

July 21-25, 1997

Aveiro, Portugal

Programme and Abstracts Book

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Defects in Semiconductors

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 23 January 1998		3. REPORT TYPE AND DATES COVERED Conference Proceedings	
4. TITLE AND SUBTITLE Nineteenth International Conference of Defects in Semiconductors				5. FUNDING NUMBERS F6170897W0091	
6. AUTHOR(S) Conference Committee					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Aviero University 3810 Aveiro Aveiro Portugal				8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD PSC 802 BOX 14 FPO 09499-0200				10. SPONSORING/MONITORING AGENCY REPORT NUMBER CSP 97-1035	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.				12b. DISTRIBUTION CODE A	
13. ABSTRACT (Maximum 200 words) The Final Proceedings for International Conference of Defects in Semiconductors, 21 July 1997 - 25 July 1997 Emphasis will be given on the properties of wide-bandgap materials, including quantum enhancement of effective band-gaps, semiconductors (silicon and III-V materials), plus radiation effects on detector materials. Topics will also include: GaN, Nanostructures, Large bandgap materials, defects in Epitaxial growth, self-organizing rare earth, metastable defects, pairs and complexes, defect reactions, radiation effects on detector material.					
14. SUBJECT TERMS Semiconductors, Electronic Devices				15. NUMBER OF PAGES 358	
				16. PRICE CODE N/A	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL		

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102



Nineteenth International Conference of Defects in Semiconductors

Programme and Abstracts Book

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UNIVERSIDADE de AVEIRO

AVEIRO - PORTUGAL

Ficha Técnica

Título

NINETEENTH INTERNATIONAL CONFERENCE OF
DEFECTS IN SEMICONDUCTORS
Programme and Abstracts Book

Autor

Vários

Editor

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Prof. M. H. Nazaré

Edição

Universidade de Aveiro
Campus Universitário de Santiago
3810 AVEIRO

Julho de 1997

Tiragem

300 Exemplares

Artes Gráficas e Serviços de Pré-Press



Impressão

Tipave, Industrias Gráficas de Aveiro



Nineteenth International Conference of Defects in Semiconductors

July 21-25, 1997

**Department of Physics
University of Aveiro
AVEIRO - PORTUGAL**

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NINETEENTH INTERNATIONAL CONFERENCE OF DEFECTS IN SEMICONDUCTORS

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The International Conferences of Defects in Semiconductors are the leading international meetings for reporting advances in understanding and controlling the properties of semiconductor materials. The meetings have a special emphasis on the behaviour of impurities and other defects which are found in the semiconductors, including those generated during the processing. The meetings are the most important gathering for academic and industrial researchers working on the subject, and the discussion of current issues at this meeting greatly influences the course of the field.

The Conferences are held every two years. The last three meetings have been held in the USA in 1991, in Austria 1993, and in Japan in 1995.

This meeting will take place at University of Aveiro in Portugal, from 21 to 25 of July 1997. The co-chairs will be Professor Helena Nazaré from the Physics Department of Aveiro University and Professor Gordon Davies from the Physics Department of King's College London. The Physics Department of University of Aveiro has been chosen to host the meeting.

Work content

At each meeting there is of course, a different emphasis in the work presented, and at this meeting there is a strong presence of work on the wide-band -gap semiconductors (GaN being a key issue), with their possible applications in high-temperature devices and optoelectronics. The choice of topical sessions and of invited speakers emphasizes current issues. Topical sessions are:

• Hydrogen	(Monday 2:00 pm-17:30 pm)
• II-VI semiconductors	(Monday 2:00 pm -17:00 pm)
• GaAs	(Tuesday 9:10 am -12:30 am, 14:00 pm – 17:00 pm)
• Growth	(9:10 am – 10:50 am)
• Germanium	(Tuesday 11:10 am -12:30 am)
• Low Dimensional structures	(Tuesday 2:00 pm – 17:00 pm)
• Erbium	(Wednesday 9:10 am – 12:30 am)
• SiGe	(Wednesday 9:10 am – 10:50 am)
• Local Vibrational Modes	(Wednesday 11:20 am – 12:30 am)
• Silicon	(Thursday 9:10 am -12:30 am, 14:00 pm – 17:30 pm)
• GaN	(Thursday 9:10 am – 12:30 am)
• SiC	(Thursday 14:00 pm – 17:30 pm)
• Mobility and Doping	(Friday 9:10 am – 12:30 am)
• Diffusion	(Friday 9:10 am – 12:30 am)

Technical Programme

The programme consists of one plenary session, followed by parallel sessions plus 2 poster sessions. In these sessions we have planned for the presentation of 3 plenary lectures, 19 invited papers, 78 contributed papers and 200 posters. Plenary papers will be allotted 50 minutes for presentation, invited and contributed papers will be allotted 40 and 20 minutes respectively. All these times include 5 to 10 minutes discussion.

Conference Proceedings

Proceedings will be published in Material Science Forum Series of TransTec Publication

Conference facilities

The meeting will be held in Aveiro Cultural and Conference Centre. This is a modern building with Conference facilities, space for Poster Display and an exhibition area where companies can display their products. This is located in the City Centre at walking distance from the University Campus (10 minutes) and from the Hotels. Student-style accommodation is available at the University Campus and block bookings have been made at some of the many Hotels within walking distance.

Sponsors

The organisers of ICDS'19 wish to thank the following for their generous contribution to the success of this conference:

- United States Air Force European Office of Aerospace research and Development
- Fundação Luso Americana para o Desenvolvimento
- Fundação Calouste Gulbenkian
- Junta Nacional de Investigação Científica e Tecnológica
- European Union-DGXII-Science Research and Development
- Transtec Publications

Without their financial assistance it would not be possible to bring such a range of expertise to the meeting

We also acknowledge:

- Biótica
- CRIOLAB
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Programme

PROGRAMME

21 JULY 97-MONDAY

- 9:15 Welcome
Plenary Session (Room C)
Chair-E.Haller
- 9:30 Recent developments in understanding localized vibrational modes and Gap modes in compound semiconductors.
R. Newman, E.G. Grosche, D.A. Robbie, R.S. Leigh and M.J.L. Sangster
- 10:20 Optically induced defects in Si-H nanoparticles.
R.J.Baierle, *M.J.Caldas*, E.Molinari and S.Ossicini
- 11:10 COFFEE BREAK
- 11:30 Defects and doping in III-V nitrides.
Chris G.Van de Walle
- 12:20 LUNCH

HYDROGEN 1 (RoomC) • Chair:B. Bech Nielsen

- 14:00 INVITED - Hydrogen molecule in crystalline silicon.
M.Kitajima, K.Ishioka, K.G. Nakamura, N. Fukata, K. Murakami, J. Kikuchi and S. Fujimura.
- 14:40 Formation and structure of hydrogen molecules in crystalline silicon.
A.W.R.Leitch V.Alex and J.Weber
- 15:00 Low temperature migration of hydrogen in silicon:interaction with oxygen.
K.Bonde Nielsen B.Bech Nielsen and J.Hansen
- 15:20 Vibrational absorption from oxygen-hydrogen (O_i-H₂) complexes in hydrogenated CZ silicon.
R.E.Pritchard M.J.Ashwin, R.C.Newman, J.H. Tucker, E.C.Lightowlers, M.J.Binns, R.Falster and S.A.McQuaid
- 15:40 COFFEE BREAK

HYDROGEN 2. (RoomC) • Chair:J.Weber

- 16:00 INVITED-STM nanofabrication and deuterium post metal annealing of mosfets for improved hot carrier mobility.
J.W. Lyding, Karl Hess and I.C. Kizilyalli

II-VI SEMICONDUCTORS 1 (RoomD) • Chair:

- 14:00 Defect structures in heavily In doped II-VI semiconductors.
V.Ostheimer, T.Filz, J.Hamann, St.Lauer, D.Weber, H.Wolf and Wichert
- 14:20 Compensation of donors by fast diffusors in II-VI compounds:model and experimental evidences for Cu doped CdS.
U.V.Desnica, I.D.Desnica-Frankovic, R.Magerle, A.Burchard and M.Deicher
- 14:40 Microscopic properties of N implanted into ZnSe.
K.Marbach, M. Fullgrabe, M.Heemeier, B.Ittermann, F.Kroll, F.Mai, P.Meier, D.Peters, H.Thiess, Ackermann, H.J.Stockmann, W.D Zeitz, H. Wensch, D.Hommel.

- 15:00 INVITED-Anion-site vacancies:donor and acceptorlike defects.
J.Chadi

15:40 COFFEE BREAK

II-VI SEMICONDUCTORS 2 (RoomD) •

Chair:W.Carlos

- 16:00 Characterization of II-VI semiconductors by positron lifetime spectroscopy with in situ optical excitation.
G.Tessaro and *P.Mascher*

PROGRAMME

- 16:40 Hydrogenation of copper related deep states in n-type Si containing extended defects.
J.Kaniewski, M.Kaniewska, L.Ornoch, T.Sekigouchi and K.Sumino
- 17:00 The I centre: a hydrogen related defect in silicon.
J.Gower, G.Davies, E.C.Lightowers and A.N. Safonov
- 18:00 POSTER SESSION P1 (Room A)

22 JULY-TUESDAY

- GaAs1 (RoomC) • Chair: R.Newman
- 9:10 INVITED-Lithium induced vacancy formation and its effect on the diffusivity of lithium in gallium arsenide.
H.Gislason, K.Leosson, H.Svavarsson, K.Saarinen and A.Mari
- 9:50 Point defects after post-growth annealing in GaAs studied by positron annihilation.
R.Krause-Rehberg, J.Gebauer, M.Lausmann
- 10:10 Defect control in As-rich GaAs.
P.Specht, S.Jeong, R.Lutz, M.Luysberg, A.Prasad, H.Sohn, J.Gebauer and E.R.Weber
- 10:30 As antisite-related defects detected by spin-dependent recombination in Si doped GaAs grown by MBE at low temperature.
K.Krambrock and M.V.B. Pinheiro
- 10:50 COFFEE BREAK
- GaAs 2 (RoomC) • Chair: H.Gislason
- 11:10 Creation of GaAs antisites in GaAs by transmutation of radioactive ⁷¹As to stable ⁷¹GaAs.
R.Magerle, A.Burchard, D.Forkel-Wirth and M.Deicher
- 11:30 Observation of metastable electron capture in n-type gallium arsenide studied by optically detected magnetic resonance.
K.Krambrock, M.V.B.Pinheiro, K.H.Wietzke, Niklas and J.M.Spaeth
- 11:50 Metastable amorphous structure in ion implanted GaAs.
I.D.Desnica-Frankovic, U.V.Desnica, M.Ivanda and T.E.Haynes

- 16:20 NMR Study of carrier states and trapping complexes in the transparent conductor ZnO:Mn.
W.W.Warren Jr, N.Roberts, R-P.Wang and W.Sleight
- 16:40 INVITED-Degradation of II-VI laser diodes.
Kazushi Nakano and Akira Ishibashi
- 18:00 POSTER SESSION P1 (Room A)

GROWTH (Room D) • Chair: P.Mooney

- 9:10 Dislocations activities in bulk SiGe alloys.
I.Yonenaga and K.Sumino
- 9:30 Electrical characterisation of electron beam induced defects in epitaxially grown Si_{1-x}Ge_x
M.Mamor, F.D.Auret, P.N.K.Deenapanray, G.Myburg and S.A.Goodman
- 9:50 Defect engineering in GaN technology.
N.N. Faleev, W.V. Lundin, B.V. Pushnyi, A.V. Sakharov, N.M. Smidt, V.I. Ushakov, A.S. Usikov
- 10:10 INVITED-Defects in SiGe
A.Nylansted Larsen

10:50 COFFEE BREAK

GERMANIUM • Chair: A.N. Larsen

- 11:10 Isotopic shifts of the rotational states of interstitial oxygen in germanium.
N.Aichele, U.Gommel, K.Lassmann, F.Maier, F.Zeller, E.E.Haller, K.M.Itoh, L.I.Khirunenko, V.Shakhovtsov, B.Pajot, E.Fogarassy and H.Mussig
- 11:30 Deep level transient spectroscopy combined with perturbed angular correlation on radioactive ¹¹¹In atoms in germanium.
Ch.Zistl, R.Sielemann, H.Hasslein, S.Gall, D.Braunig, J.Bollmann
- 11:50 Microscopic study of the vacancy and self-interstitial in germanium, by PAC.
H.Hasslein, R.Sielemann and Ch.Zistl

PROGRAMME

12:10 ODMR investigation of 2.3 MeV proton irradiated GaAs.

S.A.Goodman, F.K.Koschnick, Ch.Weber, J.M.Spaeth and F.D.Auret

12:30 LUNCH

22 JULY —TUESDAY

GaAs 3 (Room C) • Chair: J. Langer

14:00 INVITED- Positron annihilation and scanning tunneling microscopy used to characterise defects in highly Si-doped GaAs.

J.Gebauer, R.Krause-Rehberg, C.Domke, Ph.Ebert and K.Urban

14:40 Ga vacancies as compensating centers in homogeneously or d-doped GaAs(Si) layers.

T.Laine, K.Saarinen, P.Hautojärvi, C.Corbil, L.N.Pfeiffer, P.H.Citrin, M.J.Ashwin and R.C.Newman

15:00 Decay kinetics of growth-induced alignment of the first neighbor shell of CaS in AlGaAs.

J.Zhou, M.Stavola, J.F.Zheng, C.R.Abernathy and S.J.Pearton

15:20 Defects in InP and InGaAsP grown by He-plasma enhanced molecular beam epitaxy.

H.Pinkney, B.J.Robinson, D.A.Thompson, Zhao Jie, S.Junique and P.Mascher.

15:40 COFFEE BREAK

GaAs 4 (RoomC) • Chair:M.Stavola

16:00 EL2 induced enhancement of donor-acceptor pair luminescence in GaAs.

V.Alex, J.Weber

16:20 Detection and identification of the EL2 metastable state in GaAs.

J.C.Bourgoin

16:40 The microstructure of the EL2 defect in GaAs-A different look to former spin resonance data

F. Wirbeleit and J.R. Niklas

12:10 The hydrogen saturated self-interstitial in silicon and germanium.

M.Budde, B.Bech Nielsen, P.Leary, J.Goss, R.Jones, P.R.Bridson, S.Öberg and S.J.Breuer

12:30 LUNCH

LOW DIMENSIONAL STRUCTURES 1

(Room D) • Chair:

14:00 Defect related recombination processes in low-dimensional structures of ZnCdSe/ZnSe, CdTe/CdMnTe and GaAs/AlGaAs.

M.Godlewski, D.Hommel, T.Wojtowicz, G.Karczewski, J.Kossut, K.Reginski, M.Bugajski, J.P.Bergman and B.Monemar

14:20 Se and ZnSeS Epilayers by DLTS and admittance spectroscopy.

I.H.Hauksson, D.Seghier, H.P.Gislason, K.A.Prior and B.C.Cavenett

14:40 Acceptor states in boron doped SiGe quantum wells.

M.S.Kagan I.V.Altukov, K.A.Korolev, d.V.Orlov, V.P.Sinis, S.G.Tomas, K.L.Wang, K.Schmalz and I.N.Yassievich.

15:00 Array of nanoholes on a silicon surface created by uniform-intensity electron irradiation.

S.Takeda, K.Koto, M.Hirata, J.Yamasaki, S.Ijima and T.Ichibashi

15:20 Nanotubes in GaN and their formation mechanism.

Z.Liliental-Weber, Y.Chen, S.Ruminov and J.Washburn

15:40 COFFEE BREAK

LOW DIMENSIONAL STRUCTURES 2

(Room D) • Chair:W.M.Chen

16:00 INVITED-Self-assembly of nano-scale structures at semiconductor surfaces.

M.Scheffler

16:40 Spin dependent processes in self-assembly impurity quantum wires.

W. Gehlhoff

17:00 Auger type nonradiative recombination processes in bulk and quantum well structures of II-VI semiconductors containing transition metal ions.

M. Godlewski, M. Surma, A.J. Zakrzewski, T. Wojtowicz, G. Karczewski, J. Kossut, J.P. Bergman and B. Monemar

PROGRAMME

17:30 POSTER SESSION P2 (Room A)

23 JULY WEDNESDAY

ERBIUM 1 • Chair: V.Emtsev

9:10 INVITED-Erbium related defects in Si and GaAs.

A.R.Peaker

9:50 Energy transfer processes at erbium ions in silicon.

J.Palm, L.V.C.Assali, S.H.Ahn, J.Michel and L.C.Kimerling

10:10 Energy transfer rate between erbium 4f shell and Si host.

A.Taguchi, K.Takahei, M.Matsuoka and S.Tohno

10:30 Photoluminescence study of erbium in silicon with free electron laser.

I.Tsimperidis, T.Gregorkiewicz, H.P.Th.Bekman, C.J.G.M.Langerak and C.A.J.Ammerlaan

10:50 COFFEE BREAK

Er 2 • Chair: A.R.Peaker

11:20 Direct evidence for stability of tetrahedral interstitial Er in Si up to 900°C.

U.Wahl, J.G.Correia, G.Langouche, J.G.Marques, A.Vantomme and ISOLDE

11:40 Electron paramagnetic resonance of erbium in bulk silicon carbide crystals.

P.G.Baranov, I.V. Ilyin and E.N. Mohov

12:00 1.54µm photoluminescence of Er and Er+ O implanted 6H SiC.

A.Kozanecki, W. Jantsch, W. Heiss, G. Prechte, C. Jeynes and B.J. Sealy

12:20 LUNCH

THURSDAY 24 JULY

SILICON:Metals • Chair: M. Kleverman

9:10 INVITED-Iron in p-type silicon: A comprehensive model.

S.H.Ahn, L.L.Chalfoun, X.Duan, H.Nakashima, M.T.Platero, A.L.Smith, S.Zhao and L.Kimerling

17:30 POSTER SESSION P2 (Room A)

SiGe • Chair: K.Lassmann

9:10 Optical investigation of Ge rich Si_{1-x}Ge(0.9<x<1) alloys.

M.Franz, K.Pressel, K.F.Dombrowski, A.Barz, P.Dold and K.W.Benz

9:30 Substitutional carbon in Ge and Si_{1-x}Gex

L.Hoffmann, J.C.Bach, B.B.Nielsen, P.Leary, R.Jones, S.Öberg, A.N.Larsen and J.L.Hansen

9:50 Point defects and impurities in relaxed Si_{1-x}Gex

P.Kringhoj, F.Nikolajsen, E.Monakov, A.Mesli and A.N.Larsen

10:10 INVITED-Dislocation related electronic states in strain-relaxed Si_{1-x}Ge_x/Si epitaxial layers grown at low temperature.

P.Mooney and K.Shum

10:50 COFFEE BREAK

LOCAL VIBRATIONAL MODES • Chair: B. Clerjaud

11:20 Atomic configuration of oxygen negative-u center in GaAs.

A.Taguchi and Kageshima

11:40 Resonant interaction between local vibrational modes and extended lattice phonons.

M.D.McCluskey, E.E.Haller, W.Walukiewicz, P.Becla.

12:00 Anomalous shift of the 1075cm⁻¹ oxygen hydrogen defect in silicon.

R.Jones, B.Hourahine, P.R.Bridgdon and S.Öberg

12:20 LUNCH

GaN 1 • Chair: K. Thonke

9:10 ODMR studies of As-grown and electron-irradiated GaN and AlN.

G.D.Watkins, M.Linde, P.W.Mason, H.Przybylinska, S.J.Uftring, V.Härle, F.Scholz, W.J.Choyke and G.A.Slack

PROGRAMME

- 9:50 Mossbauer spectroscopy of Fe in silicon with the novel laser-ionized $^{57}\text{Mn}^+$ ion beam ISOLDE.
G.Weyer, S.Degroote, M.Fanciulli, V.N.Fedoseev, G.Langouche, V.I.Mishin, M.Van Bavel, A.Vantomme and ISOLDE.
- 10:10 Copper in silicon: quantitative analysis of internal and proximity gettering.
S.A.McHugo, T.Heiser, H.Hieslmair, C.Flink, E.R.Weber, S.M.Myers and G.A.Petersen
- 10:30 Recombination-enhanced Fe atom jump of Fe-acceptor pairs in silicon.
T.Takahashi and M.Suezawa
- 10:50 COFFEE BREAK

SILICON: Extended Defects • Chair: L.Kimerling

- 11:10 INVITED-Defect clusters in Silicon: Impact on the performance of large area devices.
B.L.Sopori
- 11:50 Infrared induced emission from silicon quantum wires.
N.T.Bagraev, E.I.Chaikina, W.Gehlhoff, L.E.Klyachkin
- 12:10 High resolution eels study of extended defects in Silicon.
N.Arai, H.Kohno, Tmabuchi, M.Hirata, S.takeda, M.Kohyama, M.Terauchi and M.Tanaka.

12:30 LUNCH

24 JULY — THURSDAY

SILICON: Oxygen • Chair: M.O. Henry

- 14:00 INVITED - An investigation of the possibility that oxygen diffusion in czochralski silicon is catalysed during clustering.
S.A.McQuaid and R.Falster

- 9:30 Electrical and optical characterization of defects in GaN generated by ion implantation.
D.Haase, M.Burkard, A.Dörnen, H.Schweizer, H.Bolay, F.Scholz
- 9:50 Implantation doping and hydrogen passivation of GaN.
A.Burchard, M.Deicher, D.Forkel-Wirth, E.E.Haller, R.Magerle, A.Prospero, A.Stötzler and ISOLDE
- 10:10 INVITED-Electrically and optically detected magnetic resonance in GaN based LEDs.
W.Carlos and S.Nakamura

10:50 COFFEE BREAK

GaN 2 • Chair: E.Pereira

- 11:10 Donor acceptor pair transition in GaN.
K.Kornitzer, M.Mundbrod, K.Thonke, M.Mayer, A.Pelzmann, M.Kamp, H.J.Ebeling, R.Sauer
- 11:30 Ab-initio studies of atomic-scale defects in GaN and AlN.
T.Mattila and R.M.Nieminen
- 11:50 Photoluminescence kinetics in the near bandgap region of homoepitaxial GaN layers.
K.P.Korona, J.M.Baranowski, K.Pakula, B.Monemar, J.P.Bergman, I.Grzegory, S.Porowski
- 12:10 Observation of native Ga vacancies in GaN by positron annihilation.
K.Saarinen, T.Laine, S.Kuisma, J.Nissilä, P.Hautojärvi, L.Dobrzynski, J.M.Baranowski, K.Pakula, R.Stepniewski, M.wodjak, A.Wysmolek, T.Suski, M.Leszczynski, I.Grzegory and S.Porowski

12:30 LUNCH

SiC 1 • Chair: B. Monemar

- 14:00 Zeeman study of the 6H-SiC:Cr.
A.Dornen, B.Kaufmann, M.Kunzer, U.Kaufmann, P.Baranov
- 14:20 A deep photoluminescence band in 4H SiC related to the silicon vacancy.
E.Sörman, N.T.Son, W.M.Chen, J.L.Lindström and E.Janzén

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- 14:40 The Oxygen dimer in silicon:some experimental observations.
T.Hallberg J.L.Lindström,L.Murin and V.P.Markevich
- 15:00 High field spectroscopy of thermal donors in silicon.
R.Dirksen, F.B.Rasmussen, T.Gregorkiewicz and C.A.J.Ammerlaan
- 15:20 INVITED-Local vibrational modes of a weakly bound H-O complex in Silicon.
B.Bech-Nielsen, K.Tanderup, M.Budde, K.B.Nielsen and J.L.Lindström
- 16:00 COFFEE BREAK

SILICON:Radiation damage • Chair: C.A.J. Ammerlaan

16:20 Vacancy aggregates in silicon.
J.L.Hastings, *S.Estreicher* and P.A.Fedders

- 16:40 Identification of VH in silicon by EPR.
P.Johannesen, J.R.Byberg, B.B.Nielsen, P.Stallinga and K.B.Nielsen

- 17:00 Vacancies and interstitial atoms in irradiated Si.
H. Zillgen and *P.Ehrhart*

20:00 BANQUET

FRIDAY 25 JULY

Mobility v Doping • Chair: A. Fazzio

- 9:10 INVITED Intrinsic modulation doping in InP based heterostructures.
W.M.Chen, I.A.Buyanov, A.Buyanov, T.Lundström, W.G.Bi and C.W.Tu

- 9:50 Pressure dependent 2-dimensional electron transport in defect doped InGaAs/InP heterostructures.

D.Wasik, L. Dmowski, J.L. Lusckowski, L. Hsu, W. Walukiewicz, W.G.Bi and C.W. Tu

- 10:20 INVITED Molecular-dynamics simulations of fundamental defects in Silicon.
S.Estreicher

- 14:40 Vacancy type defects in proton irradiated SiC.
W. Puff, P.Mascher, A.G.Balogh and H.Baumann

- 15:00 INVITED Theory of 3d transition metal defects in 3C SiC.
H.Overhof

16:00 COFFEE BREAK

SiC 2 • Chair: J.Spaeth

- 16:20 Thermal activation energies for the three inequivalent lattice sites for the BSi acceptor in 6H SiC.
A.O.Eywaraye, S.R.Smith, *W.C.Mitchel* and H.McD.Hobgood

- 16:40 The microscopy structure of the boron acceptor in 6H and 4H SiC studied with magnetic resonance.
S.Greulich-Weber, M.Feege, E.N.Kalabukhova, S.N.Lukin and J.M.Spaeth

- 17:00 INVITED- High frequency EPR studies of Shallow and deep boron acceptors in 6H-SiC.
J.Schmidt, T.Matsumoto, O.G.Poluektov, A.Arnold, T.Ikoma and P.G.Baranov

20:00 BANQUET

DIFFUSION • Chair: J. Vanhellemont

- 9:10 Formation kinetics of the Al-related shallow thermal donors:a probe for oxygen diffusion in silicon.
P.Kaczor, L.Dobaczewski, T.Gregorkiewicz and C.A.J.Ammerlaan

- 9:30 Segregation of Au at dislocations confirmed by gold diffusion into highly dislocated silicon.
H.Bracht, A.R.Schatrup and I.Yonenaga

- 9:50 Gold diffusion experiments as a tool for investigations of self interstitial interaction with extended defects.
E.Yakimov

PROGRAMME

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11:20 Ionized impurity scattering in isotopically engineered compensated Ge:GaAs.

K.M.Itoh, T.Kinoshita, W.Walukiewicz,
J.W.Beeman, E.E.Haller, J.Muto, J.W.Farmer and
V.I.Ozhogin

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G.Kaiblinger-Grujin, H.Kosina, S.Selberherr

Plenary Session.

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12:05 Summing up M.A.Stoneham

12:25 James Corbett award E.Weber

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11:20 INVITED- The behaviour of grown in point defects in CZ silicon and their importance in the 64Mbit era and beyond.

R.Falster

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RECENT DEVELOPMENTS IN UNDERSTANDING LOCALIZED VIBRATIONAL MODES AND GAP MODES IN COMPOUND SEMICONDUCTORS

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Key Words: LVMS, gap modes, isotopic shifts, force constants, dipole moments.

The lattice location and identity of impurity atoms and their complexes in semiconductor crystals can be established by the detection of impurity and host lattice isotopic fine structure in infrared absorption spectra of localized vibrational modes (LVM). Systematic differences are found in the nearest neighbour force constants for donors and acceptors compared with isoelectronic impurities in compounds with the zinc-blende structure and not all LVMS have the same linewidth. Much of the available data relates to GaAs.

Ab initio calculations have now been used to obtain eigenvectors, as well as frequencies for the perfect lattice modes of III-V compounds without using empirical models [1]. Green's functions for the defective lattice can then be formed by the Lifshitz procedure, using adjustable parameters to allow for changes in the mass of an impurity and local force constants [2]. This is an important advance since impurity - induced gap modes may be more extended spatially than LVMS. Nearest neighbour isotopic fine structure is predicted and detected for GaP:As_p, while second neighbour interactions are evident for GaP:B_{Ga}. S_p donors show strong gap mode absorption in their ionized S⁺ state but not in their neutral charge state S⁰. It is proposed that the dynamic vibrational dipole moment is shielded by an induced opposite moment of the bound electron. New results will also be presented for S-Cu_{Ga} pairs in GaP and GaAs. Isolated S_{As} donors do not give an LVM in GaAs but the longitudinal mode of the S_{As}-Cu_{Ga} mode is observed. Comparisons will be made with published data relating to impurities in ZnS[3].

It is clear that there are two types of gap modes. When a light impurity (e.g. B_{Ga} in GaP) occupies a heavy atom lattice site, the gap mode involves only small displacements of the impurity because its eigenvector must be orthogonal to that of the LVM. However there is no such restriction when a heavy atom (As_p) occupies the light lattice atom site and appreciable displacements may occur as in an LVM.

[1] P. Gianozzi, S. de Gironcoli, P. Pavone and S. Baroni, Phys Rev. B43, 7321 (1995).

[2] D. A. Robbie, M. J. L. Sangster and P. Pavone, Phys Rev. B51, 10489 (1995).

[3] M. D. Sciacca, A. J. Mayur, H. Kim, I. Miotkowski, A. K. Ramdas and S. Rodriguez, Phys. Rev. B53, 12878 (1996).

OPTICALLY-INDUCED DEFECTS IN SI-H NANOPARTICLES

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Key Words: surface reconstruction, porous Si, Hydrogen in Si

The optical properties of nanometer-size structures are currently object of debate, both from the experimental and theoretical points of view. In this scenario, Si nanoparticles are interesting in that their optical behavior shows a clear dependence on the particle size.

A reliable theoretical description of these systems is very difficult because of the need to account for atomic relaxation at a microscopic level, and to treat the optical properties consistently from the smallest cluster limit, where correlation effects are expected to be important, up to large crystallites. Most of the studies to date cannot account for all these effects at the same time in such systems.

To address this problem, we have used self-consistent semiempirical Hartree-Fock schemes of the NDO (Neglect of Differential/Diatomic Overlap) family, completely reparametrized to describe the bulk Si crystal as well as small molecules. As a result, we reproduce the key properties of the crystal, such as lattice constant, bulk modulus and phonon frequencies (MNDO/Crystal), as well as valence band ionization energies, the indirect character of the gap, and the bulk gap value when extrapolated from nanocrystal values (INDO/Crystal), while still describing relevant features of the silane, disilane, siloxane molecules. For a given nanoparticle, we therefore obtain consistent predictions for the equilibrium atomic structure, the vibrational frequencies, the optical spectra (electron correlation being included through Configuration Interaction), as well as the spatial and orbital composition of the states contributing to the optical transitions.

Our results for hydrogenated Si particles unveil a strong and spontaneous distortion that occurs under optical excitation, thus creating a localised luminescent center at the surface. For particles ranging from 29 to 71 Si atoms, with the surface perfectly saturated with H atoms, the first absorption is essentially a HOMO-LUMO transition, that leaves the particle in an excited electronic state corresponding to a one electron excitation.

By allowing full atomic relaxation in such excited state, we find a minimum-energy configuration where a hydrogen atom bridges a surface Si-Si bond, with very little relaxation of the remaining atoms in the particle. Luminescent decay occurs then mainly (60% of the optical strength) from this localised configuration-defect.

Also we find that optical absorption originates clearly from the crystalline core of the cluster, and presents a large, size-dependent blue-shift with respect to bulk Si, essentially due to quantum confinement effects. The absorption ranges approximately from 3.5 to 2.5 eV for particles with 17 to 71 Si atoms; luminescence is however 'pinned' by the configuration-defect at much lower energies (Stokes shift around 1.2 eV for the 35-Si particle).

The above results allow us to understand recent experimental data on Si-H particles, and provide a clue to understanding the optical properties of porous Si. Furthermore, they reveal a mechanism for reversible defect creation, that is expected to be relevant to the behavior of rough surfaces, interfaces, and other 'soft' environments.

DEFECTS AND DOPING IN III-V NITRIDES

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Key Words: GaN, nitride, doping, defects, compensation

GaN is successfully being used for green, blue, and UV light emitters and for high-temperature or high-power applications. The ability to control doping is crucial for device fabrication; wide-band-gap semiconductors such as GaN have long suffered from limitations on the achievable doping levels. I will discuss how theoretical results for native defects and dopant impurities, combined with state-of-the-art first-principles calculations, can be used to understand the various factors that govern doping.

p-type doping of GaN has become possible through a post-growth activation step in MOCVD-grown material. Hydrogen plays a crucial role in this process. The behavior of hydrogen in GaN is broadly similar to that in other semiconductors, including the stability of H^+ in p-type material and the negative-U character (in this case with a very large magnitude of U) [1]. Intriguing differences occur, however, for instance in the structure of hydrogen-acceptor complexes. I will discuss how hydrogen affects acceptor incorporation in GaN, and why the presence of hydrogen is detrimental to p-type doping in ZnSe. Results for interactions between hydrogen and native defects will also be presented.

The origin of the background n-type conductivity observed in almost all GaN material has been debated until recently. We have shown that the n-type conductivity can **not** be attributed to nitrogen vacancies, but is due to unintentional incorporation of donor impurities such as silicon or oxygen [2]. Comprehensive studies of GaN under pressure and of AlGaN show that the oxygen donor undergoes a *DX*-like transition: a large outward relaxation introduces a deep level in the band gap, explaining the observed carrier freezeout [3]. Si donors do not exhibit this transition. Investigations of the interaction between O and native defects produce a large binding energy between O and the gallium vacancy; we have proposed the latter to be the source of the "yellow luminescence" [2]. Finally, we have studied the interaction between O and Mg acceptors. The presence of oxygen during growth is detrimental to obtaining p-type doping in the nitrides.

I gratefully acknowledge my collaboration with Jörg Neugebauer and the support of DARPA.

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HYDROGEN MOLECULE IN CRYSTALLINE SILICON

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Key Words: crystalline silicon, hydrogen atom treatment, Raman scattering

Hydrogen impurities are incorporated during various stages of semiconductor processing, and forms various complexes with crystal defects and impurities. Among the hydrogen-related defects in silicon, hydrogen molecule is predicted by theoretical calculation to be stable at tetrahedral site [1]. However, no direct observation had been reported on hydrogen molecule in silicon, until we found that hydrogen exists in molecular form in crystalline silicon treated with hydrogen atoms in the downstream of a hydrogen plasma [2].

In this paper, we present furthermore a detailed study on the hydrogenation-temperature dependence of the formation of hydrogen molecules using Raman measurements. The vibrational Raman line of hydrogen molecule was observed at 4158cm^{-1} for crystalline silicon hydrogenated at substrate temperatures between 180 and 500°C . The intensity of the vibrational line had a maximum for hydrogenation at 400°C . The rotational Raman line of hydrogen molecule was also observed at 590cm^{-1} at hydrogenation temperature between 300 and 500°C .

The Raman shift of the vibrational line of hydrogen molecule showed little dependence on the hydrogenation temperature. The vibrational line was asymmetric and consists of at least two components at 4160cm^{-1} and 4130cm^{-1} . The relative intensity of the 4130cm^{-1} component to the 4160cm^{-1} component decreased with increasing hydrogenation temperature. Correspondingly the line width of the vibrational line decreased with increasing hydrogenation temperature, from 50cm^{-1} at 180°C to 30cm^{-1} at 500°C . The width for hydrogenation at 500°C is still much larger than that of gaseous hydrogen molecule: no more than 3cm^{-1} even for gaseous hydrogen pressurized up to 200MPa, typical pressure for bubbles in solids. The line width was not affected by lowering the sample temperature during Raman measurements down to 90K. The results suggest that the large width of the vibrational line is not explained by collisional or motional broadening but is attributed to the inhomogeneous broadening.

The Raman band of Si-H stretching was observed for crystalline silicon hydrogenated between 100 and 500°C . The formation of hydrogen molecule is discussed in comparison with that of Si-H bonds and $\{111\}$ platelets. The hydrogenation-time dependence of the formation of hydrogen molecule is also described.

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FORMATION AND STRUCTURE OF HYDROGEN MOLECULES IN CRYSTALLINE SILICON

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Key Words: Hydrogen, Silicon, Spectroscopy

We report on an investigation into the formation of H_2 molecules in crystalline Si after treatment in a hydrogen plasma. Both n- and p-type Si material having a wide range of doping concentrations were studied. Hydrogenation at temperatures as low as 125 °C was found to be sufficient for forming H_2 in the Si lattice. The expected isotope shift of the Raman frequency was measured when the H-plasma was replaced by a deuterium plasma. Furthermore, a mixture (50:50) of hydrogen and deuterium in the plasma resulted in a new Raman line, which we attribute to the H-D molecule. The linewidth of the Raman signal is about an order of magnitude broader than what has recently been measured for molecular hydrogen in GaAs.[1] We will discuss probable configurations of the H_2 molecules in the Si lattice.

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LOW-TEMPERATURE MIGRATION OF HYDROGEN IN SILICON: INTERACTION WITH OXYGEN

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Key words: Hydrogen, Oxygen, Diffusion, Metastability, DLTS

It has been recognized for some time that the presence of interstitial hydrogen leads to significant enhancements of the diffusion of oxygen and related processes, such as the enhancement of the rate of thermal donor formation and the incorporation of hydrogen in shallow thermal donors. The understanding of these catalysis phenomena require elucidation of oxygen-hydrogen structures and the interactions that occur during defect evolution in low temperature anneals. In this work, we present the results of a detailed *in situ* DLTS study, in which the annealing properties of interstitial hydrogen were examined in the temperature range from 50 to 300 K. The samples were prepared by low-dose proton implantation at 60 K in such a way that DLTS could be applied directly to the implanted layer without intervening heating of the sample. We show that two metastable donor states associated with isolated hydrogen are formed in n-type silicon. One of these states E3' is ascribed to bond-centred hydrogen and the other E3'' is tentatively assigned to hydrogen occupying a position in the low-density region of the silicon crystal. Both states transform under zero-bias annealing to the same reservoir state from which they can be recovered reversibly. The E3' signal recovers by forward-bias injection of holes while E3'' recovers by illumination. Further important features are: (I) During reverse-bias annealing E3'' converts thermally into E3'. (II) The (subsequent) reverse-bias annealing of E3' is controlled by trapping on the native oxygen impurities. (III) A weakly bound hydrogen-oxygen structure is present in the temperature range 200-275 K. (IV) This structure is associated with a migration stage in which hydrogen diffusion is retarded. (V) The hydrogen migration eventually leads to passivation of a phosphor dopant. (VI) After passivation, the E3' and E3'' signals can no longer be retrieved by hole injection at low temperature. We shall discuss the outlined annealing scenario in detail emphasizing on the role of oxygen.

VIBRATIONAL ABSORPTION FROM OXYGEN-HYDROGEN (O_i-H_2) COMPLEXES IN HYDROGENATED CZ SILICON

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Key Words: Si, oxygen, hydrogen, O_i-H_2 complexes, LVMs

CZ silicon heat treated at $T \sim 1200^\circ\text{C}$ in H_2 or D_2 gas followed by a quench to room temperature leads to the formation of infrared absorption lines at 1075.1 cm^{-1} and 1076.6 cm^{-1} that have been attributed to O_i-H and O_i-D pairs respectively [1]. These defects were lost during a subsequent anneal at $T > 120^\circ\text{C}$ but were restored by further heating at 50°C . However the defects were annihilated by heating at $T > 250^\circ\text{C}$.

We have now examined similarly treated samples held at 10 K using high resolution (0.1 cm^{-1}) FTIR. The previous assignment of the incorporation of an O_i atom, that was only circumstantial (it could have been a carbon or nitrogen atom) has been verified by the observation of satellite lines due to ^{29}Si and ^{30}Si as found for the absorption spectrum of isolated bond centered O_i atoms. Analysis of our samples containing mixed H and D impurities, shows that the defect incorporates two hydrogen atoms and not one H atom, as reported in [1]. The oxygen mode of the complex involving H-D atoms is closer in energy to that of the corresponding mode with two D atoms than that with two H atoms. The total concentration of hydrogen present in these complexes is estimated to be comparable with solubility data for [H] (at the quench temperatures 1100-1300°C) for which we have previously determined a heat of solution of 1.8 eV.

When the O_i-H_2 complexes are present (1075 cm^{-1} structure), we observe two correlated hydrogen stretch modes at 3788.8 cm^{-1} and 3730.8 cm^{-1} in thick samples: these two modes are extremely weak but sharp ($\Delta \sim \text{cm}^{-1}$). There are corresponding analogues for both O_i-D_2 and O_i-HD complexes. The existence of two hydrogen stretch modes, implies that two slightly different types of center are present. This is consistent with the observation that the oxygen modes of the O_i-H_2 and O_i-D_2 complexes always appear as a close doublet and a line with a shoulder respectively. There is an anti-correlation of the 1075 cm^{-1} structure with a third H-H mode at 3618.3 cm^{-1} that also has corresponding D-D and H-D isotopic analogues. Since this third mode is observed in FZ silicon, the centre responsible is very unlikely to incorporate oxygen. These observations provide evidence for the presence of three types of H-H bonded centers that appear to be identified with H_2 molecules. The presence of a small dipole moment would require the molecules to be polarised non-uniformly so that the 2 H atoms are inequivalent. Possible mechanisms are currently under investigation [2].

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STM NANOFABRICATION AND DEUTERIUM POST METAL ANNEALING OF MOSFETS FOR IMPROVED HOT CARRIER RELIABILITY

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Key Words: STM, silicon nanofabrication, hot electron effects

Electron stimulated desorption (ESD) of hydrogen from Si(100) by an ultrahigh vacuum scanning tunneling microscope (UHV STM) is being used to develop nanofabrication methods [1] and to study hydrogen desorption mechanisms [2]. Quantitative measurements show the existence of two regimes for hydrogen desorption. For STM tip voltages above ~ 6.5 V (tip negative) direct bonding-to-antibonding transitions are excited with a desorption yield of ~ 1 H atom/ 10^6 electrons. At lower voltages, a vibrational heating mechanism requiring multiple excitations leads to H desorption that depends strongly on voltage and current density. Also consistent with the vibrational heating model is the fact that hydrogen is much easier to desorb at lower low temperatures.

In a parallel set of STM experiments on deuterated surfaces, suggested by Avouris, we found that $\sim 10^8$ electrons are required to desorb each D atom [3]. This large isotope effect is consistent with the Menzel Gomer Redhead model which predicts an exponential dependence of desorption on the isotope mass. In addition to the isotope mass, the shorter excited state lifetime of Si-D vs Si-H also contributes to the isotope effect.

By lateral analogy to the STM experiments we tried deuterium instead of hydrogen in the post metal anneal of CMOS wafers. The idea was that the desorption of hydrogen at the oxide/Si interface by channel hot electrons might also exhibit a strong isotope effect. This is indeed the case since switching to deuterium increases transistor lifetimes by factors of 10 to 50 in accelerated aging tests [4]. Using deuterium instead of hydrogen does not change any other properties of the transistors. These results have now been confirmed by several major semiconductor manufacturers.

The large isotope effect observed in CMOS aging leads to other predictions by analogy to the STM experiments. These include the lack of a voltage threshold for transistor degradation, a strong dependence of aging on channel current density, and increased degradation for low temperature device operation. The key point here is that at high current densities transistor degradation arises from current flow within the channel without requiring carrier injection over the oxide barrier.

This work is supported by the Office of Naval Research University Research Initiative under grant N00014-92-J-1519 and the Beckman Institute for Advanced Science and Technology.

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HYDROGENATION OF COPPER RELATED DEEP STATES IN N-TYPE SI CONTAINING EXTENDED DEFECTS

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Key Words: Si, extended defects, copper related deep states, hydrogenation, DLTS.

We present results of DLTS studies performed on specimens prepared from n-type, P-doped, 28 Ωcm CZ-Si. Copper was introduced at high temperature 1100°C for 1h to the four groups of samples: as grown, free of extended defects, containing dislocation loops (DLs) with the density $2 \times 10^5 \text{cm}^{-2}$ and containing stacking faults (SFs) with the density $5 \times 10^5 \text{cm}^{-2}$. High density of DLs and SFs was induced by oxygen precipitation in different multistep annealing: DLs - 600°C/20h+725°C/ 15h+ 1000°C/ 15h, and SFs 725°C/ 15h+ 1000°C/ 15h, respectively. Hydrogen plasma treatment of all types of the samples were done at 400°C.

As it was confirmed by DLTS spectra, as grown samples were free of deep states. However, spectra in samples contaminated with copper were dominated by main trap with thermal activation energy $\Delta E_c - (0.14 + 0.02)\text{eV}$ (for $c_n = 100\text{s}^{-1}$ at 100K). Low temperature peak, of similar height has been also found in copper diffused samples containing SFs. The result confirm the dependence of energy of copper related state on diffusion temperature [1,2]. In the case of copper diffused samples containing DLs, low temperature peak was significantly reduced and additional peak at 150K appeared. Due to the very high population changes of low temperature state, DLTS technique did not allow for proper determination of deep trap concentration. Therefore thermally stimulated capacitance characteristics were measured. The huge effect of capacitance changes, "freezing effect" was observed in copper diffused samples. This result suggests that Cu and P atoms can form deep complex. The effect is very pronounced since at liquid nitrogen temperature capacitance of the samples nearly disappears. This result confirms the first suggestion of Takahashi et al [3] on possibility of generation of complexes involving transition metal and P atoms (Fe-P) in Si.

All Cu related deep states observed in free of extended defects n-type Si can be completely passivated at 400°C with atomic hydrogen in Si. However in the presence of dislocation loops as well as stacking faults the effectiveness of passivation of deep states is limited.

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THE I CENTRE: A HYDROGEN RELATED DEFECT IN SILICON

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Key Words: Hydrogen, luminescence, silicon, isoelectronic centre

In recent years there has been intense interest in hydrogen in silicon. It is becoming apparent that many radiation damage centres (both interstitial centres and vacancy centres) involve hydrogen. It is important to understand the evolution of these centres and their inter-relationships. We report here the properties of the 'I centre' (zero phonon line at 965 meV), which is created in Czochralski silicon by thermal treatment in the temperature range 400-600 C. The luminescence intensity of the I centre is greatly enhanced by deliberate hydrogen incorporation and radiation damage prior to thermal treatment. This treatment in oxygen-lean material produces the 'T-centre' (zero phonon line at 938 meV), which has recently been established as containing two carbon atoms and one hydrogen atom [Safonov et al, Phys. Rev. Lett., Vol. 77, No. 23, (1996)]. We show here that the I centre is very closely related.

The effect of changing the isotopes on the energy of the zero-phonon line and the local vibrational modes establishes the presence of hydrogen and two inequivalent carbon atoms, as for the T centre. Furthermore, the magnitudes of the isotope effects on each feature are very similar at the I and T centres. Uniaxial stress perturbations on the I centre are also shown to be quantitatively similar to the data for the T centre, and establish the same monoclinic I symmetry for both centres.

Analysis of the Zeeman data, the uniaxial stress data and the temperature dependence of the luminescence show that the I centre, like the T centre, is isoelectronic. The ground electronic state is paramagnetic as a result of one unpaired electron. Qualitatively, we may think of the proton of a single hydrogen atom as providing charge compensation for that electron. The bound exciton of the excited state is trapped by the short range attraction of the electron to the neutral centre and the Coulomb attraction of the hole to the complex. This results in the observed effective-mass-like hole.

We have not, as yet, direct evidence for oxygen being involved in the centre, except the strong requirement that it is produced in oxygen-rich silicon. Given the similarities of the I and T centre we postulate that the I centre is a T centre perturbed by the presence of a nearby oxygen atom.

DEFECT STRUCTURES IN HEAVILY IN-DOPED II-VI SEMICONDUCTORS

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Key Words: II-VI compounds, Donors, Indium, A-centre, compensation, PAC

The local atomic configuration of compensated In-donors was investigated as a function of the total In-concentration using perturbed gg-angular correlation spectroscopy (PAC). The compensation of In-donors is observable on an atomic scale by detecting characteristic electric field gradients (EFG) at the site of the radioactive probe atom ^{111}In , that are caused either by the formation of close pairs with acceptor like defects or by the relaxation of the ^{111}In probe.

From PAC-experiments in weakly In-doped ZnSe, ZnTe, ZnS, CdSe, CdTe, and CdS crystals ($[\text{In}] < 10^{16} \text{ cm}^{-3}$), the compensation of In-donors by pairing with cation vacancies V_M is known, forming the A-centre complex In_M-V_M ¹⁾. In this complex the vacancy is detected via its characteristic EFG at the lattice site of the ^{111}In nucleus. In heavily In-doped II-VI compounds other EFG are observed, indicating the formation of other local configurations of the In-donors. In case of CdS:In and CdTe:In, these EFG were also reported by Magerle²⁾ and Wegner³⁾, respectively and a preliminary interpretation in terms of In-defect complexes was given.

We present a detailed study of these new In-configurations which was performed by comprehensive PAC investigations. Single crystals of the respective II-VI semiconductor were simultaneously doped with stable In and radioactive ^{111}In by diffusion under presence of the respective chalcogen element. If the In-concentration exceeds approximately 10^{18} cm^{-3} , the PAC spectra reveal new defect structures in all II-VI compounds. The new defects are characterised by up to three, slightly different, EFG, which always occur simultaneously. In all investigated II-VI compounds, the strength of these EFG is about double the value of the A-centre defect measured in weakly In-doped crystals.

The identical defect complexes are observed in ZnSe, CdTe, or CdS that are heavily doped with Ga instead of In. For ZnSe and ZnS a partial transformation of the A-centre into the new defect structures is observed if the temperature is reduced below 100 K. PAC-measurements performed as a function of sample temperature show that the new defects are more stable than the A-centres. The obtained experimental results suggest that the new In-configurations observed at higher donor concentrations also consist of an In-donor and a cation vacancy but in a different charge state and local configuration than the A-centre defect observed in the weakly In-doped II-VI compounds. It is proposed that a singly charged cation vacancy and a doubly charged cation vacancy is bound to the In-donor in the weakly and heavily doped II-VI semiconductors, respectively.

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COMPENSATION OF DONORS BY FAST DIFFUSORS IN II-VI COMPOUNDS: MODEL AND EXPERIMENTAL EVIDENCES FOR Cu DOPED CdS

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Fast diffusors (Cu, Ag, Au, Li...) are important impurities in semiconductors. Penetrating easily, they dramatically influence electrical, optical and photoelectronic properties. In II-VI compounds they commonly compensate donor dopants in a way not fully understood.

Here we present a model which explains electrical compensation of CdS by Cu: The diffusion of Cu donors into CdS provokes simultaneous creation of cadmium vacancies, V_{Cd} , which are double acceptors. Cu compensates CdS crystal indirectly, by bringing into the crystal new V_{Cd} , that pair with existing group-III donors causing their electrical compensation. Theoretical arguments for the model are based on high bond ionicity (69%) in CdS and are analogous to those in truly ionic (89-96%) I-VII compounds, where the presence of II-row-atoms produces spontaneously equal number of compensating cation vacancies. Our model reconciles two widely accepted but apparently contradictory assumptions: one, that Cu in CdS is a fast diffusor which moves as an interstitial, and hence is a donor, and the other, that Cu compensates donors in CdS and hence effectively acts as an acceptor.

To check the model experimentally, CdS samples were prepared by pre-doping pure CdS with ^{111}In via implantation. The immediate surrounding of ^{111}In atoms is determined by Perturbed Angular Correlation (PAC) spectroscopy. Samples were engineered by appropriate annealing to contain both, isolated In atoms in substitutional Cd lattice site, In_{Cd}^+ , that are donors, and In atoms forming pairs with cadmium vacancy, V_{Cd} , at next-neighbor position, $(In_{Cd}^+ - V_{Cd}^{2-})^-$, that are acceptors. Then Cu was evaporated on the surface of CdS. Following Cu evaporation no new, Cu related, PAC frequency was obtained, the only change being gradual increase of the $(In_{Cd}^+ - V_{Cd}^{2-})^-$ component with simultaneous decrease of In_{Cd}^+ component. After one week at room temperature the fraction of In atoms forming $(In_{Cd}^+ - V_{Cd}^{2-})^-$ pairs reached 100%, and the PAC signal of isolated In_{Cd}^+ atoms disappeared totally.

In the light of the presented model previously reported results on electrical compensation of Cu doped CdS and results obtained with a number of other experimental techniques should be re-interpreted: Donors are compensated by cadmium vacancies which are spontaneously created due to the presence of Cu, and trapped by donors - they are *not* compensated directly by Cu acceptors. Our model is compatible with the only PAC results on fast diffusors hitherto reported in II-VI's, where Li doping also considerably increases the concentration of $(In - V_{Cation})$ pairs in CdS, ZnS and ZnTe, although at higher temperatures². Considering the similarities between Cu and other fast diffusing species like Ag, Au, Na, Li... and relatively high ionicity of most II-VI compounds (49-90%), it seems plausible that the same mechanism of indirect compensation caused by diffusion-induced cation vacancies, can explain compensation effects observed for other fast diffusors in CdS and in many other II-VI compounds as well.

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MICROSCOPIC PROPERTIES OF N IMPLANTED INTO ZnSe

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Key Words: ZnSe, nitrogen, acceptor doping, ion implantation

We report our first results on microscopic properties of N implanted into single-crystalline ZnSe obtained by β -radiation detected nuclear magnetic resonance (β NMR).

Spin polarized, β -active ^{12}N probe nuclei were produced in a nuclear reaction and recoil-implanted into the undoped sample (MBE grown on GaAs substrate) with an energy of up to 1.5 MeV. ^{12}N ($T_{1/2} = 11$ ms) decays into ^{12}C , the concentration of implanted N never exceeded $10^7 / \text{cm}^3$ (less than 10^3 probes simultaneously present in the sample). This high sensitivity of a nuclear technique combined with the resolution of nuclear magnetic resonance makes β NMR quite a useful tool to investigate microscopic properties of isolated impurities after implantation.

From the observation of an unperturbed Larmor resonance we conclude that already at room temperature part of the implanted N ends up at lattice sites with full cubic symmetry and is in a diamagnetic charge state. A definite identification of this site still has to be done, for a group V impurity, however, symmetry and charge state strongly favour the interpretation that this signal corresponds to N_{Se}^- , i.e., the regularly ionized acceptor.

The signal intensity as a function of implantation temperature stays constant up to about 500 K, followed by an increase by a factor of six. Saturation is reached at 900 K. A preliminary analysis of this temperature dependence suggests the following picture: at room temperature the implanted N is predominantly trapped at some paramagnetic defect where it gets rapidly depolarized. At higher temperatures this complex breaks up and we get isolated N_{Se}^- . Within this model we obtain a value of 0.51(6) eV for the dissociation energy.

Even in this early stage of our experiments it may be concluded that our data considerably shake the widespread assumption that the introduction of electrically active acceptors into ZnSe is not possible by ion implantation.

ANION SITE VACANCIES: DONOR AND ACCEPTORLIKE DEFECTS

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It is well known and generally well accepted that in III-V and II-VI semiconductors anion-site vacancies are donorlike whereas cation-site defects are acceptorlike. A surprising result we have obtained recently from first-principles calculations is that, depending on atomic relaxation, anion-site vacancies in III-V and II-VI semiconductors can be either donorlike or acceptorlike. For example, we find that an As vacancy in GaAs can be either a triple donor or a triple acceptor and that a Te vacancy in ZnTe can be either a double donor or a double acceptor. This duality of electrical behaviour is not found for cation site vacancies. The result that anion site vacancies can be acceptorlike has important implications for the n-doping of semiconductors. Since both anion and cation site vacancies can be acceptorlike defects, it becomes possible to consider stoichiometric defects consisting of equal numbers of each vacancy and to calculate the absolute formation energy involved in the passivation of donor impurities by vacancies. Using this approach we find that vacancy formation in n-doped ZnTe is: highly exothermic; cannot be avoided by changing growth conditions; and is, therefore, the most likely cause of the problems encountered in the n-type doping of this compound. Our results provide an explanation for the unexpected identification [1] of Se-site vacancies in n-type ZnSSe alloys from positron annihilation experiments because up to now these vacancies have been thought to be positively charged and not detectable by positrons. We show that it is not necessary to assume complex formation with an acceptor defect to explain the negative charge state of this vacancy.

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CHARACTERIZATION OF II-VI SEMICONDUCTORS BY POSITRON LIFETIME SPECTROSCOPY WITH IN-SITU OPTICAL EXCITATION

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Semiconductor devices such as light-emitting diodes that operate in the blue-green to near infrared region of the spectrum are of substantial interest for optoelectronic applications. For superior device performance, defects in these semiconductors must be thoroughly identified and characterized. One of the techniques to perform this task is positron lifetime spectroscopy (PLS), which is a powerful tool for characterizing vacancy type defects in single crystal materials.

In this report we will present the results of a systematic investigation of the vacancy type defects in several single crystal Cd and/or Zn based semiconductor samples (CdTe, CdZnTe, CdTeSe, ZnSe, and ZnS) using a state of the art PLS system. In the as grown state, CdTe contains defects of monovacancy character, with positron lifetimes in good agreement with the published literature. The addition of about 8% Se, however, changes the defect profile dramatically, resulting in significantly smaller concentrations (by about a factor 3) of larger vacancy complexes. A detailed study of the electronic charge state(s) of these defects as well as their thermal stabilities is in progress. The Zn-based materials also contain vacancy-type defects in the as grown state, with concentrations ranging from about 4×10^{16} to $> 1 \times 10^{17} \text{ cm}^{-3}$ for ZnSe and ZnS, respectively.

The experimental setup also allows both low temperature measurements and illumination of the samples with monochromatic light during the positron lifetime measurement. The purpose of the illumination is to investigate the influence of optical excitation on the PLS signals. Photoluminescence results are used as a guide for the PLS measurements to indicate possible defects in the materials that are optically active and to determine the ideal wavelengths with which to illuminate the samples.

NMR STUDY OF CARRIER STATES AND TRAPPING COMPLEXES IN THE TRANSPARENT CONDUCTOR $\text{ZnO}:\text{M}_{\text{III}}$

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Key Words: II-VI compounds, NMR, impurity state, complexes, transparent conductors

Zinc oxide can be doped with high concentrations of group III donors to yield conductivity values exceeding $1000 (\text{ohm cm})^{-1}$ while retaining high transparency to visible light. Using NMR of the impurity nuclei (^{69}Ga , ^{27}Al) we have investigated the structural and electronic environments of Ga and Al dopants in ZnO. The experiments cover the range of dopant concentration from 0.03 at. % up to 3.0 at. % which is close to the solubility limit. The small axial distortion revealed by the quadrupolar perturbed ^{69}Ga NMR line establishes that most of the ^{69}Ga observed in "stoichiometric" samples, $\text{Zn}_{1-x}\text{Ga}_x\text{O}$, is substitutional Ga_{Zn} . The NMR shift and nuclear spin-lattice relaxation rates of ^{69}Ga and ^{27}Al at such sites are dominated by magnetic hyperfine coupling to the spins of conduction electrons. At high concentrations ($x > 0.005$) the shift and relaxation rates are characteristic of coupling to carriers introduced into the host crystal conduction band by shallow effective mass donors. However, a distinct impurity band with a sharply enhanced density of states develops rapidly as the dopant concentration is reduced below this concentration. The carrier spin dynamics revealed by the impurity nuclear spin-lattice relaxation rate show that the carriers behave essentially as weakly interacting, nearly free electrons, even within a narrow impurity band. This observation contrasts markedly with impurity NMR results^{1,2} in Si:P and Si:B in which strong carrier spin-fluctuations develop in heavily-doped samples well above the metal-insulator transition.

Our ZnO:Ga samples also contain a second class of Ga sites, whose broad NMR lines show that their local environments are highly distorted compared with Ga_{Zn} . The relative concentration of distorted sites increases strongly with increasing oxygen content in a series of "non-stoichiometric" samples $\text{Zn}_{0.98}\text{Ga}_{0.02}\text{O}_{1+z}$ with values of z ranging from -0.012 to +0.010. In our most oxygen-rich sample ($z = 0.010$), the proportion of Ga_{Zn} substitutional sites is reduced to about 5% of the total observed Ga. Their spin-lattice relaxation rates show that the distorted sites are decoupled from the conduction electron spin density, i.e. these are diamagnetic defects. Increase in the relative proportion of distorted sites, and corresponding decrease of Ga_{Zn} sites correlates with decreasing conduction electron density at Ga_{Zn} and a sharp drop in DC electrical conductivity, especially in samples with excess oxygen ($z > 0$). We propose, therefore, that the carrier density is controlled by the concentration of Ga_{Zn} and that the distorted sites are two-electron traps. Their relationship to excess oxygen suggests that Ga in these defects is complexed with an oxygen interstitial to form, for example, $\text{Ga}_2^{3+}\text{O}_i^{2-}$.

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DEGRADATION IN II-VI LASER DIODES

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Key Words: ZnMgSSe, laser diode, recombination enhanced defect reaction

Since Haase *et al.* demonstrated the first II-VI laser diodes (LDs) at 77 K[1], LDs based on II-VI semiconductors have been further developed. We have recently achieved a device lifetime exceeding 100 hours under room-temperature continuous-wave operation by reducing the density of pre-existing stacking faults which are nucleation sources for the rapid degradation[2]. However, further extension of the device lifetime is necessary for practical applications. Understanding the degradation mechanism is a key to further improvement. During device operation, semiconductor materials are never in thermal equilibrium conditions but excited conditions, where excess electrons and holes exist and could recombine and the energy could be released either radiatively or nonradiatively. In such conditions, defect reaction in the material could not be pure thermal process. The important concept of recombination-enhanced defect reactions (REDR) by nonradiative recombination of free carriers in the vicinity of defects was proposed by Weeks *et al.*[3] In this case, pre-existing defects are needed as seeds of defect reaction.

The other defect reaction process could also occur. That is the defect generation by e-h recombination from the host lattice itself. This process is known as weak-bond-breaking model for amorphous Silicon[4]. In this case, the material will degrade easily if there is no pre-existing defect. Since bond energy is smaller than bandgap energy in II-VI wide-gap materials, this process was suspected to happen in II-VI devices.

To investigate the degradation process, we analyzed the time dependence of the optical output degradation under constant current aging condition and obtained time-dependence of t^{-1} , which is obtainable by assuming pre-existing defects are seeds of the degradation. We conclude that the II-VI LDs degrade not catastrophically, but gradually as well as III-V materials.

REDR process implies that there are three ways to improve the device reliability: the first is to lower the operation current density to suppress nonradiative e-h recombination. The second is to reduce pre-existing defect density. The third is to suppress the generation or propagation of defects. Based on these degradation-suppression ways, further improvement of reliability will be possible.

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LITHIUM INDUCED VACANCY FORMATION AND ITS EFFECT ON THE DIFFUSIVITY OF LITHIUM IN GALLIUM ARSENIDE

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Key Words: Diffusion, bound excitons, vacancies, positron annihilation, GaAs, lithium

In this work we show that the diffusion of lithium in GaAs is trap-limited at high doping levels. We determine the intrinsic diffusivity of lithium in GaAs experimentally for the first time. Previously published values for the diffusion coefficient were obtained from measurements on heavily doped material where the diffusivity was strongly reduced due to the formation of Li-related complexes [1]. From our work, we determine a migration energy $E_m = 0.67$ eV, indicative of an interstitial diffusion process. We also find, in accordance with previous studies, that complexes involving several Li atoms and native defects are formed in heavily Li-doped samples, effectively reducing the diffusivity of Li by several orders of magnitude. We address the identity of these lithium-related defect complexes using a combination of different experimental techniques.

Sharp bound exciton lines appear in the photoluminescence spectrum of semi-insulating GaAs after lithium diffusion at 400–500 °C. In *n*-type GaAs heat treatment at 950°C produces the same lines, which were attributed to excitons bound to a double V_{Ga} -GaAs acceptor [2]. In order to test the effect of lithium diffusion at low-temperatures on the gallium vacancy concentration of GaAs, positron lifetime experiments were performed. We observe a clear correlation between the V_{Ga} concentration and the intensity of the bound exciton lines. The role of Li in lowering the formation energy for gallium vacancies in GaAs will be discussed.

We also present investigations on undoped, *n*-type, *p*-type and semi-insulating GaAs, diffused above 700°C to Li concentrations well above the shallow doping. This always produces highly resistive samples through self-compensation of lithium. Heat treatment below 500°C caused *p*-type conductivity in all types of starting material. We find that the hole concentration obtained by the out-diffusion of lithium is connected to the acceptor concentration established by the high-temperature Li-diffusion for all of the starting materials. This agrees with previous observations for undoped and *n*-type GaAs [1]. The effect of the acceptors in the as-diffused samples on the eventual hole concentration is supported by infrared absorption measurements which reveal the same local vibrational mode spectrum in all the as-diffused samples. Positron measurements show that all of the heat-treated samples exhibit strongly enhanced V_{Ga} concentrations irrespective of starting material, thus establishing the involvement of V_{Ga} in the acceptors. In the paper we discuss the defect reactions in the two-step process resulting in the *p*-type conduction.

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POINT DEFECTS AFTER POST-GROWTH ANNEALING IN GaAs STUDIED BY POSITRON ANNIHILATION

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Keywords GaAs, equilibrium defects post-growth annealing, positron annihilation

Equilibrium defects in GaAs are not well understood and are still a matter of continuous discussion. Especially little is known on the formation of vacancies at high temperatures. This is mainly due to the lack of appropriate experimental tools. A powerful method for the study of vacancies in semiconductors is positron annihilation. This method is limited to the detection of negative and neutral vacancies as well as to negatively charged ions, such as $\text{Ga}^{2-}_{\text{As}}$. This is not a strong restriction in n-type material, since both monovacancy types are expected to be negatively charged. The positron technique is hardly applicable at the required high temperatures, such as 1000°C. Thus, the vacancies introduced by post-growth annealings were preserved by fast quenching. The annealings were performed in a quartz-glass ampoule arranged in a two-zone furnace, allowing us to tune the As-vapour pressure and the sample temperature independently. Using this equipment, we studied the equilibrium defects introduced during high-temperature annealings under defined As-vapour pressure. We systematically varied annealing temperature, As-partial pressure, annealing time, and quenching rate for Te-doped GaAs. The results will be discussed in the light of the existing theoretical knowledge on equilibrium defects.

DEFECT CONTROL IN As-RICH GaAs

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key words: non-stoichiometric GaAs, LT-GaAs, antisite defects, Ga vacancies, ultrafast phenomena

The incorporation of non-stoichiometric, excess As in GaAs produces native defects such as As_{Ga} , antisite defects, As_i interstitials or V_{Ga} vacancies. In GaAs grown by MBE at temperatures near 200°C (LT-GaAs) we found with magnetic resonance and optical absorption spectroscopies neutral As_{Ga}^0 in concentrations up to 10^{20} cm^{-3} and ionized As_{Ga}^+ around 10^{18} cm^{-3} . These concentrations are decreasing with increasing growth temperature, but can be well reproduced if careful control of substrate temperature and As/Ga flux ratio is established. The concentration of the ionized As_{Ga}^+ antisite defects was found to correlate surprisingly well with three times the concentration of V_{Ga} vacancies detected by slow positron annihilation in these thin films. This finding allows the conclusion that V_{Ga} triple acceptors are indeed the dominant native acceptor in these layers. Subpicosecond electron response time, as measured e.g. optically by pump-probe transient absorption or reflection, was found to be related to $[\text{As}_{\text{Ga}}^+]$, indicating that electron trapping dominates these ultrafast processes. In undoped LT-GaAs, the ionized $[\text{As}_{\text{Ga}}^+]$ may amount to about 5% of the total concentration of As_{Ga} .

In order to decrease the trapping time in MBE-GaAs grown at higher temperatures, we studied p-doping with Be to introduce in a controlled way further acceptors. For high Be-doping levels we found subpicosecond response times even at growth temperatures of $T=300^\circ\text{C}$, together with an increased $[\text{As}_{\text{Ga}}^+]$. The ratio $[\text{As}_{\text{Ga}}^+]/[\text{As}_{\text{Ga}}^0]$ was found to be increased above 50%. Furthermore, the $[\text{As}_{\text{Ga}}]$ in Be-doped LT-GaAs turned out to be higher and more stable upon annealing than in undoped LT-GaAs grown at the same temperature. Compensation of the compressive strain of As_{Ga} by the tensile strain around the small Be_{Ga} acceptors is suggested to play a role in this stabilization. A thermally stable, high As_{Ga}^0 and As_{Ga}^+ concentration due to the incorporation of appropriate impurities offers new prospects for the application of As-rich GaAs such as in ultrafast optoelectronics.

AS ANTISITE-RELATED DEFECTS DETECTED BY SPIN-DEPENDENT RECOMBINATION IN D (SI) DOPED GAAS GROWN BY MBE AT LOW TEMPERATURE

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key words: intrinsic defects, GaAs, MBE, EDMR, spin-dependent recombination, SDR

Investigations of electrically detected magnetic resonance (EDMR) via spin-dependent recombination (SDR) in a delta doped (Si) GaAs sample grown by the molecular beam epitaxy at 300°C (LT-MBE) in a [311]-A direction have shown the signals due to an arsenic antisite-related defect. The sample consists of a delta doped region with a two dimensional Si concentration of about $N_{2D} = 3.4 \times 10^{12} \text{ cm}^{-2}$ within 0.2 μm of MBE GaAs grown at 300°C. The observed EDMR spectrum shows the well-known quartet hyperfine split spectrum of an As antisite-related defect with a g - factor of 2.045 and a hyperfine splitting due to ^{75}As ($I = 3/2$) of 2600 MHz. The EDMR parameter are very similar to those for the EL2 defect observed in bulk GaAs.

Optically detected magnetic resonance (ODMR) investigations in similar grown MBE GaAs have shown high concentrations of As antisite-related defects [1]. Whether these defects belong to EL2 or another As antisite-related defect is not the matter of the present discussion. In this contribution we concentrate our discussion on the mechanism which can be responsible for the observation of the EDMR spectrum in terms of spin-dependent recombination processes, i.e. donor - acceptor recombination and the role of spin polarization effects. The observation of an As antisite-related defect in this slightly n-type GaAs under illumination is only explainable in terms of conduction in two distinct conducting channels. The present discussions are important for the investigation of other devices based on III-V semiconductors.

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CREATION OF Ga_{As} ANTISITES IN GAAS BY TRANSMUTATION OF RADIOACTIVE $^{71}\text{As}_{\text{As}}$ TO STABLE $^{71}\text{Ga}_{\text{As}}$

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Keywords: GaAs, Ga_{As} antisite, transmutation doping

An important class of intrinsic defects in compound semiconductors of type AB are antisites where an A atom is placed on a B site or vice versa and it is an interesting topic to know the energy levels of these defects. It is still an open question what the levels of the Ga_{As} antisite in GaAs are. From valence arguments Ga_{As} should act as a double acceptor. In agreement with this GaAs grown from a Ga rich melt is often p-type with an acceptor state at 78 meV and exhibits a photoluminescence (PL) emission at 1.441 eV [1]. Therefore this level and this emission is often assigned to the Ga_{As} antisite [2], however, there is also evidence that this level is due to B_{As} [3].

The only way to create Ga_{As} antisites in GaAs in a controlled way and to avoid the introduction of any other defect during the formation process is the transmutation of radioactive ^{71}As to stable ^{71}Ga . In addition, this approach offers the possibility to use the nuclear life-time of the involved isotopes as element specific labels to identify the levels of the Ga_{As} antisite.

We doped GaAs with radioactive ^{71}As by ion implantation (260 keV , $3 \times 10^{12} \text{ cm}^{-2}$) at ISOLDE at CERN followed by annealing at 1123 K. After this ^{71}As occupies As lattice sites in GaAs. Then it transmutes via the radioactive decay chain $^{71}\text{As}_{\text{As}}$ ($T_{1/2} = 64 \text{ h}$) $\rightarrow$ $^{71}\text{Ge}_{\text{As}}$ ($T_{1/2} = 11.2 \text{ d}$) $\rightarrow$ $^{71}\text{Ga}_{\text{As}}$ to stable ^{71}Ga creating Ga_{As} antisites in GaAs. This chemical transmutation was monitored with PL spectroscopy at 4.2 K. Within the first days after doping with ^{71}As the intensity of the $(e, \text{Ge}_{\text{As}})$ line at 1.479 eV is increasing since $^{71}\text{Ge}_{\text{As}}$ acceptors are created by the decay of $^{71}\text{As}_{\text{As}}$ to $^{71}\text{Ge}_{\text{As}}$. Then the $(e, \text{Ge}_{\text{As}})$ -intensity is decreasing with the half-life of $^{71}\text{Ge}_{\text{As}}$ (11.2 d) since $^{71}\text{Ge}_{\text{As}}$ is transmuting to $^{71}\text{Ga}_{\text{As}}$ and after 100 days no $(e, \text{Ge}_{\text{As}})$ emission can be detected any longer. This transient behavior confirms the assignment of the 1.479 eV line to the acceptor state of Ge_{As} and it proves that finally all $^{71}\text{Ge}_{\text{As}}$ acceptors transmuted to $^{71}\text{Ga}_{\text{As}}$ antisite defects. From this and the implanted ^{71}As dose we conclude that finally the implanted layer is doped with Ga_{As} antisites distributed in a Gaussian shaped profile centered at 110 nm depth with a width of 50 nm and a peak concentration of up to $2 \times 10^{17} \text{ cm}^{-3}$.

Remarkably, at this final state the PL spectra of all Ga_{As} doped samples do not differ from spectra of samples which have been only annealed and not implanted. This shows that there is no intense PL emission from Ga_{As} antisites between 1.515 and 0.9 eV. In particular we do *not* observe a PL line at 1.441 eV! This line and the corresponding 78-meV acceptor level is often assigned to Ga_{As} antisite defects. However, our results show, that this assignment is not correct and that the 78-meV acceptor level in Ga-rich GaAs belongs to another defect (a possible candidate might be B_{As} [3]).

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OBSERVATION OF METASTABLE ELECTRON CAPTURE IN N-TYPE GALLIUM ARSENIDE STUDIED BY OPTICALLY DETECTED MAGNETIC RESONANCE

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Key words: intrinsic defects, GaAs, metastability, ODMR

A set of slightly n-type GaAs materials ($10^{14} < n < 10^{16} \text{ cm}^{-3}$ at room temperature) from different suppliers have been studied by optical absorption and optically detected magnetic resonance (ODMR) via the magnetic circular dichroism of optical absorption (MCDA). In all samples the spectrum of neutral EL2, EL2^0 have been measured by optical absorption. By using a weak measurement light intensity (photon flux about $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$) a metastable population of paramagnetic EL2^+ , have been observed by MCDA within a few minutes at 1.5 K. As expected by extrapolation of the measurement light intensity to zero, no paramagnetic EL2 could be observed in darkness in these slightly n-type GaAs samples. In addition, MCDA and optically detected electron paramagnetic resonance (ODEPR) have shown the spectrum of a defect of unknown origin, previously called D1 [1]. However, the signals due to D1 were not affected by the metastable population of EL2^+ .

The observations suggest that electron centers with high optical cross sections different from EL2^0 exist in n-type GaAs with energy levels in the upper part of the bandgap. The electrons liberated from EL2^0 via the process $\text{EL2}^0 \Rightarrow \text{EL2}^+ + e^-_{\text{CB}}$ must be captured by these electron centers. The population of the defects by electrons is metastable in the sense that the depopulation takes place only by heating the samples up to about 100 K, a temperature near to the recovery temperature of about 130 K of metastable EL2. From the determination of the metastable population of paramagnetic EL2 we estimate a concentration of electron capture centers of the order of 10^{15} cm^{-3} . The existence of defects with metastable properties in GaAs other than EL2 have been demonstrated for the oxygen defect [2] and probably for defects which belong to reverse contrast [3]. Our samples do not contain any oxygen-related defects. Further, a correlation to reverse contrast could not be established. In the present contribution we discuss different models for those new electron capture centers which show metastable properties.

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METASTABLE AMORPHOUS STRUCTURE IN ION IMPLANTED GaAs

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Key Words: GaAs, implantation, amorphous structures, order/disorder

Disorder is introduced into GaAs by implantation of $^{30}\text{Si}^+$ ions and studied by Raman scattering, RS. A very wide range of ion doses (8×10^{12} - $3 \times 10^{16} / \text{cm}^2$), dose rates, and implant temperatures was used. RS spectra were deconvoluted in a novel way so that the apparent 'background' signal was also included in the analysis. New arguments are given that: a) this 'background' is in fact a low frequency peak and hence a meaningful signal, equivalent to the analogous 'boson peak', BP, regularly observed in glassy solids, and b) represents a specific amorphous phase, different than a well known continuous-random-network amorphous phase, a-CRN.

A systematic and self-consistent behavior of the BP signal is observed in all studied implantation conditions. BP is the only component of RS spectra whose relative intensity was always proportional to the total disorder, as evaluated by RBS, regardless as to whether higher disorder is produced by higher dose, or higher rate or lower implant temperatures. BP increases monotonically with the total disorder at the expense of fractions of other crystalline and a-CRN components. Particularly, for already completely amorphized layer, after all crystalline-phase-related peaks had disappeared, further implantation converts the a-CRN into a-BP. Relative fractions of these two amorphous components can be changed in a predictable way by varying implantation parameters: dose, rate, and implant temperature.

These results are consistent with the physical picture in which the BP signal in a-GaAs has been interpreted within the fractal model¹. The amorphous phase in GaAs is then understood as a two-phase composite of strained nanometer-size regions within relaxed continuous random network. The excess vibrational states in RS and the resulting 'boson peak' originate from the strained bonds within these 'blobs' and at the interfaces of these two regions. Analysis of temperature dependence revealed that for any selected dose and rate a-BP component is much more sensitive to the implantation temperature, T_{impl} , than a-CRN. For example, for the dose $3 \times 10^{16} / \text{cm}^2$ the a-BP/a-CRN intensity ratio is 400% lower for $T_{\text{impl}} = 40^\circ\text{C}$ than for $T_{\text{impl}} = -2^\circ\text{C}$. Hence, a-BP structure is thermally less stable and can be drastically decreased by appropriate selection of implantation parameters. On the other hand, a-BP relative fraction can be considerably increased by additional implantation, i.e. by additional impact-energy transfer to the layer. a-BP can thus be envisioned as a metastable structure of amorphous phase having higher free energy than a regular a-CRN

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ODMR INVESTIGATION OF 2.3 MEV PROTON IRRADIATED GaAs

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Key Words: GaAs, ODEPR, radiation effects, defects, metastability

Magnetic resonance studies on radiation damage in GaAs have primarily been conducted on material irradiated with electrons. There have been many studies on the electronic and structural characterisation of defects introduced during this type of particle irradiation. Proton and heavier particle irradiation are used extensively in device isolation and definition, yet there is very little know regarding the structural properties of defects introduced by these particles.

In this study, using optically detected magnetic resonance (ODMR) via the magnetic circular dichroism of the optical absorption (MCDA) we investigated the defects introduced in bulk Te-doped and semi-insulating (SI) GaAs during 2.3 MeV proton irradiation at 300 K. From ODEPR measurements in K-band and modelling we conclude that proton irradiation of Te-GaAs introduced the anti-structure pair ($\text{As}_{\text{Ga}} - \text{Ga}_{\text{As}}$, As antisite defect with a Ga antisite in the next nearest neighbour shell¹). This is the same defect as observed in similar material irradiated with high energy (2 MeV) electrons to a fluence of $5 \times 10^{17} \text{ cm}^{-2}$. This anti-structure pair exhibits the typical metastability associated with the arsenic antisite family of defects. Illumination with 1.05 eV light at 1.5 K for 20 minutes converts this defect to a metastable state which is electrically and optically inactive.

Proton irradiation of SI GaAs introduced what appeared to be an arsenic antisite type defect, however, the measured ODEPR spectrum is not entirely consistent with this speculation. The peak intensities are not equal and the hyperfine splitting does not follow the trend as would be expected for the presence of only an arsenic antisite type defect. It is also seen that this defect does not exhibit the expected metastability and it is believed that there is another defect with an EPR signal superimposed on that of the arsenic antisite type defect.

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POSITRON ANNIHILATION AND SCANNING TUNNELING MICROSCOPY USED TO CHARACTERIZE DEFECTS IN HIGHLY SI-DOPED GaAs

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Keywords: GaAs, positron annihilation, STM, $\text{Si}_{\text{Ga}}\text{-V}_{\text{Ga}}$ complexes

Positron annihilation and scanning tunneling microscopy (STM) were combined to characterise defects in highly silicon doped GaAs. An increasing density of mono-vacancies, having a positron lifetime of 262 ps, was observed by positron lifetime spectroscopy with increasing Si-doping concentration. These vacancies were identified by STM as $(\text{Si}_{\text{Ga}}\text{-V}_{\text{Ga}})$ complexes. The concentration of shallow positron traps increased with the Si concentration too. The shallow traps are identified by STM as Sj_{As} acceptors. The STM results suggest that positron trapping at shallow traps can also be related to small Si clusters. We demonstrate that the combination of positron annihilation and scanning tunneling microscopy is a powerful tool to obtain microscopic data about the concentration and nature of point defects.

Ga VACANCIES AS COMPENSATING CENTERS IN HOMOGENEOUSLY OR δ -DOPED GaAs(Si) LAYERS

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Key words: superlattice, compensation, positron spectroscopy

The n -type doping of GaAs by Si atoms is a straightforward procedure until above 10^{19} cm^{-3} a strong deactivation of free carriers occurs. This phenomenon has been tried to explain with the autocompensation mechanism which follows from the amphoteric nature of the Si impurity. The Si-doping of GaAs in delta planes (δ -doping) has been proposed as a method to overcome the problems. However, also the δ -doped samples become compensated when the planar doping increases above $1 \times 10^{13} \text{ cm}^{-2}$.

Highly Si-doped GaAs samples were grown by molecular beam epitaxy (MBE) on (100)-oriented GaAs substrates at temperature of 900 K. The Si-doping concentration of these samples varied between $1 \times 10^{18} \text{ cm}^{-3}$ and $5 \times 10^{19} \text{ cm}^{-3}$. Above $5 \times 10^{18} \text{ cm}^{-3}$ the strong reduction of free carriers was seen. Positron annihilation experiments reveal negative vacancies and ion-type acceptors in the compensated layers.

Si δ -doped GaAs samples were grown by MBE on (100) oriented GaAs wafers at temperature of 670 K. Each sample contained 100 δ -doping planes with areal concentrations of 0.01-0.3 ML (1 ML = $6.2 \times 10^{14} \text{ cm}^{-2}$) and with adjacent planes separated by 500 Å of undoped GaAs. The noticeable electrical deactivation was seen in two samples which were well above the critical planar Si-doping concentration $1 \times 10^{13} \text{ cm}^{-2}$. Positron annihilation experiments reveal vacancies and ion-type defects, which are located in undoped material between the delta planes.

The vacancies are identified as V_{Ga} . The ion-type acceptors are assigned to Si_{As} and Ga_{As} in homogeneously and δ -doped layers, respectively. The compensation of free carriers can be explained by these defects which have concentrations in the range 10^{19} cm^{-3} .

DECAY KINETICS OF GROWTH-INDUCED ALIGNMENT OF THE FIRST NEIGHBOR SHELL OF CAs IN AlGaAs:

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Key Words: Carbon in AlGaAs; Vibrational spectroscopy; Growth-induced alignment

We have recently discovered that the first neighbor shell of CAs in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is aligned in some samples following growth by metalorganic molecular beam epitaxy.¹ The C atom's Al neighbors lie preferentially in a particular {110} plane perpendicular to the (001) growth surface. This alignment of the first neighbor shell was detected from the polarisation dependence of the vibrational absorption bands assigned to C_{As} .² I.e., for light incident along the [001] direction, the intensities of the C_{As} vibrational bands depend strongly on whether the light is polarised with $E//[110]$ or $E//[1\bar{1}0]$. Further, if the C_{As} is passivated by hydrogen, it is known that the H preferentially interrupts C_{As} -Ga bonds rather than the stronger C_{As} -Al bonds.³ This leads to an alignment of the C_{As} -H complexes for samples in which the C atom's first neighbor shell is aligned. The alignment of the C_{As} -H complexes gives rise to a strong polarisation dependence of the H-stretching vibrational absorption bands that has also been used as a probe of the alignment associated with the C atom to which the hydrogen is bound.¹

Stress-induced alignment techniques have long been used to study the motion of defects in solids. Here, we report studies of the decay kinetics of the growth-induced alignment upon thermal annealing. Presumably the loss of alignment is due to motion of the C atom. Thus the decay kinetics provide a novel source of information about the motion of C in the alloy.

Work performed at Lehigh University was supported by the U.S. Navy Office of Naval Research under Contract No. N00014-94-1-0117.

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DEFECTS IN InP AND InGaAsP GROWN BY He-PLASMA ENHANCED MOLECULAR BEAM EPITAXY

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Key Words: Molecular Beam Epitaxy, Plasma, Positrons, Resistivity

InP and $\text{In}_{0.6}\text{Ga}_{0.4}\text{As}_{0.85}\text{P}_{0.15}$ grown using gas source molecular beam epitaxy with the growth surface simultaneously subjected to a He-plasma, generated by an electron cyclotron resonance source, have shown some interesting properties that have significant technological potential. For example, InP grown in the temperature range $\sim 400\text{--}450^\circ\text{C}$ exhibits a resistivity of $>10^5 \Omega\text{-cm}$ without the need for introducing deep level impurities such as iron. The InGaAsP also has high resistivities relative to material grown without a plasma, but more importantly it exhibits ultra-fast (sub-picosecond) optical response times with wavelength tunability allowing high speed optical switches operating on band-to-band absorption saturation.

In this paper we will report on our current knowledge of the grown-in defects that account for the material properties. Samples have been grown with and without Be-doping. Rapid thermal anneal studies up to 700°C have been carried out for 10 s time periods.

Results of temperature dependent resistivity and current injection measurements on InP indicate the presence of a trap lying at $\sim E_C - 0.4 \text{ eV}$ with a net trap density of $\sim 1 \times 10^{17} \text{ cm}^{-3}$. The effect of doping with 10^{18} cm^{-3} Be is to increase the resistivity by a factor of 5. Similar effects are seen in the InGaAsP where the resistivities are ~ 40 and $500 \Omega\text{-cm}$ without and with Be doping respectively. The anneal behaviour of the resistivity shows a factor of 5 increase at temperatures of ~ 550 and 650°C for InP, with and without Be doping. After annealing at 700°C the doped sample becomes low resistivity p-type, while the undoped sample recovers to the as-grown resistivity. The Be-doped InGaAsP samples show similar behaviour with a factor of 8 increase in resistivity after anneal at $\sim 500^\circ\text{C}$ while the undoped sample exhibits only a small resistivity increase for anneals in the range $550\text{--}650^\circ\text{C}$.

The defect characteristics of the samples were probed by a variable energy positron beam through measurement of the Doppler broadening of the annihilation line. The S-parameter values for both InP and InGaAsP grown with the plasma revealed the existence of vacancy-type defects independent of Be doping. After annealing at 700°C the size of the defects is found to increase substantially in the undoped materials while Be-doping appears to prevent defect agglomeration. More detailed anneal experiments are in progress to establish a correlation with the resistivity data.

EL2 INDUCED ENHANCEMENT OF DONOR-ACCEPTOR PAIR LUMINESCENCE IN GaAs

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Key Words: GaAs, EL2, photoluminescence, metastability

Band-edge photoluminescence in semi-insulating GaAs at 2K can be excited in a two step process via the mid-gap EL2 level. The efficiency of this mechanism is a few percent in comparison with conventional above band gap excitation at the same excitation power level. While the conventionally excited luminescence of our samples is dominated by conduction band to shallow acceptor transitions, the two step-excited spectra entirely consist of donor-acceptor pair transitions. The superposition of an above and below band-gap excitation source leads to a luminescence intensity, that exceeds by far the sum of both intensities. The spectra excited with the two superimposed laser beams show an especially strong enhancement of the donor-acceptor pair luminescence. We explain this preferential excitation of donor acceptor pairs in the two step and double beam excited spectra by the involvement of the shallow donor like hydrogenic $EL2^0_{n=2}$ state in the transition, that was found to participate in the deep EL2-PL at low temperatures [1]. Above band gap light can regenerate the EL2 defect from its metastable state. The photoluminescence intensity rises considerably during this recovery, when measured in the maximum of the donor-acceptor luminescence band, but not in the free to bound band. This lets us suppose that the shallow EL2 level also plays an important role in conventionally excited luminescence.

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DETECTION AND IDENTIFICATION OF THE EL2 METASTABLE STATE IN GaAs

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Keywords: GaAs, EL2, metastable, antisite, excited state.

Although a considerable amount of works has been devoted to its study, the metastable state induced by photo-excitation of the EL2 defect at low temperature, has escaped so far detection. We will report a study of the photocapacitance kinetics versus the illumination flux, wavelength and temperature. It is performed on a n-type, Si doped (at a level of $7 \times 10^{16} \text{ cm}^{-3}$), Czochralski grown GaAs which contains $2.8 \times 10^{16} \text{ cm}^{-3}$ EL2 defects, as determined by Deep Level Transient Spectroscopy. This study demonstrates unambiguously that the EL2 metastable state possesses the same charge than the filled stable state and is associated with a level located at $\sim 40 \text{ meV}$ below the conduction band. This determination is confirmed by a study of the temperature dependence of the apparent recovery of the metastable to the stable state, in the absence of photo-excitation and in the range 70-100 K, which is in fact related to the occupancy of the metastable state in thermodynamical equilibrium. We will demonstrate that the metastable level corresponds to the first excited state of the stable EL2 state. This excited state is derived from the L band, providing a simple explanation for the metastable character of the level. Electron localised on the excited (metastable) state cannot decay down to the ground (stable) state at low temperature because the electron-electron interaction is too large. This decay can only occur when a large enough atomic distortion of the As antisite can be induced to compensate for the electron-electron interaction. We will account quantitatively for the temperature and free carrier concentration dependences of the rate of transformation from the metastable to the stable state in terms of this metastable energy level and of the energy difference between the L and r bands.

THE MICROSTRUCTURE OF THE EL2 DEFECT IN GaAs - A DIFFERENT LOOK TO FORMER SPIN RESONANCE DATA

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Despite of more than one decade of research activities the micro structure of the EL2 antisite defect in GaAs is still under discussion. It was concluded from ODENDOR experiments, that the EL2 defect consists of an Arsenic on a Gallium site with an Arsenic interstitial in [111] direction [1]. However, there are many arguments against this model. Up to now no attempt was made to check this model conclusively by investigating whether or not the hyperfine and ligand hyperfine interaction constants for the nearest As neighbours including the [111] As interstitial as derived from ODENDOR are consistent with the shape of the corresponding ODEPR spectrum and with conventional EPR spectra of other authors. It turned out in our investigation, that due to the relatively large hyperfine interactions approximate solutions of the spin Hamiltonian using perturbation theory are not sufficiently accurate when recalculating EPR spectra from the ODENDOR interaction data. Therefore we have faced the problem by an exact diagonalisation of the spin Hamiltonian for the electron with up to the five neighbour nuclei with strongest interaction and taking into account any forbidden transition with its proper intensity. This way it was found, that taking into account the interstitial As results in a simulated ODEPR spectrum significantly broader than the experimental one. This means, that the ODENDOR analysis is definitely at least partially wrong, and these data must no longer be taken as evidence for the existence of an [111] As interstitial as claimed. Additionally we introduced a new way to efficiently calculate large spin Hamiltonian matrices based on the fact that they can be built up diagonal dominant. This made it possible to simulate also the line shapes of EPR spectra with many magnetic field steps. Using these technique we simulated also different conventional EL2 EPR spectra. This again verified, that leaving out the [111] As interstitial is essential to obtain a good fit to the experimental data. At the same time, the fact that both the ODEPR and conventional EPR spectra can be fitted using the same input data provides a good piece of evidence that the same defect species was measured in both experiments.

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DISLOCATION ACTIVITIES IN BULK GeSi ALLOYS

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Key Words: GeSi, alloy, dislocations, velocity, hardening, growth

GeSi alloy is of important in view of its variable band gap and lattice parameter according to the alloy composition. Though dislocations affect the electrical and optical properties of GeSi alloys and limit their application in various electronic and opto-electronic devices, very little is known on their dynamic properties and interaction with solutes in the alloys except the generation of misfit dislocations related to the mismatch at the film/substrate interface. Such misfit dislocations are introduced and move by the unrelaxed biaxial residual stress, which hinders the study of the native properties of dislocations. Consequently, it is necessary to grown bulk GeSi alloys and to measure the dynamic activities of isolated dislocations under defined stress distribution. Moreover, little attention has been paid to the appearance of the unique properties of dislocations due to alloying. This paper reports the dislocation activities and alloying effects in GeSi alloys grown as bulk crystals.

We succeeded in growing GeSi bulk alloys by the Czochralski technique. Full single and partly single crystals were obtained. - Especially, a single crystal of 60 mm in length and 20 mm in diameter with Si content 2 at% and a single crystal of 40 mm in length and 30 mm in diameter with Si content 6 at% were obtained. With an increase in Si composition, the crystals changed from single material to polycrystal in the middle part of the boule, which relates to the occurrence of constitutional supercooling.

Velocities of dislocations are found to decrease monotonously with increasing Si content, reaching about a quarter of that in Ge at 5.3 at%, in the temperature range 450 - 700 °C and the stress range 3 - 20 MPa. The velocities of dislocations in GeSi alloys can be described as a function of stress and temperature by the same type of empirical equation as those in other semiconductors. The yield stress of the GeSi alloy increases with increasing Si content from 0 to 40 at% and is temperature-insensitive at high temperatures. These results mean that the dislocations in GeSi alloys move overcoming built-in a thermal stress fields which is absent in elemental or compound semiconductors and it gives rise to hardening effect.

ELECTRICAL CHARACTERISATION OF ELECTRON BEAM INDUCED DEFECTS IN EPITAXIALLY GROWN $\text{Si}_{1-x}\text{Ge}_x$

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Key Words: DLTS, SiGe, IV, CV, Schottky diodes, Defect engineering, Barrier height

The properties of SiGe/Si heterostructures have recently received considerable attention, since they offer the possibility of bandgap engineering and improved device (heterojunction bipolar transistors) performance. The optimal use of these alloys in Si-based integrated circuits requires strict control over metallisation processes. Electron beam (E-beam) deposition enables the controlled deposition of refractory metals at high rates, and yields better metal adhesion to the substrate. During this process low energy electrons create damage in the lattice, introducing electron and hole traps at and below the metal-semiconductor interface.

We have fabricated Ti and Sc Schottky barrier diodes (SBDs) on n- and p-type $\text{Si}_{1-x}\text{Ge}_x$ by electron beam deposition. The electrical properties of Sc SBDs on p-type $\text{Si}_{1-x}\text{Ge}_x$ show that the reverse current increases and the barrier heights decrease with concentration of Ge and varies as the band gap with Ge content for strained films. These results suggest that the Fermi level is pinned to the conduction band at the interface of the binary alloy.

We have used deep level transient spectroscopy (DLTS) to investigate the electronic properties of defects introduced during E-beam metallisation in n- and p- $\text{Si}_{1-x}\text{Ge}_x$ with different compositions of Ge during E-beam metallisation. To learn more about the physical origin of these defects and their dependence on Ge content, we have compared their electronic properties to those of primary defects induced during 5.4 MeV alpha-particle irradiation. E-beam deposition introduced more defects than alpha-particle irradiation in both n- and p-type material. The most prominent defect observed in n- $\text{Si}_{1-x}\text{Ge}_x$ after E-beam deposition has a level at $E_c - 0.44$ eV. The energy level of this defect was not influenced by a change in Ge content, indicating that it is pinned to the conduction band. In p-type Si the main defect has an energy level at $E_v + 0.52$ eV, in p- $\text{Si}_{1-x}\text{Ge}_x$ this defect has an energy level that varies as $E_v + (0.52 - 1.1 x)$ eV. This variation in energy level position follows the same trend as the valence band offset in $\text{Si}_{1-x}\text{Ge}_x$ ($0.84 x$), suggesting that the main defect detected in p- $\text{Si}_{1-x}\text{Ge}_x$ is the same as that observed in p-Si.

The electronic properties of E-beam induced defects were the same for Ti and Sc SBDs. This shows that these defects do not depend on the metal used, but only on the interaction of the electrons from the electron beam with the substrate.

DEFECT ENGINEERING IN GaN TECHNOLOGY

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Key Words: GaN buffer layer, defects, stress, MOCVD

Early attempts at application of defect engineering in the GaN technology are presented. Our investigations have shown that during GaN growth on sapphire substrates the small changes of stress (smaller than the total stress in the common buffer layer) in the modified GaN buffer layer accompanied by the variation in the point defects (self-interstitials and vacancies) population in the main GaN layer.

The GaN layers were grown in a conventional metalorganic chemical vapor deposition (MOCVD) system. The growth process included the growth of the buffer layer at temperature of 500°C followed by a GaN main layer growth at temperature of 1040°C. A growth mode of the main GaN layer was found to vary from polycrystalline to epitaxial mode with the small changes of stress in the buffer layer. The surface morphology and the stress variation have been displayed by electron microscope and X-ray investigations.

Moreover, photoluminescence study showed that the variations affected an intensity of a yellow band and blue band relationship in the ranges of 2.2~eV and of 3.05~eV. As it took place, the α - β characteristics and Hall effect measurements detected variations in the carrier concentration and mobility. The buffer layer influences an activation of the impurity introduced in the main GaN layer. The undoped GaN layers have the following parameters: a free carrier concentration $n = 3 \times 10^{15} - 1 \times 10^{14} \text{ cm}^{-3}$, the full width at half maximum of the photoluminescence peak of 3.483~eV-5~meV at 6K.

DEFECTS IN SiGe

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Epitaxial layers of SiGe are mainly known from their use in fast, silicon-based microelectronics, e.g. as base layers in hetero-junction bipolar transistors; however, the improvement of their crystalline quality has made samples available which are suitable for defect studies in group-IV semiconductors.

Using epitaxial-growth techniques, such as molecular-beam epitaxy (MBE), layers of high-crystalline quality of tensile- and compressive-strained material as well as of strain-relaxed material of any composition can be grown on silicon substrates; in these layers tailored impurity distributions can be included during the growth. Hence, the band gap, and the size and type of strain can be varied over fairly wide ranges, offering a flexible system for studies of the influence of these parameters on defects in Si and Ge, in very well-defined samples.

The growth of strain-relaxed layers of crystalline $\text{Si}_{1-x}\text{Ge}_x$ of any x , on a $\langle 100 \rangle$ -Si substrate, with a sufficiently low concentration of as-grown defects such that intentionally induced defects can be studied, has been and still is a challenging task. The progress in growing these layers will be reviewed with the main emphasis on our own MBE-based efforts which, for the time being, has resulted in layers of $x \leq 0.50$ of sufficient quality for defect studies.

As an example of the use of strain and strain-relaxed SiGe in defect studies, the Sb-vacancy interaction will be discussed. Antimony is known to diffuse predominantly via vacancies in Si and Ge, and, as such, its diffusivity is relatively simple. By studying both the strain and the chemical effects of the presence of the Ge in the SiGe layers on the Sb diffusivity, it has been possible to isolate the influence of tensile and compressive strain on vacancy-assisted diffusion, and to compare it to theoretical predictions. The question as to whether the acceptor level in the forbidden gap, related to the Sb-vacancy pair, is pinned to the conduction or to the valence band or to none of them is important for a theoretical modelling of the diffusivity of antimony. The strain-relaxed SiGe system is particularly well suited for such investigations. We have studied the Sb-vacancy pair in strain-relaxed SiGe using deep level transient spectroscopy after low-temperature particle irradiation. By varying the composition of the SiGe layers we have established that this level is pinned to the conduction band.

ISOTOPIC SHIFTS OF THE ROTATIONAL STATES OF INTERSTITIAL OXYGEN IN GERMANIUM

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Key Words: Ge:O, isotope shift, phonon spectroscopy

It has been shown recently that there is a series of phonon scattering resonances between .18 meV and 4.08 meV in germanium that can be associated with rotational states up to $l = \pm 5$ of interstitial oxygen[1]. For rigid rotation of a free Ge-O-Ge quasi-molecule around its inertial axis parallel to $\langle 111 \rangle$ the momentum of inertia would be given by the reduced mass and by the distance r_0 of the oxygen from the Ge-Ge axis. From the fit to the resonance energies this would lead to $r_0 = 93$ pm and to small Ge-isotope shifts lying within the observed linewidth. However, to unravel the contribution of the oxygen, its immediate germanium neighbours, and the lattice to these states it is necessary to determine the level positions in several isotopically enriched germanium crystals as well as for the oxygen isotopes.

We report on such measurements which show that the Ge-associated shifts are distinctly larger and the ^{18}O -associated shift is smaller than calculated with the above assumption. The Ge-associated shifts appear to be even larger than compatible with an isotope-induced inhomogeneous linewidth of the resonances in natural germanium. This could indicate some average coupling of the lattice to these low-energy excitations.

Through the reduction of the strong isotope scattering at high phonon energies the use of isotopically enriched Ge has facilitated the observation of a higher resonance around 5.8 meV (position depending on Ge-isotope) which probably belongs to the rotational state $l = \pm 6$. A weak further resonance observed near 4.75 meV is possibly associated with a transition to the first excited radial state. If so, this could mean a relatively low central barrier of about 12 meV.

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DEEP LEVEL TRANSIENT SPECTROSCOPY COMBINED WITH PERTURBED ANGULAR CORRELATION ON RADIOACTIVE ^{111}In ATOMS IN GERMANIUM

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Key words: Germanium; DLTS; PAC; Impurities; Vacancies; Pairing reaction

Deep level transient spectroscopy (DLTS) is an important method to study deep centre defects in semiconductors [1]. A weakness of this method, however, is that DLTS does not contain information on the chemical nature and microscopic structure of the observed defects. This deficiency makes it difficult to correlate DLTS with structural sensitive methods like, e.g., Electron Paramagnetic Resonance (EPR). In a recent development it was shown that chemical information may be added by applying DLTS to radioactive impurity atoms [2,3]. The decay of unstable elements then may lead to an increase or decrease of the measured DLTS signals as function of the decay time.

We have further developed this technique by using radioactive impurities which at the same time serve as probe atoms for the Perturbed Angular Correlation technique (PAC). In this way we get the chemical information and can exploit the capability of PAC to measure structure information at the atomic scale. This allows not only to focus on isolated impurities or impurity pairs but also, e.g., to study the pairing process of these impurities with intrinsic defects as will be shown in the following.

Ge crystals (n(Sb)- and p(Ga)-doping concentration $1 \cdot 10^{15} \text{ cm}^{-3}$) were implanted with the well known PAC probe ^{111}In (half-life $T_{1/2} = 2.8$ days) within a layer of 4 μm thickness resulting in a concentration of $5 \cdot 10^{13} \text{ cm}^{-3}$. Annealing at 600 °C removes the implantation damage and electrically activates the probe atoms. Subsequently Schottky contacts on n- and p-type Ge were prepared.

In one type of experiments the decay of the shallow level of ^{111}In to the deep level ^{111}Cd is directly monitored by the appearance of a DLTS signal at $E_v + 145 \text{ meV}$ which grows with the half-life of the decaying ^{111}In . In a second type of experiments the ^{111}In doped Ge crystals were additionally irradiated with 1.2 MeV electrons. In the following DLTS we observe among others an additional deep level at $E_v + 325 \text{ meV}$ which disappears with the half-life of ^{111}In . Combining this result with our PAC experiments [4] performed in the same way we can identify this level as the $[^{111}\text{In}^- \text{Vacancy}^0]$ -pair. Further experiments aimed at identifying the pairing of ^{111}In with self-interstitials as seen by PAC [4] will be discussed.

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MICROSCOPIC STUDY OF THE VACANCY AND SELF- INTERSTITIAL IN GERMANIUM BY PAC

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Key Words: Germanium; Vacancy; Self-Interstitial; Frenkel Pairs; PAC

The elementary point defects in Germanium have attracted intensive research for a long time but contrary to the defects in silicon no microscopic identification of either the vacancy or the self-interstitial has yet been accomplished for a variety of reasons. Nuclear probe techniques like PAC (Perturbed Angular Correlation) have increasingly been used to study defects in semiconductors on the atomic scale [1]. The application to intrinsic defects, however, has remained difficult due to the basic problem of defect identification. We report on experiments solving this problem by a direct correlation of the defect production close to the production threshold with the microscopic PAC analysing technique.

The experiments are performed with ^{111}In PAC probes implanted into Ge crystals in a μm thick region. Following implantation the crystals are completely annealed. Subsequently two types of experiments are performed:

(1) The ^{111}In probe serves as primary knock-on atom due to a recoil energy of 29 eV from a neutrino produced in the 13-decay of the probe's precursor, ^{111}Sn . This leads to the production of Frenkel pairs with the ^{111}In probe adjacent to a vacancy, resulting in a PAC frequency $V_{Q1}=54\text{ MHz}$ which identifies the vacancy signal.

(2) By 1.2 MeV electron irradiation performed at 77K mostly single Frenkel defects are produced. In a subsequent annealing sequence monitored by PAC two defect signals occur with $V_{Q1}=54\text{ MHz}$ and $v_{Q2}=420\text{ MHz}$ showing trapping of irradiation induced defects at the ^{111}In probe. This trapping is studied as function of the Fermi level (n- and p-doping) and trapping temperature. Some preliminary results have been presented in [2].

Combining the results of (1) and (2) numerous microscopic properties are obtained:

Vacancies (via V_{Q1}) and, by exclusion experiments, self-interstitials (via V_{Q2}) can be identified. Pair formation of the ^{111}In negative acceptor with neutral vacancies and positive self-interstitials is deduced at $T=200(5)$ and $T=220(5)\text{K}$, respectively, which explains a frequently observed stage in the literature which occurs around 200 K. An acceptor state for the vacancy at $E_v+0.20\text{ eV}$ and, tentatively, a donor state for the interstitial close to the conduction band ($E_C-40\text{ meV}$) result from the Fermi level dependence of the trapping behaviour.

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THE HYDROGEN-SATURATED SELF-INTERSTITIAL IN SILICON AND GERMANIUM

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Key Words: Silicon, hydrogen, self-interstitial, local modes, uniaxial stress

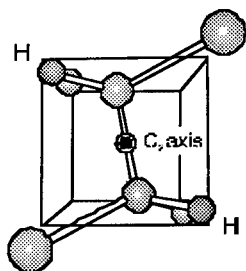


FIG. 1. The IH_2 defect

For more than two decades it has been known that implantation of protons into crystalline silicon gives rise to sharp infrared absorption lines due to excitation of hydrogen-related local vibrational modes. In the original work by Stein, a line at 1980 cm^{-1} was observed at room-temperature. This line was later shown to split into two at 1987 and 1990 cm^{-1} when the sample was cooled to liquid helium temperature. These two lines always appear with the same relative intensities which indicates that they originate from the same centre. In 1991, Xie *et al*¹ ascribed the two lines to the stretch-modes of the di-hydrogenated vacancy (VH_2). This assignment, however, disagrees with the recent work in which two other lines were shown to originate from VH_2 . In conclusion, the origin of the 1987 - and 1990-cm^{-1} lines remain unclear.

In this work the 1987 - and 1990-cm^{-1} lines have been investigated in detail. We show that these lines are correlated with two other lines at 743 and 748 cm^{-1} which we ascribe to Si-H bend-modes of the same defect. Isotope substitution experiments reveal that this defect contains two equivalent and weakly coupled hydrogen atoms. The line splittings observed when uniaxial stress is supplied to the sample show that the defect has monoclinic C_2 symmetry, i.e. a C_2 point group with the two-fold axis along $[100]$. Defects with this symmetry are rare in silicon. The orientations of the two equivalent Si-H bonds are determined. Similar investigations have been performed on the lines observed at 700 , 706 , 1882 , and 1884 cm^{-1} in proton-implanted germanium. The four lines in each material obviously originate from the same type of defect. The structure and the local vibrational

modes of the hydrogen-saturated self-interstitial (IH₂) in silicon and germanium have been calculated with *ab initio* local density functional cluster theory (see Fig. 1). The structural information on the defect giving rise to the lines at 743, 748, 1987, and 1990 cm⁻¹ in silicon and at 700, 706, 1882, and 1884 cm⁻¹ in germanium is in excellent agreement with the *ab initio* calculations on IH₂. Therefore, we ascribe these absorption lines to the IH₂ defect.

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DEFECT-RELATED RECOMBINATION PROCESSES IN LOW-DIMENSIONAL STRUCTURES OF ZnCdSe/ZnSe, CdTe/CdMnTe AND GaAs/AlGaAs

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Key Words: defects in heterostructures, II-VI and III-V semiconductors, bound excitons

Two-line structure of photoluminescence (PL) emission from quantum wells (QWs) of nominally undoped II-VI and III-V semiconductors is often related to a simultaneous observation of free and bound (typically neutral donor bound (DBE)) excitons. In this work we discuss defect-related recombination processes in doped and undoped QW structures of II-VI and III-V semiconductors. We show first (on the example of PL and time-resolved PL investigations) that formation scenario for DBEs in low dimensional structures can be different from that observed in bulk samples. Trapping of free excitons by donor impurities is relatively inefficient in the QW structures which show at low temperature PL emission of either localized (by potential fluctuations) or quasi-localized excitons. PL emission (intensity, PL excitation (PLE) spectrum and decay time) of such excitons is then weakly dependent on the doping level of QW regions of the structure.

We further show that DBE contribution to the overall PL emission can in some cases be strongly enhanced. This may lead to a confusing overestimation of the doping/contamination level. Such case we demonstrate on the example of GaAs/AlGaAs QW structure showing the presence of QW islands of a thickness smaller by 1 ML from the nominal. A fast inter-island exciton migration can be considerably slowed down once excitons are trapped by impurities. PL emission from QW islands is then dominated by DBE transitions even though defect concentration is low.

For undoped high quality structures defect-related peaks are not observed in the PL excitation spectra. We show however a puzzling observation of the strong DBE peaks in the PLE spectrum of CdTe/CdMnTe heterostructures consisting of three or four QWs and containing low (about 10%) Mn fraction in the barriers. A strong inter-QW exciton transfer is observed even though CdMnTe barriers are relatively thick (50 nm). The relevant mechanism of the transfer will be proposed and we will explain why DBE-related PLE peaks are then observed.

Se AND ZnSSe EPILAYERS BY DLTS AND ADMITTANCE SPECTROSCOPY

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Key words: ZnSe, ZnSSe, nitrogen, DLTS, admittance, p-type

In the effort of making blue-light emitting devices using II-VI large band gap materials it is well known that the compensation of nitrogen doped ZnSe epilayers causes difficulties in obtaining good p-type conductivity [1]. So far, optical methods have mainly been used to study the nitrogen level which is responsible for the p-type conductivity in ZnSe. In this paper, we report for the first time the observation of the nitrogen level in p-type ZnSe by electrical method using deep-level transient spectroscopy (DLTS) and admittance spectroscopy (AS). We have investigated nitrogen doped ZnSe epilayers grown on GaAs substrates by molecular beam epitaxy (MBE). The thickness of the epilayers was about 1 μm . The nitrogen was introduced from a nitrogen plasma source and doping levels ranging from 3×10^{16} to $5 \times 10^{17} \text{ cm}^{-3}$ were studied. Four major hole traps were observed with energy levels at 0.11, 0.46, 0.56 and 0.7 eV from the valence band. We attribute the level at 0.11 eV to a nitrogen acceptor which controls the p-type conduction of the material. A crude estimation of the 0.11 eV trap concentration obtained from DLTS data shows correlation with free carrier concentration due to nitrogen. No other direct observations of this important acceptor level in p-type ZnSe by electrical method have been reported in the literature so far. The three remaining levels may originate from the nitrogen doping process.

We also report on the observation of the nitrogen level by DLTS in p-type ZnSSe epilayers. They are grown approximately 1 μm thick on p-GaAs substrate with 20 nm ZnSe:N buffer. The nitrogen hole trap is observed at 0.13 eV from the valence band or slightly deeper in energy than in ZnSe. Sulphur mainly acts on the valence band so the activation energy of the nitrogen level is expected to increase, in a good agreement what we measure.

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ACCEPTOR STATES IN BORON DOPED SiGe QUANTUM WELLS

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SiGe quantum wells, acceptor states

The selectively doped *SiGe* quantum well structures (QWs) are of great interest for study of acceptor states which are degenerate in bulk material and should be split in two-dimensional (2D) systems due to space quantization and/or strain. The energy positions of ground and excited states of an acceptor can be controlled in a wide range by alloy composition, QW width, doping level and space position of an acceptor center. In this report the binding energies of 2D neutral (A^0) and positively charged (A^+) acceptor states in boron doped *SiGe* QWs for structures with the same QW width and doping level and different alloy composition are determined. So-called A^+ states (acceptors binding an additional hole) are of specific interest as they should exist in *SiGe* QWs in thermal equilibrium in contrast to bulk material where they can appear only due to excitation, f.i., by light.

The *p*-type *Si/SiGe/Si* QWs MBE-grown on the *n*-type *Si* substrate and selectively doped with boron were investigated at the temperatures of 4 up to 300 K. The QW thickness was of 200 Å. The *B* concentration inside the QW was of $3 \cdot 10^{17} \text{ cm}^{-3}$. Two delta-layers outside the QW with *B* concentration of $2 \cdot 10^{11} \text{ cm}^{-2}$ were used to obtain A^+ centers. Study of temperature dependence of conductivity and magnetoconductivity and electric field ionization of acceptor states allowed us to identify the boron acceptor A^+ and A^0 states. The binding energy of the A^+ state (about 2 meV) weakly increases with *Ge* content, *x*, while that of A^0 increases much stronger (for *x*=0.1 and 0.15 it is 11 and 18 meV, respectively). The experimental data are compared with theoretical calculations using zero-radius potential model.

This work was made possible in part by Grant No 96-02-17352 from Russian Basic Research Foundation and Volkswagen Grant.

ARRAY OF NANOHOLES ON A SILICON SURFACE CREATED BY UNIFORM-INTENSITY ELECTRON IRRADIATION

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Key Words: silicon, electron irradiation, nanoholes

We report the entirely novel phenomenon in nanometer space in Si; the creation of a two dimensional array of holes of a few nanometers in diameter on a Si crystal surface by uniform-intensity electron (140 to 200keV) irradiation. High-resolution transmission electron microscopy observation (HRTEM), combined with standard TEM techniques, has revealed that the nanoholes are created on the electron exit surface of a thin foil, and they are from 2 to 3nm in diameter and deeper than 10nm along the electron beam. It is also shown that they are distributed about 10 nm apart over the uniformly irradiated area and exhibit the habit planes of {111} and {100} which are parallel to the electron beam. The formation of the holes is observed regardless of the types of Si specimens, i. e. {111}, {110}, FZ and CZ.

This phenomenon is related to the formation of not Frenkel defects inside crystal but defects near the surface, since it is caused by the irradiation of electrons of even lower energy (140keV) and very sensitive to the pre-treatment of surfaces before irradiation. Concerning the formation process of the holes, TEM observation shows that the faint spot-like contrasts appear at the early stage, and with the increase of electron dose, the contrasts are gradually enhanced with their locations unchanged. With these experimental evidences, we suggest that moveable surface vacancies, accumulated at the steady state under electron irradiation, form spatially correlated shallow pits, and then the succeeding irradiation causes the deepening of the holes under the condition that the migration of surface atoms is suppressed. Even though arguments about the formation mechanism are ongoing, it is stressed that a narrow experimental window, through which we can observe the novel electron-irradiation-effect in Si involving surface vacancies, has been found.

NANOTUBES IN GaN AND THEIR FORMATION MECHANISM

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The mechanism of formation of the deleterious defect in GaN called a nanotube is proposed based on cross-section transmission electron microscopy. Formation of open-core dislocations that appear to be very similar to nanotubes has been reported in a number of crystals including SiC and ZnO. These defects have received a lot of attention especially in SiC because they are known to limit breakdown voltage of high power devices. The original explanation for these defects was given by Frank who suggested the formation of hollow-core screw dislocations. The open-core should represent an equilibrium between the extra surface free energy and the decrease in lattice strain energy. According to Frank's theory the radius of the hole is proportional to the square of the Burgers vector. However, the Frank equilibrium model can hardly explain the presence of these empty holes in GaN, since the measured and calculated Burgers vector differ by at least one order of magnitude. It will be shown that in GaN two related types of defects can be formed: nano-tubes along the c-axis and pinholes formed in the subsurface area. Both these defects start with V shaped facets on $\{10\bar{1}1\}$ polar planes.

The polarity of GaN was found to have large consequences on defect formation and a crystal growth rate. The growth rate turned out to be the slowest on $\{10\bar{1}1\}$ polar planes. Faceting on these planes in the early stage of growth or the presence of dopants or other impurities in later stages of growth, and the slow growth rate on these polar planes is proposed to be responsible for initiation of these defects. Development of pinholes into tubular, hollow nanotubes appears to depend on impurity attraction to these hollows which can stabilize their growth as tubes along the growth direction. Particular dislocations or inversion domains which are often found to be associated with these nanotubes (pinholes) appear not to be associated with their formation. The growth rate hierarchy for different polar facets might explain formation of these defects in a broad range of materials.

SELF-ASSEMBLY OF NANO-SCALE STRUCTURES AT SEMICONDUCTOR SURFACES

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Formation of quantum dots and quantum wires with properties satisfying device requirements on those structure's size, shape, uniformity, and density became possible by utilising self-ordering phenomena on crystal surfaces. In this talk I will discuss two basic theoretical aspects which crucially influence the growth of nano-scale structures:

- i) self-diffusion of cations on AlGaAs surfaces and
- ii) an analysis of surface energies and stress relief.

While the first is relevant for the formation of quantum wires on V-grooved sub-strates, the latter determines the shape of quantum dots.

*Work done in collaboration with E. Pehlke, A. Kley, and N. Moll

SPIN-DEPENDENT PROCESSES IN SELF-ASSEMBLY IMPURITY QUANTUM WIRES

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Key Words: quantum wires, spin-dependent confinement, EPR-EDEPR. We present the first findings of quantized conductance and EPR-EDEPR techniques which reveal the spin-dependent confinement and quantization phenomena in the silicon quantum wires created by electrostatically ordering self-assembly dipole boron (B^+-B^-) and phosphorus (P^+-P^-) centres. These C_{3v} symmetry dipole impurity centres are regularly arranged along the barriers of single longitudinal and lateral quantum wells (LQW and LaQW) which are naturally formed inside ultra-shallow silicon diffusion p-n junction. Short-time diffusion of boron and phosphorus, respectively, was performed from gas phase into n- and p- type Si (100) wafers using controlled surface injection of self-interstitials and vacancies. By varying the parameters of the surface oxide layer and diffusion temperature (800°C-1100°C) it was possible to define the criteria leading to the ultra-shallow p-n junction (5 nm-30 nm), which were controlled using SIMS and STM techniques. The cyclotron resonance (CR) and current-voltage (CV) dependencies, which are brought about the deflection of the bias voltage from the normal to the p-n junction plane, show that the p^+ - and n^+ -diffusion profiles consist of LQW or LaQW as a function of diffusion temperature. The logarithmic temperature dependence of resistivity and the quantized conductance finding obtained at 77K and 300K have revealed the quantum wire systems in a weak localization regime, which are induced by applied voltage inside both LQW and LaQW. Thermo-emf and tunnelling CV measurements demonstrate that these quantum wires seem to be created by electrostatic confining potential of self-assembly dipole B^+-B^- and P^+-P^- centres. The quantized conductance technique has identified new near-edge resonances that appear in $I(V)$ dependence and are due to hole scattering on single iron-related centres because of the interaction between the d-levels and minibands in quantum wires.

Spin-dependent electron/hole confinement has also made it possible to study single impurities, which are present in quantum wires, by the EPR-EDEPR method using the versions of both spin-dependent scattering and spin-dependent recombination. Besides signals from the iron-related centres, phosphorus and oxygen thermal donors, a new line that seems to be due to the C_{3v} symmetry B^+-B^- dipoles is found. Finally, the quantized conductance technique is applied, for the first time, to investigate the electrically- and optically-induced nuclear polarization in a weak magnetic field as a result of the hyperfine interaction of the lattice nuclei and spin-polarized Tomonaga-Luttinger Liquid in dipole impurity quantum wires.

AUGER-TYPE NONRADIATIVE RECOMBINATION PROCESSES IN BULK AND QUANTUM WELL STRUCTURES OF II-VI SEMICONDUCTORS CONTAINING TRANSITION METAL IONS

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Key Words: transition metal ions, II-VI and III-V materials, nonradiative recombination

Transition metal (TM) ions, such as iron, chromium or nickel, are common contaminants of bulk semiconductor materials. Intensive studies of recombination processes in TM doped/contaminated II-VI materials show a high efficiency of nonradiative transitions via TM ions. In addition to a known so-called bypassing process, recent photoluminescence (PL) and electron spin resonance (ESR) studies indicate importance of a new nonradiative process, in which energy of recombining electron-hole carriers is transferred to a nearby TM ion, which is then ionized. This, Auger-type, nonradiative process was first observed for Fe ion in ZnS:Cu. New experimental results of the authors indicate that the Auger-type processes are also important in ZnSe. A new type two-center Auger process is discussed based on the results of photo-ESR investigations of iron recharging processes in ZnSe. We show that electron trapping rate by Fe^{3+} ions is enhanced by Auger-type energy transfer to a nearby chromium ion.

TM-related recombination processes in low-dimensional structures were not studied till now. In this work we discuss first results of PL and time-resolved PL investigations of recombination processes in quantum well structures containing chromium. CdCrTe/CdMgTe and ZnCrTe/ZnMgTe quantum well (QW) structures were grown by molecular beam epitaxy. The former QW structure contained two CdTe and two CdCrTe QWs. In the latter case, three different structures were grown. Each of them contained a different chromium concentration in a QW. PL investigations show a strong reduction of PL emission intensity from chromium doped QWs, which, from the PL kinetics measurements, we explain by a rapid decrease of PL decay times of excitons in chromium containing QWs.

Two processes of TM-related nonradiative recombination of excitons in QWs are discussed. The first is an analog of the so-called bypassing process, in which exciton formation rate is reduced by efficient carriers trapping via TM ions. We show, however, that the present results indicate that the second process, Auger-type energy transfer from excitons to chromium ions, is likely responsible for the PL deactivation.

ERBIUM RELATED DEFECTS IN SILICON AND GALLIUM ARSENIDE

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Key words: erbium, silicon, gallium arsenide, defects, luminescence, quantum dots This paper reviews our experimental work on erbium in gallium arsenide and erbium in silicon. Comparisons are made with other work (elsewhere and at UMIST) on rare earths hosted in group IV and III-V compounds. Although there are still many facets of defect behaviour associated with rare earths that are uncertain, we can move towards generalising behaviour by defining three distinct regimes.

1. Very dilute systems. Here the electrical (and to some extent the optical properties) of the erbium are dependent on the impurities in the semiconductor host. The detailed behaviour is due to the chemical affinity of the erbium for the mobile impurities present and the complexes that are formed. In the case of float zone or epitaxial silicon for this regime to be operative the erbium concentration must be less than $5 \times 10^{15} \text{ cm}^{-3}$ but may be much higher in less pure hosts.
2. "Native" regime. Here the role of complexes is insignificant and the behaviour is defined solely by the interaction of erbium with the host semiconductor. In general the crystal field split luminescence bands indicate high symmetry and the electrical properties are reproducible.
3. Precipitated or phase separated systems. This regime occurs at high erbium concentrations, i.e., $[\text{Er}] \geq 10^{18} \text{ cm}^{-3}$ in near equilibrium growth but at much higher concentrations ($\geq 5 \times 10^{19} \text{ cm}^{-3}$) in grossly non-equilibrium systems (eg, ion implant with controlled solid phase regrowth). We have used this regime in MBE to produce three dimensional arrays of self organised quantum dots (10-20 diameter).

The electrical, optical and, in the third case, magnetic behaviour of the erbium related defects will be described for each of the regimes and related to the observable properties of the doped semiconductor

ENERGY TRANSFER PROCESSES AT ERBIUM IONS IN SILICON

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Key words: silicon, rare earths, erbium, LEDs, energy transfer

Erbium-doped silicon light emitters are being developed to establish an integrated silicon optoelectronic technology. Materials research focuses on the incorporation of high Er concentrations ($>10^{19} \text{ cm}^{-3}$) that exceed the equilibrium solubility by three orders of magnitude. We employ both ion implantation and CVD processes because of their compatibility with standard IC process technology. Optimum light output requires co-doping with a proper Er-ligand field of electronegative atoms such as N, O, F.

Electroluminescence from erbium-doped silicon is different from other recombination processes in semiconductors due to the involvement of the 4f core electron shell. The excitation and relaxation of the discrete energy levels of the 4f shell require resonance energy transfer that is facilitated by dissipative electronic and phonon mechanisms. We show that the spin energy stored in the excited 4f shell can be transferred back to the silicon host by either an Impurity Auger process or a phonon-mediated charge transfer process. We isolated the Auger process by the junction bias dependence of the electroluminescence decay time. Energy is transferred from the Er 4f core levels to an occupied valence state of the ion. Occupied states (zero bias) give shorter decay times than empty states (reverse bias).

The optical activity of Er in Si is linearly dependent on the donor concentration added by the presence of Er. Outdiffusion studies confirm that the donors consist of Er-ligand complexes. Temperature dependent junction photocurrent spectroscopy on erbium-doped silicon light emitting devices give direct evidence that the phonon process is facilitated by a state in the band gap at $E_c - E_T = 160 \text{ meV}$ which is associated with the optically active erbium-oxygen donor complex. The photocurrent response at 0.8 eV corresponds to excitation of the internal 4f shell, and energy back transfer from the excited core level gives ionization and the photocurrent.

In summary, erbium-ligand complexes in silicon introduce donor states in the gap. These valence electron states are very weakly coupled to the optically active, 4f core electron states. The donor levels, however, play a major role in providing a path for resonant energy transfer between the free electron system and the Er^{3+} ion.

ENERGY TRANSFER RATE BETWEEN ERBIUM 4F SHELL AND Si HOST

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Key Words: Er, Si, energy transfer probability, decay time

Erbium (Er) in Si has received much attention recently due to its potential use for Si-based optical devices using its very sharp and temperature-stable Er 4f-shell luminescence. It is well accepted now that the Er 4f shell is excited by the recombination of an electron-hole pair at an Er-related level in the bandgap. The energy transfer rate between the Er 4f shell and the electron-hole pair is an important parameter that determines optical properties. Several groups have measured the time response of the Er luminescence and observed that the Er luminescence intensity increases after a pulse photo-excitation of the host, with a time delay of the peak intensity after the pulsed excitation as large as several tens of μsec [1]. Based on this fact, it was claimed that the energy transfer rate is rather small. In this paper, we discuss the energy transfer rate based on the investigation of the temperature dependence of the Er luminescence decay time and the time response of the Er luminescence.

We have already shown that the energy transfer rate of Yb-doped InP can be evaluated by assuming a non-radiative multiphonon-assisted (NRMA) energy transfer mechanism[2]. If we assume this mechanism for Si:Er,O, the energy transfer rate estimated based on the experimentally obtained temperature dependence of the decay time is $4 \times 10^9 \text{ s}^{-1}$. The previously observed tens of μsec delay is inconsistent with this large value of the transfer rate.

Time response measurements using a fast response-time system can determine the minimum value of the transfer rate. We measured the time response of the Er luminescence for Si:Er,O samples grown by ion beam epitaxy, that shows Er luminescence dominantly from one type of Er-O complex center under the host excitation[3]. A Nd YAG laser-pumped dye laser was used as an excitation source with a fast response photo-multiplier operating at $1.5 \mu\text{m}$. An analysis of experimental results indicates that the energy transfer rate is at least 10^6 s^{-1} . This is consistent with our estimation of the energy transfer rate mentioned above assuming the NRMA energy transfer mechanism. The previously observed rather large delay is probably not due to the small energy transfer rate, but likely due to some yet unidentified extrinsic nature of the material.

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PHOTOLUMINESCENCE STUDY OF ERBIUM IN SILICON WITH THE FREE-ELECTRON LASER

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Key Words: silicon, RE-doping, photoluminescence, free-electron laser

Er doping of silicon is intensively investigated as the prominent approach to the photonics of this most important electronic material. In spite of a considerable progress recorded in this field recently, the physics of the excitation process of an Er atom embedded in the silicon lattice is still insufficiently understood. Optimization of this mechanism is of key importance for efficiency increase as required for the development of Er-based silicon devices. In the currently discussed models of the energy transfer between the 4f shell of the Er core and the crystal the existence of an intermediate state, usually referred to as Er-bound exciton, is frequently postulated. The same state is then also believed to be responsible for quenching of the Er PL at higher temperatures. However, the actual fingerprint of this state is very difficult to give, and its characteristic parameters such as binding energy and lifetime can be either speculated upon, or very indirectly estimated.

We present the first investigation of intensity and decay kinetics of the low temperature PL of Er-doped silicon under the influence of infrared radiation from a free-electron laser. The Er PL is excited by a 532 nm pulsed NdYAG laser; upon some variable delay the infrared pulse (tunable between 6.5 and 18 μm) is applied. The results show quenching of the PL by the IR pulse only at delays shorter than approx. 200 μs . At longer delays no influence of the infrared pulse on the PL decay can be observed within the experimental error. Such a result can be readily explained if one assumes that the quenching process is only possible for the Er-related BE state, and not for the considerably slower decaying excited Er state. Following this interpretation the effective lifetime of the intermediate state could be determined as approx. 30 μs . This value is considerably longer than the ones estimated within the current theoretical models. The fact that the quenching effect was observed for all the wavelengths used would then set the upper limit for the exciton binding energy at approx. 70 meV. No resonant quenching of Er PL has been found for the investigated energy range.

The current results are very likely to represent the first direct experimental data on the BE state intermediating Er core excitation which constitutes the most important step in the energy transfer process.

DIRECT EVIDENCE FOR STABILITY OF TETRAHEDRAL INTERSTITIAL ER IN SI UP TO 900°C

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Key Words: rare earth doping, erbium, silicon, lattice location, implantation

Recent photoluminescence (PL) spectroscopy studies have identified a number of Er related defect centers with different crystal surroundings in Si [1]. The most intense PL yield at higher temperatures was due to a cubic Er center, which was suggested to be isolated Er on tetrahedral interstitial (T) sites. While theoretical investigations also predict that T sites are the most stable sites for all oxidation states of isolated Er atoms in Si [2], direct lattice location using the Rutherford backscattering (RBS) channeling technique has failed so far in identifying tetrahedral Er in Si and only indicated substitutional (S) sites [3] or hexagonal (H) interstitial sites [4].

In this contribution we will report on direct lattice location of Er in Si using the emission channeling technique of charged particles emitted from radioactive isotopes. Radioactive ^{167}Tm ($t_{1/2}=9$ d) was implanted with 60 keV into FZ and CZ Si single crystals at doses around $4 \times 10^{13}/\text{cm}^2$ using the ISOLDE facility at CERN. This isotope decays into the excited state $^{167\text{m}}\text{Er}$ which has a 2.3 s half life. Conversion electrons emitted in the subsequent decay of $^{167\text{m}}\text{Er}$ were recorded with a position sensitive electron detector. This technique allowed to monitor the lattice sites of $^{167\text{m}}\text{Er}$ directly after room temperature implantation, after subsequent isochronal annealing steps, and also in situ during annealing up to 900°C. The angular distribution of emitted conversion electrons gives direct evidence that the major fraction (>55%) of $^{167\text{m}}\text{Er}$ occupies tetrahedral interstitial (T) sites, once the samples are annealed above ca. 600°C. While we cannot exclude that in our case the lattice positions of Er are still influenced by the chemical nature of its parent Tm, it is clear from the lattice location results during annealing, that, once Er occupies T sites, it will be stable even at temperatures of 900°C, at least within the accessible time window of a few seconds. This gives direct evidence that the tetrahedral position indeed represents a minimum of the configurational energy.

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ELECTRON PARAMAGNETIC RESONANCE OF ERBIUM IN BULK SILICON CARBIDE CRYSTALS

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Key Words: silicon carbide. rare earth doping. erbium.

In this letter we report the first EPR observation of rare-earth impurities in silicon carbide crystals. The samples were erbium doped 1 mm-thickness epitaxial layers which were grown by the sublimation sandwich-method in vacuum at temperatures 1700-1750 °C. Several anisotropic groups of sharp lines were observed which were identified as arising from Er^{3+} centres having a g tensors exhibiting axial and nearly orthorhombic symmetry. A direct identification of erbium ions have been established by the presence of hyperfine interaction with ^{167}Er nuclei. Three lines for axial Er^{3+} centre which seem to arise from different lattice sites in 6H-SiC:Er can be indicated with close principal g values. For the most intense line the g -values are $g_{\parallel}=1.073$, $g_{\perp}=8.071$; where the parallel axis coincides with the hexagonal c -axis of the crystal. Besides, three groups of lines which seem also to arise from different lattice sites have been observed. The similarity of the EPR spectra orientation dependencies implies that all centres have the same nearly orthorhombic symmetries. The g -factors for the most intense lines are: $g_{I_x}=12.2$, $g_{I_y}=4.192$, $g_{I_z}=2.54$; The local z -axes directed along the 6 equivalent orientations Si-C which are $\sim 110^\circ$ (or $\sim 70^\circ$) away from the c -axis within the hexagonal crystal lattice. The directions of the x -axes are in a plane spanned by the c -axis and their z -axis (in $\{11\bar{2}0\}$ plane) whereas their y -axis is perpendicular to this plane. The average g values of the axial and orthorhombic centres will be ~ 5.7 and ~ 6.3 , respectively, and this suggests that the parent cubic ground state may have Γ_6 representation for axial centre and Γ_7 one for orthorhombic Er center. Possible structures for the erbium centres are discussed. Presumably, erbium substitute for silicon and lies in a regular environment for axial center. In addition, the EPR spectrum of the excited state of Er^{3+} in 6H-SiC seems to be observed at higher temperature.

1.54 μm PHOTOLUMINESCENCE OF Er AND Er+O IMPLANTED 6H SiC

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Key words: silicon carbide, erbium, photoluminescence, quenching mechanisms

Photoluminescence in the neighborhood of 1.54 μm due to the $^4I_{13/2} - ^4I_{15/2}$ intra-4f-shell transitions of Er^{3+} ions is studied in 6H SiC bulk crystal (nitrogen donor concentration 10^{17} cm^{-3}). Erbium ions were implanted into SiC samples at room temperature at an energy of 800 keV, and with the ion doses ranging from 10^{13} to $2 \times 10^{15} \text{ cm}^{-2}$. After implantation the samples were thermally annealed (1 hour) at 1000, 1100, and 1500°C. The 4f-4f emission of Er^{3+} ions was observed only in samples annealed at 1500°C.

Rutherford backscattering measurements showed that for amorphizing doses of erbium most of the Er atoms diffuse out from SiC during annealing at 1500°C. As a result, the highest emission intensity was observed for a low dose (10^{13} cm^{-2}) implantation.

The effect of oxygen co-implantation on the 4f-4f luminescence of Er^{3+} was studied. Some enhancement of the emission intensity was observed, but no differences in the number of lines and their wavelengths between the Er^{3+} spectra in Er and Er + O implanted SiC were observed, on the contrary to the situation found in other semiconductors. It is concluded that the 1.54 μm emission of erbium in SiC originates from Er+O complexes, which are always formed as a result of annealing at temperatures exceeding 1500°C.

Temperature dependence of the integrated Er^{3+} emission intensity and the decay lifetime are measured in Er- and Er+O -doped SiC to investigate quenching mechanisms of the Er^{3+} luminescence. The characteristic decay time of 6 msec at 2K has been found. Possible models of the excitation and quenching mechanisms of Er^{3+} in SiC are discussed.

OPTICAL INVESTIGATION OF Ge-RICH $\text{Si}_{1-x}\text{Ge}_x$ ($0.9 \leq x \leq 1$) ALLOYS

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key words: SiGe, defects, photoluminescence, absorption, phonons, local modes

We have used Fourier-transform infrared photoluminescence (PL), near and far infrared absorption, and Raman spectroscopy to investigate nominally undoped and intentionally doped (e.g. B, P, Sb, Te) Ge-rich $\text{Si}_{1-x}\text{Ge}_x$ ($0.9 \leq x \leq 1$) alloys grown by a modified Bridgman method. The small full widths at half maxima (FWHM), that are between 2.5 and 4 meV for the excitonic near bandedge luminescence, are the best values reported in literature up to now. They show the excellent quality of the samples. Thus, we have been able to study new features of Ge-rich SiGe doped and undoped alloys.

We compare the near bandedge shallow bound exciton luminescence and the associated phonon sideband with near bandedge absorption measurements, which were performed on the same samples. We determine the Si concentration from the position of the no-phonon (NP) excitonic near bandedge luminescence lines using the equation of Weber and Alonso.¹ These data agree well with X-ray measurements. The FWHM of the excitonic NP line of our samples increases with rising Si concentration. In contrast to our results a decrease of the FWHM with increasing Si concentration is reported in the literature.¹ As a consequence, this decrease of the FWHM, which has been explained by alloy fluctuations¹, is not general for Ge-rich $\text{Si}_{1-x}\text{Ge}_x$. The formation of the second derivative of the absorption data not only reveals an excellent fingerprint of the LA phonons but also offers a possibility to determine the absorption threshold. We discuss the onset for absorption, which does not coincide for all the samples with the bound exciton luminescence peak. In Te and Sb doped samples we observe the emission of a deep luminescence center, which shifts with the near band edge luminescence. The FWHM of only 1.5 meV and the absence of phonon coupling reveal a strong localization of the center.

We compare far infrared absorption measurements of Ge-rich $\text{Si}_{1-x}\text{Ge}_x$ with Raman measurements. The latter reveal the appearance of high energy peaks in the energetic range of the local vibrational mode of Si ($\approx 390 \text{ cm}^{-1}$ depending on the Si concentration). These additional peaks cannot be observed in absorption measurements. In contrast to Gaisler et al.² these peaks together with two other absorptions at about 440 and 460 cm^{-1} appear already at Si concentrations of less than 3 % and they are discussed in respect to a near field ordering. Furthermore a simple shift of the Ge-Ge mode ($\approx 300 \text{ cm}^{-1}$ depending on Si concentration) to lower energy with rising Si concentration can be detected. Fuchs et al.³ did not observe this shift and they explained their different results with disordering. As a consequence, our measurements most definitely reveal that this observation is not a general feature of Ge-rich $\text{Si}_{1-x}\text{Ge}_x$.

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SUBSTITUTIONAL CARBON IN Ge AND $\text{Si}_{1-x}\text{Ge}_x$.

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Key Words: Carbon, Ge, $\text{Si}_{1-x}\text{Ge}_x$, IR-spectroscopy, ion-channeling, ab-initio calculations

Carbon is an important impurity in silicon and it forms a range of complexes among which substitutional carbon C_s is the most prominent. This defect has tetrahedral symmetry and gives rise to a single three-dimensional local vibrational mode at 607 cm^{-1} . C_s is also expected to exist in crystalline Ge due to the similar chemical properties of Si and Ge. However, the lengths of C-C and Ge-Ge bonds differs by 2.09 Å. This implies that a considerable strain field will be introduced around C_s in Ge and, therefore, the defect may be unstable. $\text{Si}_{1-x}\text{Ge}_x$ C_y layers of arbitrary thickness and low dislocation density can be grown on pure Si in contrast to $\text{Si}_{1-x}\text{Ge}_x$ layers. The reason is that the carbon atoms compensate the 4 % mismatch between the Si and Ge lattice constants. This makes C_s an interesting and important defect in $\text{Si}_{1-x}\text{Ge}_x$ compounds. So far, only the Si-C mode at 607 cm^{-1} has been observed in such materials and it remains unknown whether Ge-C bonds are formed.

In the present work, carbon is implanted into monocrystalline Ge and into relaxed epitaxial MBE-grown $\text{Si}_{1-x}\text{Ge}_x$. The samples are studied with infrared absorption spectroscopy along with ion-channelling studies on the Ge samples. Finally, ab-initio local density functional cluster theory is applied to calculate the structure and the local vibrational modes of C_s in Ge. After implantation of ^{12}C in Ge at room-temperature and subsequent annealing at 350°C , a sharp absorption line is observed at 531 cm^{-1} . When ^{12}C is substituted by ^{13}C , the line shifts down in frequency to 512 cm^{-1} and co-implantation of $^{12}\text{C}^+$ and $^{13}\text{C}^+$ does not give rise to additional lines. Thus, the 531 cm^{-1} line represents a local vibrational mode of a single carbon atom. From ion-channeling measurements on samples annealed at 450°C , it is found that $31 \pm 3\%$ of the carbon atoms are located at substitutional sites. The population of the substitutional site and the intensity of the 531 cm^{-1} mode have identical annealing behaviour and it is concluded that the 531 cm^{-1} mode is the three-dimensional T_2 stretch mode of C_s in Ge. The calculated frequencies and isotope shifts for this mode are in good agreement with the observations.

In $\text{Si}_{0.6}\text{Ge}_{0.4}$, two broad absorption lines are observed at 551 and 592 cm^{-1} after implantation of ^{12}C and subsequent annealing at 700°C . From measurements on samples implanted with ^{13}C and co-implanted with ^{12}C and ^{13}C we conclude that these lines represent local vibrational modes of defects containing a single carbon atom. When the germanium concentration is increased the modes shift downwards in frequency and broaden. However, their frequencies are always in the range from 531 to 607 cm^{-1} , corresponding to the frequencies of C_s in Ge and Si. A simple harmonic oscillator model in which it is assumed that the modes originate from C_s bound to four atoms (Si and Ge) can at least qualitatively account for the experimental data. It is concluded that carbon in $\text{Si}_{1-x}\text{Ge}_x$ binds to both Si and Ge.

POINT DEFECTS AND IMPURITIES IN RELAXED $\text{Si}_{1-x}\text{Ge}_x$

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Key words: defects, impurities, band gap, $\text{Si}_{1-x}\text{Ge}_x$ alloy, DLTS

The interest in SiGe alloy layers is rapidly increasing and a large effort is being made to integrate both strained and unstrained SiGe layers into the main stream Si device industry. However, today's needs for sub micron technology and band gap engineering give rise to new questions regarding the behavior of point defects. Among them the relationship between a given level in the gap and the energy bands it interacts with is of prime importance. In a $\text{Si}_{1-x}\text{Ge}_x$ alloy the band gap shrinks significantly when the Ge fraction x is changed. For instance, for $0 < x < 25\%$, the corresponding band gap reduction is close to 100 meV, thus offering a powerful tool to master the band gap effect. In Si the temperature variation from 100 to 300 K or a change in the pressure from 0 to 10 kbar allow a band gap reduction of few tens of meV only. Consequently investigation of pinning effect becomes much easier in $\text{Si}_{1-x}\text{Ge}_x$ alloys than in pure Si.

Using deep level transient spectroscopy we have studied and identified several band gap levels in relaxed, molecular beam epitaxy grown $\text{Si}_{1-x}\text{Ge}_x$ ($x < 30\%$). The levels investigated correspond mainly to substitutional gold and to a large variety of point defects formed by proton irradiation. The point defects are related to C and B impurities, E-centers and di-vacancies, all of them introducing levels in both the upper and lower half of the gap. In addition, the Au related defect has both donor and acceptor levels. Using thermodynamic concepts linking the carrier exchange rates to the Gibbs free energies of the thermally activated processes, all levels were found to be pinned to the conduction band. These observations will be described and the impact of the statistical Ge fluctuation on the transport kinetics clearly established.

DISLOCATION-RELATED ELECTRONIC STATES IN STRAIN-RELAXED $\text{Si}_{1-x}\text{Ge}_x$ /Si EPITAXIAL LAYERS GROWN AT LOW TEMPERATURE

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Key Words: SiGe, dislocations, D-lines, excitons, interdiffusion, hole traps

Strain-relaxed step-graded $\text{Si}_{1-x}\text{Ge}_x$ /Si structures have low densities of threading dislocations and thus are used as buffer layers for modulation-doped field-effect transistors. The extraordinarily high electron mobilities at low temperature observed in modulation-doped strained Si layers and the high hole mobilities observed in strained $\text{Si}_{1-x}\text{Ge}_x$ or Ge layers grown on these buffer layers confirm their excellent quality. The threading dislocation densities are low enough that they have no effect on the carrier mobility. For device reliability and for other potential device applications, however, it is important to understand the effects of threading dislocations on the electronic and optical properties of relaxed $\text{Si}_{1-x}\text{Ge}_x$ layers.

Low temperature photoluminescence (PL) and deep level transient spectroscopy (DLTS) have been used to study electronic states associated with threading dislocations in relaxed $\text{Si}_{1-x}\text{Ge}_x$ buffer layer structures. The dominant two peaks in the DLTS spectrum are due to hole traps having thermal emission activation energies of 0.06 and 0.14 eV in $\text{Si}_{0.7}\text{Ge}_{0.3}$. The annealing behaviour of these deep levels indicates that they arise from defect complexes at the dislocation core and a correlation between the defect concentration and the oxygen concentration in the film suggests that oxygen may be a constituent of these defect complexes. The low temperature PL spectra show near-band edge features due to excitonic recombination and also the well-known D-lines associated with dislocations. We have shown that the most intense near-band-edge features arise from the recombination of single excitons and biexcitons confined in local potential wells due to alloy composition (or strain) fluctuations in the layers. The annealing behaviour of the D-lines indicates that they very likely arise from recombination at intrinsic states of the dislocations. Detailed measurements of the energy shift of the D_1 and D_2 lines upon annealing show that D_1 is not a phonon replica of D_2 . The energy shift of D_1 is due to strain-driven interdiffusion of Si and Ge, which results in the widening of the local band gap at the dislocation core.

These results, along with other recently published theoretical and experimental work, lead to the view that in the region of the dislocation core there is an energy shift of the valence band compared to that in the $\text{Si}_{1-x}\text{Ge}_x$ crystal, due to the strain field of the dislocation. This results in a potential well for holes at the dislocation. Localized states also occur at intrinsic defects such as reconstruction defects, kinks or jogs and at point defect complexes the dislocations. Although most of the volume of the epitaxial layer has the properties of "bulk" $\text{Si}_{1-x}\text{Ge}_x$, the dislocations act as "wires" with a reduced band gap and localised electronic states.

ATOMIC CONFIGURATION OF OXYGEN NEGATIVE-U CENTER IN GaAs

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Key words: GaAs, Oxygen, atomic configuration, charge state, negative-U

Oxygen is one of the most common contaminants in semiconductors. For the dominant oxygen center in GaAs, infrared local vibrational mode (LVM) absorption measurements show three absorption lines at around 730 cm^{-1} , indicating that one oxygen atom couples with two Ga atoms[1]. Detailed experiments under short time illumination and thermal treatments show that this center has a negative-U character[2]. The atomic configuration of this oxygen center has been thought to be similar to that of the A center in silicon: an oxygen atom occupies the As substitutional site, but it moves along the (001) direction, coupling with two Ga atoms. The center is termed O- V_{As} . This atomic configuration seems to be well accepted, but the calculations by using a local-density-functional cluster method indicated that this configuration is not stable for a neutral charge state[3]. To clarify the atomic configuration of the oxygen center in GaAs, we calculated the stable atomic configurations at various sites and various charge states. The calculations were carried out within the local density functional approximation. Soft-pseudopotentials for Ga, As, and oxygen were used[4]. A 32-atom supercell was used and the lattice was relaxed for each configuration and each charge state.

Our calculated results for the O- V_{As} center also show that this configuration is not stable for the neutral state. Moreover, our calculations show that the reaction of $As_{inter} + O_{As} \rightarrow O_{inter}$ occurs easily, suggesting the interstitial oxygen is more stable than the substitutional oxygen. For the neutral charge state, the calculated stable position of the interstitial oxygen is the site which is shifted from the Td interstitial site toward the As atom along the (001) direction. Hence, the oxygen atom couples with two Ga atoms. For 1- and 2- charge states, the oxygen atom moves back toward the Td interstitial site. For these states, the Ga-O bonds become weaker than that for the neutral state. This tendency is consistent with the observed LVM frequencies for different charge states. We also calculated the formation energy as a function of the Fermi level. It was found that the O- V_{As} center does not have the negative-U character, but the interstitial oxygen shows the negative-U character. Thus, the present calculations show that the experimentally observed LVM signals are not due to the O- V_{As} center, but due to the interstitial oxygen.

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RESONANT INTERACTION BETWEEN LOCAL VIBRATIONAL MODES AND EXTENDED LATTICE PHONONS

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Key Words: Local vibrational modes (LVM's), anti-crossing, hydrogen, AlSb, GaAs.

Resonant interactions between weakly coupled systems play an important role in a variety of phenomena in solid state physics. The study of such interactions has led to discoveries of new quasi-particles such as polarons and polaritons. Thus far most of these studies have been limited to interactions between electronic and vibronic subsystems of the lattice, since small changes in electronic properties can be easily detected and the energy levels may be tuned by external perturbations such as magnetic field or pressure. We report evidence of a resonant interaction between local vibrational modes (LVM's) and extended lattice phonons that gives rise to a new collective excitation called a "localon."

Using infrared spectroscopy we have observed localons in AlSb and GaAs. In AlSb, the LVM-phonon interaction leads to a splitting of the Se-H stretch mode into three peaks at 1606.3, 1608.6, and 1615.7 cm^{-1} at liquid-helium temperatures. The Se-D stretch mode, by contrast, does not show any splitting. We propose that the anomalous splitting of the Se-H mode is a result of the local mode interacting with two different multi-phonon combinations. As the temperature or hydrostatic pressure is varied, the stretch mode and multi-phonon modes show anti-crossing behavior. We can quantitatively explain our observations with a three-level model.

In GaAs, the interaction between the $^{12}\text{C}_{\text{As}}$ LVM and a two optical phonon mode gives rise to a sideband on the low energy side. As the temperature increases from 200 to 500 K, the main peak merges with the sideband and broadens. We use a Green's function approach to describe the temperature dependence of the line shape. Although it is unclear which phonons in the Brillouin zone interact most strongly with LVM's, the fact that resonant interactions are observed in two very different defects and hosts suggests that this is a general phenomenon.

ANOMALOUS SHIFT OF THE 1075 cm⁻¹ OXYGEN-HYDROGEN DEFECT IN SILICON

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Key Words: oxygen, hydrogen, anomalous isotopic shift, silicon.

The observations of an enhancement in the oxygen diffusion rate in Si caused by H and a shallow thermal donor defect incorporating H has stimulated a study of oxygen-hydrogen defects. The recent detection of an oxygen vibrational mode at 1075 cm⁻¹ in samples soaked in hydrogen, which is shifted *upwards* by about 1 cm⁻¹ for the deuterium case, has provoked a great deal of interest. Here we show that this anomalous shift can be explained by the presence of a small H-containing molecule near to interstitial oxygen and lying at an interstitial cage site. Results are given for H₂ and for a water molecule, both of which lead to an upward shift of the frequency of the interstitial oxygen mode. Both types of molecules lead to vibrational modes in the 3500-4000 cm⁻¹ region but those of the H₂ molecule are close to modes recently detected using FTIR [1].

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IRON IN P-TYPE SILICON: A COMPREHENSIVE MODEL

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Key words: gettering kinetics, Fe-acceptor pairs, solubility, precipitate, silicon processing

Contamination by transition metal impurities is a major concern in Si processing. In particular, Fe is incorporated as highly mobile and soluble interstitials (Fe_i) either during device processing or due to starting material impurity. (Fe_i) and Group III impurities (B, Al, etc.) form Fe-acceptor pairs in Si. Both isolated and paired Fe_i introduce deep levels in the bandgap, which act as recombination centers causing the decrease of minority carrier lifetime. Fe_i is removed from Si by gettering mechanisms that include precipitation at defects and outdiffusion. For integrated circuit applications, precipitation in bulk region of the wafer, "intrinsic gettering", can be effective in cleaning the surface device region. For solar cells, outdiffusion gettering is necessary to clean the entire wafer bulk. The gettering kinetics and the associated defect thermodynamics for these processes are not completely understood within a self-consistent framework. In this paper, for the first time, we give a detailed picture of the Fe gettering kinetics for highly contaminated Si and characterize Fe-related defects generated in the gettering process.

Fe is introduced into B-doped $\langle 100 \rangle$ -type Cz and FZ Si at its solubility limit at 1000°C. The donor levels of Fe_i , $\text{Fe}_i \text{B}_s$ and $\text{Fe}_i \text{Al}_s$ pairs are used as fingerprints to determine the dissolved $[\text{Fe}]$ by DLTS measurements. The minority carrier lifetime and diffusion length are measured by EBIC and RFPCD techniques, respectively. For Cz Si, variation of the annealing temperature (620°C, 700°C, and 800°C) and time (10min-15hrs) reveals that two different kinetic regimes exist in the Fe gettering process. The first regime is dominated by rapid Fe precipitation at O-precipitate nuclei with limited Fe_i outdiffusion. The Fe precipitate size and density are estimated to be on the order of 10-20 nm and $5 \times 10^8 \text{ cm}^{-3}$, respectively. The second regime features dissolution of Fe precipitates in balance with the Fe outdiffusion process. For samples with $[\text{Fe}] \ll [\text{B}]$, the $\text{Fe}_i \text{B}_s$ pairs are found to be the dominant minority carrier recombination centers by correlation of $[\text{Fe}_i \text{B}_s]$ versus the minority carrier diffusion length. Similar experiments on FZ Si and high temperature rapid thermal anneal (RTA) pre-treated Cz Si explore the outdiffusion regime, independently. TEM is used to study Fe precipitate structure and size distribution. Our data is used to develop a comprehensive kinetic model for Fe gettering processes including the roles of temperature, time, doping level, solubility, and precipitate nuclei. The model includes both atomistic pair equilibria and continuum diffusion and segregation analyses. The model predicts contamination tendency, gettering rate and minority carrier lifetime for wafers of arbitrary thermal history.

MÖSSBAUER SPECTROSCOPY OF Fe IN SILICON WITH THE NOVEL LASER -IONIZED $^{57}\text{Mn}^+$ ION BEAM AT ISOLDE

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Over 30 years of experimental efforts to identify the Mössbauer spectra of (differently charged) interstitial and substitutional Fe in silicon, comprising diffusion and ion implantation of both radioactive ^{57}Co parent and stable ^{57}Fe Mössbauer isotopes, have led to a generally accepted identification of the spectrum for interstitial Fe, whereas conflicting interpretations still prevail for substitutional Fe. Here, we present first results obtained from ion implantations of radioactive $^{57}\text{Mn}^+$ parent isotopes, an approach, which is shown to have striking advantages over the previous experimental schemes; the results, excitingly, both corroborate and challenge previous interpretations and lead to a conceivable reinterpretation.

Laser resonance ionisation has been applied to produce ions of radioactive Mn isotopes obtained from proton-induced fission in a UC_2 target at the ISOLDE on-line mass-separator at CERN with a 1 GeV proton beam from the PS-Booster accelerator. The radioactive ion beams were found to have unprecedented intensity ($>10^8/\text{s}$ for $^{57}\text{Mn}^+$) and purity owing to the efficiency and chemical selectivity of the laser ionisation scheme. The $^{57}\text{Mn}^+$ ($T_{1/2} = 1.3 \text{ m}$) probe atoms were implanted into n- and p-type silicon with an energy of 60 keV at 77 and 297 K to fluences $<10^{12}/\text{cm}^2$. In the β^- -decay to the 14 keV Mössbauer state of ^{57}Fe an average recoil energy of 20 eV is imparted on the Fe daughter nucleus. Thus with a high probability the Fe atoms are displaced from the Mn parent site, presumably predominantly the tetrahedral interstitial site, and both single lines attributed to interstitial Fe_i and substitutional Fe_s are observed in the spectra apart from a small fraction in a defect structure characterized by a quadrupole split line. As only the nuclear charge changes in the β^- -decay and interstitial (and substitutional) Mn are known to have negative, neutral and positive charge states in the band gap, the charge state of the Fe daughter atoms can be controlled by the Mn parent charge state and its Fermi-level dependence. Thus a difference in isomer shift observed for interstitial Fe_i in n- and p-type material is attributed to the known $\text{Fe}_\text{i}^{0/+}$ charge states, whereas no difference, i.e. no charge state in the band gap, is indicated for Fe_s . The $\text{Fe}_\text{i,s}$ isomer shifts, i.e. electron densities, are found to be in an overall fair agreement with theoretical predictions as well as with a previous experimental value from ion implantations of $^{57}\text{Co}^+$ for Fe_s , whereas a previous value for Fe_i^0 from recoil implantations of Coulomb excited ^{57}Fe is argued in the light of the present results to be due to Fe_i^+ . However, the difference in electron densities for the $\text{Fe}_\text{i}^{0/+}$ states is opposite to that expected from *ab-initio* LMTO calculations. The possible origin of these deviations will be discussed and ^{57}Mn experiments will be proposed to resolve open questions concerning the atomic and electronic structure of $\text{Fe}_{\text{i,s}}$ point defects in silicon as well as the $\text{Fe}_\text{i}^{0/+}$ charge state dependent diffusivities.

COPPER IN SILICON: QUANTITATIVE ANALYSIS OF INTERNAL AND PROXIMITY GETTERING

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Keywords: copper, silicon, gettering, implantation

Copper is a prevalent contaminant in silicon with nefarious effects on device performance. Removal or gettering of unintentional Cu contamination out of the device region is desired. A standard method to remove impurities from the near surface/device region is via internal gettering which utilizes oxygen precipitates in the material bulk. This method requires undesirable, long/low temperature anneals for efficient gettering. To obtain effective gettering under any annealing condition, "proximity" gettering methods located near the device region have been the focus of recent research with a particular interest in mechanisms which do not require an impurity supersaturation. One promising method uses cavities formed by He implantation which getter metal impurities on the cavity wall by chemisorption as well as metal-silicide precipitation. In order to quantify the Cu gettering capability of these mechanisms, a characterization technique which provides an unambiguous fingerprint for Cu with high sensitivity is strongly desired. Established techniques have not fulfilled these requirements. Our research has concentrated on detecting low concentrations of Cu in silicon together with determining the gettering efficiencies and stabilities of cavities and internal gettering sites.

In this work, we measure interstitial Cu (Cu_i) concentrations in silicon with use of the transient ion drift (TID) technique which exploits the capacitance change induced by Cu_i transient drift in the depletion region of a Schottky barrier. TID allows for detection of Cu_i contamination down to $10^{11} \text{ Cu}_i \text{ atoms/cm}^3$. After Cu in-diffusion at elevated temperatures and rapid quenching, we have determined the majority of the Cu remains in the interstitial state after the quench with agglomeration transpiring over many hours at room temperature. Also, we have quantitatively determined the total Cu concentration in silicon by completely dissolving precipitated Cu back into the interstitial state with the use of rapid thermal annealing followed by a rapid quench.

Additionally, we have monitored Cu behavior in the presence of various gettering mechanisms. Specifically, TID and secondary ion mass spectroscopy (SIMS) were used to quantitatively study the gettering of Cu to implantation-induced cavities and standard internal gettering sites in silicon. The cavities were formed in the near surface region by He implantation and annealing while the internal gettering sites were created in the bulk by oxygen precipitation. Long furnace anneals were used in the gettering treatments to establish which mechanism provided the most stable site for the Cu. Based on our SIMS results, the cavities possess a significant fraction of the in-diffused Cu while our combined SIMS and TID measurements show the internal gettering sites have captured only a small fraction. Based on these results, we can conclude that the cavity layers provide a highly stable gettering site and possess a higher gettering efficiency for Cu than internal gettering sites.

RECOMBINATION-ENHANCED FE ATOM JUMP OF Fe-ACCEPTOR PAIRS IN Si

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Key Words; recombination-enhanced jump, Fe-acceptor pair, Si, ESR

We studied the recombination-enhanced Fe atom jump between the first (1st) and second (2nd) neighbor sites of Fe-Ga and Fe-In pairs in Si with the use of electron spin resonance (ESR) method which distinguishes those neighbors easily.

Specimens were floating-zone grown Si doped with Ga, In and Al at about $3 \times 10^{15} \text{ cm}^{-3}$. Iron was doped in specimens by annealing them in Fe vapor followed by quench. Fe-acceptor pairs were generated by annealing specimens at 80°C for 50 min after quench. Specimens were illuminated by monochromatic light at appropriate temperatures around 150 K. The concentrations of various Fe-acceptor pairs were determined from the absorption intensity of ESR at 10 K after illumination.

Under optical illumination, activation energies of Fe atom jump between the 1st and 2nd neighbor pair were about 0.11, 0.08 and 0.02 eV which were much smaller than those of thermal activation energies without illumination 0.82, 0.75 and 0.69 eV for Fe-Al, Fe-Ga and Fe-In pairs, respectively. The magnitude of reduction of activation energies were interpreted to be supplied by the recombination energy of electron and hole at Fe-acceptor levels. Threshold energies of optical illumination for the enhanced motion of Fe atom were 1.095, 1.091 and 0.99 eV for Fe-Al, Fe-Ga and Fe-In pairs, respectively. These threshold energies were interpreted to be the energy differences between the bottom of conduction band and acceptor levels of those Fe-acceptor pairs.

We interpret above results as follows. Free holes in the valence band are captured by Fe-acceptor which become positively charged. Electrons in the conduction band are captured acceptor levels of Fe-acceptor pairs and then recombine with holes. Recombination energy is therefore the energy difference between the acceptor levels and donor levels of Fe-acceptor pairs. Some part of the recombination energy are consumed to enhance the Fe atom motion. Applying Sumi's theory¹ to our experimental results, we estimated the fraction of the recombination energy used for enhancing the Fe atom motion to be about 0.7.

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DEFECT CLUSTERS IN SILICON: IMPACT ON THE PERFORMANCE OF LARGE-AREA DEVICES

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Defect clusters are observed in the rapidly grown silicon used for low-cost devices such as solar cells. Defect clusters consist of local agglomerations of dislocation networks and stacking faults that are caused by the strong, non-uniform, thermal stresses that can exist in rapidly growing material. Because the defect clusters can be efficient nucleation sites, they become decorated with impurity precipitates during crystal growth. Consequently, the gettering and passivation processes that are the conventional methods to ameliorate the effects of impurities and defects do not work well in the regions of defects clusters. These characteristics enhance the electrical activity of defects and, hence, their ability to degrade the performance of large-area devices. Indeed, the performance of large-area solar cells is limited primarily by the defect clusters.

Defect clusters influence a device via a number of mechanisms. They act as sites of high carrier recombination by lowering the local minority carrier lifetime and producing severe shunting of a device. Furthermore, because the defect clusters are not uniformly distributed, their effect on various device parameters depends on their spatial distributions. This paper describes a comprehensive electronic model that can be applied to determine the effects of defect clusters in large-area power devices such as solar cells. This model combines both the microscopic and the macroscopic behaviors of defects.

To determine the effect of defect clusters on a large-area device, we first model the microscopic behavior of dislocations in a N/P junction device. This model describes the carrier recombination effects associated with dislocation segments in various regions of a small-area, isolated device on its I-V characteristics. In particular, it calculates the influence of defects on the minority-carrier properties of the substrate and the voltage-dependent dark currents of the device. Next, a given spatial distribution of dislocations in a large-area device is simulated by a network of microscopic devices with an appropriate distribution of the defects. This composite model accurately predicts various parameters of a large-area solar cell and explains some counter-intuitive phenomena that have been experimentally observed. For example, the results show that in a large-area device the defect clusters produce local shunts that act as "sinks" to dissipate power internally in the device. Likewise, it is found that the influence of defect clusters depends not only on the total number of dislocations, but on the distribution of dislocations as well.

INFRARED INDUCED EMISSION FROM SILICON QUANTUM WIRES

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Key Words: silicon quantum wires, lasing oscillations, impurity dipoles

We present the first findings of the infrared induced emission from the silicon quantum wires, which is due to the formation of a correlation gap in the DOS of degenerate hole gas. The quantum wires of this art are created by electrostatic confining potential due to impurity correlations inside ultra-shallow p^+-n junctions which are realized using controlled surface injection of self-interstitials and vacancies in the process of non-equilibrium boron diffusion.

The diffusion experiments involving boron were performed from gas phase into 350 μm thick n-type Si (100) wafers. The working and back sides of wafers were previously oxidized using the thermal oxidation process. The parameters varied in the course of the short time diffusion of boron were the oxide overlayer thickness, diffusion temperature (800°C-1100°C) and Cl levels in the gas phase. Diffusion profiles measured using SIMS technique demonstrate the depths in the range from 5 nm to 20 nm. The cyclotron resonance findings and current-voltage characteristics measured at different angles between the $p-n$ junctions plane and the bias voltage show that the p^+ diffusion profiles consist of both natural longitudinal and lateral quantum wells, the relative number of which is determined by the non-equilibrium diffusion conditions. Besides, the crystallographically dependent quantized conductance obtained at high temperature (77 K and 300 K) has revealed the quantum wires induced inside natural quantum wells by the strong electrostatic confining potential due to ordering B^+-B^- dipole centres.

Using Temperature dependencies of thermal friction coefficient as well as direct and reversal CV characteristics, the C_{3v} symmetry B^+-B^- dipole centres are demonstrated to cause the formation of a correlation gap in the DOS of degenerate hole gas in the crystallographically oriented quantum wires. The dispersion in the energy of a correlation gap is dependent on local fluctuations in the dopant distribution along a quantum wire, which represent the places of the creation of isolated quantum dots under the gate voltage.

The generation of similar quantum wires with isolated quantum dots using external electric fields has been found to be responsible for the infrared emission in the range 1-10 μm , which is induced by the injection of non-equilibrium carriers into quantum wire systems. These results represent the basis toward the infrared silicon lasers in which both electrons/holes and photons are fully quantized. The dipole impurity microcavity that is a length of quantum wire restricted by two isolated quantum dots is shown to produce the lasing oscillations at the wavelengths determined by a correlation gap value, which coincide with the resonance wavelength of the microcavity. The threshold character of the irradiative power and dynamic spectrum narrowing found at 3591 nm, 3744 nm, 3969 nm, 4457 nm and 4881 nm as a function of the current that traverses the quantum wire with isolated quantum dots are evidence of light stimulated emission from silicon nanostructures.

HIGH RESOLUTION EELS STUDY OF EXTENDED DEFECTS IN SILICON

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Key Words: EELS, planar defect, interband transition, JDOS

We have applied high-resolution electron energy loss spectroscopy (HR-EELS) to exploring localized electronic structures of extended defects in Si. In contrast to applications of conventional EELS such as an analysis of chemical bonding, our study aims to observe directly the interband transitions due to the extended defects.

The extended defects in Si have a strong tendency to cause the lattice reconstruction. Consequently, the defects are usually thought to be neither electronically nor optically active. Therefore, the defects have never been detected by transmission electron microscopy (TEM) observation unless they grow larger than nanometer. However, the recent electronic computations of extended defects based on the atomic structure data have shown that the reconstructed extended defects yield the defect-localized states near the band edges and inside the valence bands.

We have performed HR-EELS measurements using a TEM-based spectrometer equipped with a field-emission-type electron gun and monochromators. The incident electron energy was 60 keV and the energy resolution was about 0.1 eV. The electron probe was 180 nm in diameter. We have obtained the complex dielectric functions of both perfect crystal and the {113} defects through the Kramers-Kronig transformation of the EELS spectra in a low-loss region. Analyzing the imaginary parts of the dielectric function in which the two peaks appear at about 2.2~2.5 eV and 4.5 eV, we have found that the lower-energy peak shifts to the lower energy by 0.3 eV and is intenser in the defects. The results are analyzed in terms of the joint density of states (JDOS) obtained by a tight binding calculation and a first principle calculation. We suggest that the defect localized states near the band edges contribute to the dielectric function.

AN INVESTIGATION OF THE POSSIBILITY THAT OXYGEN DIFFUSION IN CZOCHRALSKI SILICON IS CATALYSED DURING CLUSTERING.

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Key Words: oxygen, thermal donor, Si-interstitial, Si-vacancy, precipitation, nucleation.

The technologically important process by which oxygen (O_i) in Czochralski silicon clusters is not understood. At high temperatures ($T > 700^\circ\text{C}$), and for times beyond those associated with nucleation, the rate of precipitate growth appears to be controlled by the diffusivity of O_i atoms (D_{Oxy}) and implied values are close to measured ones. The same has not been established during the nucleation stage. Meanwhile, there has been a long debate about whether or not D_{Oxy} during clustering at lower temperatures can be assumed to be close to an extrapolation of these results. Enhancements of D_{Oxy} would be necessary to explain how the series of thermal donor (TD) defects might be distinguished by the incorporation of different numbers of clustered O-atoms, though the structure of these defects has not been established. On the other hand, measurements of out-diffusion imply values which are much larger than normal but they exhibit a complicated dependence on $[O_i]$ and anneal time. The kinetics of the loss of $[O_i]$ from solution at these low temperatures are now well defined. At the lowest temperatures ($T < 400^\circ\text{C}$) the rate depends on $[O_i]^2$ and is directly related to an extrapolation of measurements of the loss of stress-induced dichroism at even lower temperatures. The straight-forward interpretation is that clustering is limited by D_{Oxy} that its' value is not significantly greater during clustering than is expected for the singly activated process with E_a 2.53eV, and that O_2 dissociation is not significant. For anneals at higher temperatures ($400 < T < 500^\circ\text{C}$), the rate depends on increasingly large powers of $[O_i]$ and is reduced relative to an extrapolation (E_a 2.53eV) of the lower temperature results. It is clear that a reverse reaction is becoming competitive, but a quantitative explanation seems to require that relatively large clusters are being formed at rates close to those at which O_i - O_i interaction has been assumed to occur: there is little alternative but to assume that O_2 must diffuse relatively rapidly. While the kinetic observations can thus be explained together TDs could be associated with the series of large stable agglomerates ($O_n; n > 7$) that would then form by dimer agglomeration, this scheme does not naturally account for a wide range of other observations: fast realignment of TDs, their complicated annealing, the detection of other clusters with concentrations proportional to $[O_i]$ in as-grown material, and their evolution during anneals together with the early TDs. Although the concept of the rapidly diffusing dimer provides a mathematical solution to the kinetic problem, it may not be physically realistic. In this work we present calculations which demonstrate that a fundamentally different explanation of the kinetic observations is possible, one that does not require that any complex diffuses rapidly. As a proof of principle, it is demonstrated that if a rapidly diffusing defect is ejected by ϕ_2 which subsequently catalyses the rate of O_i hopping and dimer dissociation then the observation of second order kinetics need not imply that O_2 is stable. The underlying activation (E_a 2.5eV) implied by the measurements would then relate to the rate of catalyst generation by O_2 . The challenge then is to explain, the absence of even larger enhancements at the lower temperatures at which the rate of loss of stress-induced dichroism has been measured. While the catalyst might be the self-interstitial, it seems that vacancies would also have to be released as a second dissociation step.

THE OXYGEN DIMER IN SILICON: SOME EXPERIMENTAL OBSERVATIONS

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Key words: silicon, oxygen dimers, annealing, binding energy

The oxygen dimer should be the first step in the clustering process of oxygen in silicon. However, no strong experimental indications of its existence have been presented so far. Recently a model for the dimer formation has been presented and it was suggested that an infrared absorption band observed at 1012 cm^{-1} originates from the oxygen dimer [1].

In this investigation correlated bands at about 1012 , 1060 and 1105 cm^{-1} have been studied using heat-treatments at temperatures in the range 350 - 1000°C . The duration of the treatment was chosen to achieve the equilibrium concentration of dimers. Due to the estimated lifetime of the dimer a quenching procedure had to be used at higher temperatures. From the results it was possible to determine the binding energy of the dimer to be about 0.3 eV . An additional support for the assignment of the bands at 1012 , 1060 and 1105 cm^{-1} to the oxygen dimer was found from the correlation between the strength of these bands and the interstitial oxygen concentration.

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HIGH-FIELD EPR SPECTROSCOPY OF THERMAL DONORS IN SILICON

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Key Words: silicon, oxygen, high field EPR, aggregation, thermal donor

Thermal donors (TD), produced by annealing of Czochralski-grown silicon at $\sim 450^\circ\text{C}$, are among the most studied defect centers. In spite of that their microscopic structure is not unambiguously established.

The aggregation process, in which oxygen atoms are involved, generates a family of very similar but distinctly different defects. Magnetic resonance investigations of thermal donors are handicapped by this multispecies character because individual EPR spectra cannot be separated in the traditional experiment. In the present study we have applied magnetic resonance spectroscopy at high magnetic fields, $\approx 5\text{T}$, to resolve the individual species.

The measurements, performed at 140 GHz, allow for the first time the EPR identification of the individual TD species, which are observed in their singly ionized charge state TD^+ . In this way the growth kinetics of individual species as well as the structural changes upon the development of thermal donor centers could be followed. The results are compared with those obtained from the high-resolution field-swept ENDOR studies [1], the magneto-absorption experiments in high fields around 12.5 Tesla [2], and the TD development kinetics as revealed by the infrared absorption studies [3]. Special attention is paid to the bistability effect as reported for the first two TD species.

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LOCAL VIBRATIONAL MODES OF A WEAKLY BOUND H-O COMPLEX IN Si

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Key Words: Hydrogen, Oxygen, Complex, Silicon, Local Modes

In crystalline silicon, hydrogen and oxygen are important impurities and they have therefore been studied intensively over the years. In spite of this, it was only recently found that the presence of hydrogen enhances the migration of oxygen in silicon at moderate temperatures 300-500 °C. This suggests that hydrogen and oxygen impurities form a weakly bound complex since a strongly bound complex would retard the migration and the absence of bonding would imply that the migration was largely unaffected by hydrogen. The objective of this work has been to clarify whether such weakly bound H-O complexes exist.

Protons or deuterons were implanted into oxygen-rich and oxygen-poor materials at temperatures below 20 K. Implantations at several energies and doses were performed to yield a uniform distribution of hydrogen or deuterium with a local concentration of $3.3 \times 10^{17} \text{ cm}^{-3}$. After the implantation, infrared absorption measurements were carried out at 8 K without intervening heating of the sample. In the as-implanted sample one intense line associated with a Si-H stretch is observed at 1998 cm^{-1} with the same intensity in oxygen-rich and oxygen-poor material. The 1998-cm^{-1} line disappears after annealing at about 180 K and a series of new lines appear. Of particular interest for this work are lines at 1029 and 1830 cm^{-1} which show up only in oxygen-rich material. In deuterium-implanted silicon, the 1830-cm^{-1} line shifts down in frequency to 1329 cm^{-1} while the 1029-cm^{-1} line shifts up by 3 cm^{-1} only, to 1032 cm^{-1} . The 1830-cm^{-1} line is assigned to a Si-H stretch mode whereas the 1029-cm^{-1} line is ascribed to a Si-O stretch mode. The two modes have the same annealing behaviour and they disappear together at $\sim 220 \text{ K}$. Moreover, in samples coimplanted with overlapping profiles of protons and deuterons no additional modes are observed. On this basis, we conclude that the 1029- and 1830-cm^{-1} modes originate from a center containing oxygen and a single hydrogen atom. The observed frequencies and isotope shifts are discussed in connection with the results of *ab initio* calculations and plausible models are discussed.

VACANCY AGGREGATES IN SILICON

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Keywords: theory, vacancies, silicon, ring-hexavacancy

Monovacancies are rapidly diffusing intrinsic defects in silicon. They form complexes with impurities (donors, acceptors, oxygen, and others) as well as with other vacancies. Positron annihilation spectroscopy data imply that a wide variety of vacancy aggregates exist. However, there is little microscopic information on their configurations, stability, or electrical and optical activity.

We have calculated the lowest-energy configurations, stability, and electronic structures of vacancy aggregates containing up to $n=7$ vacancies. The calculations were done using a first-principles tight-binding molecular-dynamics method (based on density-functional theory) in large periodic supercells as well as at and near the ab-initio Hartree-Fock level in molecular clusters. These two approaches are very different in the way Schrodinger equation is solved and in the way the host crystal is approximated. However, many of the predicted key features of the defects are the same. Our results lead to the following conclusions.

1. One gains energy by adding one vacancy to an aggregate of $\{n-1\}$ vacancies.
2. Up to $n=6$, the lowest-energy configuration of the n -vacancy cluster (V_n) occurs when Si atoms are successively removed from a hexagonal ring.
3. The binding energy of V_n strongly varies with n . The most stable aggregate, by far, is the ring-hexavacancy (this was predicted by Chadi and Chang in 1988 using an empirical model).
4. The lowest dissociation energy corresponds to the process $V_n \rightarrow V_{n-1} + V_1$.
5. Up to $n=7$, all the V_n 's have deep levels in the gap except the ring-hexavacancy, which theory predicts to be electrically and optically inactive.

The ring-hexavacancy cannot form at temperatures higher than those at which the divacancy dissociates. However, once formed, it should survive high-temperature anneals and grow by trapping additional vacancies. The ring-hexavacancy is trigonal, planar, and remarkably stable. It is therefore a plausible nucleus for extended defects such as H-related platelets and prismatic dislocations. Since it is a large void in the crystal, it also likely to be a gettering center for a range of impurities.

IDENTIFICATION OF VH IN SILICON BY EPR

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Key words: Silicon, hydrogen, dangling bonds, vacancy, EPR.

It is well known that hydrogen and silicon atoms may form strong covalent bonds. The monovacancy in silicon possesses dangling bonds and is thus expected to form the rather stable complexes VH, VH₂, VH₃, and VH₄ with hydrogen. Recently, the Si-H stretch modes of VH₂, VH₃, and VH₄ were identified, but the simplest structure VH has not been observed. Furthermore, no detailed study of the electronic properties of vacancy-hydrogen defects has been reported. In this work, the structure of VH is identified by Electron Paramagnetic Resonance (EPR).

Float-zone grown silicon crystals were implanted with protons or deuterons at about 100 K. The energies and doses were chosen so that the distribution of hydrogen or deuterium was uniform throughout the sample. Subsequently, the samples were annealed at room temperature to form vacancy-hydrogen defects. EPR spectra were recorded in the temperature range from 35 to 225 K. The spectra contain a family of signals previously labelled S1. In addition, a strongly temperature dependent signal, which displays monoclinic-I symmetry below 65 K and trigonal symmetry above 100 K is observed. Comparison of the spectra recorded in proton- and deuterium-implanted samples allows identification of the hyperfine splitting from a single proton. Weak satellites arising from ²⁹Si hyperfine interaction show that most of the electron spin density is associated with a single silicon atom. On this basis, we conclude that the temperature dependent signal originates from VH⁰, the neutral charge state of a vacancy containing a single hydrogen atom. The transformation from monoclinic-I to trigonal symmetry may be explained as the result of thermally activated jumps of the defect among its three equivalent configurations that leaves the hydrogen atom bound to the same silicon atom. Additional support for the assignment made above is obtained from a simple analysis of the dipolar part of the hydrogen hyperfine interaction. This indicates that the distance from the hydrogen to the silicon atom carrying the dangling bond is ~2.7 Å, which is consistent with the structure of VH⁰ as expected from theory. Apart from the hydrogen hyperfine splitting, the properties of the temperature dependent signal, including the spin Hamiltonian parameters, are very similar to those of the E-center (VP⁰). In this context, the Si-H unit can thus be viewed as a "pseudo-atom", acting like a group-V impurity.

VACANCIES AND INTERSTITIAL ATOMS IN IRRADIATED Si

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Key Words: Silicon, vacancies, interstitials, irradiation effects, diffuse X-ray scattering

Vacancies and interstitial atoms are produced in by MeV electron irradiation in differently doped Si wafers and we show that a high concentration of defects ($>10^{19} \text{ cm}^{-3}$) can be frozen in at 4K. From X ray diffraction experiments we deduce that, similar to the observations with III-IV compounds/1/, a large fraction of the defects is stabilized in the form of close Frenkel pairs. The structure of these bound pairs is characterized by the nearly perfect cancellation of the long range displacement fields of the interstitial atom and the vacancy. We discuss the absolute size of these displacements, which are characterized by a relaxation volume of $+0.5$ atomic volumes respectively, as well as the introduction rate of the defects, which is of the order of $\sim 1 \text{ cm}^{-2} \text{ s}^{-1}$. Additional larger defect agglomerates are observed at higher irradiation doses. These results are rather independent of the oxygen content of the samples and of the position of the Fermi level: i.e. for weakly doped Cz-Si or oxygen free FZ-Si and for highly doped degenerate p-type Si(B) and n-type Si(As). These high defect introduction rates are at variance to the results of electrical and EPR investigations/2/ and indicate that these methods detect only a few percent of the total defect concentration which is produced and frozen in at 4K. The consequences for the understanding of the defect production in Si and for the assumption of an athermal migration of interstitial atoms are discussed. The defect patterns observed after 4K irradiation are compared to those of room-temperature irradiations where thermally activated migration is expected. In addition the thermally activated defect reactions observed during annealing at temperatures up to 1000K are discussed with special emphasis to the trapping and detrapping reactions of the defects. The observed defect reactions are discussed and compared to the observations during transient diffusion after ion implantation and to the results of high temperature diffusion experiments.

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ODMR STUDIES OF AS-GROWN AND ELECTRON-IRRADIATED GaN AND AlN

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Key Words: GaN, AlN, wide bandgap, electron-irradiation

There is considerable interest in the role of point defects in the III-V nitrides, stimulated by their successful application in blue light emitting and laser devices. We here describe optical detection of magnetic resonance (ODMR) studies in GaN and AlN, before and after 2.5 MeV electron irradiation. This first such study of defects produced by electron irradiation in these materials has been initiated because it may shed light on the properties of their intrinsic defects about which little is presently known.

In the case of epitaxial wurtzite layers of GaN grown on sapphire, ODMR is studied via photoluminescence (PL). Before electron irradiation, we observe the two ODMR signals previously reported by many workers in the luminescence band at 2.2 eV. After electron irradiation, two new bands are produced at ~0.85 eV and ~0.93 eV, from which four previously unreported ODMR signals are observed. One of these reveals resolved hyperfine interaction with a single Ga nucleus, indicating a displaced Ga atom of some kind. It is tentatively identified as a complex involving interstitial Ga_i⁺⁺.

In the case of AlN, small single crystals are available and ODMR could be performed both via PL and magnetic circular dichroism (MCD) in absorption. At least six well-resolved distinct ODMR signals are observed before electron irradiation in a broad luminescence band near 2 eV, four with S=1, two with S=1/2. The chemical identity associated with these signals has not as yet been established. Studies of electron-irradiated samples are currently in progress and will be described.

This research was supported jointly by the U.S. Navy Office of Naval Research under Grant No. N000014-94-1-0117 and the National Science Foundation under Grant No. DMR-92-04114.

ELECTRICAL AND OPTICAL CHARACTERIZATION OF DEFECTS IN GaN GENERATED BY ION IMPLANTATION

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Key Words: GaN, Implantation, DLTS, Luminescence

Radiation damage of GaN by N-ion implantation can result in an enhanced n-type carrier concentration and in generation of deep traps D2 and D3 [1]. In this paper we study samples which were grown by metal-organic vapor phase epitaxy (MOVPE), implanted with various ions and subsequently treated by rapid thermal annealing to investigate electrical properties of impurities doped by implantation. By Hall effect, capacitance-voltage measurements, deep level transient spectroscopy (DLTS), and by photoluminescence spectroscopy we study the carrier concentration, defect generation, and defect annihilation.

Implantation of GaN with Mg and following annealing results in samples which are significantly different if Mg is replaced by N or Ga. For doses around 10^{12} cm^{-2} the sample remains clearly n-type with a carrier concentration around several 10^{16} cm^{-2} . In photoluminescence spectroscopy a donor-acceptor band shows up. For higher doses of 10^{14} cm^{-2} a considerable drop in the n-type carrier concentration is found. The traps found in DLTS are those known from radiation damage.

Implantation of K ions at doses of 10^{12} cm^{-2} and subsequent annealing reduces the carrier concentration by three orders and produces a new trap 0.49 eV below the conduction band. This level is energetically close to a level which is found if C is implanted instead of K. Implantation of K and C seems to strengthen the level D3 against annihilation. After implantation the 3.365-eV-luminescence line shows up, which recently was assigned to an exciton strongly bound at extended defects [2].

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IMPLANTATION DOPING AND HYDROGEN PASSIVATION OF GaN

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Keywords: GaN, hydrogen passivation, Cd acceptors, ion implantation

The possibility of p-type doping of GaN by ion implantation has been studied using the perturbed γ angular correlation spectroscopy (PAC) [1]. To determine the lattice site of the implanted ions and to discriminate between defects created by the heavy ion implantation and their interaction with implanted Cd-acceptors, both the group III probe atom ^{111}In and the group II acceptor ^{111}mCd have been implanted ($E = 60 \text{ keV} - 350 \text{ keV}$, doses $5 \times 10^{11} \text{ cm}^{-2} - 3 \times 10^{12} \text{ cm}^{-2}$) into n-type GaN grown on sapphire by MOCVD. The annealing of the implantation damage has been studied up to annealing temperatures of 1300 K and shows that up to 80% of the implanted ^{111}mCd ions reside on substitutional Ga lattice sites without defects present in the immediate neighborhood after annealing at 1100 K.

We also report on the microscopic observation of the formation of Cd-H pairs in GaN using the radioactive acceptor ^{111}mCd as probe atom which has been implanted at 60 keV with $5 \times 10^{11} \text{ cm}^{-2}$. After annealing at 1100 K, the hydrogen loading has been performed between 295 K and 425 K using a mass-separated 100 eV H^+ ion beam (dose $1 \times 10^{15} \text{ cm}^{-2}$). After H-loading at temperatures up to 323 K, the formation of two Cd-H complexes involving about 30% of the Cd-acceptors is observed. Both complexes show axially symmetric electric field gradients ($\eta = 0.0(1)$). The less stable configuration characterized by $\nu_Q = 572(2) \text{ MHz}$ is only observed at H-loading temperatures at or below 323 K and its symmetry axis is oriented along directions with an angle of about $110(20)$ degrees with respect to the c-axis of the hexagonal wurtzite structure. The dominant Cd-H configuration ($\nu_Q = 362(2) \text{ MHz}$) is symmetric along the c-axis and stable up to 550 K corresponding to a dissociation enthalpy of 1.8 eV. The observed symmetry and stability of the formed Cd-H pairs will be discussed in the framework of theoretical calculations [2].

We acknowledge the Hewlett-Packard Optoelectronics Division for supplying the GaN samples. This work has been supported by the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie under Grant No. 03-RE4KO1-5.

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ELECTRICALLY AND OPTICALLY DETECTED MAGNETIC RESONANCE IN GaN-BASED LEDS

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Key Words: GaN, EDMR, ODMR, Magnetic Resonance, LED, EPR, Recombination

Electrically detected magnetic resonance (EDMR) has emerged as a highly sensitive probe of defects in semiconductor device structures. In this work we combine EDMR with electrically excited, optically detected magnetic resonance (i.e., electroluminescence detected magnetic resonance - ELDMR) to study and quantitatively compare radiative and non-radiative recombination in GaN-based single quantum well (SQW) LEDs. These bright green and blue LEDs have found application in full color displays and have many of the same elements of nitride-based laser diodes. The electroluminescence (EL), due to bandedge emission from a SQW of undoped InGaN, is especially impressive given the high densities of stacking faults and other defects in these devices. Here we study the role of point defects in these diodes.

The dominant magnetic resonance feature detected by either technique in both the green and blue diodes is a broad line (DB^a13 mT) at g^a2.01 due to a deep defect. Depending on bias, this defect results in either an increase or a decrease in electroluminescence at resonance and, similarly, we observe a current enhancing or current quenching signal at resonance depending on bias and temperature. By comparing the amplitudes and phases of the electrically and optically detected resonance signals we are able to conclude that the resonance signal is due to nonradiative recombination channels in a parallel leakage path and in the depletion region of one of the contacts. Furthermore, we have been able to determine the amplitudes of the contributions from the different regions of the devices.

A second resonance with g^a1.99 and DB^a7 mT is very similar to the deep donor trap, previously observed in double heterostructure diodes and, by optically detected magnetic resonance, in GaN thin films. This defect produces a decrease in both the current and electroluminescence at resonance in both SQW diodes. While the bias dependence of this resonance is different in the two diodes, the lineshape and position are very similar leading us to suggest that this defect is located in the low x In_xGa_{1-x}N buffer layer between the n-AlGaIn layer and the quantum well.

We have also used these spectroscopic techniques to study degradation mechanisms in the SQW diodes and found the amplitude and phase of the signals to be a complex function of current stressing. The results for unstressed and stressed diodes provide important insights into the location and nature of the defects responsible for the magnetic resonance spectra and for degradation processes.

DONOR ACCEPTOR PAIR TRANSITIONS IN GaN

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Key Words: GaN, PL, Donor-Acceptor transitions

We report the observation of several new photoluminescence bands in the near-bandgap energy range of GaN. The 6H GaN layers were grown by MBE at temperatures around 650°C on sapphire substrates with an intermediate AlGaIn nucleation layer.

In addition to the well-known donor-bound exciton line at 3.475 eV and the oxygen-related 3.418 eV line (at 4 K), we find weaker defect-related lines in the energy range extending to 400 meV below the bandgap, but no 'yellow band'. Variation of the sample temperature between 4 K and room temperature and variation of the excitation power allows us to identify two lines at 3.345 eV and 3.285 eV as donor-acceptor pair transitions. The estimated binding energy of the acceptors involved is no more than 130 meV and 190 meV, respectively.

Further lines at 3.365 eV and 3.21 eV are studied as well, but not finally assigned.

AB INITIO STUDIES OF ATOMIC-SCALE DEFECTS IN GaN AND AlN

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Key Words: GaN, AlN, oxygen, DX, compensation, luminescence

The plane-wave pseudopotential method is applied to study point-defects and their complexes in GaN and AlN. The calculations predict a qualitative difference in the donor behaviour between the two materials: the dominant impurity-related donors are shallow in GaN while in AlN they have a deep character, in good agreement with the experimentally measured electrical conductivity. Oxygen is found to act as a self-compensating DX-like center in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys with sufficient Al concentration. Effective compensation through metal vacancies (V_{Ga} , V_{Al}) and related complexes is shown to occur in both materials. The induced electronic levels in the bandgap are found to closely correlate with the commonly detected broad-band luminescence (yellow in GaN and violet in AlN).

PHOTOLUMINESCENCE KINETICS IN THE NEAR BANDGAP REGION OF HOMOEPITAXIAL GAN LAYERS

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Keywords: GaN, homoepitaxy, MOCVD, photoluminescence, transients, donors, acceptors.

Homoepitaxial MOCVD-grown gallium nitride (GaN) layers have been studied by photoluminescence (PL) measurements, picosecond (ps) time-resolved luminescence spectroscopy (TRL) and by photoluminescence excitation spectroscopy (PLE). The investigated nominally undoped homoepitaxial layers have the emission spectrum dominated by the donor bound exciton (DBE) recombination. The obtained PL decay times τ for the A free excitons (FE) and the DBE at 2 K were equal to 120 ps and 260 ps, respectively. These decay times of the excitons are nearly as long as the radiative ones, which have been observed in bulk GaN grown by hydride vapor phase epitaxy [1]. The measured PL decay times τ are correlated with the nonradiative defects present in the material, and are dependent on the excitation intensity. The corresponding delay times (measured as a difference between the laser pulse and emission maximum) were $\tau_d = 30$ ps and 110 ps for FE and DBE emissions, respectively. These delay times relate to the capture processes for the excitons down to the A ground state and the DBE state, respectively.

The investigation of the spectral region just below the DBE emission revealed presence of at least two processes. The first relatively weak emission line, connected with acceptor bound excitons at 3.466 eV (and the phonon wing connected with this line) has the delay time τ_d equal to 130 ps. The second process gives a weak but clearly visible emission peak at the energy 3.450 eV. It has been found that the shorter delay time τ_d equal to 110 ps is connected with this emission. This value exactly corresponds to the delay which is characteristic for the DBE ($\tau_d = 110$ ps). We suggest that the 3.450 eV emission peak corresponds to the so called two electron transition connected with the DBE. Recombination of the DBE in this process leaves the neutral donor in the excited state. It gives the transition energy between donor 1s-2s states equal to 22 meV, which corresponds to the ionization energy of the residual shallow donor of about 29 meV.

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OBSERVATION OF NATIVE GA VACANCIES IN GAN BY POSITRON ANNIHILATION

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Key Words: GaN, yellow luminescence, compensation, positron annihilation

The role of various defects in the properties of GaN still awaits a detailed description. For example, the parasitic optical transition leading to the yellow luminescence band at about 2.2 - 2.3 eV is observed both in GaN bulk crystals and layers, but the nature of the electronic levels participating in this optical process are under discussion. There is an increasing amount of evidence that this transition takes place between a shallow donor and a deep acceptor. The Ga vacancy has been suggested as the defect responsible for the acceptor level.

In this work we use positron annihilation spectroscopy to obtain structural information on native point defects in GaN materials. Bulk crystals grown under 1.5 GPa nitrogen pressure at 1500 °C were studied by positron lifetime and Doppler broadening techniques. Epitaxial layers grown by MOCVD on sapphire substrates were characterized by a low-energy positron beam.

The results show that negative vacancies are present at concentrations $10^{17} - 10^{18} \text{ cm}^{-3}$ in both GaN bulk crystals and layers. The vacancies are in the Ga sublattice and their concentration correlates with the intensity of the yellow luminescence. We conclude that the Ga vacancies contribute to the electrical compensation of n-type GaN and their acceptor levels are involved in the yellow luminescence transition.

ZEEMAN STUDY OF 6H-SiC:CR

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Key Words: SiC, Transition Metals, Luminescence, Zeeman Effect, EPR

Silicon carbide of the 6H polytype shows three luminescence lines I_1 (9587 cm^{-1}), I_2 (9516 cm^{-1}), and I_3 (9321 cm^{-1}) which were previously reported by Gorban and Slobodyanyuk [1]. We find these lines as the dominant luminescence transitions in chromium-doped material. The Zeeman splittings of the lines are studied.

Each line splits into a triplet with a g factor around 2.0 and which is almost isotropic within the resolution of optical Zeeman spectroscopy. Only line I_2 shows a small zero-field splitting with $|D| = 0.2\text{ cm}^{-1}$. Additionally, each Zeeman triplet-line of I_1 and I_3 undergoes a doublet splitting which is strongly anisotropic. The doublet splitting vanishes for the field aligned parallel the c -axis. If the field is aligned along the c -axis, the splitting corresponds to an effective g factor of $aS = 1/2$ system with $|g| = 0.65, 0$, and 0.25 for I_1, I_2 , and I_3 , respectively.

Electron-paramagnetic resonance studies performed at the identical sample show the presence of $\text{Cr}^{2+}(3d^4)$ and $\text{Cr}^{3+}(3d^3)$ in absence of illumination. The Zeeman spectra clearly rule out, participation of the Cr^{2+} and Cr^{3+} in the luminescence transitions. Instead, we assign the lines to transitions between the state $^3A_2$ of $\text{Cr}^{4+}(3d^2)$, not observed in EPR, and two further doublet states. We discuss the luminescence spectra on the background of charge-transfer transitions in which an electron or hole radiatively recombines with Cr^{4+} .

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A DEEP PHOTOLUMINESCENCE BAND IN 4H SiC RELATED TO THE SILICON VACANCY

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Key words: 4H SiC, silicon vacancy, photoluminescence, ODMR

The primary defects, such as the vacancies in SiC, are of great scientific and technological interest since they are thermally stable at room temperature. Among the various polytypes, 4H SiC seems to be the most promising material for high temperature and power device applications, because of its relatively large band-gap and high nearly isotropic electron mobility. In this work we have studied a new deep photoluminescence (PL) band in 4H SiC, which we by optically detected magnetic resonance (ODMR) can show is related to the silicon vacancy. The PL band is irradiation induced and gains in strength with the dose. It has, as expected for the 4H polytype with its two inequivalent defect sites, two sharp no-phonon lines at 1354 meV and 1440 meV.

Optically detected magnetic resonance (ODMR) on this PL band with above band-gap excitation, reveals several signals corresponding to spin-triplet states ($S=1$). The signals all have axial symmetry along the c-axis and a relatively small zero-field splitting of the magnetic sub-levels (D-value). The true correspondence between PL lines and triplet-states is revealed when selective excitation with no-phonon energies of the two PL lines is used. Only then can the two triplet-states that directly corresponds to the two PL lines be detected separately and only then is the well documented and characteristic hyperfine interaction of the silicon vacancy in SiC resolvable.

Because of the correlation between the irradiation dose and the signal strength and the characteristic hyperfine pattern, we suggest that this PL band is related to the isolated silicon vacancy in 4H SiC. The well known electron spin resonance signal from negative charge state of the silicon vacancy 4H SiC has an effective spin of $1/2$. An integer spin like $S=1$ can then not be formed by this charge state and it is reasonable to assume that the signal that we detect originates from either the neutral or the doubly negative charge state of the vacancy.

Interesting comparisons with the analogue defect system in 6H SiC will also be made.

VACANCY-TYPE DEFECTS IN PROTON-IRRADIATED SiC

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Key Words: SiC, point defects, proton irradiation, positron annihilation

In this contribution we report results of an investigation of proton-irradiation induced defects in 6H-SiC using positron lifetime and Doppler-broadening spectroscopies. The experiments were performed on N-doped (n-type) and Al-doped (p-type) crystals with carrier concentrations, $N_D - N_A = 1.7 \times 10^{18} \text{ cm}^{-3}$ and $N_A - N_D = 6.2 \times 10^{18} \text{ cm}^{-3}$, respectively. The samples were irradiated with 5 MeV protons at a sample temperature of 220 K.

In an earlier paper¹, we showed that SiC wafers of both 6H and 4H polytypes contain only small amounts of vacancy type defects in the as-grown state. These defects exhibit a positron lifetime of about 300 ps, which suggests complexes with divacancy character. Upon irradiation to a dose of $1 \times 10^{16} \text{ cm}^{-2}$, the positron lifetime spectra showed two new distinct, defect related lifetimes, with values of about 160 and 260 ps. Dannefaer et al.² obtained very similar results for 2.2 MeV electron irradiation and assigned the lifetimes to carbon and silicon vacancies. In their case however, the required dose was about a factor of 20 higher and the relative intensities of the two components, related to the respective defect concentrations, were significantly different, indicating markedly different defect introduction rates. The stability of the observed defects is investigated by annealing studies. The effect of proton irradiation on p-Type SiC, where electron irradiation did not produce positron traps², but lead to an EPR signal associated with (positively charged) carbon vacancies³, will also be discussed.

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THEORY OF 3D TRANSITION METAL DEFECTS IN 3C SiC

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Key Words: 3d transition metal impurities, hyperfine interactions

We present ab-initio total energy calculations for the electronic structure of 3d transition metal (TM) defects in 3C SiC. We employ the standard local spin-density approximation of the density functional theory. The electronic structure of the point defects is calculated using a Green's function approach based on the linear Muffin-tin orbitals Method in the atomic-spheres approximation. This method allows to accurately calculate the hyperfine interactions of the paramagnetic 3d TM states with the paramagnetic nuclei of the TM and also with the ^{13}C and ^{29}Si ligand nuclei. It further allows to include all charge states and possible spin state configurations without any additional approximation. Unfortunately the method does not allow to include lattice relaxations.

3d TM are ubiquitous contaminants in most semiconductors including SiC and the identification of these defects is often quite cumbersome. In this situation a theoretical survey of the defect's electronic structure can be quite helpful, in particular if the hyperfine interactions are determined which in most defect identifications play a dominant role.

Although both constituents of the lattice are group IV atoms, the SiC lattice is very ionic. Consequently, the electronic states of the 3d TM ions located on one of the two different substitutional positions in 3C SiC turn out to be quite site-dependent. We explain the differences for the 3d TMs on the two substitutional sites within the vacancy model: the difference of the electronic structure between the carbon vacancy V_{C} and the silicon vacancy V_{Si} is responsible for the differences of the 3d TMs. In all charge states of the defects the ground states are found to be low-spin states and only in a few exceptional cases there is the possibility for excited high-spin states.

The electronic properties of 3d TMs on the two tetrahedral interstitial sites differ even more: the TMs surrounded tetrahedrally by four silicon atoms experience an exceptionally large crystal field which prohibits the formation of high-spin states even as excited states. In contrast, the crystal field splitting for 3d TMs tetrahedrally surrounded by four carbon atoms experience virtually no crystal field at all. It is only in this case that high-spin ground state configurations are predicted. The resulting hyperfine interactions and ligand hyperfine interactions are compared with the experimental data. We show that in almost all cases a satisfactory agreement is found with experimental data whenever available.

THERMAL ACTIVATION ENERGIES FOR THE THREE IN-EQUIVALENT LATTICE SITES FOR THE B_{Si} ACCEPTOR IN 6H SiC

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Key Words: Silicon Carbide, boron, admittance spectroscopy

Electron spin resonance (ESR) studies show that boron substitutes for silicon in the SiC lattice. In 6H SiC it occupies three in-equivalent sites (h, k¹ and k²) and is expected to display three separate energy levels in the band gap. Reports for the activation energy of B_{Si} as measured by Hall effect and admittance spectroscopy range from $E_v + 0.30$ to $E_v + 0.39$ but only as a single level.

We have used both high temperature Hall effect and thermal admittance spectroscopy (TAS) measurements to study the boron levels in bulk 6H-SiC. The samples used were all grown by physical vapor transport (PVT). With TAS we were able to identify, for the first time, three separate energy levels and have assigned them to the h, k¹ and k² sites of B_{Si}. The energies are: $E_h = E_v + 0.27$ eV, $E_{k1} = E_v + 0.31$ eV and $E_{k2} = E_v + 0.38$ eV. To the best of our knowledge, this is the first report for the activation energies due to the in-equivalent sites of an acceptor in SiC. We note that these levels are not related to the deeper D-center, which is also associated with boron in SiC but is a different defect. Initial results on the shallow levels reported here indicate that the degree of compensation determines which of these levels is observed by less highly resolved techniques such as temperature dependent Hall effect. This accounts for the scatter in the activation energies reported in the literature.

THE MICROSCOPIC STRUCTURE OF THE BORON ACCEPTOR IN 6H- AND 4H-SiC - STUDIES WITH MAGNETIC RESONANCE

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Key Words: EPR, ENDOR, SiC, boron, acceptor, effective mass theory

Boron is a common contaminant in SiC and also next to aluminium the most important acceptor. In its paramagnetic charge state, it has been intensely investigated with electron paramagnetic resonance (EPR) [e.g. 1-3]. In a 6H-SiC sample enriched with ^{13}C [3] it could be shown that the largest hyperfine (hf) interaction was not measured with the two magnetic isotopes ^{10}B and ^{11}B , but with one neighbouring ^{13}C nucleus. It was argued [3] that about half of the unpaired hole resides on a nearest C atom and that only very little is found at the B nucleus. Recently, with electron nuclear double resonance (ENDOR), the $^{10,11}\text{B}$ hf and quadrupole interactions of B^0 in 6H-SiC were measured with high precision and it was confirmed that B carries almost no spin density [4,5,6]. Müller et al [4] concluded that the hole was oriented in a C-Si bond almost perpendicular to the B_{Si} -C bond. A re-examination of the ENDOR measurements as well as pulsed ENDOR measurements [5] yield that the relative signs of the anisotropic B hf interaction constant and the quadrupole interaction constant are the same instead of having opposite signs [4]. From the interpretation of the ENDOR data, the following model for the B acceptor is proposed: B occupies an Si site, the C-2p hole is oriented within the B_{Si} -C connection line as was originally postulated by Zubatov et al [3]. At low temperature, the symmetry of the B acceptor on the two quasi-cubic sites is monoclinic, while it is C_{3v} on the hexagonal site. At higher temperatures ($\sim 50\text{ K}$) the hole at the C of the two quasi-cubic site acceptors becomes thermally activated with the result that the acceptors display a C_{3v} symmetry in their EPR spectra. It was proposed that the acceptor property is transferred to the nearest C, and B_{Si} is only a ligand to the hole-carrying C. The shallow B-acceptor was denoted as 'boron-induced carbon acceptor' [4]. We report also on similar investigations of B acceptors in 4H- and 3C-SiC, which were undertaken to see whether this unexpected behaviour of B acceptors also applies to other polytypes of SiC.

Measurements with photoluminescence-detected EPR, in which the B^0 EPR spectrum in 6H-SiC is measured as a microwave-induced change of the N^0 -donor- B^0 -acceptor pair recombination luminescence, confirmed the level of the B acceptor to be at $E_{\text{v}} + 300\text{ meV}$. But these experiments also revealed that the B acceptor has a different microscopic structure if the hole is captured at very low temperature, e.g. 1.5 K . The symmetry of the defect is now C_{3v} and the hf interaction is reduced to half of the value measured when capturing the hole at higher temperature. Apparently, the hole carrying carbon has a thermal barrier against the relaxation towards B_{Si} [7].

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HIGH-FREQUENCY EPR STUDIES OF SHALLOW AND DEEP BORON ACCEPTORS IN 6H-SiC

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Key Words: EPR, Acceptors, SiC

Boron is known to produce shallow and deep acceptors in SiC. The shallow boron acceptor (ionisation energy 350 meV) has been studied extensively in the last 30 years and the theoretical model for its geometric and electronic structure has been reinterpreted several times. EPR experiments on a ^{13}C -enriched 6H-SiC crystal established that B replaces Si and that it occupies 3 sites with equal probability: two quasi cubic (k1 and k2) and one hexagonal (hex) [1]. In the model proposed by Zubatov et al. [1] the main spin density was located in the dangling bond of a C atom along the B-C connection line. In more recent publications [2-4] a new description was given on the basis of ENDOR and ODMR investigations. In this model the valence electron is donated to B by a neighbouring C atom thus forming a $\text{B}^-\text{Si}-\text{C}^+$ bond. The unpaired electron of C^+ is uniformly distributed among the three back bonds. The authors call this model the boron-induced carbon acceptor.

EPR and ENDOR spectroscopy at 95 GHz on the shallow B acceptor in a ^{13}C -enriched 6H-SiC crystal has allowed us to measure accurately the g-tensors of the 13(!) magnetically inequivalent B sites. Moreover we have measured the hyperfine tensors of the ^1B , and ^{13}C nuclear spin of the neighbouring C atom. From the results we conclude that the main density of the unpaired electron is located on the B-C bond as originally suggested by Zubatov et al. [1]. From a ^{29}Si and ^{13}C ENDOR study it is further concluded that 60-70% of the spin density is distributed in the crystal with a Bohr radius of 2.2 Å, a value in reasonable agreement with effective-mass theory.

The deep B acceptor (ionization energy ~ 600 meV) in 6H-SiC has also been studied by EPR and ENDOR spectroscopy at 96 GHz. In particular the ENDOR results on ^1B support the model proposed by Baranov et al. [5-7] in which the deep B-acceptor consists of a B-vacancy pair. This model explains in a consistent way all EPR and ENDOR data.

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INTRINSIC MODULATION DOPING IN InP-BASED HETEROSTRUCTURES

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Key Words: intrinsic, doping, antisite, InP, InGaAs, off-stoichiometric, MBE, HEMTs

We review our recent results from a new approach for n-type modulation doping in InP-based heterostructures, where grown-in intrinsic defects are utilized to provide charge carriers without requiring an external shallow impurity doping source. Such an intrinsic doping concept stems from our experimental observation that intrinsic P_{In} antisites can be preferably introduced during off-stoichiometric growth of InP at low temperatures (LT) (~260 - 350 °C) by gas source molecular beam epitaxy (GS-MBE). LT-InP grown as such is highly n-type conducting, and is shown to be due to the auto-ionization of the P_{In} antisites via the (0/+) level resonant with the conduction band at $\sim E_c + 0.12$ eV. The doping level can be conveniently controlled by varying the growth temperature. When such intrinsically doped LT-InP epilayers are used as doped regions in InP-based heterostructures, modulation doping can readily be achieved without invoking an external doping source. The success of such an intrinsic modulation doping concept is clearly demonstrated by the example cases of InGaAs/InP heterostructures [1], designed to resemble high electron mobility transistor (HEMT) structures or modulation-doped quantum wells. All the layers were intentionally undoped and were grown at a normal growth temperature 480 °C except for the top InP layer which was grown at 265 °C, by GS-MBE. Though the entire structures are intentionally undoped, n-type modulation doping in the LT-InP barrier is readily realized. Unambiguous experimental evidence on the formation of a dense two-dimensional electron gas ($> 1 \times 10^{12} \text{ cm}^{-2}$) in the InGaAs active layer near the InGaAs/InP heterointerface, as a direct consequence of electron transfer from the intrinsically doped LT-InP barrier, is provided from magneto-transport and magneto-optical studies. Experimental results from other types of device structures and from undoped and extrinsically doped reference samples with identical structures will be presented for comparison.

Important issues such as doping efficiency, electron mobility, thermal stability, etc., will be addressed. Advantages and disadvantages of the intrinsic modulation doping approach will be discussed as compared to the extrinsically doping method by shallow dopants. Interesting physical properties connected to the intrinsic doping in InP-based heterostructures and their potential in device applications will also be discussed.

Though it has only been demonstrated for InGaAs/InP heterostructures, the principle of the intrinsic doping concept is in fact rather general and can be extended to applications in other electronic material systems.

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PRESSURE DEPENDENT 2-DIMENSIONAL ELECTRON TRANSPORT IN DEFECT DOPED InGaAs/InP HETEROSTRUCTURES

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Key Words: pressure, heterostructure, InGaAs, InP

We have studied effects of hydrostatic pressure on the transport characteristics of a 2-D electron gas in defect doped InGaAs/InP heterostructures. In these structures the electrons originate from resonant donor-like native defects formed in a low temperature grown InP layer rather than from intentionally introduced shallow donors [1]. Since the resonant donors are highly localized and have a pressure derivative different from that of the InGaAs conduction band, an external hydrostatic pressure offers a unique method for changing the energy of the donor levels relative to the conduction band of InGaAs, affecting the charge transfer from the barrier to the well. External pressure can thus be used to control the 2-D gas density and study the effect of changing of the occupation of the 2-D subbands on the electron mobility.

Lattice-matched InGaAs/InP heterostructures were grown by gas-source MBE on semi-insulating InP substrates. The donor defects were located in an InP layer grown at low temperature (265 ;C) and separated from InGaAs by a variable thickness spacer of InP grown at normal temperature (480 ;C). The 2-D electron density increases from $2.7 \times 10^{12} \text{ cm}^{-2}$ to $4.8 \times 10^{12} \text{ cm}^{-2}$ as the spacer width decreases from 10 to 5 nm. Calculations of the charge transfer indicate that more than one subband is occupied at these high densities. Application of hydrostatic pressure leads to a significant reduction of the electron density and an increase of the electron mobility. The pressure induced reduction of electron density can be explained by a large negative pressure derivative of the donor level relative to conduction band edge of InGaAs. We find that the electron mobility in InP/InGaAs decreases with increasing electron density, indicating that it is limited by scattering from remote Coulombic defects. In addition, it clearly shows a change of slope at the onset of the occupation of higher electric subbands. Our theoretical calculations show that this type of dependence is expected in InGaAs/InP structures where alloy disorder scattering becomes a dominant mechanism limiting electron mobility at high electron densities.

This work was supported by US DOE under contract DE-AC03-76SF00098 and by an AASERT grant from the U. S. Air Force Office of Scientific Research (AFOSR, F49620-93-1-0367TU).

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MOLECULAR DYNAMICS SIMULATIONS OF FUNDAMENTAL DEFECTS IN SILICON

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Since the pioneering work of Car and Parrinello about 10 years ago, the use of MD simulations to study defects in crystalline Si and other materials has greatly increased. First-principle, tight-binding, and now linear-scaling techniques allow the study of an ever wider range of defect problems. Simulated anneals quickly provide local and global minima of complicated potential surfaces, while constant-temperature simulations provide vibrational frequencies, diffusivities, and the observation of defect interactions. A number of tricks can be used to speed up slow reactions and observe in real time processes that are too slow to be calculated.

In this talk, I will discuss the key ingredients and implementations of MD simulations as well as the limitations of these techniques. Then, I will review some of the recent work done in the area of fundamental defects in crystalline silicon. This includes the vacancy and vacancy aggregates, the self-interstitial, some impurities (in particular hydrogen), impurity-impurity and impurity-defect interactions.

IONIZED IMPURITY SCATTERING IN ISOTOPICALLY ENGINEERED, COMPENSATED Ge:GaAs

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Key words; Ionized impurity scattering, Mobility, Compensated semiconductors

The development of a method to accurately determine the compensation ratio (K)^{*1} in a given semiconductor has become important especially for the recent studies on defects that hinder heavy doping in compound semiconductors. It has been proposed that a quantitative understanding of the carrier scattering by ionized dopants and defects could be used to determine the compensation ratios (K) based solely from Hall mobility measurements. [2] This ionized impurity scattering is routinely calculated using Brooks-Herring (BH) theory. [3] The theory has been originally developed for lightly compensated semiconductors and its applicability has never been tested in heavily compensated materials.

In this work we demonstrate much improved understanding of the carrier scattering by ionized impurities leading to accurate determination of K up to 0.6. This is the consequence of our transport studies using isotopically engineered Ge with precisely controlled majority and minority impurity concentrations, i. e., compensation. Neutron transmutation doping (NTD) of high purity Ge single crystals with controlled ⁷⁰Ge and ⁷⁴Ge isotopic compositions led to eight p-type Ge:Ga,As samples of $0.082 < K < 0.93$. The Hall mobility measurements were performed for all samples in the temperature range $T=10-300\text{K}$. A parameter-free calculation of the Hall mobility as a function of temperature was performed for each sample in the relaxation time approximation using three different ionized impurity scattering models; (i) BH theory, (ii) Falicov-Cuevas (FC) theory [4], and (iii) Stern theory. [5] Here the FC and Stern models are two independent attempts to modify the BH theory for compensated semiconductors. Our calculation also includes scattering by neutral impurities, acoustic phonons, and optical phonons. The results of the direct comparison between calculated and experimental mobilities can be summarized as follows. For $K < 0.3$ all the three models predict essentially the same mobilities for T between 10 and 300 K that agree very well with the experiments. For $0.3 < K < 0.6$ only the FC model agrees with the experiments while the BH and Stern models overestimate the mobility by more than factor of three at $T=100\text{K}$. For $K > 0.6$ all the three models fail by overestimating the mobility severely.

These results indicate that the widely used BH approach is not applicable to heavily compensated semiconductors ($K > 0.3$) while the FC model extends its range up to $K=0.6$. For $K > 0.6$ more refined treatment of the screening and multiple ion scattering may be required to explain carrier mobilities in materials with large concentration of ionized impurities in the presence of much smaller concentration of free carriers. A quantitative estimation of the error in K determined by the BH and FC models for $0.3 < K < 0.9$ samples will be given at the conference presentation.

The work at Keio was supported by grant in aid from KAST and the Ministry of Education, Japan. The work at Berkeley was supported by US NASA W17605 and US DOE DE-AC03-76SF00098.

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- * Compensation ratio $K = \frac{[Minority\ impurity\ concentration]}{[Majority\ impurity\ concentration]}$

DEPENDENCE OF ELECTRON MOBILITY ON DOPANTS IN HEAVILY DOPED SEMICONDUCTORS

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Key Words: electron mobility, ionized impurity scattering, semiconductors

We introduce a new theoretical approach to study the dependence of the low-field electron mobility on the atomic number and on the electron number of the dopants in doped semiconductors. The charge distribution of the impurities is described within the Thomas-Fermi theory in the energy functional formulation. By means of a variational principle one obtains a unique charge distribution for each dopant. It can be shown that the failure in the past to describe successfully the different mobilities for different dopants lies in the neglect of the spatial extension of the electron charge density. The corresponding atomic form factor of the charge distribution in Fourier space is significantly different for different dopants, especially for acceptors. The scattering cross section as a function of the atomic and electronic number of the impurities is derived. The Schwinger amplitude which is superior to the 2. Born approximation is used to calculate the scattering rates. To obey the Friedel sum rule we have to correct the Debye screening length. The new formula for the screening length depends on the dopants, i.e. screening differs for an attractive potential from a repulsive one which is a consequence of the different effective scattering potentials for minority- and majority electrons. Monte Carlo simulations including all important scattering processes have been performed for silicon, GaAs, and InP in the doping concentration range from 10^{15} cm^{-3} to 10^{21} cm^{-3} . The agreement with experiments is excellent. Our results confirm not only the experimental data of the mobility enhancement of minority electrons by a factor of about 2 compared to majority electrons in degenerated semiconductors but also the generally lower electron mobility in arsenic-doped silicon compared to phosphorus-doped silicon.

FORMATION KINETICS OF THE AL-RELATED SHALLOW THERMAL DONORS: A PROBE FOR OXYGEN DIFFUSION IN SILICON

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Keywords: shallow thermal donors, oxygen diffusion in silicon, defect reactions

In this paper we investigate in detail the formation kinetics of the new type of shallow thermal donors, the K-donors, found in Al-doped silicon. A modeling of this kinetics in terms of diffusion controlled chemical reactions of oxygen and aluminum provides a new insight into the problem of oxygen diffusion in silicon at annealing temperatures of about 450 °C.

The dependence of the shallow thermal donor (STD) concentration on the annealing time has been investigated by means of the infrared absorption spectroscopy. Two types of acceptor-doped Cz-silicon samples were used: boron- and aluminum-doped. The generation of shallow thermal donors is observed in both types of samples, but only in Al-doped ones a new species called the K-donors developed. Its formation kinetics was similar to the other STD, the K-donors were thus related to aluminum-oxygen complexes.

Although the K-donors give rise to the well resolved 1s-2p shallow donor transitions in the far infrared and there is almost no chemical shift present, their nature is far more complex than that of the shallow hydrogenic donors. They were found to exhibit a DX-type metastability with a critical transition temperature of about 180 K. At liquid nitrogen temperatures they spontaneously undergo a most probably entropy-driven transition to an other configuration.

The growth kinetics of the K-donors was modeled in terms of diffusion-controlled second-order chemical reactions. Several reaction schemes involving one Al and one or more oxygen atoms were proposed and compared with the experimental data. The results are presented in terms of the oxygen diffusion coefficient and a characteristic interaction radius for the defect-oxygen reaction.

It has been established that some reaction paths may proceed when the oxygen diffusion coefficient has a value of approximately $5 \cdot 10^{-19} \text{ cm}^2/\text{s}$ at 470 °C which is an extrapolation of the higher temperature diffusion data. Thus, it seems, that no anomalously high oxygen diffusion coefficient is necessary to explain the phenomenon of thermal donor generation. Additionally, it has been found that the incorporation of the Si-selfinterstitial as a catalyst into the reaction pathway greatly enhances the overall efficiency of the K-donor formation reaction.

The formation kinetics of the aluminum-related shallow thermal donors is related to the agglomeration of other thermal donors through the common diffusing reagent - oxygen. However the reactions involved are not as complex and therefore easier to handle and interpret theoretically. Their investigation in terms of the nonlinear diffusion-controlled processes seems to give a clear insight into the phenomena governing the oxygen diffusion and precipitation at 470 °C.

SEGREGATION OF Au AT DISLOCATIONS CONFIRMED BY GOLD DIFFUSION INTO HIGHLY DISLOCATED SILICON

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Key Words: silicon, gold, neutron-activation, segregation

We report on diffusion of Au into highly dislocated Si monocrystals, undoped and uniformly doped with B. The boron concentration of the samples exceeds the intrinsic carrier concentration even at high temperatures resulting in extrinsic diffusion conditions. A high density of dislocations of 10^7 cm^{-2} or higher was obtained by plastic deformation of Si bars. After indiffusion of Au into Si, the samples were neutron irradiated. The stable ^{197}Au transforms into the radioactive isotope ^{198}Au by neutron transmutation. The distribution of ^{198}Au was followed by mechanical sectioning and counting the activity of each section.

Au profiles measured after diffusion at temperatures between 900°C and 1100°C show Au-diffusion to be faster in heavily boron-doped Si than in undoped samples. All profiles are accurately described by complementary error functions yielding an effective diffusion coefficient $D_{\text{Au}}^{\text{eff}}$ and a boundary concentration $C_{\text{Au}}(x=0)$. Data for $D_{\text{Au}}^{\text{eff}}$ and $C_{\text{Au}}(x=0)$ extracted especially after diffusion at 900°C are considerably lower and higher, respectively, than expected from the extrapolation based on the high-temperature results. Although the temperature dependence for $D_{\text{Au}}^{\text{eff}}$ and $C_{\text{Au}}(x=0)$ individually deviate from an Arrhenius equation the product $D_{\text{Au}}^{\text{eff}} C_{\text{Au}}(x=0)$ both for boron- and undoped Si follows an Arrhenius expression.

On the basis of interstitial-substitutional exchange mechanisms which are well established for the analysis of Au diffusion in Si and a mechanism which additionally takes into account segregation of Au at dislocations, the temperature dependence of $D_{\text{Au}}^{\text{eff}}$, $C_{\text{Au}}(x=0)$ and their product is explained. Within these models Au profiles in highly dislocated Si yield information about the enthalpy of segregation. Furthermore, the influence of doping on Au diffusion enables us to deduce for the first time the charge state and energy level of interstitial Au in Si.

The strong segregation tendency of Au found at 900 °C motivates us to simulate the distribution of Au diffusion in a Si structure consisting of buried layers with a high dislocation density. Theoretical profiles show that the foreign-atom concentration inside the buried layer exceeds the concentration in the dislocation-free regimes by several orders of magnitudes. This finding which has potential application in the formation of buried micro-wires, can be checked experimentally by appropriate structures grown by molecular-beam epitaxy

GOLD DIFFUSION EXPERIMENTS AS A TOOL FOR INVESTIGATIONS OF SELF INTERSTITIAL INTERACTION WITH EXTENDED DEFECTS.

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It is well known that gold in Si crystals diffuses via the kick-out mechanism therefore during gold diffusion self interstitials are generated in the bulk and gold concentration is determined by the self interstitial annihilation. Thus investigations of gold distribution after diffusion annealing allow to study interaction of self interstitials with extended defects, annihilation efficiency of these defects and generation of self interstitials by the other sources during the diffusion annealing. In dislocated samples the interstitial annihilation predominantly takes place on dislocations and if the annihilation velocity is not very high measurements of gold concentration allow to estimate the dislocation efficiency as a sink for self-interstitials as a function of impurity content, thermal treatment conditions, dislocation structure etc. It has been shown that the gold concentration after the diffusion in the temperature range from 850⁰ to 1000⁰ C in Cz and FZ dislocated p-type Si with the same boron concentration (about 10¹⁶ cm⁻³) is rather different although in the both types of crystals the gold concentration inside the samples in accordance with the kick-out mechanism increases with the dislocation density as $(N_D)^{1/2}$. It was obtained that efficiency of dislocations as a sink for Si interstitial is much smaller in Cz Si than that in FZ one. The **Error! Bookmark not defined.** coefficient describing this efficiency in Cz Si at 850⁰C is about 0.01, i.e. much smaller than that (**Error! Bookmark not defined.**-1) estimated for the case of very high annihilation velocity, and exponentially increases with temperature while in FZ Si it is practically independent of temperature. The results obtained can be explained by dislocation pinning by oxygen precipitates as it was demonstrated by well know experiments studied the formation of locking stresses for dislocation gliding and by the thermostimulated release of dislocation from these obstacles or by the dissolution of oxygen precipitates under gold diffusion conditions. It has been shown that from such measurements the part of dislocations able to climb can be estimated. The influence of self interstitials created due to oxygen precipitates formation on the gold concentration has been revealed. It has been shown that gold diffusion experiments can give a valuable information about the oxygen precipitation and reconstruction of oxygen precipitates.

THE BEHAVIOR OF GROWN-IN POINT DEFECTS IN CZCHROLSKI SILICON AND THEIR IMPORTANCE IN THE 64MBIT ERA AND BEYOND.

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Grown-in intrinsic point defects and their agglomerates in Czochralski silicon are taking on an ever increasing importance to the successful manufacture of integrated circuits especially at the 64Mbit level of integration and beyond. The primary issue is the agglomeration of excess vacancies during crystal growth into small (50-100nm) octohedral voids in densities on the order 10^6 cm^{-3} . Under certain circumstances agglomerates of silicon self interstitials may also be important. At the moment, however, it is the vacancy agglomerates which are of the greatest interest. Such "grown-in" voids can act as sites for dielectric breakdown events in thin gate oxides. As chip sizes and complexity increase, the presence of these defects in the "typical" densities can be a yield limiting factor. Epitaxial silicon presents a straightforward solution to the problem, but rapid advances in fundamental silicon science and crystal growth engineering may yet prove successful in bringing these defects under sufficient control for the GigaBit era and beyond.

This paper presents a survey of recent advances in the understanding intrinsic point defects and their reactions during crystal growth. Of primary concern is 1) the incorporation of excess intrinsic point defects into a growing silicon ingot, 2) the processes which control their agglomeration into large low density defects 3) methods by which their size and density distributions may be controlled and 4) the effects of residual concentrations of intrinsic point defects left over from the main agglomeration reactions on, primarily, the clustering of oxygen at temperatures lower than those of the main agglomeration reaction.

Poster 1

CHEMICAL TRENDS IN ELECTRONIC PROPERTIES OF ARSENIC VACANCY-3D TRANSITION METAL PAIRS IN GALLIUM ARSENIDE

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Key words: arsenic vacancy, transition metal, GaAs

In this work we report theoretical investigations of the chemical trends in the electronic properties of transition metal impurity pair complexes in GaAs. Self-consistent electronic state calculations have been carried out for the arsenic vacancy-3d transition metal pairs using the Watson-terminated molecular cluster model within the framework of the multiple-scattering $X\alpha$ method.

The analysis of the one-electron energy spectra of the $\theta_{As}TM_{Ga}$ with $TM = V, Cr, Mn, Fe, Co, Ni,$ and Cu , lead to the conclusion that the pairs in trigonal symmetry can be described by two different microscopic models. For $TM = V, Cr, Mn,$ and Fe the gap energy levels are 3d-related orbitals and are formed by a covalent interaction between them and the host atoms electronic states. For $TM = Co, Ni,$ and Cu the gap energy levels are divacancy-like states, i.e., they have a dangling-bond character. Therefore the electronic and magnetic properties of the pairs are related to molecular orbitals which have distinct characteristics depending on the occupation of the 3d orbitals of the TM impurity.

LONG RANGE LATTICE RELAXATION FOR DONOR CENTERS IN SUPERCCELL METHOD

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Key Words: donor centers, lattice relaxation, supercell approximation

When applying the supercell approximation to a point defect in semiconductor, there arise problems connected with a description of a lattice deformation around the defect. In the present work, these problems are revealed and discussed. The supercell method can be successfully applied to the short-range lattice deformation around the point defect, for which only the nearest-neighbour ions are shifted from their equilibrium positions. However, the long-range lattice deformation, which accompanies the impurity centers in semiconducting compounds, involves small, slowly vanishing displacements of the remote ions and cannot be properly treated by this method. If we try to describe the long-range deformation by introducing the supercell, which usually consists of no more than a hundred of ions, we neglect the displacements of the ions outside the supercell. Moreover, the symmetric distribution of the supercells does allow to take into account the relaxation of a part of the ions inside the supercell. This problem is considered in the present work with the help the phonon representation for the ion displacements. The largest contribution to the lattice deformation energy results from the interaction with LA and LO phonons, which are described by the deformation potential and polar coupling, respectively. We have calculated the displacements of ions around donor centers in the charge states: D^0 , D^+ , and D^{+} , and determined their contribution to the total energy of the donor-relaxed lattice system as a function of the size of the supercell. The calculations have been performed in the frame of the one-band approximation for strongly and weakly localized shallow-level donor states in GaN, GaAs, AlAs, CdS, CdTe, ZnSe, and CuCl. The results show that the short-range interaction with LA phonons leads to the lattice distortion around the impurity center of an intermediate range, which means that the supercell consisting of several hundreds of atoms is sufficient to account for the major energetic contribution. However, the correct treatment of the lattice deformation resulting from the long-range polar interaction with LO phonons requires the application of the supercell, which contains several thousands of atoms. The energy and the range of the LO-phonon induced lattice relaxation increase with increasing polar character of the binding of semiconducting compound. This effect is essential for the strongly polar crystals (CuCl, GaN), but even for the weakly polar GaAs, becomes important for the donor states of strong electron localization at the impurity center. The estimated energetic contribution and the range of the lattice deformation around the donor center are of particular importance in planning the large-scale ab initio calculations with the use of supercells and interpreting their results.

AB INITIO INVESTIGATIONS ON DIFFUSION OF HALOGEN ATOMS IN GaAs

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Key Words: GaAs, halogen, diffusion, first-principles calculations

The behavior of halogen atoms incorporated in semiconductors is of great importance in various processes in device fabrication. The reaction and diffusion of halogen atoms in the bulk semiconductor and the near-surface region is essential for chemical etching processes. The diffusion properties determine the concentration of halogen atoms near the surface during etching. The presence of large concentrations of ionized halogen atoms induces band bending near the surface, changes carrier concentrations around the halogen atoms, and affects the etching reactions of halogens. The degradation of AlInAs/GaInAs system caused by thermal treatments is reported to be due to the diffusion of fluorine atoms from the surface into the Si-doped AlInAs layer, which causes the formation of complexes between the F and Si atoms and leads to the passivation of Si donors [1]. The thermal degradation is peculiar to the AlInAs ternary system, in which F atoms may exhibit high diffusivity. In spite of their technological importance, the properties of halogen atoms are poorly understood.

In this paper, we present first-principles calculations of the properties of halogen atoms in crystalline GaAs, such as stable configurations, migration paths, charge-state effects, and interactions with dopant atoms. The calculations are based on the local density functional theory using first-principles pseudopotentials in a supercell geometry. We have determined the stable charge state of an isolated halogen atom as a function of the Fermi energy, and found that chlorine and fluorine atoms exhibit quite different behaviors in GaAs. The Cl atom prefers the bond-center site of a Ga-As bond in the positive charge state, in spite of its high electronegativity, and diffuses through the GaAs crystal via a path in the region of high electron density. On the other hand, the F atom prefers the negative charge state at the tetrahedral interstitial site which has Ga atoms as the nearest neighbors, and diffuses through the low-electron-density region. In Si-doped GaAs, both the Cl and the F atom occupy the tetrahedral interstitial site with the substitutional Si donor atom as a nearest neighbor and form a neutral halogen-Si complex. The Cl-Si complex is weak and easily dissociates into the isolated Cl and Si atoms, while the dissociation energy of the F-Si complex is much larger than that of the Cl-Si complex, which implies that F atoms more effectively passivate Si donors in GaAs. The thermal degradation of AlInAs system will be also discussed in terms of the obtained results of the behaviors of F atoms in GaAs.

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AB INITIO STUDY OF THE C_{AS} LOCAL OSCILLATOR IN GALLIUM ARSENIDE

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Key Words: GaAs:C, anharmonicity, local vibrational mode, density-functional theory

We studied the anion-site substitutional impurity C_{AS} in GaAs because of its importance for growing semi-insulating GaAs crystals. The local vibrational mode (LVM) at this defect shows a distinct fine structure due to a ligand induced isotope effect. However, the fine structure and the isotope shift due to the $^{12}C \rightarrow ^{13}C$ replacement can not be explained within the harmonic approximation [1]. Recently, a second thermally activated line of the LVM was discovered [2].

We performed an ab-initio density-functional theory treatment of the LVM at this impurity center. First, the phonon dispersion curves of the GaAs bulk crystal were calculated in the harmonic approximation in order to account for the hybridization effects between the local and host vibrational modes. After one Arsenic atom of the supercell had been replaced by Carbon, we relaxed the four innermost shells of atoms of the host crystal around the impurity. The Gallium neighbors are displaced 0,39 Å towards the Carbon atom. Using the relaxed positions we calculated the second order harmonic and third and fourth order anharmonic force constants between the atoms close to the defect.

In the harmonic approximation, the theoretical impurity isotope shift was 2.56 meV in good agreement with the experimental value of 2.60 meV. However, the harmonic approximation failed for the ligand induced isotope shift, for which we calculated a value 25% too low. Our first analysis showed, that the vibration of the impurity atom with frequency $\nu = 1.7 \cdot 10^{13} \text{ s}^{-1}$ couples to vibrations of the ligands with $\frac{1}{12}\nu$ due to the third order terms of the potential. This increases the localization of the mode at the ligands. We use a Green's function technique for the quantitative determination of this mode coupling to obtain a better understanding of the observed ligand induced isotope shift.

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ANALYSIS OF CU-INDUCED TRAPS IN GaAs BY INFRARED QUENCHING AND RECOVERY OF THERMALLY STIMULATED CURRENT

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Key Words: GaAs, Cu, diffusion, TSC, quenching, compensation.

In previous work we have shown that semi-insulating materials can be obtained from n-type GaAs by in-diffusion of copper through a conventional compensation mechanism [1,2]. The analysis was based on Hall effect and dark current measurements. We have also investigated the compensation process by monitoring directly the carrier traps introduced by copper in the n-type starting material using optical DLTS and photo-induced current spectroscopy which enables us to trace the traps through the semi-insulating phase.

In this work we investigate semi-insulating samples which were obtained by diffusion of copper in n-type GaAs starting materials. Thermally Stimulated Current (TSC) spectroscopy has been used to study the dominant energy levels in the samples. Three energy levels were observed : the copper acceptors at $E_v + 0.15$ eV and $E_v + 0.4$ eV as well as a deep donor level at $E_c - 0.7$ eV. The donor peak is shifted in temperature with respect to EL2 present in the starting materials. The microscopic structure of this deep donor is not known. The infrared quenching and recovery mechanism of the photoconductivity at 90 K and the TSC signal from the observed defects have been investigated. Similar photoconductivity quenching is observed in the copper diffused semi-insulating samples and the semi-insulating reference material. Since EL2 is completely suppressed by the copper diffusion, this means that the new deep donor has the same photoquenching properties as EL2. In addition, close values of the optical capture cross sections are measured for the two defects. Hence, we deduce that the deep donor very likely involves the As_{Ga} defect.

No correlation between the dynamics of the photoconductivity quenching and the quenching of the TSC signal from the copper acceptors was observed. We deduce that the microscopic structure of the related defects does not include EL2. This is a direct evidence against a connection between the microscopic structure of the acceptor defects induced by the Cu-diffusion in GaAs and the As_{Ga} antisite.

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AS INTERSTITIAL PAIRS IN GaAs*

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Key Words: interstitial, complex, gallium arsenide

Extensive analysis [1] of titration, density, and lattice constant measurements indicates that the most numerous point defects in melt-grown GaAs are As interstitials. The electrical behavior at growth appears to be controlled by As vacancies, indicating that the As interstitials remain neutral. After post-growth cooling, these interstitials are expected to be present primarily in complexes or extended defects, since isolated As interstitials are quite mobile. However, there is no direct experimental evidence on the precise microscopic structure of the As interstitials either during high-temperature growth from the melt, or in the diffuse interstitial clusters [2] which have been observed after cooling.

In order to obtain very high resistivity and short carrier lifetimes, GaAs can be grown by MBE at low substrate temperatures, resulting in extremely As-rich material (LT GaAs). As in melt-grown GaAs, measured As antisite concentrations in LT GaAs are often too low to account for the reported deviation from stoichiometry. Formation energies of As interstitials and As antisites in As-rich GaAs have been found to be comparable, and lower than the Ga vacancy formation energy [3], suggesting that substantial numbers of As interstitials may be present in LT GaAs, as well as in melt-grown GaAs. The lowest energy isolated As interstitials are acceptors [4]. However, since large numbers of electrically active As interstitials are not observed in either melt-grown or LT GaAs, As interstitials may be present in these materials primarily in the form of electrically inactive complexes.

We will discuss the results of first-principles molecular dynamics studies of the low-energy configurations for As interstitial pairs. The lowest energy As interstitial pairs are found to be electrically inactive. These interstitial pairs also contribute only a modest amount of lattice strain, in agreement with experimental evidence that As interstitials do not make a large contribution to the lattice strain.

* This work was supported in part by the AFOSR under Grant F49620-96-1-0167, and by grants of HPC time on the SGI Power Challenge at the DOD Aberdeen Center and on the Cray C90 at the DOD CEWES Center.

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CHARACTERISTICS OF THE COMPLEXES RESPONSIBLE FOR THE 1.2 EV LUMINESCENCE BAND IN N-TYPE GaAs:TE (Sn OR Si): RESULTS OF PHOTOLUMINESCENCE STUDIES AT RESONANT POLARIZED EXCITATION

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Key words: complex, GaAs, Jahn-Teller effect, polarized photoluminescence

A photoluminescence (PL) band with a maximum near 1.2 eV associated with complexes involving a gallium vacancy (V_{Ga}) and a donor (Te_{As} , Sn_{Ga} or Si_{Ga}) in GaAs was studied at excitation by light with photon energy lower than the Ga_{As} gap. PL spectra, PL excitation spectra and PL polarization induced by polarized resonant excitation have been measured in the temperature (T) range of 2-240 K. The induced PL polarization was invariant up to $T \approx 130$ K for any type of donors under investigation, suggesting that at $T < 130$ K the Jahn-Teller distortions of the complexes do not reorient in the light-emitting state. In the simple models of these complexes [1] this means that the barrier between equivalent configurations of the complex in the light-emitting state (and hence the energy of the Jahn-Teller stabilization) is higher than ~ 200 meV. Reorientation of distortions, revealed from their alignment under uniaxial pressure at $T = 2$ K [1], occurs in the ground state which is also distorted.

From the low-temperature values of the induced polarization of PL at different crystal orientations relative to the directions of the exciting light and its electric vector, we have evaluated parameters of optical dipoles describing in one-dipole approximation absorption and emission of light by the complexes. For all complexes, the direction of the optical dipole was found to be not too different from the $\langle 111 \rangle$ -type axis. (In the case of $V_{Ga}Te_{As}$ this axis does not coincide with the initial axis of the complex). This demonstrates that the splitting of vacancy state of any complex under investigation due to the donor effect is less than that due to the Jahn-Teller effect. From the values of angles characterizing direction of optical dipole, we estimated the relative values of the Hamiltonian parameters [1] describing the effect of a donor in the complex. In $V_{Ga}Sn_{Ga}$ and $V_{Ga}Si_{Ga}$ for both possible models of these complexes (one or two configurations with the lowest energy), the donor effect is weaker than in $V_{Ga}Te_{As}$ complex, what is consistent with difference in donor position relative to V_{Ga} in these complexes.

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DEFECT IN THICK EPITAXIAL GaAs LAYERS

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Keywords: Growth, GaAs, VPE, DDX, Hall effect, SIMS, IR absorption, EL2.

Epitaxial growth is classically used to produce thin layers and heterostructures of good quality for micro- and opto-electronics. The up-to-date techniques (molecular beam and chemical vapor phase deposition techniques) are expensive, often polluting and do not allow the growth of layers more than few microns thick. However, there are many fields, such as high power electronics, optics, nuclear detection, in which the use of thicker epitaxial layers is required. Such thick layers cannot be produced by the above mentioned techniques. We shall describe a simple, inexpensive and non polluting technique that allows the growth of very thick layers (from typically few microns to mm). This is a vapor phase technique which allows to vary the growth rate in a very large range (from 1 μm per hour to 10 μm per minute). It has been used to grow GaAs thick layers, namely several hundred of microns thick. Structural, electrical and optical studies have been performed in order to evaluate their potentialities for specific applications. Double X-ray diffraction shows that the layers are mono-crystalline and no deviation from stoichiometry can be detected. Secondary ion mass spectroscopy shows that the main impurities that contaminate the layers are Si and C at a level of 10^{16} cm^{-3} . Infrared absorption detects only the presence of EL2 defects with a concentration which is directly related to the growth rate. This dependence of EL2 concentration versus the growth rate will be described and explicated. The way to obtain semi-insulating layer will be deduced and demonstrated. Photoluminescence spectra of these layers exhibit a strong bound exciton line accompanied by the donor-acceptor line, that illustrates their good quality. Hall effect shows that the layers can be slightly n- or p-type (at a level of 10^{16} cm^{-2}) depending on the growth conditions and on the concentration of the EL2 defects. The mobilities are characteristics of phonon scattering, indicating that the concentration of charged defects or impurities is low. We shall finally describe how all these properties vary with the conditions of growth. We shall discuss how these layers could be used for the fabrication of fast photodetectors and high power optically activated switches.

METASTABLE DEFECTS IN PLASMA-IRRADIATED *n*-GaAs

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Keywords: Metastability, Plasma-induced defects, Photorefractive, GaAs, Bias-annealing

The Si donor reactivation in Ar plasma-irradiated GaAs under Reverse Bias Annealing, RBA, at elevated temperature was first reported in the last ICDS-18 [1]. The reactivation was proposed to be induced by emission of two-electrons from complexes between donors and point defects to the conduction band. Such emission induces structural instability of the complexes due to coulombic repulsion, resulting in point defect dissociation. We have recently found that such reactivation is also induced by Reverse Bias *Injection* Annealing, RBIA, i.e., RBA under laser irradiation [2]. The present paper reports that the change would be reversible due to a metastable character of the complex under RBIA.

The donor reactivation reaction under RBA at elevated temperatures was proposed [1]:



On the other hand, the dissociation occurred during RBA even at room temperature under laser illumination. Charge densities in the surface layer was recovered and exceeded the original donor density in the samples, i.e., $2.5 \times 10^{17} \text{ cm}^{-3}$ in a way reported [1]. This suggests that point defects would become positively charged by RBIA as well as under RBA. In other words, this reactivation occurs due to two-photo-excited hole capturing instead of two electron emission. The rate constant of reactivation kinetics under RBIA had an activation energy of 0.1 eV which is reduced from 0.73 eV under RBA.

It is interesting to note that the charge density near the surface region, which was increased once by RBIA, decreased after heat treatment around 100 °C and its profile is nearly the same as before RBIA. This suggests that point defects are not completely dissociated from the complexes with donors, Si^+Y^+ , under RBIA, yet the complexes show optically induced metastability.



The transition temperature was as high as around 100 °C.

Since the metastability occurs even at room temperature, they have potential applicability for Fermi level modulation at relatively high temperatures.

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DEFECTS IN NEUTRON IRRADIATED LEC SI-GaAs

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Key Words: Semiinsulating, GaAs, compensation, radiation damage, α -DLTS, PICTS

Neutron irradiated Liquid Encapsulated Czochralski Semi-Insulating GaAs was studied in order to identify the traps that are introduced by irradiation and their relation with the Charge Collection Efficiency of the diodes when used as high energy particle detectors. Different LEC starting materials were used to make prototype Schottky-Ohmic diodes that were irradiated with fast neutrons up to $1.9 \times 10^{15} \text{ Ncm}^{-2}$, which is the expected annual dose that the detectors will receive near the interaction point at the Large Hadron Collider at CERN.

The traps were studied using three different techniques, namely: α -DLTS, PICTS and Capacitance-Voltage measurements. The measurement techniques require special consideration because the material is highly compensated and is 'relaxation-like' so that some conventional semiconductor analysis needs care. The first technique uses alpha particles to create electron-hole pairs in a reverse biased diode and to collect them using a charge sensitive preamplifier. The charge transient produced has a "fast" component with time constant τ^+ which is related to the trapping of the charge and one or more "slow" components with time constant τ_{D_i} which is related to the detrapping of the charge carriers. A temperature scan produces a change of the detrapping time constant τ_{D_i} which is fitted to a multi-exponential function and the activation energies and capture cross sections are obtained from an Arrhenius plot and the concentration of the trapping centre is proportional to the ratio of τ_{D_i}/τ^+ .

In the second technique the capacitance of the diode is measured as function of voltage, frequency and temperature. The time constant of the trapping centres, as well as the concentrations can be obtained from the fitting to a Debye curve of Capacitance-Frequency data as function of temperature.

Finally the diodes were studied using Photo-Induced Current Transient Spectroscopy. A pulse of sub-bandgap light is shone onto the diode and the current transient analysed using the high resolution multi-exponential fitting function already mentioned.

Several traps were identified and a calculation of the effect of shallow donors and shallow acceptors on the compensation of deep acceptors was performed. There was good consistency between the methods. Well known traps such as EL14 and EB10 were identified using the above mentioned techniques although a broad spectrum of traps was found in the different samples. No relation between a specific trap and the CCE of the diodes was found. Some of the diodes have traps that were not observed in other samples although the starting material is nominally the same. Most of the observed traps are electron traps but hole traps were also found.

δ - DOPING SEMICONDUCTOR SUPERLATTICES UNDER IN-PLANE MAGNETIC FIELDS

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Keywords: δ -doping - Magnetic field effects - Electronic Structure

δ -doping quantum wells and superlattices are new semiconductor systems of considerable interest for basic research and device applications. In the present work, we report on selfconsistent subband- and miniband-structure calculations in the effective mass approximation of n-type δ -doping multi-quantum wells and superlattices under the effect of in-plane magnetic fields. The silicon δ -doped GaAs superlattices are built up of periodically thin layers of Si impurities 2Å wide immersed in bulk GaAs. The dopant layer generates a V-shaped potential well that confines the electrons released by the donors, forming a quasi two-dimensional electron gas which screens the potential of the positive charges. The study is extended to superlattices in which Si δ -doped layers are introduced in the center of GaAs/GaAlAs quantum-wells, and the system is repeated periodically. The magnetic field B, parallel to the layers was taken in the y direction, for which the gauge $A=(Bz,0,0)$ has been assumed. The miniband wavefunctions and eigenvalues are obtained by solving the one-dimensional Schrodinger equation in conjunction with the Poisson equation which determines the electrostatic Coulomb potential. Many body effects such as exchange and correlation are taken into account within the local density approximation. In order to satisfy Bloch theorem, we adopt the Wigner-Seitz-Slater version of the cellular method with space filling one-dimensional cells and impose the continuity of the wavefunction and its normal derivative at the cell boundaries. The electronic subband structures, miniband occupations, potential profiles, and Fermi level position for several donor concentrations and superlattice periods are obtained. We show results for magnetic fields varying from 0 to 20 T and discuss the magnetic field effects on the electronic structure of these δ -doping systems in contrast to what has been observed in usual compositional superlattices.

DETECTION AND IDENTIFICATION OF ELECTRON AND HOLE TRAPS IN HIGH-RESISTIVITY LEC-GaAs IRRADIATED WITH PROTONS

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Key Words: GaAs, high-resistivity, PITS, DLTS, proton irradiation.

For many years liquid encapsulated Czochralski (LEC) semi-insulating (SI) GaAs has been widely used as a substrate material in GaAs integrated circuits. In addition, it has recently found application in radiation-hard solid state detectors [1,2]. The characterization of deep level native defects and defects created by irradiation is important to tailor the quality of the material. Since DLTS is not useful for high resistivity materials, a technique known as photoinduced transient spectroscopy (PITS) has been introduced to characterize the traps present in such materials [3]. This technique however, has some limitations compared to DLTS, such as difficulties in identifying the nature of traps and their concentration.

In this work an analysis of deep levels related to defects in high-resistivity LEC-GaAs, generated during growth or by proton irradiation (2.6×10^{10} - 1.3×10^{11} cm⁻²) was made using PITS. In order to compare the effects of defects in the volume and defects close to the surface of the material on the PITS signal, sandwich Schottky diodes and planar samples with two ohmic contacts on the front face were studied. Five main traps are observed. In addition to apparent activation energies, it is shown that the nature of traps can also be identified. The irradiation creates a deep level defect with an apparent activation energy of 0.72 eV. This defect was identified as an electron trap. Furthermore, it is shown that the wavelength of the excitation light significantly modifies the PITS spectra. Probable reasons for such modifications are discussed.

In order to confirm the identification of traps deduced from PITS, DLTS measurements under a continuous illumination [4] of the sample were also performed. General comparison is made between results obtained from these different techniques.

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DLTS CHARACTERISATION OF DEFECTS INTRODUCED IN GaAs DURING REACTIVE AND NON-REACTIVE ION-ETCHING

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Key Words: GaAs, Schottky barrier diodes, dry etching, DLTS, defects, metastability

Dry etching is a key processing step in microelectronics manufacturing. Both reactive and non-reactive ions, and sometimes combinations of these, are used to achieve the desired etch rate and semiconductor surface morphology. Dry etching does, however, introduce electrically active defects into semiconductors which alter their properties and hence influence the quality of devices fabricated on them.

Using deep level transient spectroscopy (DLTS), we show that the electronic properties and concentrations of defects created in n-GaAs during dry etching depend on the type of etchant (He, Ar and SiCl₄) and etch conditions (plasma pressure and deposition power), respectively.

In low energy (1-5 keV) He-ion bombarded GaAs we observed five prominent electron traps, EHe1 - EHe5. Whereas EHe1 (E1¹) and EHe2 (E2¹) are two charge states of V_{As}, EHe4 (E3¹) is related to V_{As} - As_I close pairs. Some of the defects introduced during Ar ion-etching [e.g. EAr2 (E2)] were similar to defects formed by He ion bombardment. We could, however not detect the E1 charge state of V_{As} in Ar-etched GaAs, probably due to stress fields caused by extended defects which prohibit its filling. The set of defects introduced during SiCl₄ reactive ion etching, ER1 - ER6, is interestingly different from those introduced by He and Ar. We could not detect any V_{As}-related defects (E1 - E3) after in SiCl₄ etched GaAs. Only one common defect is introduced by He, Ar and SiCl₄ processing (EHe3 = EAr3 = ER3). This defect has the same electronic and metastable properties as Eα3 created by high energy α-particle irradiation.² It can be reversibly removed by hole injection at 100 - 120 K and re-introduced by annealing above 200 K. ER3 is the main defect created by SiCl₄ etching where its concentration approaches 10¹⁶ cm⁻³ at the surface and decreases sharply into the GaAs.

The properties of Schottky barrier diodes (SBDs) fabricated on He and Ar ion processed surfaces are all poor. Compared to SBDs on unetched surfaces, they show lower barrier heights and large generation-recombination currents due to the high degree of etch-induced surface and sub-surface disorder. In contrast, despite the high surface concentration of some defects (e.g. ER3), SBDs on fabricated SiCl₄ etched surfaces have excellent properties - in some cases at least as good as SBDs on unetched surfaces. We ascribe the different defects introduced by He, Ar and SiCl₄ processing and the different behaviour of SBDs fabricated on surfaces processed with these etchants to the different etch rates and etch mechanisms. Whereas SiCl₄ etching occurs rapidly via chemical reactions and desorption, Ar ion etching proceeds much slower via sputtering, while the sputter yield of He is almost negligible.

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ELECTRICAL PROPERTIES OF LOW TEMPERATURE GROWN GaAs

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Keywords: Admittance spectroscopy, TLG, GaAs, percolation, precipitates, EL2.

GaAs layers have been grown by molecular beam epitaxy in the range 150-400 K. These layers have been characterized by admittance spectroscopy, i.e. by measuring the admittance, the conductance (real part of the admittance) and the susceptance (imaginary part), versus frequency in the range 5 Hz - 13 MHz, at various temperatures. We find that the conductance is frequency independent and varies with temperature in a way which demonstrates that it must be ascribed to band conduction with electrons thermally ionized from a band of deep defects. The ionization energy increases with the growth temperature, and with annealing temperature, as the width of the defect band decreases, showing that the defects involved are the EL2 ones. The susceptance varies linearly with frequency and is temperature independent. Because the admittance presents a minimum at a frequency which is directly related to the d.c. conductance, we interpret this susceptance behaviour as due to electron transport via a percolation regime. This percolation is characterized by a dimensional factor that corresponds to the average distance between As precipitates. Consequently, we understand the admittance characteristics in terms of percolation induced by insulating regions developed around As precipitates, as a result of the existence of capacitances induced by space charge regions due to the metallic character of these precipitates.

ESTABLISHMENT OF QUANTITATIVE CORRELATION BETWEEN RAMAN AND RBS DISORDER ASSESSMENT: ACCUMULATION OF DAMAGE IN $^{30}\text{Si}^+$ IMPLANTED GaAs

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Both Raman spectroscopy, RS, and Rutherford back scattering ion channeling, RBS, have been used extensively to monitor overall changes in microstructure of implanted semiconductors. However, an analysis which would provide a direct quantitative comparison between two methods is still lacking.

In this study, GaAs monocrystals were implanted with $^{30}\text{Si}^+$ ions in a wide range of ion doses, dose rates, and implant temperatures and analyzed with RS and RBS. All RS spectra were deconvoluted in the same, consistent, and novel way, such that the change in a low frequency peak, (usually interpreted as a background and ignored) was also taken into account. An excellent fit was obtained for all RS spectra. For a quantitative disorder assessment the LO phonon peak was analyzed within the 'spatial correlation', SP, model in which it is assumed that implantation induced defects partition the crystal into regions of finite size L in which order and translational symmetry has been preserved. The correlation length L_{RS} is then obtained as a fitting parameter in the expression for RS intensity.

To obtain a quantitative estimate of the amorphization process we have postulated inter cascade distance, ICD, model which estimates the average distance, L_{ICD} , between implantation induced cascades as a function of ion dose. The model also allows for the overlap of different cascades for higher doses.

Disorder was monitored in RBS as a damage fraction, f_{RBS} , defined as a volume fraction of disordered atoms in implanted layer. By combining the ICD model with the Morehead-Crowder model, in which f_{RBS} corresponds to the fraction of damaged area, an independent estimate of the undamaged regions size, L_{RBS} , can be obtained from RBS experimental data.

A very good agreement was found when the results of all three approaches were compared: the L_{ICD} calculated from the ICD model, correlation length L_{RS} determined from the LO fit, and L_{RBS} , determined from RBS data. This enabled a straightforward comparison of relevant signals and a direct quantitative correlation between RS and RBS. While measure of disorder in RBS, f_{RBS} , reflects the disordered volume fraction of the implanted layer, RS measures simultaneously the lowering of the translational symmetry (an effect important at low doses) and a fraction of disordered volume (prevailing at higher doses). A considerable differences in sensitivity of two methods to particular defects were used to differentiate several types of implantation induced disorder: a) line and/or planar defects which primarily reduce crystal translational symmetry (present at low doses and in annealed samples as residual extended defects); b) micro- and nanometric-size crystallites having the virgin wafer orientation; c) polycrystallites of other orientations resulting from post-implant recrystallization d) clusters of interstitials and other small volume defects; e) amorphous phase, being a continuous random network of atoms; and f) second amorphous phase characterized with a boson peak in Raman spectrum.

EVIDENCE FOR THE PRESENCE OF DIFFERENT MODIFICATIONS OF COMPLEXES RESPONSIBLE FOR THE 1.2 eV PHOTOLUMINESCENCE BAND IN GaAs:Te

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Key words: complex, photoluminescence, GaAs, uniaxial stress, reorientation

In this work, we demonstrate that the broad 1.2 eV photoluminescence (PL) band in GaAs:Te associated with the $V_{Ga}Te_{As}$ complexes is formed by several modifications of the complex. The PL bands related to different modifications are unresolved because of their close positions and substantial widths. However, some experimental results testify that there are at least two types of defects responsible for the PL band under study. One of them is marked by reorientation of the Jahn-Teller distortions in the ground state of the complexes and by their alignment under uniaxial pressure even at very low temperature. In defects of the second type, the distortions are fixed and cannot be aligned by uniaxial pressure.

This conclusion has been made from analysis of the low-temperature behavior of the 1.2 eV band at interband excitation under uniaxial pressure and from comparison of this behavior with the results of investigation of the induced polarization of the PL at resonant polarized excitation. It is based mainly on the following experimental evidence.

1. A “jump” of polarization of the 1.2 eV PL band due to alignment of the defect distortions under uniaxial pressure at low temperature is different for different samples.
2. The value of this “jump” is varied through the spectrum of the PL.
3. The polarization of the PL at resonant polarized excitation at low temperature was the same for all investigated samples and its value is inconsistent with the values of “jump” derived from the uniaxial stress study.

We suppose that the defect with reorientable distortions is the usual $V_{Ga}Te_{As}$ complex and the defects with the fixed distortions are associates of this complex with some other defects.

LOW-TEMPERATURE INTRINSIC DIFFUSION COEFFICIENT OF LITHIUM IN GaAs

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Key Words: Diffusion, defect reactions, defect complexes, GaAs, lithium

The determination of the intrinsic diffusivity of reactive impurities is complicated by the trapping mechanisms commonly involved. One such reactive species is interstitial Li in GaAs which is positively charged and shows affinity to other impurities and native defects. In order to derive the intrinsic diffusion coefficient of Li in GaAs, we employed sequential annealing and space-charge profiling measurements on Zn-doped material with a low Li-concentration. This system exhibits a particularly weak pairing interaction. A kinetic model for trap-limited diffusion was used to calculate the intrinsic diffusivity, yielding values of D_i in the temperature range 280–330 K. The migration energy for lithium in GaAs was determined to be $E_m=0.67$ eV which agrees with commonly observed values for interstitial diffusion. The diffusion behaviour was compared to that of Li in heavily doped material where the migration is governed by an activation energy of 1.2 eV which agrees with the lowest complex dissociation energy measured in the material. The value of the Li diffusion coefficient tabulated in the literature was derived from measurements on similar material [1], yielding a value of $E_m=1.0$ eV in high-temperature measurements. The presence of a trapping process was recognized but, nevertheless, no detailed measurement of the intrinsic diffusivity of Li in GaAs has been provided until now. The previously measured value is easily accounted for within the model of trap-limited diffusion.

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MAGNETIC RESONANCE AND POSITRON ANNIHILATION OF INTRINSIC ACCEPTORS IN ITC-TREATED GALLIUM ARSENIDE

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key words: intrinsic defects, GaAs, positron annihilation, ODMR, EPR, acceptors

The quality of semi-insulating (SI) GaAs substrate material is strongly influenced by thermal treatments. For substrate improvements the knowledge of defects present and their electrical and optical properties is fundamental. Heat treatments of semi-insulating (SI) GaAs near the melting point, i.e. 1200 °C for 16 hours, followed by a rapid quench to room temperature destroy almost all of the EL2 defects that were found in the as-grown material [1]. This type of GaAs material is called inverted thermal annealed (ITC) GaAs because of the fact that this heat treatments change the conductivity type from n-type SI to slightly p-type.

In this work we report on correlation experiments made by positron annihilation spectroscopy (PAS), conventional electron paramagnetic resonance (EPR) and optically detected magnetic resonance (ODMR) via the magnetic circular dichroism of the optical absorption (MCDA). In the positron annihilation experiments signals due to a new negative charged vacancy-related defect and negative ion-type defects were detected. From Hall experiments it was known that the samples were slightly p-type at room temperature (pError! Bookmark not defined. 10^{11} cm⁻³) after annealing at 1200 °C for 16h and rapid quench to room temperature. In optically detected electron paramagnetic resonance studies signals due to at least three different defects were observed [2]. Conventional EPR showed strong signals due to the so-called BE1 defect [3]. Correlation experiments have been done under illumination on the same samples by both methods: the positron lifetime and ODMR. Different defect models will be discussed to explain the results of both studies and to explain the resistivity change from n-type SI to p-type.

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METASTABILITY OF THE ANTI-STRUCTURE PAIR IN GaAs

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Key Words: Metastability, defects, III-V semiconductors

We have studied the metastability of the anti-structure (arsenic-antisite—gallium-antisite) pair in GaAs using self-consistent, parameter-free total energy methods [1]. Our calculations predict that this defect complex exhibits metastability similar to that of the isolated arsenic-antisite. However, the anti-structure pair has ionization levels in the band gap in the metastable configuration, unlike the isolated arsenic-antisite. The ionization levels enable absorption of infrared light in the metastable state. The results are used to discuss and interpret the arsenic-antisite-type defects observed experimentally in electron-irradiated GaAs [2,3].

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MICROSCOPIC NATURE AND OPTICAL PROPERTIES OF METASTABLE DEFECTS IN ELECTRON-IRRADIATED GaAs

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Key Words: GaAs, metastability, electron irradiation, antisite defects, positron annihilation

Introduction of As antisite defects in electron irradiation of GaAs has been often reported. However, most infrared absorption studies on this defect have revealed only minor metastable effects which have often been related to the native EL2 defect remaining in the sample after irradiation. The detection of irradiation-induced EL2-like metastable defects has been reported in some electron-paramagnetic-resonance (EPR) and magnetic-circular-dichroism of absorption (MCDA) experiments [1]. However, no structural information on the metastable states of the irradiation-induced defects have been obtained in these experiments.

Systematic correlation of infrared absorption and positron annihilation experiments allows us to identify two metastable defects in electron-irradiated GaAs. The first one is present already in as-grown material, and it can be identified as the native EL2 defect by its photoquenching and subsequent thermal annealing properties. The second one is introduced by irradiation at 300 K, and it disappears in thermal annealing at 520 K. Its metastable state is optically active, anneals at 70 K and exhibits optical recovery at 25 K. Positron experiments indicate that both these defects have a vacancy in their metastable state, in good agreement with the vacancy-interstitial model of the As antisite defect. Therefore, the native defect is attributed to an As antisite and the irradiation-induced one to an As antisite complex. The metastable state of the As_{Ga} complex can be generated with 1.075-eV photons and recovered with 1.35-eV photons with optical cross sections of $2 \times 10^{-20} \text{ cm}^2$ and $5 \times 10^{-19} \text{ cm}^2$, respectively. The metastable state of the As_{Ga} complex absorbs 0.7 - 1.2 eV photons, indicating that it has ionization levels in the band gap.

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Mn RELATED RECOMBINATION CENTERS IN EPITAXIAL GaAs GROWN FROM BISMUTH MELT

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Key Words: GaAs:Mn, LPE from busmut melt

The photoluminescence (PL) properties of heavily doped GaAs:Mn layers grown by liquid phase epitaxy from bismuth melt have been studied. A new PL band strongly overlapped with the conduction band-to-manganese acceptor band (e,Mn) was found. Its shape is Gaussian, the halfwidth is more then 100 meV and increased with temperature rised. Peak position of the new band shifts downwards with temperature slower than the band gap of the GaAs. These feature is typical for a band attributed to a center with a strong electron-lattice coupling. An ionization energy of this new manganese-related center was determined and one equal to 41 meV. Surprisingly, in spite of the sufficiently lower ionization energy of the new center in comparison with ionization energy of the manganese acceptor center (110 meV) the new band was temperature quenched at higher temperatures than the (e,Mn) band. We have shown that this phenomenon is due to essential difference in the carrier capture coefficients at new center compared with carrir capture coefficients at manganese acceptor center.

Moreover, a sharp decrease of the low-temperature PL intensity with manganese doping was observed evidence in the creation of a nonradiative manganese-relative center.

It have been determined that the concentration of the both new manganese-related centers increased steeper than the concentration of the manganese substitutional acceptor

ORIGIN OF AN ANOMALOUS TRANSIENT INP-N STRUCTURES BASED ON OVERCOMPENSATED SEMICONDUCTOR

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Key Words: transient spectroscopy, overcompensated GaAs and AlGaAs

Many kinds of the anomalous capacitance and current transient have recently been discovered in GaAs. The theory [1-3] developed for a $n\pi p$ junction with one deep level has given us insight into the "space charge" nature of these phenomena. In the paper we outline our previous results and present new ones. The appreciable shift of the both of space-charge region (SCR) boundaries takes place during transient in such a junction provided that n is not of a high value. The capacitance of the π layer itself is independent of the SCR boundary location. As result, the large capacitance change, though of an anomalous sign, arises due to detrapping in π layer. (So capacitance spectroscopy may be effective to study an overcompensated material.) The capacitance transient is nonmonotonous and the DLTS spectrum is accordingly multi-peaked one. The anomalous current rise may occur due to electric field reversal in the π layer. One of peculiarities is that the peak of the TSC (Thermally Stimulated Current) may appear when the SCR boundary crosses a πp interface. The peak is attended with the TSCAP (Thermally Stimulated Capacitance) peak at the same temperature. The high resistivity of the π layer facilitates this mechanism to operate [3]. The solution of the problem for the case of the depth-dependent resistivity has shown that the interposition of the both of peaks and the number of TSC peaks are affected by this factor. Experimental data obtained on GaAs and AlGaAs doped with Cr or Fe are in a good agreement with the theory.

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PERTURBED ANGULAR CORRELATION MEASUREMENTS AND LATTICE SITE LOCATION OF Br IN GaAs

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Key Words: Br—double donor, Vacancy—Interstitial model

It is known that in semiinsulating GaAs after implantation of the halogen ^{77}Br and annealing at 1123 K a uniform electric quadrupole interaction ($\nu_Q=299(2)\text{MHz}$) is observed by means of the Perturbed Angular Correlation technique [1]. At low Br concentrations 100% of the probes are found in this defect configuration, producing an axially symmetric electric field gradient, whose principal component V_{ZZ} is oriented in the $\langle 111 \rangle$ direction. In order to explain this behaviour of the Br impurity in GaAs we proposed a model which is based on the assumption that Br is dissolved on the group V site in III-V semiconductors. According to theoretical calculations [2], the isolated substitutional double donor Br_{As} should then form a relaxed configuration. In this so called Vacancy—Interstitial model, a neighbouring Ga atom is displaced along the $\langle 111 \rangle$ crystal axis, thus destroying the cubic symmetry around the Br probe, which remains on the As site.

To verify the assumption that the Br impurity in the defect complex remains substitutionally on the As site in GaAs, the emission channeling technique was applied. The electron emitter ^{82}Br (^{82}Kr) was used as a probe nucleus for emission channeling experiments for the first time. After a 30 keV implantation and subsequent annealing under conditions identical to the PAC experiment, angle dependent channeling spectra were recorded around the $\langle 100 \rangle$ and the $\langle 110 \rangle$ crystal axis. In both directions a channeling effect (flux peak) was observed, as expected for a substitutional lattice site occupation of the emitters. A quantitative analysis of the data, assuming a depth distribution of the emitters according to simulations with the Transport of Ions in Matter TRIM—programme [3] yielded a substitutional fraction of $65 \pm 10\%$ of the implanted Br.

However, recent Secondary Ion Mass Spectroscopy (SIMS) measurements of stable Br implanted into GaAs showed a significant broadening of the implantation profile after the annealing process. The recalculation of the theoretical channeling effect taking into account the SIMS—data is currently in progress and is expected to result in an increase of the substitutional fraction of Br emitters deduced from the channeling experiment.

The measurements therefore support the above mentioned theoretical calculations describing the behaviour of substitutional double donors in III-V compound semiconductors.

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SILICON DONOR - GALLIUM VACANCY COMPLEXES IN LOW TEMPERATURE GROWN GaAs.

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Gallium arsenide grown by molecular beam epitaxy at low temperature (LT GaAs) has attracted much attention during the last few years [1,2]. The major feature of this material is a large number of point defects related to a high arsenic excess. The most important among them are arsenic antisite defects, which form well known deep levels close to middle of the band gap. Typical concentration of the As_{Ga} -related donors in as-grown LT GaAs is as high as 10^{20} cm^{-3} . While the nature of dominant donors in LT GaAs is well understood, the nature of compensating acceptors still remains under discussion. A probable candidate for this role is gallium vacancy [3].

In this paper we report the results of photoluminescence study of V_{Ga} -related complexes in silicon doped LT GaAs.

The LT GaAs films were grown by molecular beam epitaxy at 200°C. The films were doped with Si or with Si+In. The as-grown samples were divided into several parts. One part was kept as-grown, the others were annealed at various temperatures. Electron probe microanalysis, x-ray diffraction, and near infrared optical absorption were applied for evaluation of excess As and antisite defect concentrations. The photoluminescence (PL) spectra were recorded at 4.2 K in the spectral region of 800-1200 nm.

No evidence for gallium vacancy related complexes was found in as-grown samples. However, PL line at ~1.2 eV was revealed in the spectra of annealed samples. This line is usually attributed to $\text{V}_{\text{Ga}}\text{-Si}_{\text{Ga}}$ complex [4]. The intensity of this line was found to increase with increasing annealing temperature. It was also higher in In-free sample than in In-doped one.

The data obtained are discussed in terms of diffusion of gallium vacancies from the surface into the bulk during the annealing procedure. This process plays a key role in precipitation of excess arsenic in LT GaAs.

The work was supported by Russian Research Program «Physics of Solid State Nanostructures» and by Russian Foundation for Basic Research.

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SITE STABILITY, DIFFUSION, AND CHARGE DYNAMICS FOR MUONIUM IN GaAs

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Key Words: Muonium, Hydrogen, Dynamics, Diffusion, GaAs

A series of experiments on the states and transitions of muonium (Mu) in GaAs carried out over the last few years have provided a great deal of information on the analogous isolated hydrogen defects. The physical and electronic structure of Mu_0^{BC} has been known for some time. We have recently determined the structure and diffusional dynamics for the Mu^- center [1]; it resides at a tetrahedral interstice (T-site) with Ga neighbours (T_{Ga}), stabilized by slightly—ionic bonding and inward relaxation of the Ga atoms. Above 500K Mu^- migrates among T_{Ga} sites with an activation energy of 0.68 eV but is orders of magnitude less mobile than Mu_0^{T} . In contrast, Mu^+ should reside near a bond center (BC), although that is not yet experimentally verified. In p-type samples Mu^+ begins to move near 200K and finds a second stationary site near 400K, again becoming mobile above 600K. Evidence from weakly n-type GaAs suggests that Mu_0 is stable in a T-site (rather than at the BC location as for Si) with a $\text{BC} \rightarrow \text{T}$ site change near 200K. We observe rapid high—temperature Mu charge-state cycles in both heavily—and lightly—doped n-type samples. At high donor concentrations Mu_0^{T} acts as an electron—hole recombination center above 750K where a $\text{Mu}_0^{\text{T}} \leftrightarrow \text{Mu}_0^{\text{T}}$ cycle occurs via alternating h^+ and e^- capture. In weakly n-type and semi-insulating samples a $\text{Mu}_0^{\text{T}} \leftrightarrow \text{Mu}_0^{\text{BC}}$ electron loss/capture cycle begins near 550K with an activation energy of 0.45eV for the loss step. The Mu charge—cycle results and individual state mobilities imply that diffusion is dominated by Mu_0^{T} even when it is not the expected equilibrium state. Similar charge cycles and diffusion processes can be expected for H in GaAs.

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SPECTROSCOPIC INVESTIGATION OF NEUTRAL NIOBIUM IN GaAs

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Key Words: niobium, 4d impurities, GaAs

The knowledge on 4d transition metal impurities in III-V semiconductors is scarce compared with the one on 3d impurities. A sharp photoluminescence line due to neutral niobium in GaAs has already been reported together with its behavior under external magnetic field. In this work, in addition to photoluminescence, absorption and photoluminescence excitation spectroscopy experiments are reported. Experiments under uniaxial stress have also been performed.

In absorption, only the sharp line at 6416.4 cm^{-1} , already reported from photoluminescence experiments, is observed. Photoluminescence excitation spectroscopy of this line reveals a broad triply peaked band around 9000 cm^{-1} . Its shape is characteristic of an orbital triplet excited state coupled to τ_2 modes of vibration.

Photoluminescence and absorption experiments show a slight splitting of the 6416.4 cm^{-1} line under tetragonal uniaxial stress and no splitting under trigonal stress. More surprising is the very strongly non-linear behavior under a tetragonal stress. The most plausible explanation is that a hidden level, not evidenced directly, interacts with either the ground or the excited state of the transition.

We propose an energy level scheme which explains all these experimental observations together with the Zeeman data previously reported.

SPECTROSCOPY OF NITROGEN-RELATED CENTERS IN GaAs

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Key Words: GaAs, nitrogen, FTIR spectroscopy, SSMS

The investigation of light impurities in GaAs is of particular interest for the development and optimization of crystal growth technology as well as for the physical understanding of these defects itself. Whereas there is now a considerable amount of experimental and theoretical work available concerning C, O and B in GaAs, the phenomena related with the presence of nitrogen in this material are widely unknown.

We present the results of low-temperature Fourier transform infrared (FTIR) absorption spectroscopy and radiofrequency spark source mass spectrometry (SSMS) studies on poly- and monocrystalline GaAs samples. In particular, spectroscopic signatures are investigated which address the question whether nitrogen is introduced as an isoelectronic substitutional impurity, N_{AS} , in molecular form or complexed with other impurities such as hydrogen. Typical concentration ranges are given.

High-pressure synthesized nominally undoped polycrystalline samples show chemical nitrogen contents up to 3 ppm using a SSMS relative sensitivity coefficient of 1. Maximum concentrations in monocrystalline liquid-encapsulated Czochralski (LEC) samples are about 50 ppb. In nitrogen-rich materials strong local vibrational mode (LVM) absorption at 471 cm^{-1} (10 K) is observed which is assigned to substitutionally incorporated N_{AS} . Spectroscopic evidence at 2947 cm^{-1} is found in some samples for the nitrogen-hydrogen complex [1]. LVM absorption of N_{AS} has been reported previously only from nitrogen-implanted GaAs [2] and from epitaxial layers grown by vapour phase epitaxy under NH_3 partial pressure [3]. For the first time, the LVM line is detected with a quality sufficient for the evaluation of integrated absorption and true line shape. Results are compared with other substitutionally bonded light impurities. Based on SSMS data a first tentative calibration of the oscillator strength is given.

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STRUCTURE AND REORIENTATION OF THE $\text{Si}_{\text{As}}\text{-H}$ AND $\text{Zn}_{\text{Ga}}\text{-H}$ COMPLEXES IN GALLIUM ARSENIDE

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Key Words: Defects, Hydrogen passivation

Infrared-absorption spectroscopy measurements under uniaxial stress have shown that acceptor-hydrogen complexes in crystalline GaAs (c-GaAs) have a trigonal symmetry and activation energies for reorientation in the range of 0.2-0.5 eV[1]. It has been suggested that the H atom is bonded primarily to one nearest neighbor As in the case of Ga-site acceptors like Be_{Ga} , to the acceptor atom, instead, in the case of As-site acceptors like Si_{As} [2]. It is quite surprising, therefore, that the properties under stress of acceptor-H complexes are independent of the acceptor sublattice. On the other hand, a quite low value (0.037 eV) of the activation energy for the reorientation of the $\text{Zn}_{\text{Ga}}\text{-H}$ complex in GaAs has been recently obtained by internal friction measurements.[3]

In the present study, the geometry, the chemical bonding and the energy barrier for the reorientation of the $\text{Si}_{\text{As}}\text{-H}$ and $\text{Zn}_{\text{Ga}}\text{-H}$ complexes in crystalline GaAs have been investigated by first-principle pseudopotential- local-density-functional methods in a supercell approach. Present results show that both complexes are characterized by a stable configuration with the H atom located next to a bond centered (BC) site. Moreover, in the $\text{Si}_{\text{As}}\text{-H}$ complex the H atom forms a $\text{Si}_{\text{As}}\text{-H}$ bond weakly perturbed by the Ga neighbor, while in the $\text{Zn}_{\text{Ga}}\text{-H}$ complex the H atom is primarily bonded to the nearest As atom, thus supporting previous suggestions on the H bonding. Despite those differences, the resulting bonds have similar dissociation energies and H stretching frequencies. On the grounds of details of the H bonding, those similarities are likely due to the weak perturbation produced by the third atom in the complex. The activation energies for the reorientation of both the complexes are of order 0.2 eV, thus in a good agreement with experimental results only in the case of the $\text{Si}_{\text{As}}\text{-H}$ complex. Because present results indicate that the reorientation kinetics of the two complexes is quite similar at comparable temperatures, we suggest that two different regimes occur at different temperature in the case of the $\text{Zn}_{\text{Ga}}\text{-H}$ complex, as reported in the case of nitrogen in diamond[4]. In particular, a tunneling of the H atom could account for the small value of the activation energy measured at low temperature, while the reorientation of the complex should be characterized by thermally activated jumps over an energy barrier of about 0.2 eV at higher temperature.

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STUDY OF PLASTICALLY DEFORMED SEMICONDUCTORS BY MEANS OF POSITRON ANNIHILATION

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Key Words: positron annihilation, deformation, vacancies, dislocations

Both elemental and compound semiconductor samples plastically deformed under compression were investigated by combined transmission electron microscopy and positron-lifetime spectroscopy. Additionally, annealing experiments were performed to identify the deformation-induced defects. The decomposition of the positron lifetime spectra gave evidence of the formation of vacancies, divacancies and vacancy clusters during deformation. Defect concentrations were determined for different deformation temperatures, strain rates, and deformation directions. The defect densities are distinctly higher for multiple-slip orientations. The mechanism of vacancy formation and clustering as a function of the deformation temperature could be related to dislocation cutting and the dragging of jogs along screw dislocations. Temperature-dependent positron lifetime measurements in GaAs samples exhibited the formation of shallow positron traps due to the deformation. Two types of shallow positron traps were identified depending on the deformation conditions. One type had a positron binding energy of approximately 40 meV and was related to a Ga_{As} antisite defect. Another shallow trap had a positron binding energy of about 10 meV. This trap was attributed to the undisturbed dislocation line, which behaves as in metals as a shallow positron trap.

SUBSTITUTIONAL NITROGEN AND NITROGEN-HYDROGEN COMPLEXES IN GaAs

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Key words: Nitrogen, Hydrogen, GaAs, Pseudopotential

We have investigated the electronic structure, atomic geometry and energetics of the isolated nitrogen impurity (N_{Ga}) and the complexes $N_{Ga}-H$ and $N_{Ga}-H_2^*$ in GaAs. Our calculations are performed using density-functional theory within the local density approximation and ab initio norm-conserving pseudopotential.

Our results for N_{Ga}^0 show an on-site defect with two deep levels in the gap, where the lowest one corresponds to a doubly occupied a_1 level. As others anion-antisite-like defects in GaAs, we observe a metastable structure when the N atom is displaced from the substitutional site along $\langle 111 \rangle$ direction by ~ 1.0 Å. In this structure the total energy increases in 0.31 eV with respect to the stable structure (on-site) and the calculated barrier is 0.44 eV. For the N_{Ga}^{-1} system we found a large off-center displacement along $\langle 111 \rangle$ direction, where the total energy is 0.5 eV lower than that of the on-site position. The calculated formation energy, with N_{Ga}^0 in the stable state, show that substitutional nitrogen can be found in three charge states (0, -1 and -2) with the middle one being unstable, having an U-negative behavior. At the metastable state of N_{Ga}^0 , this center was found in four charge states (from +1 to -2).

The minimum energy configuration for the neutral $N_{Ga}-H_2^*$ complex has the H atoms occupying, each one, a bond-center position of the $N_{Ga}-As$ bonds. The N-H and H-As distance are 1.09 Å and 1.96 Å respectively, for both bond-center configurations. We observed that the a_1 defect level is passivated, while the t_2 level, occupied with two electrons, is located near the valence band top. The minimum energy configuration for the neutral $N_{Ga}-H$ complex has the H atom in an off bond-center position of the $N_{Ga}-As$ bond, the N-H and H-As distance are found in 1.08 Å and 2.01 Å respectively. We also observed the passivation of the a_1 level but the t_2 level now appears in a midgap position.

THEORETICAL STUDY OF SELECTED COMPLEX-DEFECTS IN GaAs

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Among the experimental techniques used in the development of III-V semiconductor devices, the ion implantation plays a major role for establish proper n- and p-type conductivity on an initially semi-insulating (si) material, as for Si on si GaAs. Also ion or electron bombardment is often applied to convert a conductive doped layer in a highly resistive one. The electrical isolation obtained in this way is of relevance to enhance the electronic characteristics of semiconductor devices, e.g., the reduction of the backgating effect in GaAs integrated circuits.

Most of the interesting features of these materials are assumed to be related with deviations from the ideal crystal structure that can appear either as simple-defects (vacancy, antisite, interstitial, impurity) or as complex-defects (combination of simple-defects). An *ab-initio* calculation based on pseudo-potential density-functional theory is used. A supercell with 128 atoms is adopted in Car-Parrinello scheme. For the antistructure pair ($\text{As}_{\text{Ga}} + \text{Ga}_{\text{As}}$), from the total energy calculations, a first donor, a first acceptor, and a second acceptor levels are observed and a comparison is made with earlier, both theoretical and experimental, results. Two other possible complex-defects ($\text{V}_{\text{As}} + \text{As}_{\text{Ga}} + \text{Ga}_i$ and $\text{V}_{\text{Ga}} + \text{Ga}_{\text{As}} + \text{As}_i$) are discussed. It is shown that the first one presents a metastable configuration and the second one is unstable presenting a spontaneous recombination. For all complex-defects the formation energies and charge densities are discussed.

TRAPS FOUND IN GaAs MESFETS: PROPERTIES LOCATION AND DETECTION

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Key Words: traps, GaAs MESFETs, DLTS, noise, dispersion, semi-insulating substrate

Traps located within semiconductor devices degrade their performance. They result in excess noise and various transient and frequency dependent effects. These effects occur mainly at low frequencies but also affect high frequency devices in mixer and oscillator applications. They also have important effects in the device degradation processes and various 'sidegating' and 'kink' effects. In order to improve devices it is important to know the properties and location of the defects.

A systematic study has been made of the defects in GaAs MESFETs over a temperature range 77K-330K under Ohmic and current saturation bias, using a variety of techniques: conductance DLTS with gate or substrate excitation, a novel transient modelling method to determine the trap location, mutual conductance dispersion, output conductance dispersion, excess noise and substrate oscillations.

A total of nine generally occurring traps have been detected. Their properties and locations will be described and compared with values found in the literature. The values found by the different methods will be compared, but in general there is no systematic difference.

The relative sensitivity of the different techniques will be discussed. In general the conductance DLTS method using an Ohmic channel is easiest to operate and detects most traps. The reason why some traps are not detected by some methods will be discussed.

In n-channel devices both electron-like and hole-like traps are found. The 'type' is defined by the sign of the DLTS transient. The electron traps are located in the neutral channel and produce small effects. The hole-like traps are usually the most prominent and are found in the free surface (H₂) or the semiinsulating substrate. These traps also have the property that their filling and emptying times are (nearly) equal. The location, formation and reason for the activity of these traps will be discussed.

Steps or 'kinks' are found in the current saturation region. These are caused by trap filling by hot electrons to give a change in the pinch-off voltage.

TRUE AND APPARENT DEEP LEVELS DEDUCED FROM SPACE-CHARGE TRANSIENT MEASUREMENTS

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Key Words: transient spectroscopy, anomaly, false center, GaAs

Space-charge transient spectroscopy techniques being applied to heavily compensated or overcompensated semiconductor provide good possibilities to study deep-level centers in spite of the anomalous phenomena accompanying transients [1-3]. The phenomena include multi-peaked DLTS and Thermally Stimulated Current(TSC) spectra, nonmonotonic Thermally Stimulated Capacitance (TSCAP) line etc., all of them arising when the only thermal emission process is operative. Here we consider a spectroscopic value of the anomalies and ways how to distinguish true and apparent centers, including metastable ones, following from a standard analysis. We present the theory and simulations of signal forms for $n\pi$ pquad hbox and quad npp structures. The concentration profiles and ratio of shallow and deep centers, N/N_t , were assumed to be arbitrary ones. In $n\pi$ p structure the first (low-temperature) TSC peak (T_{m1}) typically arises at instant the space-charge boundary enters the π region and is accompanied by a TSCAP peak at the same T, if n is not of a high value. The second peak (T_{m2}), if any, is in the position either near that of the "ideal" one or may be shifted towards a higher temperature. In npp structure, two-peaked spectra are produced by the step-like $N_t(x)$ dependence, if $N/N_t \ll 1$ in the outer p layer and $N/N_t \geq 1$ in the inner one. The inflection point (not maximum) of the TSCAP line corresponds to T_{m1} . Experiment has been performed on the LPE-grown GaAs. Recipes of how to interpret experiment properly and the data processing scheme are presented.

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UNIAXIAL STRESS SYMMETRY STUDIES ON THE E1, E2 AND E3 IRRADIATION-INDUCED DEFECTS IN GALLIUM ARSENIDE

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Key Words: GaAs, uniaxial stress, E1, E2, E3, defect symmetries

When uniaxial stress is applied to a crystalline solid, the atomic arrangement in the local vicinities of lattice defects can be distorted, and electronic energy levels which were orientationally degenerate in the absence of stress may become non-degenerate. Measurements of the effects of uniaxial stress, applied along different crystal directions, upon the electronic levels of the defects can therefore give information on the structural symmetries of the defects and thus on their identities. We present results here from what we believe to be the first ever uniaxial stress investigations on irradiation-induced defects in gallium arsenide.

In this work we have investigated the effects of uniaxial stresses from zero to 0.4 GPa on the 10-250K majority-carrier deep level transient spectra of epitaxial n-GaAs (in the form of Schottky diodes) before and after irradiation by 1.0 MeV protons. As for high energy electron irradiation, such irradiation creates the E1, E2 and E3 electron-trapping levels, which, for zero applied stress, have electron ionisation energies to the conduction band of about 0.045, 0.140 and 0.340 eV, and are usually believed to be due to lattice defects arising from the displacement of arsenic atoms. We find that for each of these three defect levels, uniaxial stress applied along a $\langle 100 \rangle$ direction of the GaAs causes increase but no broadening of the DLTS-measured electron ionisation energy, but that $\langle 110 \rangle$ applied stress produces both broadening of the DLTS peak and increase of the mean ionisation energy of the defect. For the E1 defect the effect of 0.4 GPa $\langle 110 \rangle$ stress is to produce splitting of the E1 peak into two clear peaks. By detailed analysis of the E1, E2 and E3 DLTS peak shapes we deduce that $\langle 110 \rangle$ stress causes splitting of each of the respective electronic levels into two levels of equal populations. These $\langle 100 \rangle$ and $\langle 110 \rangle$ uniaxial stress data strongly suggest that the E1, E2 and E3 defects each has C_{3v} crystallographic symmetry, ie that each has a structure that contains a single $\langle 111 \rangle$ symmetry axis.

For the E3 defect the data are consistent with the proposal in other work that this defect is an arsenic Frenkel pair, provided that the interstitial-vacancy direction is along $\langle 111 \rangle$. However, our data for the E1 and E2 defects do not support the identification of these defects as simple arsenic vacancies of T_d symmetries in different charge states.

VACANCY DEFECTS IN LOW-TEMPERATURE-GROWN GaAs OBSERVED BY POSITRON ANNIHILATION

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Keywords: low temperature grown GaAs, Positron annihilation, vacancies

A systematic investigation of GaAs layers grown at low temperatures (LT-GaAs) was carried out by means of positron annihilation. The vacancy defects in undoped as-grown material were identified to be mainly Ga vacancies. The vacancy concentration increases up to 10^{18} cm^{-3} with decreasing the growth temperature to 200° C. It is shown that the estimated concentrations can account for the compensation of As_{Ga}^+ antisites as previously assumed. No other acceptor-like defect having significant concentrations could be detected by temperature-dependent positron measurements. Isochronal annealing up to 600° C was done at various samples. New defects different from Ga vacancies are formed during annealing. These defects are found to be vacancy clusters or As precipitates, detected by TEM.

YB LUMINESCENCE CENTRES IN MBE-GROWN AND ION-IMPLANTED GaAs

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Key Words: gallium arsenide, rare earth elements, luminescence complexes

Intensity of rare earth (RE) luminescence in semiconductors depends, among other factors, upon the probability of optical transitions within the 4f-shell of RE ions and upon the efficiency of energy transfer from the excited system of electrons and holes to RE luminescence centres. It was suggested in the literature that optical activity of Yb in III-V compounds must be related to its substitutional location largely due to covalency effects which relax the parity selection rule and make parity forbidden dipole transition in the 4f-shell possible. In GaAs the substitutional fraction of Yb (determined by Rutherford back scattering/channeling technique) was found to be below sensitivity of the method, which was thought to be the reason for very weak (if any) Yb luminescence previously reported for GaAs doped with Yb either by ion implantation or during epitaxial growth.

Due to high chemical activity of RE elements their associations with other dopants are quite common. In the present work we demonstrate that Yb can be rendered optically active in GaAs if it is incorporated in some luminescence complexes which enhance the optical transition probabilities and/or efficiency of energy transfer from electrons and holes to Yb luminescence centres. The Yb doping was produced either in the process of MBE growth or by ion implantation. It has been found that co-doping (by ion implantation) with group IV (Si) or group VI (S, Se, Te) and oxygen is a prerequisite of optical activity of Yb in GaAs. The characteristic f-f luminescence of Yb^{3+} is emitted by three-component complexes ($\text{Yb}+\text{O}+\text{S}/\text{Se}/\text{Te}/\text{Si}$). Formation and destruction of Yb related centres imply complicated reactions between their components, at least some of them being mobile at the post-implantation annealing temperatures (500-700°C). These reactions in MBE grown layers were found to be basically the same as those in the bulk material. It was found that within the group of similar centres ($\text{Yb}+\text{O}+\text{S}/\text{Se}/\text{Te}$) the optical transition energies increase and the energies of participating phonons decrease with the increase of (S/Se/Te) coactivator size (mass). Oxygen seems to be a necessary component of Yb related centres in GaAs: a number of luminescence due to associations of Yb with some background impurities were found only in the case of combined ($\text{Yb}+\text{O}$) implantation. The crucial role of oxygen in the optical activation of Yb is possibly due to its participation in the energy transfer process. The intensity of luminescence of ($\text{Yb}+\text{O}+\text{S}$) is comparable to that of Yb in GaP or even in InP, where the luminescence is attributed to isolated substitutional Yb^{3+} ions. It can be suggested the lattice position of rare earth atoms might not be the only (and even not the most important) factor of their optical activity if they are incorporated in some complex centres. In this case the relaxation of parity selection rule might be largely due to symmetry lowering interaction of RE ions with other components of the complexes.

ACCEPTOR-HYDROGEN INTERACTION IN InAs

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Key words: InAs, hydrogen passivation, Cd acceptors, ion implantation

The interaction between hydrogen and Cd acceptors in InAs was studied by perturbed angular correlation (PAC) spectroscopy. From earlier PAC experiments it is already known [1], that Cd acceptors trap hydrogen, resulting in two different complexes (C427, C577). One of them was assigned unambiguously to a close Cd-H pair (C427) oriented in $\langle 111 \rangle$ direction. The second configuration (C577) revealed a more puzzling behaviour with regard to its formation and microscopic structure and its identification required further experiments.

At the on-line mass separator ISOLDE samples of undoped, LEC grown InAs were implanted with radioactive ^{111m}Cd ions at 60 keV and a dose of 10^{11} cm^{-2} . After the removal of the implantation induced radiation damage by furnace annealing at 920 K (600 s., As overpressure) low energy H^+ implantations were performed at 295 K with a dose of $3 \cdot 10^{14} \text{ cm}^{-2}$ and energies of 100 eV and 1 keV, respectively. The following PAC experiments gave surprising results: besides the Cd-H pair and complex C577 a third, new hydrogen correlated complex (C555) was observed. The characteristic PAC parameters of C555 ($\nu_Q = 555(2) \text{ MHz}$, $\eta = 0.19(1)$) are very similar to those of C577 ($\nu_Q = 577(2)$, $\eta = 0.09(1)$), but the complexes are formed under different H^+ implantation conditions. C555 appears after H^+ implantation with an energy of 100 eV while C577 is observed after H^+ implantations with higher energy ($E = 1 \text{ keV}$). None of the three complexes are observed after He^+ implantation under similar conditions proving that these complexes are not created by the presence of implantation induced lattice defects alone and hydrogen has to be involved.

The orientation of C555 and C577 was determined by varying the angle between the lattice directions of the single crystal and the detectors. It was found, that both complexes are not oriented in $\langle 111 \rangle$ but in $\langle 110 \rangle$ lattice direction. Recording PAC spectrum at room temperature within increasing time intervals clearly show a transformation of C555 and C577 into Cd-H pairs (C427).

Our present results prove that besides Cd-H pairs two more hydrogen correlated complexes are formed. They behave very similar and our PAC data indicate an interpretation in terms of multi-hydrogen complexes (Cd-H_n) or Cd-hydrogen pairs together with some other impurity or defect (Cd-H-X). Both transform into Cd-H pairs at room temperature.

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LATTICE PARAMETER CHANGES AND DEFECT REACTIONS IN LOW TEMPERATURE ELECTRON IRRADIATED AlAs

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Key words: AlAs, Lattice parameter, point defects, e-irradiation

X-ray diffraction was employed to investigate the damage accumulation and the subsequent thermally activated annealing reactions in AlAs layers on GaAs substrates. Irradiations were performed at 4.6K with 2.5 MeV electrons up to a total dose of $2 \cdot 10^9$ electrons/cm². The irradiation induced increase of the lattice parameter amounts to about half of the changes observed in the GaAs substrates and yields the first quantitative results on the damage production in AlAs. There is no major annealing observed below 200K and, similar to GaAs, there is a major annealing step around room temperature, a rather continuous annealing up to 500K and a final recovery stage between 700K and 900K. The underlying defect reactions are discussed in comparison to the detailed results available for GaAs [1] and the lattice strain in the AlAs films is compared to the observations after ion implantations [2]. Finally these results are discussed in relation to the different models for the explanation of the unique resistance of AlAs against amorphization under ion irradiation.

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A PLAUSIBLE EVIDENCE OF THE EXSISTENCE OF DEEP ACCEPTORS IN Si D-DOPED AlGaAs

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Key Words: Photoluminescence, Deep acceptors, Si δ -doped AlGaAs

Photoluminescence(PL) by above-band gap excitation with an Ar-ion laser for Si δ -doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ has been measured in the temperature range between 10 K to 300 K. PL spectra are composed of at least three predominant peaks. As an example, the PL spectra at 70 K for $x=0.35$ with the band gap of 2.02 eV show three separated bands peaked at 1.995 eV, 1.925 eV, and 1.835 eV, respectively. They are denoted as I, II, III bands, for convenience. The temperature dependence of intensity and its line shape for each PL band were curve fitted well with appropriate forms. Based on the fitting with a theoretical form for a free-to-band(FB) recombination including an alloy effect and a lowered dimensionality effect on the density of state of conduction band, we may conclude that the I band is the FB recombination. It is also found that the I and II PL bands terminate at C_{As} and Si_{As} acceptors, respectively. A remarkable result obtained in this work is that the quenching of three PL bands reveal nearly the same amount of thermal activation energies at higher temperature range. The fact leads one to propose that the initial states of these PL bands lie at the bottom Γ conduction band. The quenching is caused via thermal activation to higher levels possibly the L band of about 90 meV higher than the bottom of the Γ band followed by the nonradiative recombination process. Based on this idea together with the large energy shift of about 200 meV of III PL band(1.835 eV) , we may propose that the final state might be related to a deep acceptor level. This PL band has been assigned before to a Si-related deep donor level. The PL studies for the δ -doped AlGaAs grown from the different origin are giving consistent results. We will address a detailed talk in the conference.

BACKGROUND DOPING EFFECTS ON Zn DIFFUSION IN GaAs/AlGaAs MULTIPLE-QUANTUM-WELL STRUCTURES

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Key words: Doping effect, column-III vacancy, column-III interstitial, Zn diffusion.

The effects of background n- and p-type doping on Zn diffusion in GaAs/AlGaAs multiple-quantum-well structures are investigated by secondary-ion mass spectrometry (SIMS) and photoluminescence (PL) measurements. Zn diffusions are performed at 575 °C into three identical multilayered structures consisting of 30 GaAs quantum wells separated by $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ barriers. The first and the second structures are uniformly doped with Si ($5 \times 10^{18} \text{ cm}^{-3}$) and Be ($1 \times 10^{19} \text{ cm}^{-3}$), respectively. The third structure is also uniformly doped with Si ($5 \times 10^{18} \text{ cm}^{-3}$) but its 10 central periods are codoped with Be ($1 \times 10^{19} \text{ cm}^{-3}$). SIMS profiles measured after Zn diffusion show that the region behind the Zn diffusion front of all structures are disordered. In particular, the effective Zn diffusivity and the disordering rate are significantly dependent on the background doping. They are enhanced by Be doping and reduced by Si doping. PL measurements give information about different point defects in the epitaxial multilayered structures and the reactions of these defects during the diffusion process. Before Zn diffusion, the Si-doped structure contains a high concentration of column-III vacancies, whereas a domination of column-III interstitials is observed for the Be-doped structure. After Zn diffusion, PL results indicate a reduction of column-III vacancy concentration in the Si-doped sample and an increase in column-III interstitial concentration in the Be-doped sample. A model based on the "kick-out" mechanism of Zn diffusion is proposed to explain our observations. The incorporation of Zn into the crystal lattice during Zn diffusion results in a column-III interstitial supersaturation responsible for the Al-Ga interdiffusion in the Zn diffused region. The effective Zn diffusivity and the disordering rate are controlled by the background donor or acceptor concentration in the structure and by the column-III interstitial concentration behind the Zn diffusion front. The effective Zn diffusivity and the disordering rate increase with increasing acceptor concentration, but they decrease with increasing donor concentration. Since column-III interstitials and column-III vacancies can mutually annihilate, the concentration of column-III interstitial and column-III vacancy in the Si-doped structures is reduced, leading to a retardation of Zn diffusion. On the other hand, the contribution of the column-III interstitial concentration in the Be-doped structures to the Zn-diffusion induced column-III interstitial supersaturation results in an enhancement of the Zn diffusivity.

GALLIUM INTERSTITIALS IN GaAs/AlGaAs HETEROSTRUCTURES INVESTIGATED BY OPTICALLY AND ELECTRICALLY DETECTED MAGNETIC RESONANCE

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Key Words: electrically detected magnetic resonance, GaAs

For the identification and analysis of defects in semiconductors electron paramagnetic resonance (EPR) has a long tradition. Despite of the tremendous success of conventional EPR investigations on defects in bulk semiconductors, the method has strong limitations for the application on epitaxial layers or quantum wells. The defect concentrations present in such structures are in most cases far below the detection limit of the conventional EPR. Two ways to overcome this drawback have been developed: optically and electrically detected magnetic resonance (ODMR and EDMR, respectively). While ODMR is a well established technique, EDMR investigations have been reported only on a rather limited number of semiconductors, especially quantum well structures.

We performed a comparative ODMR and EDMR study on GaAs/AlGaAs heterostructures containing a 50 nm GaAs quantum-well codoped with Si and Be. The donor-acceptor-pair recombination serves as sensitive detection channel for the ODMR experiments and reveals the presence of Ga interstitials in the GaAs quantum well. The signals observed in EDMR depend sensitively on the choosen experimental conditions. Three cases can be distinguished which dependent on the localization of the recombination current in the heterostructure. Surface defects are observed for the current path dominantly localized in the GaAs cap layer. Ga interstitials are observed for conditions where the current is dominantly driven through the quantum-well, and Cr^{4+} as well as arsenic antisite defects for conditions including recombination current in the semi-insulating substrate. These results indicate the high potential of EDMR in view a selective detection of defects in complicated sample structures, especially as all attempts to separate the observed defects by the standard EPR procedures fail.

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PHOTOLUMINESCENCE CHARACTERISATION OF SURFACE DEFECTS IN AlGaAs QUANTUM WELL

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It is well known that unless special precautions are taken in the substrate preparation and selection of growth conditions, the molecular beam epitaxial growth of GaAs and AlGaAs layers give rise to a particular class of surface defect; known as oval defects. Some of these oval defects, at a later stage, influence the performance of small area devices. The oval defects in GaAs and AlGaAs epitaxial layers were characterized using Raman microprobe having submicron spatial resolution and photoluminescence techniques. In this paper, the quantum well recombination results are presented from the oval defects under steady state excitation in the laser structures.

DEEP ELECTRONIC STATES AT THE INVERTED AlAs/GaAs INTERFACE UNDER DIFFERENT GROWTH MODES

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Key words: Intrinsic deep-level defects, epitaxial growth modes, interface state density

The properties of the AlGaAs/GaAs interface have significant consequences for the characteristics of various heterojunction-based semiconductor structures. It is well established that the electronic properties of the inverted (GaAs on AlGaAs) interface are inferior to those of the normal (AlGaAs on GaAs) interface. The origin for this asymmetry has not been fully understood yet. One reason might be the interface roughness induced by the lower Al mobility on the AlGaAs surface during MBE growth. In addition, the segregation of residual impurities has been discussed to generate interface charges. There is however no experimental proof up to now that indeed impurities cause the deep electronic states at the inverted AlGaAs/GaAs interface. We have recently found by DLTS a series of well-defined electron traps, which are concentrated at this inverted interface. These deep levels are not originating from impurities, but from native point defects, which are formed during growth on the AlGaAs surface.

In order to study the generation of these intrinsic defects at the AlAs surface, we have examined the inverted AlAs/GaAs interface grown under different conditions. It is known that three-dimensional (3D) growth of AlAs is occurring in a *forbidden window*. This growth mode identified by the formation of facets results in a rough surface. At lower temperature and enhanced As₄ flux, it is possible to realize a *reentrant* layer-by-layer (2D) growth mode, which is indicated by oscillations of reflection high-energy electron diffraction (RHEED) intensities and straight RHEED streaks. With this distinct mode, the effective Al mobility is enhanced, and a smooth AlAs surface is obtained. In particular, the two electron traps p4 at 0.60 eV and p6 at 0.95 eV, which are found to be dominant, depend on the growth mode. The levels p4 and p6 are most likely associated with the isolated arsenic vacancy V_{As} and a complex containing the arsenic antisite defect As_{Al}, respectively.

We will show that the carrier deficit at the inverted AlAs/GaAs interface and the densities of the interfacial levels p4 and p6 can be drastically reduced under the *reentrant* 2D growth conditions. The 2D density of intrinsic traps determined by the C/V method becomes comparable with the total electron deficit at the heterojunction. Under 3D growth conditions, the concentration of the level p6 is reduced for higher temperature, lower As₄ flux, and lower growth rate, i.e., when more time is available for the kinetic processes. The interfacial level p6 is apparently linked with the As₄ flux-dependent mobility of Al atoms, which can lead to the formation of Al vacancies and the subsequent incorporation of As on cation sites. It is therefore an indicator for imperfections on the surface. In spite of the surface roughness, which is produced by 3D growth, the levels are sharp and the intrinsic defects are usually not incorporated into the epitaxial layer. For the interface grown with the *reentrant* 2D mode, the formation of the level p6 is minimized at comparatively low temperatures and drastically enhanced As₄ fluxes, which is in sharp contrast to the behavior under 3D mode conditions. The nearly defect-free growth is thus confirmed by the very low concentration of the interfacial level p6. Because the total density of interface charges becomes also sufficiently low, we can achieve the accumulation of free electrons on the GaAs side of the inverted interface. In conclusion, the optimization of the growth kinetics on the AlAs surface can be investigated via electronic states at the inverted AlAs/GaAs interface.

DEFECT FORMATION DURING LASER INDUCED INTERMIXING OF GaAs/AlGaAs MULTIPLE-QUANTUM-WELL STRUCTURES

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Key words: Laser induced intermixing, Ga antisite related complex, cathodoluminescence.

Low-temperature cathodoluminescence and secondary electron modes of a scanning electron microscope are used to study the formation of point defects during laser induced intermixing of GaAs/Al_{0.45}Ga_{0.55}As multiple-quantum-well structures. The surface of the GaAs/AlGaAs multilayered samples is selectively irradiated with a scanned Ti:sapphire laser beam. Micron-sized melted regions where the GaAs/AlGaAs multilayered structure is totally intermixed are observed under the irradiated surface. The cathodoluminescence spectra of the melted region are dominated by a broad emission band at 1.47 eV. This emission band is believed to be due to the recombination of a Si donor-Ga antisite acceptor complex. Ga antisites are formed during laser irradiation. Si atoms originated from the Si-doped GaAs substrate dissolve into the melt when the melted region develops into the substrate. The luminescence spectra obtained for the 6 µm wide transition region adjacent to the melted region show a broadening and a blue shift of the emission peak associated with the recombination of excitons confined in the quantum wells. This indicates the partial disordering of the multilayered structure. In addition, the Ga antisite related emission band and an emission band due to the transition of free electrons to Si acceptors in the quantum wells are seen in the luminescence spectra of the partially disordered region. Our results demonstrate that Ga antisites are the main intrinsic point defects generated during laser irradiation induced intermixing of GaAs/AlGaAs multilayered structures. The Si-Ga antisite complex is formed at high concentration in the melted region. The mechanism responsible for the disordering of the multilayered structure around the melted region is discussed on the basis of the Si-Ga antisite complex diffusion.

DLTS STUDY IN Be - DOPED P-TYPE AlGaAs/GaAs MBE LAYERS.

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Key words : deep levels, DLTS, AlGaAs.

Deep hole states in p-type $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ grown by MBE have been studied by the deep-level transient spectroscopy (DLTS) method. The as grown and He-ion irradiated samples have been investigated.

In the as-grown samples four hole traps labeled by us as H1 to H4 were detected. For the traps H1, H3 and H4 thermal activation energies obtained from Arrhenius plots were equal to: $E_{H1} = 0.15 \text{ eV}$, $E_{H3} = 0.4 \text{ eV}$ and $E_{H5} = 0.46 \text{ eV}$. Hole emission from H2 trap has been found to be electric field dependent. The electric field dependence of emission rate indicates that carrier emission from the trap has to be accompanied by acquiring a net charge by the defect, i.e. the H2 trap has to be charged upon a hole emission and neutral upon hole capture. This implies that the trap H2 would then be defined as the acceptor-like levels (0/-) in a p-type material. The electric field dependence has been explained in the terms of the Frenkel-Poole mechanism.

It was found that capture processes to the trap H4 is thermally activated with energetic barrier equal to 0.18 eV . This fact indicates that large relaxation is involved in the hole capture/ emission processes.

He-ion bombardment of samples introduced a new deep trap with activation energy close to 0.65 eV .

ELECTRICAL TRANSPORT AND ODMR INVESTIGATIONS OF THE ANOMALOUS GERMANIUM ACCEPTOR IN $\text{Al}_x\text{Ga}_{1-x}\text{As}$

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Key words: Ge, acceptor, $\text{Al}_x\text{Ga}_{1-x}\text{As}$, electrical transport, PPC, ODMR

It is well known that the acceptor germanium in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ has an ionization energy which depends strongly on the Al molar concentration. The level goes from $E_v + 40.4$ meV at $x = 0$ up to $E_v + 130$ -150 meV for $x = 0.4$ [1], which is by far larger than the shift predicted by the effective mass theory for the same Δx range ($\Delta E_i = 5$ meV) [1]. In order to better understand the origin of this anomalous behavior, liquid phase epitaxy (LPE) grown p-type Ge-doped to 10^{18} cm^{-3} $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ samples were investigated by electrical transport techniques, magnetic circular dichroism of the absorption (MCDA) as well as optically detected magnetic resonance (ODMR).

The results can be summarized as follow: when cooling the sample in the dark, two distinct regimes of electrical conduction were observed. The first, dominant at higher temperatures ($T > 100$ K), shows an activation energy of 130 ± 10 meV, which is very similar to the thermal ionization energy of the isolated Ge_{As} -acceptor ($x = 0.4$). Below 100 K, the freeze-out regime is substituted by a hopping conduction process in the Ge-impurity band which is in good agreement with the Mott's law ($\ln(\sigma) \propto T^{-1/4}$). In the latter regime, after illuminating the sample with light of energy below the band gap, a weak persistent photoconductivity effect (PPC) was observed. It was verified that the PPC is present up to 190 ± 10 K.

A strong paramagnetic IR MCDA band has also been observed after cooling the sample in the dark. As a microwave induced change in this MCDA band, an ODMR line of a defect having $S = \frac{1}{2}$, $g_{[001]} = 2.03 \pm 0.01$ and $\Delta B_{1/2} = 60$ mT could be detected. This ODMR line is very anisotropic, which suggests a defect with symmetry lower than T_d . After discussing the origin of the MCDA and ODMR results, a model for the Ge-acceptor is proposed. It is based on the idea that the neutral and paramagnetic ground state of the Ge-acceptor is relaxed possibly due to the alloy disorder in the first (Al,Ga) neighbor shell.

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ODMR STUDY OF ELECTRON IRRADIATION-INDUCED DEFECTS IN $\text{Al}_x\text{Ga}_{1-x}\text{As}$

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Key Words: $\text{Al}_x\text{Ga}_{1-x}\text{As}$, As antisite defects, Ga vacancies, ODMR

The aim of this study was a comparison between the irradiation-induced defects in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and GaAs. The influence of Al neighbours on the stability and structure of these radiation-induced defects in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ was also investigated.

$\text{Al}_{0.16}\text{Ga}_{0.84}\text{As}:\text{Te}$ layers were investigated with magnetic circular dichroism of the absorption (MCDA) and optical detection of electron paramagnetic resonance (ODEPR) via the MCDA after electron irradiation. Two free standing Te-doped $\text{Al}_{0.16}\text{Ga}_{0.84}\text{As}$ layers ($n \sim 10^{18} \text{ cm}^{-3}$ at RT, thickness approx. 220 μm) grown by liquid phase epitaxy (LPE) were irradiated at 4.5 K with 2 MeV electrons. The irradiation fluences were $5 \times 10^{-7} \text{ cm}^{-2}$ and $1 \times 10^{-7} \text{ cm}^{-2}$. The samples were transferred into the ODMR spectrometer (ODMR = optical detection of magnetic resonance) at 77 K.

Prior to annealing to 300 K the MCDA and the ODEPR of two different Ga vacancy-type defects were measured. One Ga vacancy-type defect has a similar ODEPR spectrum as the one observed in GaAs (halfwidth of the ODEPR line approx. 70 mT), the other defect has a much smaller halfwidth (40 mT). In addition an As-antisite defect was found which has a similar MCDA spectrum as the anti-structure pair in GaAs (As antisite defect with a Ga antisite in the next nearest neighbour shell¹). Annealing experiments showed that the Ga vacancy-type defects in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ anneal out in a broad temperature range (200 K - 280 K) as was also observed in GaAs.

It is believed that the trigonal distortion of the Ga vacancy in GaAs is caused by a static Jahn-Teller effect². One As neighbour is relaxed to the Ga vacancy and has a prominent hyperfine interaction which causes the structure and the large halfwidth of the ODEPR line. The fact that one of the Ga vacancy-type defects in $\text{Al}_{0.16}\text{Ga}_{0.84}\text{As}$ has a reduced halfwidth of the EPR can be explained with a reduced or absent prominent hyperfine interaction of the relaxed As neighbour. It is speculated that the static Jahn-Teller effect leading to a trigonal distortion of the Ga vacancy in GaAs² is suppressed by the reduction of symmetry due to neighbouring Al atoms in $\text{Al}_x\text{Ga}_{1-x}\text{As}$.

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POLARON COUPLING FOR SULPHUR IMPURITY IN GaSb

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Keywords: magnetopolaron effect, bound polaron, metastable defects, shallow-deep transition

Although GaSb and its alloys gain an increasing importance as materials for optoelectronics it is still very little, compared to other III-V compounds e.g. GaAs or AlGaAs, known about physical properties of defects in these materials. We present for the first time a detailed far infrared absorption study of the intra-center 1s-2p shallow donor transition in GaSb:S in high magnetic fields. From this study an information about the binding energy, polaron coupling strength and metastable transition mechanism could be obtained.

The infrared absorption appears at low temperatures only after sample illumination with a near-bandgap light. Therefore, as confirmed also by Hall-effect measurements, it has to be linked to the metastable shallow state of the DX center in GaSb. The wavefunction of this state has been found to be an extended hydrogenic-like and built predominantly from the Γ minimum of the conduction band. On the other hand, the shallow state binding energy of nearly 9 meV, estimated from the line position of the 1s-2p transition, exceeds nearly 4 times the value of binding energy predicted by the effective mass theory for a shallow state connected to the Γ minimum.

The striking feature exhibited by the intracenter absorption at high magnetic fields is a large magnetopolaron effect. From the magnitude of the polaron splitting the polaron coupling strength of $\alpha = 0.5-0.7$ could be estimated. We attribute such large coupling strengths to properties of the dielectric screening of the strongly nonisocoric impurity potential.

Our study of the bound polaron in GaSb:S may give a better insight into the fundamentals of the shallow-deep transition exhibited by metastable defects in III-V semiconductors. A distinct change of the crystal effective dielectric properties is observed in GaSb in the vicinity of the sulphur impurity. It amounts to an increase of the "static" lattice screening and a reduced "dynamic" electron screening. This effect provides a justification of two basic assumptions commonly made in modeling the shallow-deep transition. a) the large amplitude of lattice vibrations, being a driving force of the pseudo Jahn-Teller effect, which stabilizes the configuration with the large lattice relaxation, b) the possible "nearly simultaneous" two electron capture necessary for the formation of a negative-U state. As a result the shallow-deep transition may be viewed as a "cooperative" action of both the long- and short-range electron-phonon couplings leading to lattice relaxation - a kind of local phase transition in the vicinity of the defect similar to a phase transition "in macroscale" found, e.g., in ferroelectrics. The values of the ratio of the static to dynamic effective dielectric constants estimated from the analysis of the polaron coupling indicate a possibility that a large bipolaron shallow state may be formed, which then is driven into the localized deep one via the large lattice relaxation.

FIRST-PRINCIPLE CALCULATION OF ELECTRONIC PROPERTIES OF $\text{Ga}_{1-x}\text{Al}_x\text{N}$ ALLOYS

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Keywords: Semiconductor, Ab-initio calculation

The electronic properties of the wide band gap semiconductors $\text{Ga}_{1-x}\text{Al}_x\text{N}$ alloys for ($x = 0.0, 0.25, 0.75$, and 1.0) have been investigated by using the first principle calculation. The calculated direct band gap for the random distribution of cation nearest neighbour tetrahedral clusters in the $\text{Ga}_{1-x}\text{Al}_x\text{N}$ alloys for any arbitrary concentration x is seen to show a quite linear variation with concentration of Al which is in agreement with the experiment. On the other hand, the indirect band gap remains invariant. We observe a direct to indirect band gap cross over at $x=0.59$.

CHARACTERIZATION OF MISMATCH-INDUCED DEFECTS AND THEIR EFFECT ON THE ELECTRICAL PROPERTIES OF ZnSe/GaAs HETEROJUNCTIONS GROWN BY MBE

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Key words: ZnSe, GaAs, hysteresis, mismatch-induced defects, MBE, admittance.

Much work has been done on ZnSe epitaxial layers grown on GaAs because of the small lattice mismatch (0.27 %) in this heterojunction. Pseudomorphic growth is possible at thickness of about 0.15 - 0.2 μm . However, many devices require ZnSe layers beyond this thickness. Therefore mismatch-induced defects are widely present in and near the heterointerface [1,2]. Because the interface has a strong effect on both electrical properties and other physical characteristics, such as defect density and degradation of the devices, the characterization and control of the ZnSe/GaAs heterointerface is important to obtain high-quality ZnSe epilayers on GaAs substrates. Although many reports have been published on the characterization and control of the MBE-ZnSe/GaAs interface, they are still subject of considerable interest.

We here present experimental results obtained from admittance spectroscopy and capacitance-voltage (C - V) measurements on p- and n-type ZnSe layers grown by MBE on highly doped GaAs substrates. The interface properties and their effects on the electrical properties of the ZnSe/GaAs heterojunctions were investigated. The C - V characteristics of these heterojunctions show a hysteresis which can be related to an unusually slow capacitance transient after the applied reverse-bias is decreased. A large frequency dispersion of the capacitance and a broad peak in the conductance spectra are observed at temperatures around 340 K. These observations strongly suggest the presence of a continuum of defects in the interface between ZnSe and GaAs. The capacitance versus frequency data was analyzed in terms of Lehocvec's model [3] of an interface state continuum with a single time constant. The density of interface states was then found to be about $4 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ for typical both n- and p-type samples. We attribute the long time constant observed in the capacitance transients to slow changes in the charge on the interface states. The scattered values of this time constant for different samples and the values of the single time constant calculated from the fitting of data are in a good agreement

The presence of interface states may seriously affect the performance of ZnSe/GaAs based devices. The correlation between their behavior and the growth conditions is of prime importance and is presently under study.

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COMPARISON BETWEEN AS-GROWN AND ANNEALED QUANTUM DOTS MORPHOLOGY

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The atomic self-organization during the first stages of the epitaxial growth on highly mismatched substrates has been used recently as a method to obtain low dimensional structures without the requirements of using other technological processes.

The present work studies the first stages of quantum dots growth and the influence of the annealing after the InSb deposition. Two samples were prepared by depositing a total amount of InSb equivalent to 2.0 and 2.8 monolayers (ML) by Atomic Layer Molecular Beam Epitaxy (ALMBE), keeping the Sb flux constant. After dots deposition both samples were annealed at a temperature of 435°C during 5 min with a continuous Sb flux. A piece of the sample with 2.8 ML was kept without annealing in order to assess the effects of the process in the structure of the islands.

High-energy electron diffraction during growth was used to assess the growth mode during the first stages of deposition. A Stransky-Krastanov mode is suggested as it was observed a transition from two-dimensional to three-dimensional growth mode. Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) were also performed in order to determine the morphology, distribution and relaxation state of the dots.

Results show that, in general, good quality dots are obtained for the annealed samples, due to the enhancement of the atoms reorganization on the wafer surface. AFM results show that the annealed samples have well defined dots with a uniform distribution over the substrate, while as grown sample presents a smooth wavy surface and InSb islands are not well distinguished from each other. For the annealed samples, the dots surface density rises with the InSb contents, and the size is higher as well. It can be also observed for the 2.8 ML samples that, in both as-grown and annealed cases, the substrate surface has developed an anisotropic rugosity that is more outstanding in the case of the annealed sample. This anisotropy is not so noticeable in the case of a growth of 2 ML which could be due to the lower InSb contents or to slightly changes in technological parameters.

TFM images confirm the above observations and display that the anisotropy of the 2.8 ML sample also affects to the dots size, being larger in the direction parallel to the undulation. The dots shape is more regular in the case of the annealed samples. High resolution images exhibit that the crystalline quality is better for the annealed case. The most common defects found are misfit dislocations and twins that relax the strain of the InSb/InP system. Finally, the Stransky-Krastanov growth mode is discussed for this samples as we have no evidence of a wetting layer.

COULOMB INTERACTION BETWEEN CARRIERS LOCALIZED IN InAs/GaAs QUANTUM DOTS AND ON POINT DEFECTS

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Key words: quantum dots, defects, DLTS

Recently, there has been considerable interest in studies of carrier localization in quantum dot (QD) heterostructures. In this work we report on the deep level transient spectroscopy (DLTS) and capacitance-voltage (C-V) studies of InAs/GaAs vertically coupled quantum dot (VECOD) structures inserted in an active region of laser diode. The QDs are formed self-organized in a p-type GaAs matrix during molecular beam epitaxy.

From C-V profiles the spatially localization associated with QDs has been determined. We apply different combinations of bias voltages V_b and of filling pulse voltages V_f to perform the DLTS study of the regions below, coincident, and above the layer with VECODs. The measurements has demonstrated clear signal due to localization of carriers in QDs. Additionally, some concentration of deep traps ($\approx 10^{11} \text{ cm}^{-2}$) and has been revealed in the region spatially coincident with QDs. These point defects originate, most probably, from low temperature GaAs growth during multiple InAs-GaAs deposition cycles. We found that DLTS spectra are changed dramatically for isochronous annealing temperatures below and above 245 K and for cooling conditions $V_f > 0$ or $V_b = 0$. After annealing at $T_a > 245 \text{ K}$, apart from well-known for GaAs EL14 and HL5 levels, E1 electron and H1 hole levels were observed. After annealing at $T_a < 245 \text{ K}$ the peaks, related to these levels, disappeared and other broader E1* and H1* peaks appeared. The position of the H1* peak in DLTS spectra depended on values of V_f , annealing temperature T_a , cooling conditions ($V_f > 0$ or $V_b = 0$) and optical illumination. A thermal activation energy of the H1* level also varied from 132 to 199 meV with V_f , T_a . After illumination and cooling at $V_f > 0$, when the carriers from QDs photoexcited, peak are shifted towards the position measured at $V_f = 0$. The effects observed demonstrate that formation of an additional potential barrier takes place and H1* level is not a metastable defect. The position of the H1 peak in DLTS spectra depends on the V_b value. On contrary, the amplitude and shape of the peak are not changed. A energy of the H1 level varied from 89 to 194 meV. A energy of the E1 and E1* are coincident and equals 110 meV. Our results allowed us to conclude that H1, E1 and H1*, E1* levels are related with the same VECOD. At annealing at $T_a < 245 \text{ K}$ and cooling at $V_f > 0$ QDs are occupied by carriers. Coulomb interaction between the charged QDs and deep centers located in regions close to QDs takes place and dipoles are formed. The electrostatic potential caused by these dipoles is superimposed to the QD potential barriers caused by conduction and valence band discontinuities. The carriers from deep levels can tunnel into quantum dots from which they were previously thermally evaporated. This effect is responsible for the appearance of the broad band in DLTS spectra which replaces the EL14 and HL5 levels. At annealing temperatures $T_a > 245 \text{ K}$ QDs the carriers are evaporated from QDs and dipoles can not be formed. In this sense, the observed shift of the energy is connected with an effect of lowering of the potential barrier for carrier emission from VECODs and with tunneling through its due to p-n junction-induced electric field

DEFECTS IN GaAs HETEROSTRUCTURES: STUDIES WITH ACOUSTICALLY DISTURBED OPTICAL REFLECTANCE AND ABSORPTION

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Key Words: interface, defect states, optical spectra, acoustic waves

We report on a new technique which is developed in order to characterize defect states localized in the vicinity of an interface. The technique combines optical studies on semiconductor heterostructures and acoustic waves employed as an external perturbative factor of optical spectra.

We present data obtained on GaAs epitaxial layers, not intentionally doped and doped with Si and Te impurities, grown by MBE on the (100) GaAs substrates. Lamb acoustic waves were utilized in order to disturb optical reflectance and absorption spectra. Comparison of these data with measured optical spectra of transverse acoustoelectric voltage (TAV) as well as photoacoustic and photoelectric images of near surface regions of the structures will also be presented.

We detect spectral features at 1.42eV and 2.88eV which have been known to arise from optical transitions at the M_0 and M_1 critical points of GaAs and thus verify our technique. We observe spectral peaks with energies of 37meV and 29meV below the band gap which are attributed to the energy levels of Si and Te impurities, respectively. We find two unknown peaks ranged from 50meV to 67meV (E_1 peak) and from 80meV to 90meV (E_2 peak) below the band gap in different samples. These peaks are observable in both the acoustically disturbed reflectance spectra and the spectra of TAV. They are suggested to be due to two energy levels of arsenic vacancy V_{As} localized in the interface and influenced by electric fields and mechanical stresses in the boundary region. An exact energy position of the E_1 and E_2 peaks is therefore indicative of an interface quality. This conclusion is in excellent agreement with an interface quality test performed by photoacoustic and photoelectric imaging of the GaAs layers. A model describing appearance of the presented spectral features due to perturbation by acoustic waves will be discussed.

EPR STUDIES OF SUPERLATTICES

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Key words: Interdiffusion, Strain, Superlattices

Magnetic resonance provides a powerful tool for the investigation of the properties of magnetic thin layers and superlattices (SL's). In this paper we present results where the EPR of isolated paramagnetic centers is used for the investigation of interdiffusion in SL's. In particular, we study Eu and Mn impurities in the diamagnetic layers of SL's of the type PbTe/EuTe and CdTe/MnTe, respectively.

Paramagnetic impurities in superlattices differ from those in volume crystals by the local strain and by a possible confinement of the conduction electrons. Strain leads to a modification of the fine structure of the magnetic impurity while the presence of the confined electron gas results in a modification of the spin relaxation rates. Thus, investigating the saturation of the EPR amplitude as a function of microwave power we are able to distinguish the spectra of impurities in the SL wells from those in the substrate also in the cases where fine structure is not resolved. In the magnetic/diamagnetic SL's, the EPR studies of impurities which diffuse into the diamagnetic well allow a quantitative analysis of the diffusion at the interface.

We demonstrate the influence of conduction electrons on the spin relaxation of localized centers in CdTe doped with Mn and N. The nitrogen acceptor exhibits metastability. The resulting giant photoconductivity leads to dramatic changes of the Mn relaxation rates under illumination.

EPR studies are applied for the investigation of local strains acting on Mn and Eu impurities in SL's. Since Eu, in contrast to Mn, is characterised by a well resolved fine structure we are able to monitor not only the mean strain but also its fluctuation.

We investigate inter-diffusion in EuTe/PbTe SL's. We analyse the amplitude of EPR spectra of isolated Eu impurities and of Eu-Eu pairs. The observation of spectra of isolated impurities is possible if the local concentration of diffused impurities is lower than 1% in the well. Since we are able to observe such spectra in SL's with a width of the diamagnetic wells of a few monolayers only we conclude that these SL's are characterised by very weak diffusion and an almost rectangular shape of the concentration profile $x(z)$, which cannot be effectively evaluated by X-ray analysis.

EXCITED STATE DYNAMICS IN QUANTUM DOTS: DYNAMIC DILATATION

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Key words: Quantum dots, excited states, dephasing

This work concerns the femtosecond and picosecond dynamics of excited states in quantum dots, typically CdS clusters consisting of 150-200 atoms, for which the excited states are of interest through their role in potential photonic devices. The effects discussed appear to be general for dots of this size, whether the excited states correspond closely to bulk excitons, or whether they are associated with defects or impurities.

The fact that the dots are at constant pressure, rather than constant volume, leads to a modest but significant energy shift on the picosecond timescale in what would normally be described simply as zero-phonon lines. This "dynamic dilatation" shift is unimportant in bulk systems, and is not important for different reasons in small molecules. In essence, the rapid optical absorption step can be regarded as a constant volume step; it is followed by a slower step as the constant pressure condition and the zero surface traction conditions are reestablished. In simple cases, the shift will be inversely proportional to the dot volume and the characteristic timescale proportional to the dot radius.

In certain experiments, the shift will have the same effect as dephasing, for the emission energy will have moved away from the absorption energy, even for what are regarded as zero-phonon lines. The predictions appear to be in line with current experimental data, for which there is a so-called elastic process of dephasing. For this process, the apparent dephasing time and its dependence on dot radius are similar to those expected from dynamic dephasing [1,2].

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IRRADIATION INDUCED LATTICE DEFECTS IN $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ PIN PHOTODIODES

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Key words: $\text{In}_{0.53}\text{Ga}_{0.47}$ epitaxial layers, Alpha ray irradiation, deep levels

Results are presented of an extended study on the lattice defects induced in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ pin photodiodes by 20-MeV alpha rays. The radiation source dependence on the generation of deep levels in the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ epitaxial layers and on the degradation of device performance is also reported taking into account the number of knock-on atoms (N_d) and the nonionizing energy loss (NIEL).

Pin photodiodes fabricated in $n^+ \text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ epitaxial layers grown on (100) InP substrates with a 500 nm $n^+ \text{InP}$ buffer layer using a hydride ($\text{Ga/In/HCl/AsH}_3/\text{H}_2$) vapor phase epitaxy system were used in this study. The nominal thickness of the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ epitaxial layer used as light absorbing layer are 3 μm . After removing the Kovar glass from TO-18 package the diodes were irradiated by 20-MeV alpha rays at room temperature in the AVF cyclotron in TIARA at the Takasaki Radiation Chemistry Research Establishment. The fluence of alpha rays was varied between 10^9 and 5×10^{13} $1/\text{cm}^2$. The irradiation was performed without applying bias to the diodes.

The electrical and optical characteristics of the diodes were measured at room temperature before and after irradiation. The deep levels in the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ epitaxial layer were studied using the deep level transient spectroscopy (DLTS) method. To investigate the recovery behavior of the irradiated diodes, isochronal thermal anneals were also carried out.

The damage coefficient of device performance calculated for alpha ray irradiation is nearly same with that for neutron irradiation, while it is about three orders of magnitude larger than that for electron irradiation. This is due to the different N_d and NIEL, which is correlated with the difference of mass and the possibility of nuclear collision. Electron capture levels around (E_c -0.38 eV) are induced in the $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ epitaxial layer for fluences above 1×10^{10} $1/\text{cm}^2$. The density of induced levels increases with increasing fluence. Induced electron capture levels are thought to be associated with the Ga vacancy and are presumably responsible for the degradation of device performance.

GROUND AND EXCITED STATES OF D-CENTERS IN SEMICONDUCTOR QUANTUM DOTS

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Key Words: semiconductor quantum dot, D^- center, singlet and triplet states of S and P symmetry

Properties of a negatively charged donor center (D^-) have been studied for spherical semiconductor quantum dots in the frame of effective-mass approximation. A spherically symmetric potential well of finite depth has been introduced as a model for the confinement potential of the single, isolated quantum dot in a dielectric material. We have considered the ground state (1^{1S}) and excited states (2^{1P} , 2^{3P} , 2^{1S} , 2^{3S}) of S and P symmetry in both singlet and triplet spin configurations. The ground-state and the excited-state energy levels have been calculated by variational means. For comparison, the energy spectrum of the neutral donor (D^0) has also been calculated. The results are presented as functions of the potential-well depth W and quantum-dot radius R . For all values of R , the energy levels of the considered D^- states are located below the continuum threshold (one electron bound in the D^0 ground state and the second — outside the dot) provided that the potential well is sufficiently deep, i.e. W is larger than about one tenth of the donor rydberg. This means that in quantum dots — on the contrary to the bulk crystals — the excited states of the D^- center can be observed. The calculated $1^{1S} \rightarrow 2^{1P}$ transition energy shows the pronounced maximum as a function of the quantum-dot radius R . The maximum energy of the transitions between the 1^{1S} and 2^{1P} states strongly depends on W and reaches the values of the order of one donor rydberg for large W . Both the bulk-crystal limits, i.e. $R \rightarrow 0$ and $R \rightarrow \infty$, and the limit $W \rightarrow \infty$, are correctly reproduced in our calculations. To the best of our knowledge, the present paper provides the first numerical results for the excited states of the D^- center in semiconductor quantum dots.

EMISSION AND CAPTURE KINETICS FOR A HYDROGEN-RELATED NEGATIVE-U CENTER IN SILICON: EVIDENCE FOR METASTABLE NEUTRAL CHARGE STATE

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Key Words: silicon, hydrogen-related center, emission, capture, electronic structure, metastable state

Processes of emission and capture of charge carriers for the centers with negative-U properties have some features related to the peculiarities of electronic structure of the defects. Carrier emission or capture can be followed by the transformation of the defect configuration and subsequent transition towards the stable state. Non-equilibrium occupancy statistics for the negative-U centers are generally rather complicated. However, from the careful study of the capture and emission kinetics a lot of important information on the electronic structure of the defects can be obtained.

This work presents the results of study of electron emission and capture processes for an amphoteric (having a donor and an acceptor levels) hydrogen-related center with negative-U properties in crystalline silicon. This center is one of the dominant electrically active defects in irradiated and heat-treated Si<O,H> crystals. Capacitance transients techniques (DLTS and ICTS) were used to investigate the above processes in n-type Cz-Si crystals with different doping levels.

It is found that only singly negatively and singly positively charged states of the defect are stable. But for the description of the transition process between these states thermodynamically unstable neutral charge state should be taken into account. Two local energy minima in configurational space are found to be present for this state, i.e., a metastable neutral charge state occurs. Hence, four different states are available for the center.

A non-equilibrium occupancy statistics for the negative-U centers with such an electronic structure has been developed. It is shown that four different terms can be dominant in the equation for the temperature dependence of time constant of the occupancy transient process with respect to the Fermi level position in the crystal. Each of the terms is characterized by its activation energy and its power dependence on the free carrier concentration.

Experimentally observed emission and capture kinetics were fitted perfectly by applying the developed statistics and the values of energy barriers for the electron capture and emission were derived. The peculiarities of electronic structure of this defect are discussed.

HYDROGENATION AND PASSIVATION OF B IN SI BY BOILING IN WATER PRESSURIZED UP TO 10 ATM

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Keyword: hydrogen, acceptor, passivation, Si, B, water boiling

It is well established that hydrogen introduced in semiconductors causes significant modifications in their electrical and optical properties. Recently, we have found that a pressurized water boiling at 2 atmospheric pressures and 120 °C accelerates hydrogenation and passivation of an acceptor B in Si[1]. In this study, hydrogenation has been extended to 10 atm and 181 °C.

Chips cut from $1 \times 10^{16}/\text{cm}^2$ ^{11}B implanted (001) p^+n Si wafers were boiled in deionized water in a stainless steel autoclave vessel at pressures up to 10 atm. FTIR measurement shows that the transmission at a range from 2200 to 1500 cm^{-1} (which corresponds to free hole absorption) for samples boiled for 6 hrs gradually increases from that for unboiled $\text{p}+\text{n}$ wafers with increasing pressure and temperature up to 8 atm. However, above 8 atm, the transmission decreases towards 10 atm. Also, the sheet resistance for p^+ layers increases due to B passivation up to 8 atm, but decreases above 8 atm. The C-V carrier profile also shows that holes near the surface are gradually depleted with increasing pressure up to 8 atm, but partly recover above 800 °C. On the other hand, boiled and B passivated $\text{p}+\text{n}$ wafers were thermally annealed in Ar gas isochronally for 30 min from 100 to 300 °C. Both the FTIR transmission and the sheet resistance gradually return from 150 °C to those respective values before boiling. In particular, there has been observed an anneal stage from 175 to 225 °C. In the 6 hrs boiling experiment mentioned above, hydrogenation rather decreases above 8 atm (176 °C). These behaviors may be understood as the results of competing effects of passivation of introduced Hydrogen and the dissociation of Hydrogen from the bond center site between B and Si.

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IR STUDIES OF Si:H BOND-BENDING VIBRATIONAL MODES IN Si

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Key Words: hydrogen in silicon, local vibrational modes

The IR analysis of Si:H bond-stretching and bond-bending local vibrational modes in proton-implanted crystalline silicon are performed. New data on the identification of Si:H bond-bending absorption bands are obtained.

At present time there are a lot of experimental and theoretical data on the nature of bond-stretching bands. However the analysis of bond-bending spectra is very difficult because of:

- bond-bending Si:H bands in the range $500-800\text{ cm}^{-1}$ are broad;
- the bands are characterized with weak or unresolved splitting;
- there is not direct correlation with behavior of the bond-stretching bands;
- there is a very intensive phonon absorption in the bond-bending range.

In comparison with bond-stretching range there are only a few IR bands in the bond-bending range. This fact indicate that the bond-bending vibrational frequencies of complexes with similar structure may be closed to each other. We have found dose dependence and annealing behavior correlation between total intensities for some groups of bond-stretching and bond-bending IR bands.

It is shown that bond-bending Si:H bands are split into two separated groups related to vacancy- and interstitial-type complexes as in the case of the bond-stretching bands. The bands in the range $580-690\text{ cm}^{-1}$ are assigned with vacancy-type complexes and the bands in the range $710-780\text{ cm}^{-1}$ are assigned with interstitial-type complexes. The main bond-stretching and bond-bending modes correlated with each other are following (the frequencies were measured at room temperature:

- a) $1950, 1960\text{ cm}^{-1}$ and $718, 750\text{ cm}^{-1}$,
- b) $2104, 2120\text{ cm}^{-1}$ and $588, 610, 694\text{ cm}^{-1}$
- c) $2161, 2184\text{ cm}^{-1}$ and $588, 610, 668\text{ cm}^{-1}$,
- d) 2211 cm^{-1} and 634 cm^{-1}

The dose dependence of the $588 \sim 610\text{ cm}^{-1}$ doublet correlates with the dose dependence of the 2161 and 2184 cm^{-1} , but the increasing of the 588 and 610 cm^{-1} doublet intensity upon isochronal annealing in the range $400-450^\circ\text{C}$ correlates with the annealing behavior of the 2104 and 2120 cm^{-1} doublet. Therefore we have concluded that the corresponding complexes have similar structure with closed frequencies of bond-bending Si-H modes.

MECHANISM OF ENHANCED HYDROGENATION IN POLY-Si THIN FILMS USING ULTRASOUND TREATMENT

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Key Words: hydrogen, ultrasound treatment, poly-Si, thin film

Manufacturing of high performance poly-Si thin film transistors is a critical process for the next generation of active-matrix-liquid-crystal-displays. High density of grain boundary defects and interface states in the gate-oxide strongly deteriorate transport and recombination properties of poly-Si films and prevent to design thin-film transistors with superior parameters. A conventional approach of post-deposition plasma hydrogenation has problems of reliability and time consumption. These problems are due to a trap-limited mechanism of hydrogen diffusion in poly-Si films. It was observed recently, that the process of a hydrogenation in poly-Si thin films can be improved by applying the low-temperature ultrasound treatment (UST).

A strong two orders of magnitude decrease of sheet resistance was observed in as-deposited hydrogenated LPCVD films after UST processing at temperatures lower than 100°C. This was accompanied by the improvement of film electrical and optical homogeneity. It was directly observed an enhancement of hydrogen passivation of grain boundary defects by the measurement of nano-scale contact potential difference mapping using an atomic force microscope. In 550°C thermally recrystallized films containing both polycrystalline phase and amorphous phase, the UST promotes a strong increase of a total photoluminescence intensity as a result of hydrogenation of non-radiative defects (dangling bonds). The most dramatic UST effect was the activation by a factor of two orders of magnitude of a "new" luminescence maximum at 0.9 eV at UST temperatures from 150 to 280°C. This process requires only a few minutes of UST processing at 280°C. The activation energy of this UST effect is close to the diffusion energy of atomic hydrogen in crystalline silicon.

The UST experiments generated a background to propose the following three-step UST mechanism: (1) ultrasonic vibrations can be coupled with trapped atomic hydrogen which can be released by UST from traps to the interstitial position; (2) this is followed by a fast interstitial diffusion of the hydrogen, and (3) accomplished by a capture of atomic hydrogen at dangling bonds.

METASTABLE DEFECTS AND RECOMBINATION IN HYDROGENATED AMORPHOUS SILICON

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Keywords: amorphous silicon, metastable defects, electronic properties

Metastable defects have been created by light exposure in thin films of a-Si:H. Effects on the electronic properties have been investigated and the interpretation is based on a proposed recombination model.

Changes in the defect density have been measured by Photothermal Deflection Spectroscopy and Electron Spin Resonance for different exposure times. The samples have been also characterized by dark conductivity as a function of temperature and photoconductivity as a function of temperature and light flux. A number of parameters have been monitored along the photodegradation process: Fermi level position, dangling bond density, Urbach slope, density of paramagnetic centers, photoconductivity dependence on temperature and the exponent of its light intensity power dependence.

The experimental results are consistent with numerical calculations with a recombination model [1] involving band tails and one class of correlated dangling-bond states. Effects of light-soaking on the temperature, light intensity and defect density dependences of photoconductivity are reproduced by the model, like the shift of the onset of thermal quenching and the faster than linear decay of the photoconductivity magnitude with increasing defect density. The calculations allow to explain light-soaking effects on the transport and recombination properties of a-Si:H as a consequence of changes in the electronic occupation of the gap states produced by light-induced defects.

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(work supported in part by Junta Nacional de Investigação Científica e Tecnológica, contract No. PBIC/C/CTM/1 385/92)

THE TRAPPING OF HYDROGEN AT CARBON DEFECTS IN SILICON

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Key Words: Silicon, Hydrogen, Carbon, Migration

Substitutional carbon is a common isoelectronic impurity in silicon. However, when it traps hydrogen, it becomes electrically active as a deep donor. Previous calculations have shown two metastable states for this complex[1], with very similar energies. This paper uses a Car-Parinello-like molecular orbital dynamics procedure to explore the trapping of the hydrogen by the carbon, the stable structures for the neutral and the charged complexes, and the energy barriers between the states.

Because the hydrogen is only trapped at the carbon when there is substantial distortion of the lattice and it is much lighter than the host atoms, it must migrate between stable sites by the sort of lattice-activated tunnelling mechanism discussed by Flynn and Stoneham[2]. Its trapping energy and the activation energy for it to move between sites are estimated by this method.

An alternative approach, recently used for the self-interstitial in silicon[3], is a molecular dynamics simulation in which the modelled silicon lattice is held at a high temperature, for long enough for the hydrogen to move sites. If this calculation is repeated the statistics of the migration step can be built up, but the hydrogen is still being treated as a classical particle. A direct comparison can be made between these two methods.

The di-carbon defect also traps hydrogen which stabilises the two carbon atoms in the higher energy configuration (C_S-C_i , the A form) of the metastable defect[4]. So as the more stable structure ($C_S-Si_i-C_S$, the B form) traps the hydrogen, a substantial reordering of the defect must take place. This transformation can be seen directly in the simulation.

Hydrogen, whatever site it occupies, will usually have local vibrational modes (LVM) associated with it. The dipole moment of the defect can be calculated while it is vibrating within the simulation. A Fourier transform of the time-dependence of the dipole moment gives a good prediction of the infrared spectrum of the defect, and can be compared directly with the experimental LVM spectrum.

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THERMAL STABILITY OF HYDROGEN MOLECULES IN CRYSTALLINE SILICON

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Key Words: H₂, crystalline silicon, isochronal annealing, diffusion

We report the first direct experimental study on thermal stability and diffusion of hydrogen molecules, H₂, in crystalline silicon. Recently we succeeded in direct detecting H₂ in crystalline silicon by means of Raman spectroscopy measurement.[1,2] The vibrational line (Q₁: 4158 cm⁻¹) of H₂ is observed in crystalline silicon hydrogenated at substrate temperatures between 180 and 500°C.

In order to investigate thermal stability of H₂ we have performed isochronal and isothermal annealing after the remote treatment of hydrogen-atoms at 250°C for 3 hours, and measured changes in the intensity and the shape of the Q₁ line of H₂. The isochronal annealing was performed at temperatures ranging from 300 to 500°C for 20 minutes. The intensity of the Q₁ line of H₂ was almost constant up to 400°C, indicating that H₂ is very stable in the crystalline silicon up to 400°C. The intensity of the Q₁ line drastically decreased after annealing at 450°C and disappeared after annealing at 500°C. The line width of the Q₁ line was large (30-50 cm⁻¹) and changed little at the annealing temperatures from 300 to 450°C. The decrease in the Raman intensity above 400°C is may not be due to the dissociation but the diffusion of H₂ in crystalline silicon, since the Q₁ line was clearly observed for a silicon sample hydrogenated at the same temperature of 500°C. The idea is also supported by isothermal annealing experiment at 400°C. We will also discuss about the formation and diffusion mechanism of H₂ in crystalline silicon.

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PALLADIUM-HYDROGEN RELATED COMPLEXES IN SILICON

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Key Words: hydrogen, transition metals, silicon

We report on studies of the electrical properties of palladium-hydrogen related defects in n- and p-type silicon using Deep Level Transient Spectroscopy (DLTS). Hydrogenation of the samples was achieved by wet-chemical etching. In non-etched Pd doped samples we find three levels: the acceptor level of substitutional palladium in n-type silicon and two donor levels in p-type silicon the deeper one being the well-known single donor of palladium [1]. Both donor levels agree in their concentration depth profiles before and after etching suggesting that the more shallow level is the double donor state of substitutional palladium.

In n-type silicon we observe after etching three hydrogen-related levels accompanied by a decrease in the palladium acceptor concentration. The new levels are only detected in the region close to the sample surface where hydrogen was incorporated. Due to differences in their concentration depth profiles we relate them to different palladium-hydrogen complexes. These complexes are stable up to 400 K, but dissociate completely at temperatures above 600 K.

In p-type silicon an additional heat treatment after wet-chemical etching is needed to form palladium-hydrogen related defects. After 10 min annealing at 400 K we observe four new levels. Depth profiling after the injection of hydrogen by reverse bias annealing shows that all these levels are formed in the region where hydrogen is located. We assume that at least two of these levels belong to the same palladium-hydrogen complex.

A comparison with the results of platinum [2] shows that both the transition metals do not only occur in the same charge states and exhibit almost identical energy levels for the isolated defects, but also show similarities in the formation of transition metal-hydrogen complexes. We find a correlation in the thermal behavior and the spatial distribution for hydrogen-related centers in Pd and Pt doped silicon, respectively. However, palladium tends to form more electrically active complexes with hydrogen than platinum.

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TRACING DIFFUSION BY LAPLACE DEEP-LEVEL SPECTROSCOPY

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Key words: Laplace DLTS , diffusion, ion-implantation, hydrogen

One of the standard applications of deep-level transient spectroscopy (DLTS) is to investigate spatial distributions (redistributions) of defect species in depletion layers of diode structures. This may include studies of impurity in-diffusion, decorated radiation damage, defect interactions etc. In this work, we show how the high resolution offered by the Laplace DLTS [1] can be utilised to quantitatively investigate the diffusion broadening of delta layers of deep donors without having to carry out defect-profiling in the usual way. In general, the Poole-Frenkel effect for defects provides a convenient transformation between an emission-rate scale and depth scale. As a result, in our case the technique having a sufficient emission-rate resolution allows to quantitatively evaluate diffusion lengths in the micron range. This approach is free of complications coming from the presence of the Debye-tail which (in high resistivity material) affects DLTS profiles of narrow distributions. We demonstrate advantages of the technique in the case of the donor states of interstitial hydrogen in silicon [2]. These states giving rise to the DLTS signals denoted E3' and E3'' are formed by ion-implantation at low temperatures, less than 80 K, and anneal to the same reservoir state. However, both states can be recovered after annealing. In the case of E3' by the forward-bias hole injection and in the case of E3'' by illumination. The forward-bias injection is associated with athermal diffusion and causes that the primary implantation profile broadens. This effect of hydrogen redistribution is clearly revealed in the peak shapes of the Laplace spectra and is here used as an example to discuss this novel diffusion application of the Laplace technique.

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TRAPPING SITE OF HYDROGEN MOLECULE IN CRYSTALLINE SILICON

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key words: H₂, hydrogen atom treatment, mc-Si:H, a-Si:H, *ab initio* calculation

Hydrogen molecule is observed by means of Raman measurements in crystalline silicon hydrogenated in the downstream of a hydrogen plasma. A possible trapping site for hydrogen molecule is the tetrahedral site of silicon crystal, which is predicted by theoretical calculations. There remains, however, another possibility that hydrogen molecules might be trapped in defects, dislocations or voids in crystalline silicon formed during hydrogenation. In the present study we have examined the effect of defects and voids on the formation of hydrogen molecule.

Microcrystalline (μ c-Si:H) and amorphous (a-Si:H) silicon samples have been treated with atomic hydrogen for 3 hours at substrate temperature 400°C. We have observed the vibrational Raman line of hydrogen molecule in microcrystalline silicon after hydrogen atom treatment. The Raman shift and width of the vibrational line are very similar to those observed in crystalline silicon after the same treatment, while its intensity relative to that of the optical phonon line is considerably smaller. In a-Si:H, no Raman signal due to hydrogen molecule is detected before or after hydrogen atom treatment. These results indicate that hydrogen molecule is formed and trapped only in non-defective bulk crystal of silicon. We have also examined silicon crystal implanted with doses of 1×10^{15} - 1×10^{17} H₂⁺/cm² and an energy of 10 keV and observed no Raman signal of hydrogen molecule; this confirms that defects and dislocations play a negative role in the formation and trapping of hydrogen molecule.

We have performed *ab initio* calculations on hydrogen molecule in silicon using cluster model. A tetrahedral site is found to be a stable trapping site for hydrogen, and the vibrational frequency of the hydrogen molecule is calculated to be 4393 cm⁻¹, in reasonable agreement with the experimental result in crystalline silicon. Our calculation supports that hydrogen molecule in hydrogenated crystalline silicon is trapped in the tetrahedral site in bulk silicon lattice.

INTERSTITIAL CARBON -HYDROGEN DEFECTS IN Si

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Key Words: carbon defects, hydrogen, silicon, *ab initio* theory.

Interstitial carbon, in contrast with substitutional carbon, forms defects with hydrogen which are electrically active and stable to high temperatures. *Ab initio* cluster calculations show that the most primitive defect, C_iH , diffuses very rapidly and is expected to complex with many other impurities notably C, H and O. We describe here the structure and properties of $C_{i,n}H_m$ defects where n and m are less than 3. The most stable defects of the type $C_iC_sH_m$ have very different structures when $m=0$ and when $m>0$. In the former case, the C-C bond is metastable and only C-Si-C bonds are formed. However in the second case, the presence of a H atom stabilises the C-C bond. These results are supported by experiment. We show that the vibrational modes of the C_s-C_iH defect are close to those observed for the T-photoluminescent centre and this defect is passivated when complexed with a further H atom. This defect then provides the first example of a fully characterised carbon centre containing a C-C bond.

ELECTRICALLY ACTIVE SILVER-HYDROGEN COMPLEXES IN SILICON

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Key Words: hydrogen, transition metals, silicon

The effect of hydrogenation on the energy levels of silver doped n- and p-type silicon is reported. After wet chemical etching new hydrogen related deep level defects are formed at the expense of the substitutional silver concentration.

The deep level spectrum and the spatial distribution of the defects are measured by the DLTS technique on Schottky diodes. We observe in addition to the donor and acceptor level of substitutional silver several other levels. Four new centres with the highest concentration are observed only near the etched surface and introduce the levels at $E_C - 0.09$, $E_C - 0.42$, $E_V + 0.27$, and $E_V + 0.38$ eV. From the spatial distribution which reveals features opposite to those of silver donor and acceptor levels and the annealing behaviour, we ascribe them to hydrogen-silver complexes. More than fifty percent of the initial silver concentration can be transformed into these complexes.

A detailed study is presented on the kinetics of formation and dissociation of the complexes.

A comparison is made with the hydrogen complexes formed in gold doped silicon.

STRUCTURE AND CHARGE-STATE-DEPENDENT INSTABILITY OF A HYDROGEN-CARBON COMPLEX IN SILICON

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Key Words: DLTS, stress, hydrogen, carbon, silicon

Hydrogen injected by chemical etching into silicon forms a H-C complex acting as an electron trap with a donor level at $E_c - 0.15$ eV. We have done DLTS measurements under uniaxial stresses to study the symmetry and structure of the H-C complex and the bonding nature of its electronic state. Application of compression stresses up to 1.2 GPa along $\langle 111 \rangle$ and $\langle 110 \rangle$ directions splitted the DLTS peak into two as ratios of 1:3 and 2:2, respectively, which are the ratios of the low-temperature peak to the high-temperature one. No splitting was observed under the stress of 0.9 GPa along $\langle 100 \rangle$ direction. These results clearly indicate the trigonal symmetry of the H-C complex, and are consistent with the previously proposed model, where hydrogen occupies the bond-centered site between carbon and silicon atoms. The observed ratio of 1:3 of the splitting under $\langle 111 \rangle$ stress means that the compression stress along the bond direction raises the electronic energy, indicating the anti-bonding nature. We have also observed stress-induced preferential alignment of the complex, which was aligned by the annealing at 250 K for 50 min under $\langle 110 \rangle$ stress to the high-temperature DLTS peak.

We have studied the stability of the complex by the annealing with and without reverse bias applied to the Schottky junction. We have found the complex is stable inside the depletion region and is unstable outside, where it is annihilated with an activation energy of 0.7 eV and a frequency factor of $10^{10.5} \text{ s}^{-1}$, while inside the activation energy is 1.3 eV and the frequency factor $10^{14.5} \text{ s}^{-1}$. From these results, we have concluded that the complex becomes unstable by capturing an electron from the conduction band outside the depletion region.

LOW-TEMPERATURE HYDROGEN DIFFUSION IN SILICON: INFLUENCE OF SUBSTRATE QUALITY AND THE SURFACE DAMAGE

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Hydrogen passivation of defects and impurities is used extensively in the commercial fabrication of silicon photovoltaic devices. In spite of being a commercial technology, relatively little is known about diffusion and passivation processes. As a result, the behavior of hydrogen in silicon continues to be quite intriguing. For example, in silicon solar cells, the effect of hydrogen passivation occurs readily in the substrates produced by certain vendors, yielding up to a 20% increase in the cell performance. However, there may be no improvement observed for cells fabricated on material from other vendors. Furthermore, it is observed that passivation also occurs when cells go through a low-temperature anneal in a hydrogen-containing forming gas (FG) ambient. These observations raise two very important questions - (i) why does the degree of passivation vary from material to material in spite of having very similar impurity and defect structures, and (ii) why does the FG anneal at temperatures as low as 400 °C (for 1 hr) lead to very effective passivation. We have carried out experimental investigations aimed at solving these issues.

Our investigations show that the diffusivity of hydrogen in photovoltaic (PV) silicon can be many orders of magnitude higher than in FZ silicon. The diffusivity increases with an increase in the crystal growth speed, increase in C concentration, and a decrease in the O concentration. It is interesting to note that the conditions that enhance vacancy formation in silicon also enhance hydrogen diffusivity. The observed results can be explained by assuming hydrogen diffusion at low temperatures occurs via a vacancy mechanism by the formation of a hydrogen-vacancy (H-V) complex. We will show some experimental results that agree with the H-V mechanism for hydrogen diffusion. This mechanism suggests that a material containing high concentrations of vacancy-related defects will have deeper penetration of hydrogen in a given process, thus, leading to a better passivation. We also determined that hydrogen diffusion from a molecular ambient of hydrogen is mediated by the surface damage. We characterized the damage needed to provide sufficient hydrogen to passivated bulk defects in PV silicon. The surface damage appears to assist hydrogen diffusion in two ways—by dissociating the molecular hydrogen and increasing the solubility of hydrogen in the surface layer. A plausible explanation for the role of damage is that $H_2 + V \Rightarrow (H-V) + H^+$. This process can further add to the diffusion by creating (H-V) species.

We have performed experiments on silicon substrates grown by several vendors under different growth conditions. The results are based on SIMS diffusion profiles of hydrogen and deuterium in silicon grown by different vendors under different growth conditions, FTIR absorption spectroscopy, TEM analyses of surface damage, minority carrier lifetime measurements by RF-PCD and SPV, CV analyses, Positron annihilation spectroscopy, and solar cell analyses. This paper will present experimental results that support the above hypotheses.

CATHODOLUMINESCENCE STUDY ON THE HYDROGENATION OF ZINC OXIDE

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Key Words: ZnO, hydrogenation, green emission, band edge luminescence, exciton

ZnO has been widely used as a fluorescent material due to its green emission. ZnO also has the potential for the UV applications with its excitonic luminescence. Since these two luminescence processes are competitive and the green emission is dominant in most of bulk crystals, control of deep levels is indispensable for the UV application. We succeeded to passivate the green emission and, in turn, to enhance the band edge luminescence of ZnO crystals by hydrogen plasma treatment.

Nominally undoped ZnO crystals were grown by a flux method using PbF_2 as a solvent. Single crystals about $10 \times 10 \times 0.3 \text{ mm}^3$ in size were obtained. They were then annealed at 1000°C for 6 h in an oxygen ambient to improve the uniformity of spatial distribution of deep levels related to oxygen. Hydrogen-plasma treatment was performed at about 400°C for 7 min. The luminescence characteristics of ZnO crystals were studied by cathodoluminescence.

CL spectra of ZnO crystals before hydrogenation consist of a sharp peak at 3.29 eV and a broad peak centered at 2.2 eV. They are due to the band edge luminescence and the green emission, respectively. The integrated intensity of the latter is more than 10 times higher than that of the former. The spectrum does not show significant temperature dependence.

After the hydrogenation, on the other hand, the green emission is completely passivated and, in turn, the band edge luminescence becomes dominant. [1] The intensity of band edge luminescence is 8 times higher than that before hydrogenation at room temperature. The band edge luminescence increases with the temperature decrease and its intensity at 30 K becomes more than 100 times higher than that at room temperature. Rough estimation suggests that the number of the emitted photon is more than several tenths of the number of excited electron hole pairs generated by the electron beam.

Similar effect of hydrogenation was found in the sintered ZnO.

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THEORY OF NITROGEN-DIHYDROGEN COMPLEX IN GAP

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Key words: GaP, N-H, defects, semiconductors, LED

Nitrogen in GaP is an isoelectronic acceptor. It is much more electronegative than phosphorus, forming bound excitons. It has made possible the fabrication of LEDs from an indirect band gap material. A spectroscopic study [1-2] of the complexes resulting from the passivation of the nitrogen-hydrogen complexes involve one nitrogen and two hydrogens, in C_{3v} symmetry, and can exist in three different states, two of them corresponding to different charged states. In one state nitrogen isotopic shifts of local modes show that both hydrogens are bonded to nitrogen. The nitrogen five-fold coordinated, a surprising result, was never found in organic molecules. We investigated this result using ab-initio theory. We performed ab-initio calculations, using Local Density Approximation and pseudo-potentials, on a $\text{HNHGa}_{22}\text{P}_{21}\text{H}_{42}$ cluster. For the neutral electric charged, we obtained 2 stable configurations: A - The lowest total energy one, both hydrogens are bonded to nitrogen; B- The other, 0.6 eV higher, the hydrogen at the bond centred position is bonded to Ga, in a way that resembles H_2^* in Si. For the negatively charged, we obtained the B configuration and for the double negatively charged, we obtained the A configuration, with a H(bc)-N bond length unusually large. Our ab-initio results show that for two different charged states, nitrogen is five-fold coordinated, in accordance with experiment.

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CHARGE TRANSFER PROCESSES IN ZNTE:TI CRYSTALS CO-DOPED WITH NI

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Key Words: Transition-Metal Doping, Luminescence, EPR, Zeeman Effect

Previously unobserved bands are investigated in low-temperature photoluminescence of Ti-doped ZnTe crystals. The ${}^3T_2(D) \rightarrow {}^3E(D)$ transition of the $Ti^{3+} (3d^1)$ ion displays three zero-phonon lines (zpl) at 3903, 4013 and 4103 cm^{-1} ; the weak ${}^3T_2(F) \rightarrow {}^3A_2(F)$ band of $Ti^{2+} (3d^2)$ exhibits a single zpl at 2855 cm^{-1} . Zeeman measurements show a threefold splitting of the isotropic Ti^{2+} line and a further splitting of the Ti^{3+} lines. In Ni co-doped crystals the known PL bands of $Ni^{2+} (3d^8)$ at 3840 cm^{-1} and $Ni^{+} (3d^9)$ at 3095 cm^{-1} occur in addition. After cooling these crystals to 4 K in the dark, practically only the luminescence of the singly ionized donor Ti^{3+} is observed. The characteristic luminescence of Ti^{2+} appears only after irradiation with light ($h\nu > 7000\text{ nm}^{-1}$). The appearance of the Ti^{2+} luminescence is interpreted as due to the charge-transfer reaction $Ti^{3+} + h\nu \rightarrow Ti^{2+} + e^+_{VB}$. Sensitization spectra show that the charge state Ti^{2+} is metastable at low temperatures (4 K), decaying slowly ($t \approx 1000\text{ s}$) back into Ti^{3+} . This decay cannot be induced by irradiation. EPR investigations confirm the charge-transfer behaviour outlined above. Under irradiation, the isotropic signal of Ti^{3+} at $g=1.9139$ which is present in thermal equilibrium at 4 K, is reduced in favour of the photo-stimulated Ti^{2+} signal at $g=1.9255$. Excitation and sensitization spectra are discussed in one-particle models for the involved ionization states of Ti and Ni.

DEEP LEVELS IN $\text{Cd}_{0.99}\text{Mn}_{0.01}\text{Te} : \text{Ga}$.

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Key words : defects, DLTS, II-VI compounds, CdMnTe .

The problem of defect centers controlling performance of the devices made of II-VI compounds has been extensively studied for last two decades. In this paper we present the results of our investigation of deep level defects in bulk $\text{Cd}_{0.99}\text{Mn}_{0.01}\text{Te}$ mixed crystal. Samples used in this work were n-type Ga doped crystals grown by the Bridgman method with net donor concentration equal about 10^{16} cm^{-3} and 10^{15} cm^{-3} . The measurements were performed by Deep Level Transient Spectroscopy (DLTS) method. Schottky diodes used for the investigation were thick Au diodes deposited in vacuum of 10^{-6} Torr on chemically prepared surface. For ohmic contacts dots of indium were soldered in temperature of about 500 K for several seconds.

In the material with higher donor concentration five electron traps have been found with activation energies equal to $E1 = 0.15 - 0.2 \text{ eV}$, $E2 = 0.33 \text{ eV}$, $E3 = 0.36 \text{ eV}$, $E4 = 0.52 \text{ eV}$. Electric field enhanced electron emission from the level E4 has been observed and described in terms of Frenkel-Pool mechanism.

In the as-grown samples with lower concentration only one dominant level with energy activation $E5 = 0.63 \text{ eV}$ has been observed in DLTS measurements. After annealing the as-grown samples at temperature 400K for one hour the concentration of the defect responsible for the level E6 decreased and two additional minima in DLTS signal appeared with energy activation $E6 = 0.65 \text{ eV}$ and $E7 = 0.74 \text{ eV}$. The trap E5 has an acceptor-like (-/0) character. The capture process of electrons on this trap is thermally activated with a capture barrier of 0.21 eV indicating strong electron-phonon coupling. This yields the true energetic distance of the E5 level from conduction band as equal to 0.42 eV.

DONOR DOPING OF ZNSE: LATTICE LOCATION AND ANNEALING BEHAVIOUR OF IMPLANTED BORON

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Key Words: ZnSe, boron, donor doping, ion implantation

The success in fabricating p-type ZnSe by means of MBE and MOVPE, with the subsequent presentation of the first laser diode in the blue-green [1] has sparked vast activities in investigating the microscopic properties of potential *acceptor* impurities like N and Li in this material. *Donor doping* of ZnSe, on the other hand, is considered a question of much lesser technological interest, since several group VII elements yield carrier concentrations of up to $10^{19} / \text{cm}^3$. It should be kept in mind, however, that concerning the n-type doping of ZnSe, there are still a lot of fundamental questions to be answered. Using the group III elements Al, Ga, or In as donors, the maximum carrier concentrations are limited to only $10^{18} / \text{cm}^3$; for B, the group III doping element in elemental semiconductors, there are not even numbers available in the literature. It is the purpose of the present investigation to study the behaviour of B implanted into ZnSe with special regards to its suitability as a donor element.

Spin polarized, radioactive ^{12}B nuclei ($T_{1/2} = 29$ ms, nuclear spin $I=1$) are produced in a nuclear reaction and recoil implanted into nominally undoped ZnSe at negligible concentrations. Temperature and orientation dependent β -radiation detected NMR measurements on these probe nuclei allow the following conclusions:

- A large fraction ($\geq 80\%$) of the implanted boron ends up at substitutional Zn sites.
- This B_{Zn} is in the diamagnetic charge state B_{Zn}^- . At least from 300 K on, therefore, the desired donor is indeed electrically active.
- The full T_d symmetry of the site is maintained. There is no reduction in symmetry which could result in a deep instead of a shallow donor.
- Only a very modest post-implantation annealing is needed to populate the unperturbed Zn sites. As activation parameters for this process we find an activation energy and a preexponential factor of $E_A = 0.61(3)$ eV and $n_0 = 10^{6.0(3)} \text{s}^{-1}$, respectively. These values mean that already 15 min at $T = 380$ K are sufficient, certainly an important fact for this temperature sensitive material.
- Once it reached its lattice position, B_{Zn} is thermally stable. Up to 950 K we could not detect any mobility (detection limit: 100 jumps/s).

In summary we find that microscopically all prerequisites for the use of boron as a donor element in ZnSe are fulfilled. Only future experiments can show, however, if these conclusions for extremely diluted boron remain valid if higher implantation doses are used.

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OBSERVATION OF FRENKEL PAIRS ON BOTH SUBLATTICES OF ELECTRON IRRADIATED ZNSE

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Key Words: ZnSe, vacancies, interstitial atoms, irradiation, diffuse X-ray scattering

[100]-oriented ZnSe crystals have been irradiated at 4K with 2.5 MeV electrons up to a highest dose of $2 \cdot 10^{19} \text{ e}^-/\text{cm}^2$. The irradiation induced defects and their thermally activated reactions have been investigated by measurements of the diffuse scattering close to different Bragg reflections and of the change of the lattice parameter. Similar to the observations with other semiconductors these measurements yield large defect introduction rates, which are of the order of 3 cm^{-1} , and small relaxation volumes of the defects. The distribution of the diffuse scattering intensity indicates the predominance of close Frenkel pairs. In contrast to the observations with the elemental semiconductors there is an increase of the lattice parameter with irradiation dose which indicates, that there is no complete cancellation between the displacement fields due to vacancies and interstitial atoms. Averaging over all defects we obtain a positive relaxation volume for the interstitial of $V_j^{\text{rel}} = 0.4$ atomic volumes and for the vacancy a negative value of $V_v^{\text{rel}} = -0.25$ atomic volumes.

We observe two well defined low temperature annealing stages which are located between 20K and 50K and between 100K and 220K respectively, and which account for the annealing of about 40% of the defects each. Only the second stage has been observed so far and has been attributed to the recombination of close Frenkel pairs on the Zn-sublattice [1]. Therefore we attribute the new low temperature stage to the recombination of close Frenkel pairs of the Se-sublattice. Remarkably this first observation of Frenkel pairs on the Se-sublattice yields a similar concentration and size for the Frenkel pairs for both sublattices. We attribute the annealing up to room temperature to the mobility of the interstitial atoms and observe the formation of small interstitial clusters by those interstitials which escape recombination. Along with the beginning of the vacancy migration we observe total annealing in the temperature range between 400K and 650K.

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NATURE OF DISLOCATION-RELATED DEEP LEVEL DEFECTS IN CdS

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Key Words: dislocations, DLTS, cathodoluminescence, DX-center, CdS

The origin of defects induced by plastic deformation of CdS single crystals was investigated by low-temperature cathodoluminescence (LT-CL/SEM), which permitted us to distinguish between screw (luminous) and edge (non-luminous) dislocations, and by deep level capacitance spectroscopy. Dislocation structures around microindentations of different surfaces of a sample with wurtzite structure were reconstructed from CL/SEM data. The ratio between different types of dislocations in the near-surface layer could be changed, choosing of the orientation of the indented surface and removing surface layers of increasing thickness. This allowed us to prepare Schottky diodes with 7-8 significantly different dislocation structures in the space-charge region of the Schottky-diode. Up to 14 different DLTS-peaks appeared after plastic deformation. Correlations between the amplitude of separate DLTS peaks and concentrations of particular types of dislocations were established. Deep levels due to edge prismatic, β -edge and screw dislocations were identified. As only three deep levels were due to particular types of dislocations, the other centers could be attributed only to point defects, either generated or activated by dislocation loops. This experimental fact gives direct evidence that the activity of dislocations in CdS is due to impurities and point defect clusters rather than the core states of dislocations themselves. Surprisingly, it was found that the main electron trap in dislocated CdS is due to screw dislocations which are usually expected to be electrically inactive.

Detailed studies of screw-dislocation related centers revealed that these centers surrounded screw dislocations and exhibited large lattice relaxation upon capture of a charge carrier. This led to a significant underestimation of its concentration in previous papers on deep levels in CdS. Capacitance studies of emission and capture processes, photo-capacitance studies of optical emptying of the center and Hall effect measurements revealed that the center has all essential properties of the DX-center. A model was suggested, in which the DX level of substitutional donors becomes detectable in the vicinity of screw dislocations under the influence of their strain fields.

ON THE TWO ELECTRON NATURE OF IN- RELATED DX STATES IN CdTe

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Key Words: DX centres

Recently, the metastable, DX like behaviour of the indium donor in CdTe at low temperatures was demonstrated. However, the microscopic model of this centre and its charge state were not verified experimentally up till now.

In this work we investigate:

- the electron concentration and mobility vs. applied hydrostatic pressure (HP) in the temperature range of 77 K - 300 K ,
- the electron emission from DX state under HP after filling this level by freeze-out under high hydrostatic pressure (HPFO)
- electron capture by the DX state under HP in steady-state photo-conductivity experiments

on CdTe:In layers grown by MBE with the In doping level in the range $5 \cdot 10^{17} - 2 \cdot 10^{18} \text{ cm}^{-3}$.

Results for the Hall effect after an HPFO cycle and photo-conductivity measurements under pressure up to 20 kbar demonstrate that the DX state is occupied by two electrons: agreement on the position of the top of the barrier as seen from emission experiments, on one hand, and capture experiments, on the other hand, is obtained only when a two-electron process is assumed for the thermal emission from the deep DX state.

The barrier for electron emission from the DX state increases with applied pressure p , according to: $E_{\text{em}}(p) = 255 \text{ meV} + p \cdot 8.5 \text{ meV/kbar}$.

A microscopic model and the configuration coordinate diagram for the DX state of In in CdTe are presented and compared with that of DX centers in III-V compounds.

PHOTOINDUCED MAGNETISM IN CdF₂ WITH BISTABLE DONORS: THE CLUE FOR THE NEGATIVE U?

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Key words: bistable donors, negative U, photomagnetism, CdF₂:In, CdF₂:Ga

In and then Ga donors in CdF₂ were the first fully characterised bistable donors in semiconductors. Recent first principle computations by Song et al. (1995) confirmed the basic feature of the early model of bistable donors in CdF₂, namely the existence of the symmetric large lattice relaxation (the lattice collapses onto the In (Ga) positively charged core upon the defect photoionisation) and the vibronic barrier separating the two bound states of the donor: deeper - localised and shallower - hydrogenic, effective mass state. In case of In, the theory reproduces well the energy levels and the barrier, while for the deeper Ga, the barrier height is strongly underestimated. Although a standard one-electron defect model of these donors explains well most of the experimental data, it cannot reconcile lack of the ESR signal for the donor in the ground localized state. Only upon illumination the ESR signal appears and it is unambiguously related to the effective mass shallower bound metastable state of the donor. Such a behavior is similar to that for the standard DX centers in III-V and II-VI compounds and could be one of the hints for the negative U character of these states. It should be pointed out that a negative U character of the DX centers comes from a covalent bond breaking and is one of the features of the sp³ bond at defects.

To clarify the situation we measured the temperature dependence ($4 < T < 300$ K) of the magnetic susceptibility of CdF₂ bulk crystals doped with In or Ga in darkness and upon illumination. At temperatures at which metastable donor photo transformation occurs, magnetic susceptibility increases and it follows a Curie law. Qualitatively this effect agrees with a hypothesis of a two-electron character of the relaxed ground state of the bistable donors in CdF₂ crystals. However, a different type of bonding implies that another mechanism should be responsible for the electron pairing (different relaxation) than for the DX centers in III-V compounds. As such a behavior was neither predicted by the available theoretical results and did not have simple and intuitive explanation for the highly ionic host, we attempted to make a quantitative analysis of the photoinduced magnetism. By assuming that additional paramagnetism comes from non interacting shallow donors with spin $S=1/2$, their concentration was computed (it is in the 10^{19} cm⁻³ range) and compared with that estimated from other measurements: the shallow donor states photoionisation and the Hall effect. Agreement is satisfactory. However in all our samples Mn was additional dopant. It is plausible that a ferromagnetic coupling occurs between spin $5/2$ of the Mn and spin $\frac{1}{2}$ of the shallow donor (its extended wavefunction allows for an overlap and thus exchange interaction with the localized Mn wavefunction). Such interaction produces spin molecule with the effective spin $S=3$ and effectively increases the magnetic susceptibility (proportional to $S(S+1)$). It may thus provide an alternative to the negative U explanation of the experiment. A detailed quantitative analysis of the observed photomagnetism will be presented at the conference.

EPR INVESTIGATION OF METASTABLE DONOR STATES IN $\text{CdF}_2\text{:In,Ga}$

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Key words: Donor - metastability, negative-U, sp-d coupling

Donors in CdF_2 recently received considerable attention because of their metastable character which implies their applicability for optical memories: both In and Ga exhibit 2 different donor states which are separated by a barrier. In the case of Ga this barrier is effective up to room temperature in this optically transparent material ($E_G > 8\text{eV}$).

In this paper we present the results of photo-EPR investigations on CdF_2 doped intentionally by either Ga or In, and unintentionally also by Mn. We observe the resonances of both the shallow donor state and that of Mn.

The EPR spectrum of the shallow donor state occurs only after illumination and it vanishes after heating the sample in darkness above the critical temperature for metastability, T_m . Below T_m , we find clear indications for motional narrowing of the EPR linewidth: thermal hops of a conduction electron from one donor to another leads to a time averaging of the fluctuating local (hyperfine) fields. As a function of temperature, the EPR linewidth changes with an activation energy equal to that of the electrical conductivity which proves that indeed we observe the shallow donor resonance and its metastable population.

The spin of Mn impurities and their concentration in CdF_2 is not photo-sensitive but their EPR spectrum changes considerably after sample illumination: it increases strongly in amplitude. We show that these changes originate from a specific mechanisms of spin relaxation: filling the shallow donor states opens a most effective channel of spin relaxation via sp-d exchange coupling between the localized Mn spins and effective mass electrons. Shortening of the spin-lattice relaxation time reduces the saturation and thus increases the signal due to Mn.

The concentration of Mn is of the order of 10^{18} cm^{-3} - too small to affect the shallow donor state (as it is the case in diluted magnetic semiconductors), but they can be treated as useful "detectors" in the presence of shallow donor electrons.

We were not able to find any trace of an EPR spectrum (nor any spin relaxation channel) which could be attributed to the deep donor state indicating that the deep state is a non-magnetic, two-electron state with the microscopic nature similar to negative U- DX states which are observed in III-V compounds.

TEM-STUDY OF FRANK PARTIAL DISLOCATIONS IN ZnSe/GaAs(001) CAUSED BY SUBSTRATE-PREPARATION

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Keywords: ZnSe/GaAs, MBE, TEM, RHEED, QMS, frank partial dislocations, hydrogen

A detailed study is presented about the formation of Frank partial dislocations in ZnSe/GaAs (001) grown by molecular beam epitaxy (MBE). The investigations were carried out by transmission electron microscopy (TEM), reflection high energy electron diffraction (RHEED) and quadrupole mass spectrometry (QMS).

The GaAs-substrates are pretreated in two steps: a wet chemical etching and a subsequent treatment with a hydrogen(H)-plasma in the growth chamber. Plan-view-TEM micrographs reveal a strong dependence of the Frank partial dislocation density on the time of chemical etching as well as on the substrate temperature during H-plasma etching. Without further precautions the RHEED pattern show thus a (2x1)-reconstruction. However, if the H-plasma treatment proceeds under Zn-stabilised conditions the (2x1)-reconstruction disappears and, furthermore, the generation of Frank partial dislocations in the growing layer is reduced. Since the (2x1)-reconstruction results from the formation of a Ga_2Se_3 -layer at the interface, it is suggested that the presence of Zn-atoms suppresses the formation of Ga-Se-bonds. The Se-source for the Ga_2Se_3 -formation is found in small amounts of H_2Se , which is observed in QMS-spectra during the activation of the H-plasma-source. The H_2Se -partial pressure can be reduced drastically by cooling the cryo-shields in the growth-chamber with liquid nitrogen. After optimising the substrate preparation on the line just described we succeeded in a reduction of the Frank defect density from 4×10^8 to $6 \times 10^6 \text{ cm}^{-2}$. Thus a pseudomorphic growth of the ZnSe-layers has been achieved up to a thickness of 400 nm.

VACANCY-TYPE DEFECTS IN ELECTRON AND PROTON-IRRADIATED II-VI COMPOUNDS

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Key Words: II-VI compounds, point defects, proton irradiation, positron annihilation

In this contribution we present a study aimed at investigating the basic properties of radiation induced defects in ZnO, ZnS, ZnSe, and ZnTe and at comparing them to those intrinsic to these materials. Positron annihilation experiments were performed on both single- and polycrystalline samples, irradiated with 1 MeV electrons at 70 K or 3 MeV protons at 223 K. Combined positron lifetime and Doppler-broadening measurements were conducted as a function of measuring temperature down to 10 K before and after annealing to explore the detailed physical nature of the induced defects and their respective charge states. The isochronal annealing was done in air or in an Ar atmosphere. It was found that both electron and proton irradiation caused significant changes in the positron annihilation characteristics and several annealing stages were observed, related to the annealing of variously sized vacancy complexes. The thermal stabilities of the induced defects as well as possible clustering mechanisms will be discussed.

RAMAN SPECTROSCOPY OF OPTICAL LATTICE VIBRATIONS IN SMALL CdS CRYSTALS EMBEDDED IN SiO₂ FILMS

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CdS-doped SiO₂ films (semiconductor volume fraction $f=0.1-15\%$) were grown on glass substrates by magnetron rf-sputtering with post-deposition annealing. X-ray studies indicated cubic modification of CdS in the films. Optical transmission measurements showed a marked blue shift of the interband absorption of CdS due to the spatial confinement of carriers. Our previous studies of films with larger CdS fraction (6-15%), in particular, by means of FIR spectroscopy, lead us to the conclusion that these films contain fractal aggregates of nanocrystalline particles.

Raman spectra of the films were taken at 20-300K using various lines of an Ar laser. They show broadened peaks corresponding to CdS LO phonons as well as to 2LO and 3LO. The main peak is practically unshifted with respect to the bulk LO phonon frequency and the lineshape is rather asymmetric for all the films studied. It was fitted fairly well by considering LO-type phonon modes confined in nanocrystalline spheres and taking account of those with $l=0$ and $n>1$, l and n being the spherical quantum numbers, which are, in fact, responsible for the low-frequency wing. This model seems to be natural for films containing less than 1% of CdS.

However, in accordance with the aggregate hypothesis, there is no much reason to consider the stuck nanocrystals as regular spheres for films with $f\sim 10\%$. Model lattice dynamics calculations have been performed for CdS clusters of irregular shape, including some voids. The numerically calculated results are shown to be able not only to fit equally well the LO Raman lineshape, but also to explain an extra feature appearing in the experimental spectra, interpreted as a disorder-activated acoustic (DALA) mode. Our model, although including only nearest-neighbour interactions, produces both the DALA and (gap) surface modes in the calculated Raman spectra.

BISTABILITY OF OXYGEN VACANCY IN SILICON DIOXIDE

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Key Words: SiO₂, Oxygen Vacancy, Bistability, Charge State

Silicon dioxide SiO₂ is a premier material in semiconductor science and technology. Silicon would not have been used as the dominant electronic material in technology without the high quality of its oxide. More fundamentally, SiO₂ possesses both ionicity and covalency so that understanding of its properties, in particular the properties of defects, would lead to an unified view of non-metallic materials. Little is known, however, about microscopic nature of intrinsic defects in SiO₂. In this work, we report total-energy electronic-structure calculations within local density approximation (LDA) in density functional theory performed for oxygen vacancy V_O in α quartz. We find (i) that the oxygen vacancy, which is theoretically shown here to be most abundant in the material, has a variety of charge states from +2 to -2 depending on the location of the Fermi level in the energy gap, (ii) that for neutral and +1 charge states the oxygen vacancy shows structural bistability where two neighboring Si atoms form a bond in one geometry (small relaxation), and in the other geometry (large relaxation) one of the two Si is displaced to a back-bond oxygen atom, (iii) that the geometry with small relaxation becomes unstable for +2, -1, and -2 charge states whereas the geometry with large lattice relaxation remain (meta)stable, and (iv) that a set of the charge states { +2, +1, 0 } forms an effective-negative-U system in which ionicity as well as covalency plays an important role.

Calculations have been carried out by use of normconserving pseudopotentials and LDA combined with conjugate-gradient minimization technique as reported elsewhere[1]. A point defect in an otherwise perfect crystal is simulated by a repeating supercell model. We use a 54-atom triclinic supercell for defects in α quartz. We find that the 60-Ry cutoff energy in the planewave basis set and one special k point suffice for obtaining converged results.

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BISTABLE CENTERS IN CDMNTESE:IN CRYSTALS STUDIED BY LIGHT-INDUCED GRATINGS

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Key words: bistable donors, negative U, holography, four-wave mixing

Indium and Gallium ions are well known bistable dopants in semiconductors and also in more ionic hosts as in CdF₂ crystals. Bistability means electron trapping either at localized or delocalized - hydrogen like state. Wavefunction of the former is very compact, while of the latter - diffuse, effective mass like. It is associated with large lattice relaxation (LLR) effect, responsible for existence of DX centers in A_{II}B_{VI} and A_{III}B_V semiconductors. Therefore a phototransformation of the center from a one state to another must lead to a large change of the local polarizability, and thus large changes of the local refractive index. The refractive index changes in the order of 10⁻⁴ are easily obtainable with the concentration of phototransformed centers about 10¹⁸ cm⁻³. Therefore such centers can be efficiently used in writing volume holographic gratings.

In and Ga ions in Cd_{1-x}Mn_xTe_{1-y}Se_y crystals exhibit photomemory effect which persist for very long time if samples are kept at liquid helium temperature (Wojtowicz et al. 1993). Using DLTS technique one deep, localized level has been found in indium doped samples with the thermal activation energy for electron emission of 0.14 eV. We performed continuous wave degenerate four-wave mixing (c.w. DFWM) experiments on Cd_{0.99}Mn_{0.01}Te_{0.97}Se_{0.03}:In sample, measuring the scattering efficiency and decay kinetics of the light-induced gratings at different wavelength in the near-infrared region. Scattering efficiency of the FWM is above 10% which means that the local changes of refractive index are responsible for the creation of the light induced gratings. The dependence of the scattering efficiency on the temperature reveals two peaks at temperatures T₁=17K and T₂=110K. They are associated with two types of deep centers with different thermal activation energy for electron emission. The second peak at T₂=110K is associated with the deep level with the activation energy of 0.14 eV, the first one is associated with the center with lower activation energy, which has not been detected in the DLTS experiment. The model derived by us describes quantitatively the origin of the peaks of FWM scattering efficiency vs. temperature. The high temperature side of the peak is due to thermal recovery of deep center which causes disappearance of the grating. Low temperature side is associated with the grating destruction mechanism as, for example, impact of non-coherent stray light. In degenerate FWM experiment also reading beam can contribute to the destruction of the grating at low temperatures since it can ultimately cause a complete phototransformation of the impurity from the deep to the metastable shallow state thus erasing the grating, too. Therefore a maximum in the diffraction efficiency vs. temperature occurs at temperature at which the speed of incoherent erasure equals the thermal recovery rate via the barrier separating the two states. The FWM scattering efficiency is not proportional to the square of the power of incident writing beams. We show that this effect is associated with negative U properties of the bistable centers in this material.

A CODOPING METHOD IN GAN PROPOSED BY AB INITIO ELECTRONIC STRUCTURE CALCULATIONS

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We propose a new type doping method, the "codoping method (doping n- and p-type dopants at the same time) " for the fabrication of low-resistivity p-type GaN with wurtzite structure on the basis of theoretical investigation using one of ab-initio electronic-structure calculation methods, the augmented spherical wave (ASW) one.

It is well known that doping problems that fabrication of both low-resistivity n- and p-type doped materials is difficult, so called uni-polarity, occur because of the self-compensation in wide-band-gap semiconductors, such as GaN. At the doping-levels, $10^{15} - 10^{13} \text{ cm}^{-3}$, we can estimate overall change in the total energy ($=\Delta E$) given by $\Delta E = \Delta\mu + \Delta E_M$ where the first and second term refer to a change in chemical potential for the electronic system and in the Madelung energy that is an intrinsic property for the lattice system, respectively. We note that ΔE_M with negative (positive) sign means that compared with undoped crystals we find a larger attractive (repulsive) force at the anion site resulting in shifts of energy levels of valence orbitals of outermost s and p levels of anion atoms towards lower (higher) energy-regions, leading to stabilization of ionic charge distributions.

We find that while sign of ΔE_M for n-type GaN doped with Si_{Ga} or O_{N} is negative, sign of ΔE_M for p-type GaN doped with Be_{Ga} or Mg_{Ga} is positive from the band structure calculations. It means that p-type doping beyond some of the doping levels leads to the generation of N vacancies due to destabilization of ionic charge distributions for N. In other words, while we increase the concentrations of acceptor dopants such as Be and Mg, there increase the concentrations of donor dopants, that is, we find little change or a decrease in net carrier densities beyond the doping levels.

We find that GaN crystals with codoping of 2Mg_{Ga} and $\text{Si}_{\text{Ga}}(\text{O}_{\text{N}})$ are p-type conductivity and there decrease the Madelung energies for the two crystals compared with that for GaN doped with two Mg atoms. In particular, for $\text{GaN}:\text{Si}_{\text{Ga}}$ and 2Mg_{Ga} , from site-decomposed DOS, we verified large delocalized impurity states. Thus, we can expect low-resistivity p-type GaN crystals with codoping of Si and two Mg atoms. On the other hand, for p-type $\text{GaN}:\text{O}_{\text{N}}$, $2\text{Mg}(\text{Be})_{\text{Ga}}$, we find that codoping of O atoms with strong electronegativity play an important role in an increase in the concentrations of acceptor dopants, Be and Mg, from the band structure calculations. It leads to high p-type conductivity in GaN codoped with $\text{Be}(\text{Mg})$ and O, which coincides with the recent experimental data by Brandt et al. [1]

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A FIRST PRINCIPLES STUDY OF MG-RELATED DEFECTS IN GaN

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Key Words: gallium nitride, deep level defect, photoluminescence

Photoluminescence (PL) studies on undoped and Mg-doped GaN films revealed the existence of deep-level defects. Although it is still debated what is responsible for the yellow luminescence (YL) peak around 2.2 eV, recent experimental and theoretical studies showed that the YL intensity is suppressed by Mg incorporation, and it seems to be originated from an acceptor-like defect such as gallium vacancy and its complex with an extrinsic impurity. On the other hand, Mg-doped GaN exhibits an additional PL peak at 2.7 - 2.9 eV. In this work we investigate the origin of blue luminescences (BL) in Mg-doped GaN through first-principles pseudopotential calculations. We find that the most probable Mg-related defect is a substitutional Mg_{Ga} , which occupies a Ga sublattice site. Because of the large discrepancy in atomic radius between the Mg and N atoms, a substitutional Mg_{N} at a N sublattice site is extremely unstable, however, it is shifted into a neighboring interstitial position and likely to form a complex of Mg-interstitial and N-vacancy ($\text{Mg}_i\text{-V}_{\text{N}}$), where N vacancies are dominant donors in the absence of other donor impurities such as Si and O. The $\text{Mg}_i\text{-V}_{\text{N}}$ complex is found to be much more stable than their isolated Mg_i and V_{N} defects for various charge states, with the vacancy-neighboring Ga atoms relaxed significantly outward from the vacancy site. This defect complex has the $(2+/3+)$ and $(+/2+)$ ionization levels at 2.28 and 2.78 eV above the valence band maximum, respectively. We suggest that in GaN samples without Si or O impurities, the BL is attributed to the transition between the shallow acceptor level and the deep donor level related to the $\text{Mg}_i\text{-V}_{\text{N}}$ complex, while the donor-acceptor pair emission is due to the transition between the Mg_{Ga} and V_{N} levels.

ANTI-CORRELATION BETWEEN IRON CONTAMINATION AND YELLOW LUMINESCENCE IN MOVPE- AND VPE-GROWN GaN

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Key Words: GaN, Fe³⁺, yellow luminescence

In an early study to compensate shallow donors in GaN grown by vapour phase epitaxy (VPE), Monemar et al. prepared and analysed iron-doped GaN layers¹. In fact, high-resistivity material was obtained, demonstrating that iron acts as a deep acceptor in GaN, as it does in InP and GaAs. Recently, Fe³⁺ was studied with photoluminescence and optical detection of magnetic resonance by Maier et al.². A zero phonon line at 1.3 eV and a phonon-sideband structure were identified belonging to the spin-forbidden internal transition $^4T_1(G) \rightarrow ^6A_1(S)$ of Fe³⁺ (3d⁵) on substitutional Ga site.

In this study, photoluminescence in the visible and infrared region at 1.5 K was measured for several wurtzite GaN layers. These layers grown by metal organic vapour phase epitaxy (MOVPE) and VPE on sapphire were supplied by the CRHEA in Valbonne. In several samples we found the Fe³⁺ luminescence in the near infrared region indicating a contamination of the samples with iron. In the visible and uv region, the donor bound exciton, a donor-acceptor recombination at 3.27 eV³ and the yellow luminescence band centered around 2.2 eV⁴ were observed. Comparing the integral intensities of the Fe³⁺ luminescence with the other luminescence bands, we found an anti-correlation between the occurrence of the Yellow band and the Fe³⁺ luminescence. Due to the long radiative lifetime of the Fe³⁺ luminescence of the order of milli seconds² it is not likely that the yellow luminescence is quenched by a competing recombination process involving the deep iron acceptor. We speculate that the introduction of iron lowers the position of the Fermi level which could be responsible for an increase in the formation energy of Ga vacancies (Neugebauer et al.⁵). It is believed that Ga vacancies are the acceptor recombination partners in the yellow luminescence process⁵. The quenching of the yellow luminescence due to the presents of Fe³⁺ could be understood as a decrease in the concentration of the Ga vacancies due to a Fermi level effect.

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CHARACTERIZATION OF THE RELAXATION BY MISFIT DISLOCATIONS CONFINED AT THE INTERFACE OF GaN / Al₂O₃(0001) STUDIED BY TEM

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Keywords: GaN, TEM, HRTEM, misfit dislocations, confinement, relaxation, MBE

A transmission electron microscopy (TEM) investigation of the relaxation process by misfit dislocations confined at the interface of the highly mismatched system GaN / Al₂O₃(0001) has been carried out.

Wurtzite type GaN was grown epitaxially by reactive ion molecular beam epitaxy (RIMBE) on the (0001) basal plane of Al₂O₃. We determined the orientation relationship between epilayer and substrate by selected area electron diffraction (SAED). The diffraction images show that the <11-20>-direction in GaN is parallel to the <10-10>-direction in Al₂O₃ whereas the [0001]-direction is the same in both materials. In this orientation the high lattice mismatch of $f = -13,8\%$ would prevent an epitaxial growth with low defect densities of 10^9 cm^{-2} in the GaN layer as reported in many publications. But high resolution transmission electron microscopy (HRTEM) revealed a relaxation process with misfit dislocations confined at the interface:

HRTEM images show (11-20)-Al₂O₃-lattice planes ending at the interface in regular intervals of about 8 lattice constants. These misfit dislocations have Burgersvectors parallel to the (0001)-interface plane, and therefore the extension of these dislocations into the GaN-layer is obviously suppressed.

An analysis of the corresponding Burgersvectors with regard to the structure model of Al₂O₃ and GaN reveals perfect 60° misfit dislocations with a large edge component. Thus the high lattice misfit is mainly compensated by a regular array of misfit dislocations confined at the interface GaN / Al₂O₃. It seems that a residual stress causes the defect densities in the GaN epilayer reported in many works.

DEFECT FORMATION AND ELECTRONIC TRANSPORT AT AlGaIn/GaN INTERFACES

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Key Words: gallium nitride, mobility, heterostructures

We calculate the effects of charged defects, located in the vicinity of an AlGaIn/GaN interface, on the electronic transport at the interface. We evaluate the effects of the interface structure on incorporation of the defects as well as their effects on the 2-dimensional (2-D) electron scattering rates. Recent studies have shown that confinement of electrons in 2-D channel at the AlGaIn/GaN interface results in large enhancement of the low temperature mobility [1, 2]. In most, if not all, of these experiments, the electrons originated from unintentional donor defects in the AlGaIn barrier rather than from intentionally introduced shallow donors. The nature of these defects is not yet firmly established. Native defects such as a N vacancy or chemical impurities with an energy level resonant with the conduction band have been previously considered as possible dopants in highly n-type conducting, undoped GaN and may also be the source of the donor defects in the AlGaIn barrier.

In this work we calculate the distribution of defects in the vicinity of the AlGaIn/GaN interface taking into consideration the fact that the formation energy of charged defects depends on the location of the Fermi level. We find that the defects in the AlGaIn barrier which provide the electrons in the GaN well are preferentially formed close to the interface. This assures an efficient charge transfer resulting in large densities of the 2-D gas in GaN. However, the proximity of the charged defects to the 2-D gas leads to strong scattering, reducing the low temperature mobility. We have performed calculations of the electron mobility in 2-D AlGaIn/GaN heterostructures. Besides scattering by charged defects we have incorporated all the phonon scattering mechanisms including acoustic deformation, piezoelectric and polar optical. Scattering by charged defects is found to be the dominant process limiting the electron mobility at temperatures below 100 K. For background impurity concentrations of less than 10^{13} cm^{-3} in the GaN well, the electron mobilities can be made as high as several hundred thousand cm^2/Vs at 4 K. If one could grow a pure AlGaIn spacer between the doped AlGaIn and the GaN, we find that theoretical low temperature mobilities can reach as high as several million cm^2/Vs . Although our calculations predict very high electron mobilities in optimized heterostructures, a significant reduction of the unintentional defect densities will be required to reach these limits in experimentally grown heterostructures.

In addition, we have calculated the 2-D electron gas density and mobility as a function of hydrostatic pressure. Since resonant native defects are highly localized, the pressure derivative of their energy with respect to the conduction band is very different from that of shallow impurities. Thus, the electron density and mobility show very different pressure dependencies for the case in which shallow donors are the sources of the electrons as compared to the case in which doping is achieved by incorporation of native defects.

This work was supported in part by US DOE under contract DE-AC03-76SF00098 and in part by NSF grant DMR-94 17763.

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IDENTIFICATION OF IRON TRANSITION GROUP TRACE IMPURITIES IN GaN BULK CRYSTALS BY ELECTRON PARAMAGNETIC RESONANCE.

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Key words: Gallium Nitride, transitional metal impurities, EPR

We report on the observation of electron paramagnetic resonance of iron, manganese and nickel trace impurities in bulk GaN crystals grown by the sublimation sandwich method. The resolved hyperfine structure due to interaction with ^{55}Mn ($I=5/2$) nuclei has been observed in GaN, allowing unambiguous identification of the impurity. Manganese and nickel exist in Mn^{2+} ($3d^5$) and Ni^{3+} ($3d^7$) charge states with electron spin $S=5/2$ and $S=3/2$, respectively, and occupy gallium sites in the GaN lattice. For Mn^{2+} we found $g=1.999$, hyperfine structure constant $A=70\cdot 10^{-4}\text{ cm}^{-1}$ and fine structure parameter $|D|=240\cdot 10^{-4}\text{ cm}^{-1}$. The EPR spectrum of Ni^{3+} in GaN had the characteristic anisotropy of an $S=3/2$ system in a strong axial crystalline field. The effective g -factor values were found to be $g_{||}=2.10$ and $g_{\perp}=4.20$ for a system with an effective spin $S'=1/2$. The zero-phonon line at 1.047 eV seems to belong to transition ${}^4\text{T}_2(\text{F})\text{-}{}^4\text{A}_2(\text{F})$ within 3d levels of Ni^{3+} ion with a $3d^7$ electronic configuration.

IMPACT OF RADIATION-INDUCED DEFECTS ON THE YELLOW LUMINESCENCE IN MOCVD GaN

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Key Words: gallium nitride, luminescence, radiation defects

Strong interest in studies of the III-V nitrides is stimulated by their potentials in important technical applications. Among them, GaN has showed rapid technological advancement and attracted close attention of researches and engineers. Some recent calculational results [1,2] cast light on intrinsic defects in GaN and can help the experimentalists in testing the defect models proposed. First of all, a yellow luminescence (YL) band at ≈ 2.2 eV associated with yet unidentified defects is of special interest because this band may be due to the presense of Ga vacancies or Ga vacancy-related complexes [2]. It is well known that electron irradiation of semiconductors provides a convenient tool for production of point defects. The aim of the present work is to ascertain whether and, if so, how radiation-induced defects in GaN may affect the YL.

GaN layers of a wurtzite structure were grown by the MOCVD technique using 6H-SiC substrates. The growth rate was about $2 \mu\text{m/h}$ and the thickness of layers ranged from 1 to $3 \mu\text{m}$. The layers studied were n- and p-type conductivity as well as not intentionally doped. The charge carrier concentrations were close to $1 \cdot 10^{18} \text{ cm}^{-3}$ and $3 \cdot 10^{17} \text{ cm}^{-3}$ for n-GaN:Si and p-GaN:Mg, respectively. The electron concentration for the undoped GaN samples was about $3 \cdot 10^{16} \text{ cm}^{-3}$. The samples with lesser internal stresses were selected for irradiation. Electron irradiation (0.9 MeV) was carried out at a beam current of $5 \mu\text{A/cm}^2$ and the sample temperature during irradiation didn't exceed 60°C . Some samples were irradiated with ^{60}Co gamma-rays at 10°C , the irradiation intensity being $7 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Photoluminescence spectra were recorded at 4.2 K and room temperature using a He-Cd (325 nm) and Ar (458 nm) laser, respectively. Electrical measurements were taken by means of the Van der Pauw technique.

Prior to irradiation, the YL band peaks at 2.23 eV for n-GaN and 2.17 eV for p-GaN (at room temperature). After electron irradiation of n-GaN, radiation-induced defects make their appearance in two ways. First, the maximum of the above band was clearly shifted to a new position at 2.34 eV, at a dose of $1 \cdot 10^{17} \text{ cm}^{-2}$. Second, the intensity of the YL was increased by a factor of three. We also observed similar effects for electron-irradiated p-GaN, although at much lower intensities of the YL at room temperature as compared to n-GaN. Nonetheless, it has been found that prolonged gamma-irradiation of p-GaN (at a dose of $1 \cdot 10^{19} \text{ cm}^{-2}$) can enhance the YL by a factor of five. Again, the maximum of this band is shifted to 2.34 eV, thus showing a contribution of the same radiation-induced defects, as in the case of n-GaN. Electrical measurements showed that electron irradiation of both n- and p-GaN results in increasing concentration of charge carriers. However, these changes reflect a net effect of the production of electrically active native defects on both sublattices and should be interpreted starting from the theoretical predictions made in [1,2].

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LOCAL VIBRATIONAL MODES AT As_N IN CUBIC GaN: COMPARING AB-INITIO CALCULATIONS TO A SEMI-EMPIRICAL MODEL

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Key Words: cubic GaN:As, local vibrational mode, density-functional theory

GaN can be grown in zincblende structure on a GaAs substrate. In this material a high number of Raman lines are observed in the range from 60 to 250 cm^{-1} at low temperatures [1]. These proposedly originate from defects resulting from diffusion of As atoms into the GaN layer and/or of N atoms into the GaAs substrate during the epitaxial growth process.

We here concentrate on the local vibrational modes (LVM) of the As_N center in GaN. The phonon dispersion curves of the host GaN crystal were calculated using the Keating-Kane model and by fitting the valence force parameters to the well known Raman frequencies at the zone boundaries. The change of the force constants in the vicinity of the defect was treated with the scaling factor approximation [2]. We calculated a cluster of up to 525 vibrating atoms embedded in the crystal and selected the modes with high vibration amplitudes in the vicinity of the defect. The energies of these local vibrational modes can be fitted to the experimental data by a variation of the scaling factor.

We also studied this defect using ab-initio density-functional theory. Due to the different ionic radii of the Ga and N atoms, we calculated first the relaxation of the atoms around the defect and then the force constants at the defect site. We also performed the same type of cluster calculations as before.

Both methods give the same results for the vibrational energies, but different results for the interatomic forces.

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LOCAL VIBRATIONAL MODES AT TRANSITION METAL IMPURITIES IN HEXAGONAL AlN AND GaN CRYSTALS

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Key Words: GaN, AlN, Transition Metals, Local Vibrations, Isotope Shifts

We present a detailed experimental and theoretical study of local vibrational modes (LVMs) at transition-metal (TM) impurities in wurtzite-type crystals. The energies of the LVMs of Fe^{3+} and Ti^{2+} in hexagonal GaN and Fe^{3+} in hexagonal AlN are calculated with a modified valence-force model of Keating and Kane, which was generalized for hexagonal symmetries including long-range Coulomb forces. Due to the anisotropy of wurtzite-type crystals in the direction of the c-axis there are 14 independent valence-force parameters. The valence-force parameters of the perfect crystals are calculated by fitting the phonon dispersion curves to experimental Raman and photoluminescence data of GaN [1] and to ab-initio calculations of AlN [2]. The valence-force parameters in the vicinity of the defect are determined using the scaling-factor approximation which is defined by $p_d = p + p_s$, where p is any of the valence-force parameters of the perfect crystal and p_d the corresponding parameter at the defect site. The dynamical matrix is set up for a cluster of 295 vibrating atoms, which is embedded in the non-vibrating crystal and taking the TM as the central atom. The eigenvalues of the dynamical matrix gives us the vibration frequencies. The LVMs were selected due to their large vibration amplitudes in the region of the defect as obtained from the eigenvectors of the dynamical matrix.

The calculated energies of the LVMs are in good agreement with the results obtained by our photoluminescence and photoluminescence excitation measurements. We present the substitutional and the ligand induced isotope shifts of the LVMs. The calculated substitutional isotope-shifts were found to be smaller than 1 meV per nucleon and therefore could not been observed because of the experimental linewidth of 1.5 meV.

We also demonstrate the delocalization of LVMs with energy in the phononbands due to hybridization with crystal phonons.

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ON THE ORIGIN OF YELLOW DONOR-ACCEPTOR PAIR EMISSION IN GaN

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Key Words: GaN, photoluminescence, donor-acceptor pair recombination

“Deep” yellow donor-acceptor pair (DAP) recombination is likely the most known but less understood photoluminescence (PL) emission of GaN. This emission is commonly observed in GaN samples grown by different techniques, as is also confirmed by the present work. Several studies indicated an anti-correlation between the strength of this PL and a morphological quality of GaN epilayers. No clear explanation of this fact was given. To verify if such anti-correlation exists we performed PL investigations (PL, its temperature dependence and PL kinetics) of several GaN samples grown either at different conditions, or at the same conditions but on three different substrates or, finally, by different growth methods. Even though strong deep DAP PL was observed in some cases, no simple correlation between intensity of this PL band and e.g. strain conditions in the sample was found. An analog of “yellow” DAP PL is also observed in cubic phase GaN samples grown on (100) silicon substrates. This PL is shifted down in energy by about 250 meV.

The origin of the “yellow” DAP emission was recently discussed based on the results of optically detected magnetic resonance (ODMR), stress and PL kinetics investigations. Two conflicting models were proposed to explain this PL. Deep donor-shallow acceptor transition was proposed based on the results of ODMR study, whereas other ODMR experiments and stress and PL kinetics measurements were explained in frame of shallow donor-deep acceptor transition model. We believe that present PL investigations may explain the reasons for such conflicting models of “yellow” DAP transitions in GaN. Even though the present PL kinetics measurements support the second model of the “yellow” DAP emission, PL study indicates a complex nature of this PL emission. In some cases an indication of a two-band nature of this PL was observed. In addition to a two-band nature of the PL, we observed in some cases that PL intensity, which first slowly decreases with increasing temperature, starts to increase at higher temperatures. This may also be explained by the presence of an underlying second PL emission related to e.g. deeper donors. All these results may explain the reasons for conflicting explanations of the results of often the same investigations (e.g. ODMR studies by two different groups).

OPTICAL MICROSTRUCTURE OF Zn-O DEFECTS IN GALLIUM NITRIDE

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Key Words: gallium nitride, luminescence, polarization diagram

It is known that the polarization diagram technique is excellent method for investigation of optical microstructure of emission defects in crystals. We report here the results of the investigation of defects in GaN at impurity and intrinsic excitation of photoluminescence using this technique.

High-quality epitaxial layers of GaN doped simultaneously with zinc and oxygen were grown by gas-phase technique in chloride-hydride system on sapphire substrate with orientation (1012). Layers of GaN were oriented in plane (1120). A luminescence band with maximum 2,55eV at 300K and linear polarization up to 60% was observed. This band was associated with presence of pair Zn-O defects and attributed to intercenter transition. The main contribution to emission and absorption in GaN(Zn,O) is that of linear oscillators, oriented in plane (0001)GaN symmetric about the C-axis in GaN.

These results were confirmed by the numerical simulation for various models of Zn-O defects.

The work was performed with partial support of Arizona University (USA).

PHOTOLUMINESCENCE OF INCLUSIONS OF THE CUBIC PHASE IN A PREDOMINANT HEXAGONAL GaN MATRIX

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We report on temperature dependent photoluminescence studies of GaN films grown by MBE on sapphire substrates. Strain has been proven to be the major line broadening mechanism of low temperature luminescence. Modification of hydrostatic and biaxial strain components were utilized to minimize the half width of the near band edge luminescence. Consequently, PL lines as narrow as 1.2 meV were observed in films that are almost strain free. No 'yellow' luminescence band was found in these samples. A sharp transition at 3.257 eV indicates the formation of the cubic GaN phase [1] in the hexagonal matrix. We find that the occurrence of the cubic phase to be stoichiometry related, the signal intensity increases with increasing Ga/N₂ flux ratio. Though the band edge PL of the cubic phase may overlap with the well-known spectrum of the donor-acceptor pair recombination of the hexagonal phase, the signals can be discriminated by temperature variation. TEM investigations confirm the existence of cubic GaN inclusions in the hexagonal films [2]. They nucleate spontaneously and account for about 1% of the matrix volume.

Being still visible at room temperature at 3.202 eV, the temperature dependence of the excitonic transitions (DX / FX) in the cubic phase can be described by Cody's formula [3]. The temperature $\theta \sim 600\text{K}$ is significantly different from the one determined for the corresponding transitions of the hexagonal phase ($\theta \sim 300\text{K}$).

$$E_{\text{gap}}(T) = E_{\text{gap}}(0) - \frac{\lambda}{\exp(\theta/T) - 1}$$

In crystals exhibiting the cubic phase, we also detect a structure at 3.146 eV consisting of the zero phonon transition plus two phonon replica. This signal is observable for temperatures up to 140K. Consequently, we identify this signal group as a donor-acceptor pair transition in the cubic phase. Our assignment is in agreement with results obtained by cathodo-luminescence of cubic GaN grown on GaAs [4].

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STRAIN RELATED PROCESSES IN GaN THIN FILMS

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GaN thin films are typically grown on sapphire substrates that do not match the GaN lattice (15% lattice mismatch) and differ in thermal expansion. Since growth temperatures are low compared with the materials melting point ($T_{\text{growth}} < 0.5 T_{\text{melt}}$) plastic relaxation appears to be difficult and the films can be strained elastically to stress levels that can reach one GPa. It is shown that physical properties of the films such as the width of luminescence lines or the surface morphology of the layers can be optimized by engineering these stresses. The growth temperature of buffer layers, their thickness and the composition of the GaN thin films are shown to be parameters that can be utilized for this purpose. This way, heteroepitaxially grown MBE films can exhibit x-ray rocking curves as narrow as 80 arcsec, 1.2 meV narrow donor bound luminescence emissions or a desired surface morphology.

Similarly, stress is introduced by the growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum wells into GaN because of a lattice mismatch that may reach 11%. A quantitative investigation of the Indium distribution in $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum wells at an atomic scale reveals that this strain causes indium segregation that increases with the indium content in the $\text{In}_x\text{Ga}_{1-x}\text{N}$ layers. Sometimes a separation of different phases in the investigated crystals with Indium concentrations $30\% \leq x \leq 50\%$ is found. The results give experimental evidence for formation of Indium clusters in $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum wells, and the existence of a miscibility gap in the GaN-InN quasi-binary system. In addition, a transition from a planar (2D) growth on {0001} surfaces to a three dimensional (3D) growth on {0001} and {01-11} surfaces is observed if the effective thickness of $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum wells exceeds a critical value. The formation of misfit dislocations is not observed though this critical thickness greatly exceeds values that are calculated from the model of Matthews and Blacklee. The 2D/3D transition influences growth rates and it is argued that it is driven by strain. Thus, strain relaxation in GaN / $\text{In}_x\text{Ga}_{1-x}\text{N}$ / GaN heterostructures occurred by surface roughening and not by plastic deformation.

ZEEMAN STUDY OF THE 0.94 eV EMISSION IN AlN AND GaN

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Keywords: AlN, GaN, transition metals, photoluminescence, Zeeman effect

Despite the enormous progress in growth and device technology there is only little information about deep defects in group III-nitrides. Transition metals (TMs) form deep defects and can be expected to be common contaminations of these materials which are grown at very high temperatures. Even though their technological relevance for growing high resistivity material, first detailed information on TM defects was reported only recently.

Up to now, five TM luminescence bands have been reported for GaN and AlN [1]. On the basis of magneto-optical measurements, the electronic configurations of the 1.30 eV and 1.19 eV TM defects in GaN were identified. The 1.30 eV luminescence is unambiguously attributed to the ${}^4T_1-{}^6A_1$ transition of Fe^{3+} (3d⁵-system) [2], whereas the 1.19 eV zero-phonon line (ZPL) is attributed to the ${}^1E-{}^3A_2$ transition of a d²-system [3]. Ti^{2+} and Cr^{4+} are discussed as luminescence centers [4]. No other magneto-optical measurements have been performed so far. In this paper we report on the first Zeeman study of the 0.94 eV ZPL in AlN and the 0.93 eV ZPL in GaN, respectively. The ZPLs were investigated in magnetic fields up to 15 T at temperatures between 1.8 K and 40 K. We observe a symmetric isotropic threefold splitting of the 0.94 eV ZPL in AlN needles. On the basis of temperature dependent Zeeman measurements, the splitting is attributed to the ground state. The g-value of 2.10 ± 0.10 is typical for a ${}^3A_2$ -state and thus we attribute the 0.94 eV ZPL in AlN to a ${}^1E-{}^3A_2$ transition of a d²-system. Possible 3d impurities are V^{3+} , Ti^{2+} and Cr^{4+} . A similar Zeeman behaviour was observed for the 0.93 eV ZPL in GaN. Because of the localized wavefunction of the deep impurity and similar lattice constants of GaN and AlN together with the large bandgap, it is expected that internal transitions of the same TM element appear approximately at the same energy. Thus, V seems to be the most promising candidate to explain the 0.94 eV ZPL in AlN and the 0.93 eV ZPL in GaN, taken into account the Cr^{4+}/Ti^{2+} attribution of the 1.19 eV ZPL in GaN.

The energies of deep levels of TMs are used to determine band offsets of semiconductor heterostructures based on the internal reference rule for these defects. Even though the internal reference rule has been validated for many semiconductor/TM combinations it is not clear whether it can be used unambiguously to predict band offsets. We discuss the band offsets of GaN, AlN and GaAs in this context and show, that the internal reference rule can not be applied for the GaN/GaAs heterojunction.

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BLUE EMISSION IN Mg DOPED GaN STUDIED BY TIME RESOLVED SPECTROSCOPY

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Key Words: GaN:Mg, blue emission, time resolved spectroscopy

A strong blue emission is present when GaN films are heavily doped with Mg. It is also known that compensation of non-intended donors reduces the free hole density at least two orders of magnitude as compared with the Mg concentration.

Previous work on the blue band in Mg heavily doped (10^{20} cm^{-3}) shows that two main emissions contribute to the band with maximum at 2.8 eV and 2.7 eV¹. The dependence with excitation density shows a shift too large to be attributed to DAP recombination.

In the present work we analyse by time resolved spectroscopy, in conditions of low excitation density, the temperature dependence of the blue emission and compare it with steady state data. From this analysis and for delays above 80 μs we see a prompt emission with maximum at 3 eV, while the bands at 2.8 and 2.7 eV are slow emissions. While the 2.8 eV band as a decay of the order of .1 ms the 2.7 eV has a lifetime of the order of tens of milliseconds at 11 K.

From the temperature dependence of the two emission intensities and decays a mechanism of excitation and deexcitation of the bands that contribute to the blue emission in these samples is proposed.

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POSITRON ANNIHILATION IN GaN: 1D-ACAR DATA

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Key Words: positrons, annihilation, GaN, point defects, 1D-ACAR spectroscopy

The angular correlation of the annihilation radiation (ACAR) of the electron-positron pairs is a sensitive probe for studying of the electron momentum density and its disturbances by defects in semiconductors. The method relies on the propensity of positrons to get localized at the regions of negative effective charges of a defect and the resulting emission of the annihilation gamma-photons that carry information about the annihilation site. Here, we consider some results that have been obtained recently for GaN by one-dimensional (1D) ACAR. It has been established that in the crystal lattice of GaN diamond-like semiconductor the annihilation of thermalized positrons with electrons of the valence band is a predominating process and so-called broad component of the 1D-ACAR curves may be attributed to the positron annihilation in the narrow zones of the outer shell core electrons.

An estimation of the enhancement of the electron density at a positron has been made by the data of 1D-ACAR measurements. Numeral value of the electron radius $rs' = 1,830$ to $1,890$ a.u. is in a qualitative agreement with the data of calculations which are based on the local-density approximation [1]: $rs = 1,887$ to $1,896$ a.u. As a whole, this result is indicative of insignificant enhancement of the ambient electron density at the screening of positrons in the crystal lattice of GaN. The influence of the effective charges of the lattice sites on the positron annihilation with electrons of outer shells of ionic cores in GaN is discussed. It has been shown a dominating role of the outer shells of "Ga" ionic cores in the process of formation of the broad component of the 1D-ACAR curves. The results obtained point to the partial localization of wave packets of thermalized positrons near "N" sites in "defect-free" GaN. The mentioned partial localization may result in significant differences of the cross-sections of positron capture by intrinsic defects of the vacancy-type. There are some reasons to believe that Ga-vacancies as well as their impurity complexes have to be an effective centers of the positron localization and the annihilation radiation of localized electron-positron pairs can carry the information about the configuration of the defects of a such type. 1. M.Puska, S.Makinen, M.Manninen, and R.Nieminen, Phys. Rev. B 39, 7666 (1989).

RAMAN SCATTERING FROM DEFECTS IN GaN

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Keywords: GaN, phonons, Raman scattering

In the last few years the wide-bandgap semiconductor GaN has received increasing attention because of its application as the favorite basic material for optoelectronic devices working in the blue to ultraviolet spectral region [1]. One of the main problems which still restricts the growth of high-quality GaN layers is the high concentration of defects which yields a high background carrier concentrations and the typical n-type conductivity of GaN layers. It is still unclear what kind of defects are responsible for these effects.

We present results of Raman-scattering experiments on p- and n-type cubic GaN layers grown on GaAs and hexagonal layers grown on sapphire. While the layers deposited on sapphire exhibit only the expected host phonon modes, we found a series of additional sharp lines in the range between 60 and 250 cm^{-1} from the layers grown on GaAs. The lines show a strong temperature dependence. Their intensity increases exponentially with decreasing temperature and the modes disappear when reaching room temperature. Wavelength-dependent measurements reveal that they are strongest under excitation around 568 nm. Some of these lines were also observed by Ramsteiner et al. [2] and have been attributed to hydrogen-like transitions between the electronic states of a shallow donor in hexagonal and cubic GaN. In order to prove this model we have performed a systematic Raman study on several series of GaN layers grown on GaAs and sapphire. We found that the attribution of some modes to the cubic and some to the hexagonal modification given in [2] is not valid and that more lines appear than expected by hydrogen-like transitions of one donor [3]. On the basis of the new experimental data including results of high-pressure Raman experiments and magnetic-field dependent measurements we discuss possible candidates of defects.

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DONOR CENTERS IN ERBIUM -IMPLANTED SILICON

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Key Words: silicon, erbium impurity, thermal donors

Oxygen aggregation processes in Si with high oxygen contents are sensitive to the presence of various impurities (C, B, H etc). Among the rare-earth elements, Er in oxygen-rich Si attracts much attention in view of its application to optoelectronics. Post-implantation annealing of Si:Er:O at 700°C for removal of radiation-induced defects leads generally to formation of donor centers with ionization energies less than 90 meV. The experimental information about these donors is meagre so far. In this work the formation of oxygen-related centers in Si:Er is studied in two ways. First, we investigated shallow donors produced in Czochralski-grown Si (Cz-Si) after implantation of Er as well as co-implantation of Er and O followed by annealing at 700°C. Second, some samples of Cz-Si:Er were subjected to additional heat treatment at 450°C to produce the well-known Thermal Double Donors (TDD) and elucidate the features of oxygen aggregation in the presence of $\text{Er}[\text{O}]_n$ -related complexes.

Commercial Cz-Si wafers doped with B ($\rho \approx 7 \text{ Ohm-cm}$) were used as substrates for the production of n-type layers by implantation of Er or co-implantation of Er and O. The energy of ions was 1.2 MeV and 0.17 MeV for Er and O, respectively. The doses used for Er were mostly $1 \cdot 10^{13} \text{ cm}^{-2}$ and those for O were always higher by an order-of-magnitude. Under such conditions, the implanted layers were far from being amorphous, as evidenced by X-ray and Raman spectroscopic measurements. All implanted samples were subjected to annealing at 700°C for 30 min in a chlorine-containing atmosphere to remove radiation damage. Further heat treatment if applied were performed at 450°C in dry nitrogen. Electrical and optical measurements were taken to estimate contributions of various donor centers.

Er-related defects were found to be effective nucleation sites for oxygen aggregation in Cz-Si:Er. In this case the distribution of donor centers over their ionization energies ranges from $\approx 0.03 \text{ eV}$ to 0.09 eV and peaks at $\approx 0.07 \text{ eV}$. With increasing oxygen content for Cz-Si:Er:O the contribution of shallow donor centers increases and their distribution has a maximum at $\approx E_C - 0.04 \text{ eV}$. However, the total concentration of shallow donors remains practically the same as in the case of Cz-Si:Er, since the concentration of Er-related nucleation sites is comparable in both cases.

Heat treatment of Cz-Si:Er at 450°C leads to enhanced formation of the lower-numbered TDD (TDD1 - TDD4) and their formation rate at the beginning of heat treatment is increased by a factor of five as compared to Cz-Si subjected to the same heat treatment. This heat treatment does not change the concentration of donor centers already existing in Cz-Si:Er after the 700°C annealing. Most likely, the oxygen aggregation path proceeds via other nucleation sites than $\text{Er}[\text{O}]_n$ -related complexes formed during post-implantation annealing.

ELECTRONIC STRUCTURE OF LIGHT EMISSION CENTERS RELATED TO ERBIUM IN SILICON

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Key words: erbium, oxygen, silicon, electronic structure

Erbium is an efficient luminescent center in silicon. The sharp line luminescence at $\lambda = 1.54 \mu\text{m}$ is interpreted as the result of an internal 4f transition and should be assigned to transitions from the first excited state $^4I_{13/2}$ to the ground state $^4I_{15/2}$ of Er^{3+} ($4f^7 1^1$). Moreover, it has been demonstrated that oxygen coimplantation enhances the Er luminescence and the origin of this enhancement is still unclear.

In this work, the electronic structure calculations of erbium-oxygen complexes in silicon have been carried out by using the self-consistent-field multiple scattering theory in within the framework of the molecular cluster model. The *quasirelativistic* theory in which the radial functions inside each atomic sphere satisfy an average Dirac equation that includes the Darwin and mass-velocity corrections, but not spin-orbit term, has been used.

The Er $4f$ and $6s$ states have been treated as valence states. The calculated results do not support the assumptions that the $4f$ electrons could be treated as a frozen core. The results also show that some kind of hybridization among $4f$, $6s$, $5d$, and $6p$ orbitals takes place in the interaction between Er, oxygen and silicon host atoms.

Based in the assumptions that the $4f$ — derived states must have an atomic-like character and a small crystal field splitting, we propose a microscopic model which provides a consistent interpretation for the photoluminescence measurements.

PHOTO- AND ELECTROLUMINESCENCE OF ERBIUM-DOPED Si

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Keywords: rare earth luminescence, non-radiative recombination

Optical transitions within the 4f shell of rare earth dopants in semiconductors can be utilised for a variety of applications like photon up-conversion, optical amplification and lasers. Last not least, because of its enormous technical potential in fibre optical communication systems, the 1.54 µm luminescence of Erbium in glasses, III-V and II-VI compounds has attracted also considerable interest in the possibility to use Si as host material for luminescence type devices. Unfortunately, the photoluminescence (PL) yield and also the electroluminescence (EL) yield of forward bias operated diodes quenches for Si already at temperatures well below room temperature, whereas diodes operated under reverse bias conditions exhibit much less efficient quenching and sizeable output even at 300 K.

In this paper we discuss the mechanisms responsible for the luminescence quenching in Si:Er. We investigate both the yield and the luminescence life time of forward biased EL diodes. We find that the EL yield and the decay time exhibit the same temperature dependence as in PL indicating the same excitation and parasitic decay mechanisms. Both the yield and the effective lifetime decrease exponentially above a temperature of about 150-200 K, depending somewhat on the Er center under consideration and on the sample preparation conditions. These findings clearly show that non-radiative deexcitation of the Er occurs as a thermally activated process.

It was demonstrated in the literature that under reverse bias conditions the luminescence quenching is less effective and for an explanation, an Auger process was considered by which free carriers are excited by radiationless deexcitation of the Er 4f shell. In order to test this assumption for our moderately doped samples (the carrier concentrations are below 10^{18} cm^{-3} in both the n- and p- type regions) we investigate the EL yield of diodes which do not show emission under reverse bias conditions. In order to excite the Er ions we apply a short forward pulse to the reverse biased diode. No difference is seen in the decay time constant as compared to the case of a forward bias close to flat band condition. We conclude thus that free carriers do not affect the non-radiative recombination in the concentration regime considered. This conclusion is supported also by the observation of identical PL under different bias conditions.

Therefore a different deexcitation mechanism must be invoked in order to explain the luminescence quenching in moderately doped samples. Here we consider bypassing mechanisms and energy backtransfer to activator states, which are shown to improve the PL yield in oxygen-codoped material.

In some samples we observe also 1.54 µm PL and EL at room temperature. We show that this emission is caused rather by dislocations and Er is not involved.

STRUCTURAL DEFECTS AND PHOTOLUMINESCENCE IN DISLOCATION-RICH ERBIUM-DOPED SILICON

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Key Words: silicon, erbium, structural defects, luminescence

Dislocation-related luminescence D bands were observed in plastically deformed silicon and strain-relieved SiGe epitaxial layers [1,2]. Recently, we found D1 and D2 photoluminescence lines in Si:Er after postimplantation annealing at 1100 °C [3]. The purpose of our work was to study an influence of implantation and annealing conditions on formation of structural defects and photoluminescence in Si:Er.

For formation of Si:Er, Er ions were implanted at 0.8 - 2.0 MeV energy and 1×10^{12} - 4×10^{14} cm⁻² dose in FZ- and Cz-Si with a resistivity of 1-20 Ωcm. Co-implantation of oxygen ions with 0.1 - 0.25 MeV energy and 1×10^{13} - 4×10^{15} cm⁻² dose was also performed. Postimplantation annealing was carried out at 1000 - 1250 °C for 0.25 - 8 h in various ambient surroundings. TEM, X-ray diffraction, optical microscopy and photoluminescence techniques were used to study the properties of Si:Er.

The different types of structural defects (dislocations, stacking faults and precipitates) were observed. The type of dominant defects depends on the Er implantation dose and the temperature and medium of annealing. For example, implantation of 1 MeV Er ions at a dose of 1×10^{13} cm⁻² and subsequent annealing at 1100 °C in a chlorine containing atmosphere led to formation of Frank loops with stacking faults of 0.7 - 3.5 μm size and 2×10^7 - 1×10^8 cm⁻² density and prismatic dislocation loops of 0.1 - 1.0 μm size and 2×10^6 - 7×10^7 cm⁻² density.

We observed formation of only the 1525 nm (D1) and 1417 nm (D2) luminescence lines. It is important to underline that there were no Er-related (1537 nm) luminescence line after annealing at temperatures higher than 1000 °C. The strictly specified wavelengths of observed D1 and D2 lines suggests that there is no deformation in samples after annealing at 1100 °C. The shape of the D1 line is practically the same in all the samples, whereas the D2 line shape depends on the sample preparing conditions. There is no a correlation between the D1 and D2 line intensities. We observed an increase of the line intensity with increasing density of Frank dislocation loops of small sizes.

In conclusion, TEM and double crystal X-ray diffraction permitted to study deformation variations and structural defect formation during high energy ion implantation and subsequent annealing. Some correlations between the defect structures observed and D line luminescence intensity took place.

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INFLUENCE OF FABRICATION CONDITIONS ON PROPERTIES OF Si:ER LIGHT-EMITTING STRUCTURES

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Key Words: silicon, erbium, luminescence, defects

The understanding of formation of Er-related electrically and optically active centers and structural defects is essential to improve the luminescence intensity of Si:Er structures. The purpose of our work was to study electrical, luminescence and structural properties of Si:Er during implantation and annealing.

For formation of Si:Er, Er ions were implanted at 0.5 - 2.0 MeV energy and 5×10^{12} - $3.2 \times 10^{15} \text{ cm}^{-2}$ dose in FZ- and Cz-Si. Co-implantation of O, F, N and C ions with 0.06 - 0.25 MeV energy and 5×10^{13} - $4.8 \times 10^{16} \text{ cm}^{-2}$ dose was also performed. Postimplantation annealing was carried out at $400 \pm 900^\circ \text{C}$ for 0.25 - 4 h in various ambient surroundings. Rapid thermal annealing was also used. SIMS, RBS, TEM, X-ray diffraction, DLTS, capacitance-voltage, photo- and electroluminescence (PL and EL) techniques were used to study the properties of Si:Er.

Dependent on technological conditions, several types of luminescence lines, Er-related ($1.54 \mu\text{m}$), free exciton ($1.124 \mu\text{m}$) and defect-related ($1.3 - 1.5 \mu\text{m}$), were observed. The Er-related luminescence intensity increases monotonically with increasing implantation dose in the intervals of 5×10^{12} - $1 \times 10^{13} \text{ cm}^{-2}$ and 8×10^{14} - $3.2 \times 10^{15} \text{ cm}^{-2}$. At the same time, the intensity decreases in the intermediate dose range. Strong variations in the spectrum of electrically active Er-related centers were also observed in dependence of technological conditions. The observed changes in optical and electrical properties of Si:Er were related to defect structure transformations. In particular, we consider that a decrease of the Er-related luminescence line intensity after implantation of Er at a dose of 1×10^{13} - $8 \times 10^{14} \text{ cm}^{-2}$ is associated with formation of Er-related precipitates (which we observed by TEM) being optically inactive centers.

Co-implantation of Er and some elements (more electronegative than Si) led to an increase of the PL and EL intensity. Such samples were characterized by a rich fine structure of luminescence and DLTS spectra. Our experiments showed that enhancement of light emission from Er after ligand introduction took place due to optimization of the excitation and back transfer processes rather than ligand gettering of nonradiative centers.

We have fabricated Si:Er:O LED demonstrating EL at 300 K. EL was observed both under forward and in reverse bias conditions. EL under reverse bias was excited by impact excitation. Its intensity was reduced by a factor of 2 with the temperature increased from 70 K to 300 K.

MECHANISM OF GENERATION OF THE ER RELATED EMISSION FROM III-V SEMICONDUCTOR HETEROSTRUCTURES

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Key Words: erbium, quantum well, light emission, laser

We propose one of possible mechanisms for realizing of an inversive distribution of the f electrons of the Er^{3+} ions placed into semiconductor heterostructure with quantum wells. The heterostructure with wells of different effective band gaps $E_g^{\text{ef}} = 1.24 \text{ eV}$ and $E_g^{\text{ef}} = 0.8 \text{ eV}$ is discussed. These energies correspond to transitions Er^{3+} ion from ground state $^4I_{15/2}$ to excited states $^4I_{11/2}$ and $^4I_{13/2}$ correspondingly.

Previously [1] it was shown that the Coulomb excitation of f-electron by electron-hole Auger recombination in a quantum well is more effective than in a bulk of semiconductor if this process is resonant. Resonance excitation of the f-electrons in a well takes place in the case when distance between quantum-size energy levels of electrons and holes $E_g^{\text{ef}} = E_g + E_{0c} + E_{0h}$ (E_{0c} and E_{0h} are magnitudes of ground state quantum-size energy levels of electron and holes, correspondingly) is exactly equal to distance between ground and excited states of the Er^{3+} ion. This Coulomb mechanism of the excitation of the erbium ion allows to exerts control over the resonance condition by varying parameters of a well. We discuss the structure with two types of wells of different depth in order for the transitions $^4I_{15/2} \rightarrow ^4I_{11/2}$ and $^4I_{15/2} \rightarrow ^4I_{13/2}$ would be excited. For both transitions the Coulomb excitation rate is equal to about 10^{10} s^{-1} . Characteristic decay time of the Er related emission is equal to $10^{-3} - 10^{-4} \text{ s}$. Hence, this mechanism of excitation of f-f transitions is effective, even though the concentration $n(\text{Er})$ is more lager than electron-hole pairs concentration $n(e,h)$. It should be noted that depth one of quantum well should be more than 1.3 eV in order to excite the $^4I_{15/2} \rightarrow ^4I_{11/2}$ transition. The reverse $^4I_{11/2} \rightarrow ^4I_{13/2}$ transitions can produce inversive distribution of the f-electrons between the $^4I_{13/2}$ and $^4I_{15/2}$ states of the Er^{3+} ions in consequence of it induced radiated transitions $^4I_{13/2} \rightarrow ^4I_{15/2}$ should take place in that system.

The optimal laser structure must content several quantum wells with $E_g^{\text{ef}} = 1.24 \text{ eV}$ and $E_g^{\text{ef}} = 0.8 \text{ eV}$. This structure would be realized on base of the InGaAsP compounds. Our estimates show that in the regime of generation the characteristic time of induced transitions is equal to about $10^{-7} - 10^{-8} \text{ s}$, and power irradiation is equal to about 100 mW at threshold current near 200 A/cm^2 .

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ELECTRON SPIN RESONANCE OF Er-OXYGEN COMPLEXES IN GaAs.

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Key Words: erbium, GaAs, oxygen, ESR, photoluminescence

Er-doped semiconductors have been widely studied because of their possible applications to new optical devices, but the atomic configurations of Er luminescence centers are not yet understood. The electron spin resonance (ESR) is an effective method of understanding these configurations. ESR signals associated with Er were recently observed in silicon implanted with Er and oxygen. [1] Here we report on ESR signals in Er-doped GaAs grown with oxygen codoping by metalorganic chemical vapor deposition (MOCVD) which shows strong Er-related luminescence. [2] An ESR signal with the effective g-value of about 6 has been observed in GaAs implanted with Er and oxygen [3] and in melt-grown GaAs crystals doped with Er. [4] In this work, we also observed a broad and weak ESR signal with $g=5.95$ in Er-doped GaAs grown by MOCVD, while in the oxygen-codoped sample, in addition to this signal, at least six narrow and strong ESR signals were observed. The relative ESR intensities of these signals were about two orders of magnitude higher than that of the signal with $g=5.95$ for the sample without oxygen codoping. These signals were anisotropic. When the magnetic field was nearly parallel to the [100] direction, the effective g-values of these signals were 2.25, 2.13, 0.92, 0.86, 0.79, and 0.75. Comparisons of signals from various samples with different Er concentrations and changes in ESR spectrum under the illumination with 632-nm laser indicate that these signals originate from at least two types of Er-oxygen complexes. We discuss the relation between the ESR spectrum and the photoluminescence spectrum due to Er centers. We also discuss the nature of the Er-oxygen complexes responsible for the Er-related spectra.

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EXCITATION AND DE-EXCITATION OF ERBIUM IONS IN SEMICONDUCTOR MATRICES

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Key words: erbium luminescence, Auger excitation, de-excitation of erbium ions

Studies of erbium photoluminescence in erbium-doped semiconductor matrices of different nature (crystalline and amorphous silicon, AlGaAs, GaAs/AlGaAs quantum structure) have shown that in most cases the main excitation channel of erbium ions is an Auger process. A free carrier is captured by a defect state induced in the bandgap of the semiconductor by an erbium ion or erbium-containing complex, while the energy released is transferred via Coulomb interaction to an f-electron to excite it to an upper state of the f-shell. The excess energy is transferred to defects and emitted as phonons.

In the case of AlGaAs, erbium induces hole traps, therefore the Auger excitation proceeds via recombination of a free electron with a localized hole. In crystalline silicon erbium-oxygen complexes produce donor states in the bandgap and the Auger excitation occurs by recombination of localized electrons with free holes. In amorphous silicon doping by erbium is accompanied by formation of dangling bond defects, and Auger excitation processes take place via capture of conduction band electrons by dangling bonds in neutral state.

Calculations are performed of the probabilities of three types of transitions leading to a capture of a free carrier by a defect level: 1) radiative transition (observed by defect luminescence), 2) multiphonon nonradiative transition, and 3) Auger excitation of erbium ion. It is demonstrated that the probability of the Auger process exceeds the probability of the radiative transition practically in all types of semiconductor matrices. With an increase of the temperature the probability of multiphonon nonradiative transitions increases quasi-exponentially, and the competition of this transition with the Auger excitation leads to temperature quenching of erbium luminescence. The reverse process of de-excitation of an erbium ion via energy transfer back to the defect level is considered in which the energy of an excited f-electron is given up to generate a free carrier from the defect level. The activation energy of this process is the difference of the energy of thermal ionization and the energy of excitation of an f-electron. The probability of such processes is calculated for AlGaAs and amorphous silicon.

Theoretical calculations are compared with experimentally determined temperature dependences of intensity of erbium luminescence in various semiconductors. Good agreement of the theory with the experiment is obtained and parameters of the theoretical model (local phonon energy, parameter of electron-phonon interaction etc.) are determined.

HIGH TEMPERATURE LUMINESCENCE DUE TO Er IN POROUS Si

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Keywords: Defect structure, rare earth luminescence

According to the empirical rule of Favenec et al.¹, the temperature induced quenching of the 1.54 μm photoluminescence (PL) of Erbium in different host crystals occurs at higher temperatures for materials with larger energy gap. Therefore also nano-porous Si has been doped with Er and first results appeared very promising: strong luminescence could be obtained also well above room temperature whereas the PL of Er in crystalline Si quenches already below 200 K. So far, however, no information concerning the structure of Er centers in po-Si were obtained.

In this contribution, we report results from excitation spectroscopy on po-Si:Er which indicate that the high temperature luminescence in our samples is rather due to Er embedded in SiO_2 - δ clusters. Porous Si layers with a thickness of 2 μm and a porosity of 75% were prepared by anodic etching. Er was introduced electrolytically from ErCl_3 dissolved in ethanol. After annealing at 1000°C for 10 s in an O_2/N_2 atmosphere the samples show a sharp and intense Er^{3+} related luminescence at 4.2 K which decreases only by a factor of 6 when the temperature is increased to 300 K. This spectrum consists of one line centered at 1539 nm and a FWHM of 3.6 nm at 4.2 K and a second line, at least three times as narrow, centered at 1548 nm. In addition, there is a second set of more than 4 lines superimposed at direct excitation. This spectrum is quenched efficiently already at temperatures as low as 40 K.

Both types of spectra clearly show resonances when excited in the 800 and 980 nm bands which correspond to the $J = 15/2 \rightarrow 9/2$ and the $15/2 \rightarrow 11/2$ excitation transitions, respectively, within the 4f shell of Er. For the sharp spectrum, we observe at least 6 sharp excitation lines close to 970 nm and 5 lines close to 800 nm. The exact line positions at 1.54 μm and their widths are comparable to those seen in crystalline Si and III-V compound semiconductors. The number of excitation lines excludes cubic symmetry of the centres responsible. We attribute only this type of spectrum to Er diffused into the po-Si. The low quenching temperature may be related to non-radiative recombination at surface defects.

We attribute the wider spectrum seen up to temperatures well above 360 K to Er in an SiO_2 -like surrounding because of its striking similarity with both the PL and the excitation PL spectra seen in fused silica doped with Er. We conclude thus that the efficient room temperature Er- luminescence seen in samples doped electrolytically with Er and subjected to annealing at 1000°C in oxygen-rich atmosphere is rather due to Er incorporated in a glass like environment.

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INFLUENCE OF THE ERBIUM DOPING ON STRUCTURE AND OPTICAL PROPERTIES OF THE InGaAs/GaAs SUPERLATTICES

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Key Words: erbium, superlattice, optical spectrum, energy level

The $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ structures at $x = 0.1-0.2$ doped with erbium have been prepared by MBE method. The quantum wells in the $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ structures were formed by alternating of 1.4 InAs monolayer and 7 GaAs monolayers of general width about 12 nm. The width of GaAs barriers was equal to 25 nm. Erbium doping of the structure was achieved by Er introduction into quantum wells at the concentration $(2-3) \cdot 10^{19} \text{ cm}^{-3}$. Characterization of the fabricated structures was done with SIMS technique with the resolution of 5 nm and with X-ray spectrometer.

The SIMS measurements have shown that the maximum of Er concentration $2 \cdot 10^{19} \text{ cm}^{-3}$ takes place on heteroboundaries. Accordingly to the SIMS data in both undoped and doped samples quantum wells are formed by $\text{In}_x\text{Ga}_{1-x}\text{As}$ compound with some difference of the average indium concentration: 14% and 15%, correspondingly. The X-ray studies of the undoped and doped samples show that the structure of superlattice doped with erbium is more perfect than the structure without erbium. Specifically, the density of defects in undoped samples is about $1.2 \times 10^8 \text{ cm}^{-2}$ and less than or equal to $1.5 \times 10^7 \text{ cm}^{-2}$ in erbium doped samples. Besides, intensity of diffraction peaks in doped sample is more and their width is less than in undoped sample. The average misfit parameters for these structures obtained from X-ray data is equal to 0.3% and 0.4% correspondingly. The X-ray study also show the absent of the interfaces separating the InAs and GaAs layers in quantum wells, the quantum wells are formed by the homogenous InGaAs compounds. The width of quantum wells in Er doped structures, 12.2 nm, are somewhat wider than in undoped ones, 10.2 nm.

Absorption spectrum of undoped structure contains the sharp band at wavelength near 0.86 μm , attributable to the excitonic transition. There are also four absorption bands at $\lambda = 860, 852, 847, \text{ and } 842 \text{ nm}$, which are attributable to transitions from the heavy hole levels to electron miniband. For erbium doped sample an absorption band has moved to region of large wavelengths. The exciton peak in this case is more broader than in spectrum of the undoped sample and the fine structure of electron-hole optical transitions disappears. Besides, a new absorption band appears at the long wavelength side of the spectra, which is attributable to transitions from the heavy hole levels to second electron miniband. The Er related emission of wavelength 1.54 μm was observed in erbium doped samples.

We calculated the energy-band spectrum of the coincided structures using X-ray and SIMS data. Obtained results allow to explain the optical spectra of undoped and Er doped samples. In particular, the appearance of the second electron miniband in Er doped structures, where the quantum wells turn out to be somewhat deeper and wider than in the undoped samples. The broadening of the absorption spectra in Er doped samples is caused by the fluctuations of the electric field induced by the high concentration of the Er^{3+} ions on the interface.

ER DIFFUSION AND Er-INDUCED Ga-Al INTERDIFFUSION IN GaAs/AlGaAs QUANTUM STRUCTURES

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Key words: erbium, MBE growth, quantum structures, diffusion, interdiffusion

It is shown that the introduction of erbium in GaAs/AlGaAs quantum well structures in the process of growth by MBE leads to efficient interdiffusion of Ga and Al and diffusion of Er.

The erbium-doped structures were grown by MBE at $\sim 600^\circ\text{C}$ on GaAs substrates and consist of an $\text{Al}_x\text{Ga}_{1-x}\text{As}$ etch stop layer 600 nm thick with $x = 0.3$, then 50 quantum wells of 10-nm GaAs:Er well and 21-nm AlGaAs barriers. The concentration of erbium introduced into the GaAs QWs was controlled by the temperature of the erbium source. In all the samples there were also 0.9-nm AlAs spikes at each end of the barriers separating the GaAs:Er and AlGaAs. On top of the 50 QWs there was another identical 600 nm AlGaAs window to symmetrize the strain. Finally about 7-nm of GaAs was grown on top to prevent the AlGaAs from oxidizing. For comparison, a structure consisting of 8-nm GaAs:Er (900°C) layers separated by 22-nm of GaAs repeated 50 times with 300-nm of GaAs on top and a sample with $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ layer doped by erbium were also grown.

SIMS profiles measured for all the structures showed that destruction of QWs and levelling of concentrations of Er, Ga, and Al occur, and more pronounced the higher the concentration of erbium introduced into GaAs layers during the MBE growth. This fact indicates unusually fast diffusion of erbium and interdiffusion of gallium and aluminum for 600°C , the temperature of the GaAs substrate.

Further support for these conclusions is given by measurements of erbium photoluminescence which in the above structures exhibit spectra characteristic of AlGaAs matrix even at very low concentrations of erbium introduced. The latter result indicates also a sort of interaction between erbium and aluminum, so that erbium ions prefer to have aluminum in their close vicinity.

Possible mechanisms of erbium-induced Ga-Al interdiffusion and Er-Al interaction are discussed.

ER-INDUCED DEFECTS AND ERBIUM LUMINESCENCE IN MBE-GROWN AlGaAs:Er

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Key words: erbium, luminescence, defects, MBE-grown AlGaAs:Er

Two types of shallow traps with binding energies of 20 and 50 meV and a deep trap with the binding energy of about 400 meV were found in MBE-grown AlGaAs:Er. We have demonstrated that excitation of erbium luminescence occurs by the Auger process involving these three types of traps.

Photoluminescence studies in erbium-doped AlGaAs reveal three series of erbium emission lines at 1540 nm differing by their temperature dependence, lifetimes, and linewidths. The intensity ratio of lines inside the series is conserved over the whole temperature range studied. These three series of erbium luminescence correspond to $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition from the lowest excited state of the f-shell to the ground state. Three defect luminescence bands were also found besides exciton luminescence. The differences in positions of defect lines and exciton line were interpreted as the binding energies of defect states. Correlation between the temperature and pumping rate behavior of erbium and defect luminescence permits to connect each erbium series with a particular type of defect state from this set. We present experimental evidence for the conclusion that excitation of erbium ions occurs via Auger processes involving these three types of defects. Since AlGaAs is a wide gap semiconductor the excitation process occurs via higher excited states of the 4f-shell of erbium ion which is demonstrated by an observation of luminescence lines with the energies of 1.49 and 1.26 eV corresponding to the transitions $^4I_{9/2} \rightarrow ^4I_{15/2}$ and $^4I_{11/2} \rightarrow ^4I_{15/2}$. This fact indicates that a three-level excitation scheme for the luminescence on 1540 nm can be realized in AlGaAs:Er favoring the conditions for laser action. Temperature quenching of high energy erbium lines is also studied.

A mechanism of Auger excitation of erbium ions is proposed which involves recombination of a free electron with a hole at a defect with a transfer of the energy released via Coulomb interaction to the erbium ion. The excess energy is transmitted to the defect and released by phonon emission. This mechanism is consistent with the whole set of our experimental results including data on temperature quenching of erbium luminescence.

EXAFS MEASUREMENT ON LOCAL STRUCTURE AROUND ERBIUM ATOMS DOPED IN GaAs WITH OXYGEN CO-DOPING

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Key Words: EXAFS, erbium, oxygen, co-doping, local-structure, GaAs

Er-doped semiconductors are important for optical communication systems since one of the prominent luminescent peaks of Er at $1.5\mu\text{m}$ is in the minimum absorption region of silica based optical fiber. luminescence is intra-4f-shell transition of Er^{3+} . intra-4f-shell transition is stable regardless of and the temperature. III-V semiconductors are useful as host semiconductors for Er-doping because advanced growth techniques are available. Recently, the Er atoms doped in GaAs with O co-doping showed high efficient photoluminescence^[1], and the local structure around the Er atoms attracts strong interest because photoluminescence excitation measurement revealed that the Er formed many types of luminescent centers.

In this work, Er doped GaAs samples with O co-doping^[2] were investigated by fluorescence EXAFS (extended x-ray absorption fine structure) in order to study the local structure around the Er atoms. The sample was grown by OMVPE (organometallic vapor phase epitaxy) at 500°C . The concentration of the Er atoms in GaAs was $4.0 \times 10^{18} \text{ cm}^{-3}$. The EXAFS measurement was conducted using synchrotron radiation at beam line BL12C of the Photon Factory in the National Laboratory for High Energy Physics at Tsukuba. Er L_{III}-edge EXAFS was measured at 100K using polarized x-ray to [110] or $[\overline{1}010]$ direction. polarized x-ray, the position of the O atoms around Er atoms could be identified if many O atoms occupy the same sites. analyzed assuming several local structures around the Er atoms. For example, theoretical EXAFS spectra of Er atoms on Ga site with one O atom and three As atoms, and with two O atoms and two As atoms on the nearest As sites (Er-O and Er-2O structures) were calculated using FEFF6 program.

The measured $\chi(k)$ spectrum was Fourier transformed into R-space. In the Fourier transformed $\chi(k)$ spectrum, two near neighbor peaks were clearly observed which corresponded to O and As, respectively. The bond lengths of Er-O and Er-As were obtained to be 2.14Å and 2.79Å, respectively. The coordination numbers of both O atoms and As atoms were two. 2.14Å is close to the Er-O bond length, 2.27Å, in Er_2O_3 . If two As atoms and two O atoms locate on tetrahedral As sites in GaAs and the Er-O bond length is 2.17Å, the Er-As bond length must be 2.82Å. This value is close the obtained value, 2.79Å. The shape of the $\chi(k)$ spectrum agreed only with the calculated spectrum assuming the Er-2O structure.

Therefore we concluded that most of the Er atoms doped in GaAs with O co-doping constructed Er-2O structure even in the sample where many types of luminescent centers were observed. This result suggests that the difference of the luminescent centers are due to the difference of the configurations of atoms further than 2nd near-neighbors around the Er atoms.

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Er CENTERS IN GaAs:Er,O STUDIED BY OPTICAL SPECTROSCOPY UNDER HYDROSTATIC PRESSURE

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Key Words: GaAs, Er, oxygen, luminescence, hydrostatic pressure, trap levels

An optical spectroscopic study of Er centers in MOCVD-grown GaAs:Er,O under hydrostatic pressure is reported. At ambient pressure the host-excited photoluminescence (HEPL) spectrum of these samples is dominated by the sharp PL lines from one type of Er center[1]. The luminescence is in the 1.5 μm region and is due to the crystal-field-split intra-4f-shell transitions $^4I_{13/2} - ^4I_{15/2}$. By resonantly exciting the 4f-shell of the Er ions directly, at least 10 different types of Er centers with distinctly different PL spectrum are observed to be simultaneously present within the sample, these different types of Er centers being different complexes of Er with other impurity elements including native defects of GaAs[2].

Under the application of hydrostatic pressure several new transitions appears at 1.5 μm in a HEPL spectrum. By comparison with photoluminescence spectra obtained by resonant excitation of the Er 4f-shell at ambient pressure, the new luminescence is attributed to two types of Er center present in the sample but silent by HEPL at ambient pressure. For the Er centers observed at elevated pressures, a study of the temperature dependence of HEPL intensity as a function of pressure was made.

If the 4f-shell of the Er ion is excited by way of the non-radiative recombination of an exciton bound to an Er center-related trap level, the temperature dependence of HEPL intensity depends on both back-transfer (the opposite of the excitation process) and carrier thermalization from the trap level, the dominance of either process being determined by the position of the trap-level within the bandgap. The appearance of Er-related luminescence under the hydrostatic pressure is found to be well explained in terms of the trap level of the Er center entering the band-gap of the host. Furthermore, by studying the effects of the Γ/X crossover at ~ 40 kbar, where the GaAs band-structure changes from direct to indirect, and by considering the pressure coefficient of the trap depth, we deduced that both electron and hole traps are formed by the Er centers having different atomic configurations.

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LUMINESCENCE AND ANNEALING STUDIES OF Nd- AND Er-IMPLANTED GaN

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Key Words: gallium nitride, erbium, neodymium, ion implantation, photoluminescence

Strong rare-earth (RE) 4f-emissions from erbium and neodymium ion-implanted GaN have been observed through photoluminescence (PL) measurements. MOCVD-grown GaN was implanted with Nd and Er at ion energies of 910 and 1150 keV, respectively, with doses of 1×10^{13} and 5×10^{13} cm⁻² at room temperature. The implanted samples were annealed in a conventional furnace in flowing NH₃ gas at temperatures ranging from 700 to 1050 °C with a proximity cap. The results of annealing temperature dependent PL measurements showed that the optimal annealing temperature was 1000 °C for both Er and Nd, and surface degradation became evident for annealing above 1000 °C. PL measurements were also performed as a function of excitation laser wavelength from an Ar⁺-ion laser ranging from above (275 nm) and below (514.5 nm) bandgap energy at the sample temperatures ranging from 2 to 300 K.

Low temperature PL of the Nd-implanted GaN showed three well-resolved 4f-transitions of the $^4F_{3/2} \rightarrow ^4I_{13/2}$ at ~ 1.46 μ m, $^4F_{3/2} \rightarrow ^4I_{11/2}$ at ~ 1.14 μ m, and $^4F_{3/2} \rightarrow ^4I_{9/2}$ at ~ 0.98 μ m, which originate from the crystal-field split manifolds of the Nd³⁺ center. An energy level model is proposed which accounts for most of the observed transitions, and it is believed that all these emissions originated from only one non-cubic Nd³⁺ center. Numerous new luminescence peaks were observed as the wavelength of the laser excitation was lowered. The annealing behavior of the sample showed that appreciable Nd-related luminescence can be observed only after annealing the sample at 800 °C, and the PL intensity increased with the annealing temperature through 1000 °C. The $^4F_{3/2} \rightarrow ^4I_{11/2}$ emissions (~ 1.10 μ m) were found to persist to room temperature with no shift in energetic location. Oxygen coimplantation with Nd was found to result in no enhancement in Nd luminescence, and no changes in the annealing properties or peak locations.

The results of PL measurements of Er-implanted GaN showed two well-resolved 4f-transitions of the Er³⁺ center, the $^4I_{13/2} \rightarrow ^4I_{15/2}$ at ~ 1.54 μ m and the $^4I_{11/2} \rightarrow ^4I_{15/2}$ at ~ 1.00 μ m from the crystal-field split manifolds. The large number of emission peaks were observed along with numerous 'hot' lines from the sample temperature dependent PL. An energy level model requiring at least two non-cubic Er³⁺-centers is proposed, which accounts for the majority of the observed luminescence peaks. The Er-related luminescence signal is first observed for samples annealed at 700 °C, and increases in intensity with the annealing temperature through 1000 °C. Although the luminescence signal decreased with increasing sample temperature, the $^4I_{13/2} \rightarrow ^4I_{15/2}$ manifold (~ 1.54 μ m) was found to lose only one-half of its integrated intensity as temperature increased from 2 to 300 K. Oxygen coimplantation with Er was found to enhance the ~ 1.54 μ m peaks and lower the optimal annealing temperature from 1000 to 800 °C. The formation of Er-O complexes was thought to be responsible.

THEORY OF DISLOCATIONS IN GaN

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Key words : dislocations, gallium nitride, theory

First-principles calculations are carried out in large clusters and supercells containing threading edge and screw dislocations in wurtzite GaN. It is shown that the relaxation of the dislocation cores leads to the elimination of deep levels from the band gap in both types of dislocations and this can be understood in terms of chemical arguments. The screw dislocation with a filled core is unstable against one with an open core.

The edge dislocation does not possess a fully rebonded core and contains three-fold coordinated Ga and N atoms.

These dislocation core structures are contrasted with those found by similar methods for dislocations in GaAs and the implication of these results to the stability of optical devices is discussed.

Poster 2

VALENCE CONTROLS AND CODOPING IN LOW-RESISTIVITY N-TYPE DIAMOND BY AB-INITIO MOLECULAR-DYNAMICS SIMULATION

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Diamond is the most promising materials for the application of the high-speed, high-temperature, and high-power electronic-devices. It is well known that the fabrication of the low-resistivity p-type diamond is easy but that of n-type diamond is very difficult because of the super-widegap ($E_g=5.4\text{eV}$) semiconductors. In order to make materials design for the fabrication of the low-resistivity n-type diamond, we study the nature of the donor states (N, P, and B) and valence controls by the "codoping method (coping n- and p-type dopants at the same time)" in diamond using ab-initio molecular-dynamics simulations including 64 atoms in super-cell.

We find that the N is a deep donor with a large C3V pseudo-Jahn-Teller distortions (22% distortion of one C-N bond in C-C distance) at low-temperatures, and the self-trapped (C3v) N state with uniaxial symmetry changes to an isotropic donor state by the dynamical-Jahn-Teller hopping at high-temperatures. The hopping potential barriers is 0.18 eV in our calculation. P donor state with C3V states is more shallow than N, but the distortions of N are mainly breathing-type (10% distortion of four n.n. C atoms and 3.6% of P in C-C bond length). We discuss the difference of the electronic structure and the atomic configuration of N and P based upon the pseudo-Jahn-Teller interaction.

In order to make materials design to fabricate the low-resistivity n-type diamond, we have calculated the stable atomic configuration and electronic structure of the codoping of n- (N and P) and p-type (B) dopants at the same time. We discuss the stability of the Madelung energy with forming p- and n-type dopant-pair and the lattice-relaxation energy with large atomic size (P) and small atomic size dopants (B) at the same time. We discuss the optimization of the codoped atomic configurations of p-type B and n-type 2N (or 2P) pairs in diamond, and the materials design how to make the low-resistivity n-type diamond.

A FIRST PRINCIPLES STUDY OF INTERSTITIAL Si IN DIAMOND

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Key Words: silicon, interstitial, vacancy model, diamond, *ab initio* theory.

Si is known to be incorporated in diamond in the form of dispersed impurities: the isotopic data available for the twelve-line, 1.682 eV zero-phonon-line structure arising from a complex of Si with a vacancy correlates with the natural abundances of Si. However there has long been suggestion that Si may also exist in the form of an interstitial.

Local-density-functional calculations are used to examine the structure of interstitial Si in diamond. It is found that Si is only marginally stable in the <100> and <110> split-interstitial configurations. When Si is placed at the T_d site, the structure spontaneously reconstructs to form a substitutional Si site close to a self-interstitial. This structure is lower in energy than the split configurations by more than 6 eV.

Consequently, calculations have also been performed on substitutional Si close to a <100> self-interstitial. It is found that there is a binding between the interstitial and Si atom: the lowest energy configuration is found where the Si atom lies at a next-nearest neighbour site from the site shared by the two carbon interstitial atoms. Separating them by a further lattice site increases the total energy by around 1 eV.

It is concluded that Si would not adopt an interstitial location in diamond, but may form complexes with interstitial carbon.

BREAKDOWN OF THE VACANCY MODEL FOR IMPURITY-VACANCY DEFECTS IN DIAMOND

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Key Words: nitrogen, vacancy model, diamond, *ab initio* theory.

Vacancy impurity complexes are important defects in large band gap materials like diamond as they often give rise to characteristic optical lines and magnetic signatures. The vacancy model for impurity vacancy defects in semiconductors assumes that the ground and low energy excited states are derivable from the four sp^3 hybrid orbitals on atoms bordering the vacancy. This means that the optical spectra and magnetic structure can be calculated with some confidence and there are many cases where this model works: for example, the substitutional impurities N, P and Si bordering a vacancy within diamond. But we describe here a counter-example concerning the lowest excited state of the [V-N₃] defect. This well-known defect has been characterised in EPR, optical absorption and luminescence studies. It is shown that the defect possesses a shallow electron trap, localised outside the vacancy, which is involved in the lowest excited state of the defect and responsible for the weak N2 and N4 optical bands associated with the defect. This shallow state has a very important effect on the lifetime of the dominant N3 luminescent band. The important point is that this state does not arise from the sp^3 hybrids of the vacancy and is then an example where the model has broken down.

The implication of this result to the general understanding of vacancy-like defects in diamond and the consequences for the recombination of photo-excited carriers in other systems will be discussed.

ISOTOPIC SHIFTS OF THE N3 OPTICAL TRANSITION IN DIAMOND

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Keywords: diamond, isotopes

The N3 centre in diamond consists of three substitutional nitrogen atoms each of which is a nearest neighbour to the same vacant lattice site. The centre is found in most natural diamonds, and has important gemmological consequences. The centre can also be created in laboratory conditions by heating any diamond which contains N atoms. Since it is now possible to synthesise diamonds with excellent control of their properties, N3 centres can be created in isotopically controlled diamonds. However, to the best of our knowledge the effects have not yet been reported. Here we show that the N3 zero-phonon line, at 2.985 eV in natural diamond, is shifted by $+0.14 \pm 0.07$ meV in ^{12}C diamond doped with ^{15}N , with no detectable change in the vibronic bandshape. In ^{13}C diamond, the phonon energies of all features in the vibronic band appear to be reduced from ^{12}C diamond in the ratio $(12/13)^{1/2}$, and the zero-phonon shift is $+4.5 \pm 0.2$ meV.

The carbon isotope shift can be understood as the sum of three terms. The first two are familiar in this type of study, the third is novel:

- 1) The lattice for a ^{13}C diamond is known to be larger than for ^{12}C , and, from the known response of the N3 line to hydrostatic stress, the expansion shifts the N3 zero-phonon line by 0.3 meV.
- 2) The vibrational frequencies are likely to be different in the ground and electronic states. The effect of the isotopic change can be estimated from the temperature dependence of the energy of the N3 line, at 2.7 ± 0.4 meV.
- 3) In addition, there is a weak Jahn-Teller effect in the excited state. This JTE coupling has the effect of reducing the zero-point energy in the excited E state compared to the ground state (where there is no JT coupling). With no JT coupling in the E state the zero-point energy of the two e-modes is $\hbar\omega$, the effective quantum of the modes. As the JT coupling increases the potential surface becomes the well-known Mexican hat, with complete rotational freedom in the e-mode space about the undistorted configuration. The zero-point energy is quenched to zero for these rotations, leaving only $1/2 \hbar\omega$ for the zero-point energy. Consequently isotope substitution changes the energy of the zero-phonon line, and the effect is estimated for the N3 centre at ~ 1 meV.

The sum of the three contributions gives an expected carbon shift of ~ 4 meV, close to the measurement. In contrast, the lack of nitrogen-induced isotope shift is surprising, and implies that qualitatively the optical electron at the centre is remote from the N atoms. This conclusion agrees with ENDOR measurements for the ground state, but still has to be reconciled with theoretical studies of the centre.

FORMATION AND RELAXATION OF HYDROGEN-RELATED DEFECTS IN THE SUBSURFACE REGION OF DIAMOND FILMS

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Key Words: hydrogen, diamond films, metastability, cathodoluminescence

It is known that the hydrogen plasma produces a *p*-type high-conductive layer near the surface of diamond films. Recently, we have found a new luminescence peak around 540 nm from the subsurface region of hydrogen-plasma-treated homoepitaxial diamond films. It is ambiguous that these two phenomena originate in the same defects or not. In order to clarify this relation, we performed cathodoluminescence (CL) spectroscopy and the current-voltage measurements of diamond films treated in various hydrogenation conditions.

Diamond films were deposited on synthetic Ib diamond (001) substrates using a plasma-enhanced CVD apparatus with 0.5 % CH₄ diluted by H₂ gas. These films were oxidized by acid solution, followed by a thermal annealing at 400 °C for 30 min in N₂ atmosphere. After the oxidation, they were again exposed to hydrogen plasma under various conditions.

A specific broad peak around 540 nm is observed in the subsurface region of diamond films treated by hydrogen plasma at 800 °C. Contrary to this, it is not observed in the films hydrogenated at 500 °C. However, this peak suddenly appears after low-energy (10 kV) electron beam irradiation. In accordance with this change, the electron beam irradiation leads to a change in the conductivity of the films. Namely, the conductivity of the films hydrogenated at 500 °C increases after the electron beam irradiation, and it becomes the same as that at 800 °C.

The accelerating voltage dependence of the CL spectra indicates that the hydrogen related luminescent state exists in the surface region and its density decrease drastically with increasing the depth from the surface. The depth distribution of these states become slightly broader with increasing hydrogenation duration, that corresponds to the SIMS depth profile of the films treated by deuterium plasma.

These results indicate that (1) the hydrogen-related luminescence is originated in the defects which bring the high-conductive layer and (2) a metastable configuration exists in this hydrogen-related defects and a relaxation into a stable state occurs by the low-energy electron beam irradiation.

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FINESTRUCTURE OF THE BORON BOUND EXCITON IN DIAMOND

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Key Words: diamond, boron bound exciton, finestructure

Natural and high-temperature high-pressure (HPHT) diamonds are studied with cathodoluminescence at low temperatures and high spectral resolution. All samples unintentionally contain boron which is optically identified by the emergence of the boron bound exciton (BE) recombination radiation in the spectra. Spin orbit interaction of the holes splits the BE emission into a doublet (BE^{TO}: 5.215 eV and 5.227 eV) as known from the literature.

No-phonon transitions of the BE at 5.356 eV and 5.367 eV are weakly allowed due to the large localization energy of 55 meV at the boron acceptor. In our samples, they are strong enough to study them in detail with the benefit of drastically reduced linewidths compared to the phonon-assisted recombination radiation. This allows us to resolve a fourfold finestructure of either spin-orbit BE^{NP} component. The observed finestructure is similar to the structure in acceptor bound exciton emission in silicon. There, valley-orbit interaction of bound electrons induced by the acceptor binding lifts the sixfold degeneracy of the conduction band minima.

The Lorentzian lineshape of the exciton no-phonon emission lines is correlated with the bound exciton lifetime and we estimate a value of ≤ 4 ps at 35 K. The temperature dependence of these transitions is also discussed.

HYDROGEN AND HYDROGEN-LIKE DEFECTS IN DIAMOND

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The importance of diamond as a semiconductor material is receiving much interest. Hydrogen is known to passivate active dopants in the diamond lattice, catalyse the growth of CVD diamond and to affect many of the properties of diamond. Positrons, muons and protons and atoms formed from these positive particles have been used to study the behaviour of implanted hydrogen in diamond. This paper reviews the results of these studies.

INVESTIGATION OF ION IMPLANTED BORON IN DIAMOND

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Key Words: diamond, boron, ion implantation, β -NMR

Boron is known to be responsible for the p-type semiconductivity of natural type IIb diamonds, where it forms an acceptor level at 0.37 eV. In the laboratory, attempts at producing p-type diamond layers by boron ion implantation have been reported by several authors. However, for the dopant atom to be electrically active it must reside on a regular lattice site, usually substitutional.

Here, we report on the determination of the fraction of implanted boron atoms that take up defect-free sites in diamond. A particularly effective technique for such a study is β -NMR in which spin-polarized nuclear probes, here: ^{12}B , are implanted at extremely low concentrations, typically 10^8 cm^{-3} into the host lattice [1]. The polarization is detected via the β -radiation emitted during the decay of ^{12}B to ^{12}C , otherwise the technique is comparable to conventional nuclear magnetic resonance. Polarized ^{12}B was produced in the reaction $^{11}\text{B}(\text{d},\text{p})^{12}\text{B}$ with 1.5 MeV deuterons, and recoil implanted into a single crystal diamond Ib target. Resonance depolarization spectra were measured in an external magnetic field of 1 kG at sample temperatures ranging from 300 to 800 K. The polarization amplitude was relatively small, yielding a fraction at defect-free tetrahedrally symmetric sites of 10(1) % at 300 K, increasing to 15(2)% at 800 K. The spectra also showed that some of the boron probes occupy low symmetry sites. Temperature dependent measurements of the polarization amplitude show evidence of an annealing stage at $T \sim 650 \text{ K}$. The results are discussed and compared to the implantation behaviour of other dopants in diamond, see e. g. [2].

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STUDY OF DEFECTS IN DIAMOND FILMS BY ELECTRICAL MEASUREMENTS

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Keywords: Diamond films, Electrical properties, Defect, Microstructure, Raman

Diamond films grown by Microwave Plasma Assisted Chemical Vapour Deposition (MPCVD) present a complex structure due to the natural formation of defects during the growth of the diamond microcrystals. In the film surface, the different crystal orientations and size create a large number of defects arising from the bulk of the crystal, the grain boundaries and from non-terminated crystal surfaces. Many of these defects electrically active are localised at the interfacial layers that are mainly non-diamond phases. They act as an effective way of carrier generation and transport, competing with the natural states of the defects in diamond phases.

Free standing diamond films about 5 μm thickness (determined by IR measurements) are used in this work. Atomic Force Microscopy shows a very uniform surface morphology with preferred $\langle 111 \rangle$ orientation crystals with an average size about 1 μm . The surface analysis is performed by a micro-Raman mapping that shows some heterogeneities along the surface, with varying relative intensities of the diamond Raman line at 1333 cm^{-1} , and contributions from non diamond phases.

Ohmic contacts with gold evaporated in both surfaces of the samples are used to study the electrical behaviour with applied fields up to 10^6 V/m in the temperature range from 10 K to room temperature. The temperature dependence of the current in the low temperature range (11-100 K) give an activation energy of 0.09 eV, much lower than the observed for higher temperatures. This contribution increases when the grain size decreases. This behaviour is attributed to tunnelling across the grain boundaries, and related with the non-diamond phases revealed by the Raman spectra.

RADIATION DAMAGE OF DIAMOND AND SILICON BY HIGH ENERGY NEUTRONS, PROTONS AND α PARTICLES

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Key Words: Silicon, Diamond, Radiation damage, Particle detectors

In the new generation of particle accelerators, such as the Large Hadron Collider, the detectors will have to operate after very high doses of radiation. The conventional silicon detectors will have to be modified to cope with the radiation doses expected and new materials such as diamond are being considered to replace them.

While the particle physicists have developed very sophisticated computer simulations to show how any sort of exotic particle penetrates materials and to simulate the detection mechanisms, they do not include any treatment of the damage caused to the materials. On the other hand, there are excellent ion implantation models which track the multiple damage caused by ions, but they do not need to model the damage due to other particles.

When a high energy particle passes through a solid it may displace an atom, transferring much of its momentum to that primary knock-on atom, and this can cause a cascade which constitutes the major damage to the material. We have used the particle physicists' simulations, GEANT, MICAP and FLUKA, to predict the damage caused by neutrons at energies from 0.1 to 10 MeV, and then used the ion implantation simulation TRIM to find the damage caused by the knock-on atoms produced from the neutron collisions with host atoms. Most of the experimental data is from neutrons with an energy profile peaking around 1 MeV, so the results are compared with that energy range. We find that the primary damage is 112 ± 2 vacancies per 1 MeV neutron cm^{-1} in silicon and 68 ± 7 vacancies per 1 MeV neutron cm^{-1} in diamond. However, most of these vacancies recombine with the displaced interstitials while the irradiation takes place, so the observed damage is only a very small proportion of this (figures around 2% are quoted for Si).

The damage due to protons and α particles can be modelled directly by TRIM, as these particles are ions themselves. The total damage due to 1 MeV protons is 7.3 ± 7 vacancies cm^{-1} in diamond and 18.4 ± 4 vacancies cm^{-1} in silicon, and for α particles the comparative figures are 51 ± 5 and 135 ± 3 respectively.

Comparison with experimental results for the damage due to proton and neutron irradiation in silicon and electron irradiation in diamond, allows us to predict how much of the damage anneals out, that is, how many of the displaced atoms recombine with the vacancies they left behind. We can use this information, with the TRIM predictions of collision processes, which tell us the energies of the displaced atoms as well as their positions, to determine the profiles of the actual damage produced by high energy particles as a function of depth into the material.

CAPACITANCE SPECTROSCOPY OF THE DEEP CENTERS IN THE SiC.

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Key Words: Deep centers, DLTS, Silicon carbide, luminescence, recombination.

In the present work parameters and distribution of deep centers in 6H, 4H and 15R SiC epitaxial layers and pn junctions made by sublimation in an open system, container free liqued phase epitaxy and CVD were investigated. In case of pn junctions structures with undoped base and with base doped by B or Al were used.

Deep levels ionization energies and holes and electrons capture cross - sections were determined with DLTS and i-DLTS technique. In 6H SiC were identified five mane types of deep centers and several analogs of it in other SiC polytypes. It has been found Deep levels which connected with blue, green and yellow (for 6H SiC) electroluminescence bands. Also it were founded Deep levels which could govern the recombination processes in the investigated p-n structures.

Compensation and overcompensation of the higly pure n-type epilayers, grown by different technological methods, by deep acceptor centers was observed. Possible structure of the observed centers was discussed.

This work was supported in part by Arizona University (USA).

THE INFLUENCE OF THE INCORPORATION AND DESORPTION OF CH_n GROUPS ON THE DEFECT CHARACTERISTICS IN α -SiC:H FILMS

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Key Words: SiC, thin films, microvoids, positron annihilation, FTIR, thermal desorption

The defect structures in carbon rich α -SiC:H films deposited on various substrates using ditertiary butyl silane (DTBS) and electron cyclotron resonance chemical vapour deposition were investigated as a function of thermal treatment.

Isochronal annealing was carried out in steps of 50 °C from 200-650 °C for 30 min at each temperature. After each annealing step FTIR and UV-VIS absorption measurements were performed. The energy gap of the α -SiC:H films was deduced from the transmittance spectra of the film deposited on a quartz substrate using a Perkin-Elmer UV-VIS spectrometer in the range of 300-700 nm. The FTIR spectra were recorded at room temperature relative to an uncoated FZ-Si substrate and the Si-C, Si-H and C-H absorption bands were analyzed. A variable energy positron beam was used to observe changes in the defect structure during *in-situ* annealing by measuring the Doppler broadening of the annihilation line. For the gas evolution experiments the samples were inserted into a desorption chamber and heated to 800 °C at heating rates of 2 and 10 °C/min. The partial pressures of H, H₂, CH, CH₂, CH₃, and other species were monitored by a quadrupole mass analyzer and were used as a measure of the evolution rate.

Films grown at high deposition rates were found to contain hydrogen trapped in voids. The origin of these microvoids was identified to be the incorporation of CH_n groups. At high gas flow rates, CH_n bonds are not sufficiently broken by the plasma and are directly incorporated in the films. The effusion of CH_n groups with increasing annealing temperature promotes void growth. At annealing temperatures above 600 °C, Si-H and C-H bonds are broken and the films become more interconnected due to the formation of additional C-C bonds. As a consequence, the void structure is annealed out and the films become more tensile.

THE MICROSCOPIC STRUCTURE OF SHALLOW DONORS IN SILICON CARBIDE - STUDIES WITH MAGNETIC RESONANCE

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Key Words: EPR, ENDOR, SiC, shallow donors, effective mass theory, valley-orbit splitting

The most important shallow donor in SiC is nitrogen which is inadvertently incorporated by the Lely growth. Although nitrogen donors have been investigated for many years by electron paramagnetic resonance (EPR) in several polytypes [e.g. 1-3], open questions have remained with respect to the differences in hyperfine (hf) interactions observed in EPR for the various inequivalent lattice sites. In order to obtain a better picture of the electronic ground state nitrogen donors in 6H-, 4H- and 3C-SiC were investigated by measuring the nitrogen hyperfine (hf) interactions with electron nuclear double resonance (ENDOR) with higher precision than possible in EPR. It was shown that the hexagonal site donor in 6H- and 4H-SiC has an unexpectedly small isotropic hf interaction constant and a significant anisotropic hf interaction constant. An explanation of the small isotropic hf constant (it is a factor of 14 smaller than that of the quasi-cubic sites) had been attempted by considering the Kohn-Luttinger interference factors and the differences in the stacking order along the c-axis [4]. It is the purpose of the present work to extend the ENDOR investigations to 4H-SiC and 3C-SiC as well as to investigate in detail the superhyperfine (shf) interactions in 6H-SiC. Shf interactions with many shells of ^{13}C and ^{29}Si were measured. The hf and shf interactions are discussed in the framework of effective mass theory and the role of the chemical nature as well as of the valley-orbit interaction are considered when taking central cell corrections into account.

It is also shown that the temperature dependence of the hf splitting of the EPR spectra can be understood on the basis of the thermal occupation of the two lowest effective mass states with A_1 and E symmetry split by the valley-orbit interaction. The interpretation of the temperature dependence of the nitrogen hf interactions led us to propose that EPR spectra of phosphorous donors observed hitherto in neutron transmuted 6H-SiC [4,5] and ascribed to substitutional phosphorous donors [5] as well as to phosphorous-vacancy pair defects [4,5] may all be due to substitutional phosphorous donors on the two quasi-cubic and hexagonal Si sites occupying a ground state with E symmetry at low temperature (<10K) and a state with A_1 symmetry at high temperature (>60K).

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THEORETICAL STUDIES ON OXYGEN IN SiC

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Keywords: oxygen, silicon carbide, theory

Knowledge about the state and motion of oxygen as well as its reactions in the bulk and on the surface of silicon carbide are required to design appropriate technological steps for preparing well controlled MOS structures. Preliminary results of an attempt to acquire general knowledge about the behavior of oxygen in various polytypes by means of theoretical methods are presented. Quasi-static semi-empirical quantum chemical and ab initio LDA calculations in cyclic and molecular cluster models, as well as quantum molecular dynamics calculations with an LDA based tight binding Hamiltonian have been carried out on cubic SiC to study the possible substitutional and interstitial configurations, charge state, and diffusion mechanism of an isolated oxygen atom. Similar calculations in 2H and 4H polytypes are in progress.

RAMAN SCATTERING ANALYSIS OF DEFECTS IN 6H-SiC INDUCED BY ION IMPLANTATION

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Key Words: 6H-SiC, Raman scattering, ion implantation, defect annealing

The development of electronic devices and integrated circuits in SiC technology has to take into account the low diffusion coefficients of impurities in SiC. This forces to use ion implantation for selective doping of the active areas in the devices. In this context, one of the main drawbacks of this material is the very high stability of the defects induced by ion implantation, which are important to be investigated. On the other hand, among the different polytypes, 6H-SiC is interesting for electronic applications due to the availability of single crystal wafers already in a commercial stage, being envisaged in the next future a strong enhancement of crystalline quality and wafer size

This work reports about the Raman scattering analysis of ion implantation processes in 6H-SiC as a function of the implant species, temperature and anneal treatment. So, SiC wafers were implanted with B or Al ions in a multiple implant process giving a 200 nm thick buried implanted layer with a concentration of $5 \times 10^{19} \text{ cm}^{-3}$ at different temperatures in the broad range between room temperature and 1000°C . Pieces from these wafers have been flash lamp annealed at 1700°C during 20 milliseconds.

The measured spectra show a strong dependence of the intensity of the main Raman modes on the treatment parameters. The analysis of the normalized intensity of these modes allows to evaluate the level of damage induced by the implantation process, as well as its recovery. There arise three defect related bands in the spectra, located at about 177 cm^{-1} , 270 cm^{-1} and 550 cm^{-1} . Having similar shape for different implantation species, these bands appear in the same spectral region as the Si-Si related vibrational modes from amorphous Si, which suggests a similar structural origin. On the other hand, the comparison between the different samples points out the higher stability of the defects induced by the Al implant and corroborate the absence of a complete defect recovery by the annealing process. These data are correlated with those previously reported from different implanted species and anneal treatments [1,2].

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ELECTRON IRRADIATION INDUCED DEFECTS IN 6H-SiC AND THEIR ANNEALING BEHAVIOUR

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Keywords: SiC; electron irradiation; positron annihilation

In this contribution, we report results of an investigation of electron-irradiation induced defects in 6H-SiC using positron lifetime and Doppler-broadening spectroscopies. The experiments were performed on n- and p-type single crystalline wafers, purchased from CREE Research, spanning carrier concentration $N_D - N_A = 5-40 \times 10^{17} \text{ cm}^{-3}$ and $N_A - N_D = 1 \times 10^{17} \text{ cm}^{-3}$. Some of the samples show that depending on doping type and doping level, defects are already present in the as received state. These defects could not be annealed out by heat treatments as high as 1400 °C.

After irradiation with 2.5 or 10 MeV electrons at room temperature within a dose range of $(0.6-12) \times 10^{17} \text{ cm}^{-2}$ two defect lifetimes could be resolved in our samples, one at 160 and the other at 260-270 ps [1]. The 160 ps lifetime arises from neutral carbon vacancies, which are introduced at much higher rates than the positively charged carbon vacancy in electron-irradiated n-type 3C-SiC as determined by EPR measurements [2].

The irradiation induced defects anneal out in three sharp annealing steps at about 100 °C, 700 °C and 1300 °C. The significant reduction of carbon vacancies at 100 °C suggests that annealing of defects occurs during the irradiation as well as during storage at room temperature. The two high-temperature annealing steps suggest that carbon vacancies have formed impurity vacancy complexes.

Low temperature measurements after electron irradiation at 100 K are currently in progress to determine the type and concentration of the initial created defects and to clarify whether annealing and/or clustering of these defects takes place between 100 and 300 K.

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LATTICE DEFECTS IN $\text{Si}_{1-x}\text{Ge}_x$ EPITAXIAL DIODES INDUCED BY 20 MeV ALPHA RAYS

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Key words; $\text{Si}_x\text{Ge}_{1-x}$ strained epitaxial layers, 20-MeV alpha ray irradiation, deep levels

Results are presented of an extended study on the lattice defects induced in $\text{Si}_{1-x}\text{Ge}_x$ epitaxial devices by irradiation with 20-MeV alpha rays. The germanium content and radiation source dependence on the generation of deep levels in the strained $\text{Si}_x\text{Ge}_{1-x}$ epitaxial layers and on the degradation of device performance are also reported taking into account the number of knock-on atoms (N_d) and the nonionizing energy loss (NIEL).

Strained layer $n^+ - \text{Si}/p^+ - \text{Si}_x\text{Ge}_{1-x}$ epitaxial diodes are used in this study. The germanium content of the strained $\text{Si}_x\text{Ge}_{1-x}$ epitaxial layer with 100 nm nominal thickness is $x = 0.08, 0.12$ and 0.16 . The boron concentration of the strained $\text{Si}_x\text{Ge}_{1-x}$ epitaxial layer is about $6 \times 10^{17} \text{ cm}^{-3}$. The diodes were irradiated by 20-MeV alpha rays at room temperature in the AVF cyclotron in TIARA at the Takasaki Radiation Chemistry Research Establishment. The fluence of alpha rays was varied between 10^9 and $5 \times 10^{13} \text{ 1/cm}^2$. The irradiation was performed without applied bias to diodes.

The deep levels induced in the $\text{Si}_x\text{Ge}_{1-x}$ epitaxial layer and Si substrate of the devices were studied using deep level transient spectroscopy (DLTS) methods. Thermal anneals of the irradiated devices were performed to investigate the recovery of the lattice defects and the device performance.

The damage coefficient of electrical performance calculated for alpha ray irradiation is close to that for proton and neutron irradiation, while it is about three orders of magnitude larger than as for electron irradiation. The degradation increases with decreasing germanium content, which is due to the different N_d and NIEL originating from the difference of mass and possibility of nuclear collision. For the $x = 0.08$ diodes, only hole capture levels ($E_v + 0.45 \text{ eV}$) are observed for fluences below $1 \times 10^{13} \text{ 1/cm}^2$, while both electron ($E_c - 0.50 \text{ eV}$) and hole capture ($E_v + 0.44 \text{ eV}$) levels are detected for a fluence of $5 \times 10^{13} \text{ 1/cm}^2$. Most probably the electron capture levels are associated with an interstitial boron complex and are related to the increase of reverse current and the decrease of capacitance in the $\text{Si}_x\text{Ge}_{1-x}$ epitaxial layer.

ELECTRONIC PROPERTIES OF DEFECTS INTRODUCED IN N- AND P-TYPE $\text{Si}_{1-x}\text{Ge}_x$ DURING ION ETCHING

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Key Words: SiGe, ion etching, particle irradiation, defects, DLTS

Surface processing and in particular dry or plasma etching of semiconductors is a key technology for device processing. As ion assisted etching becomes more widely and routinely applied for device fabrication, especially for smaller dimensions, it is important to understand the damage introduced by the processing itself. Low energy particle bombardment also plays an important role in controlling the growth and properties of MBE grown Si and SiGe layers. We have used deep-level transient spectroscopy (DLTS) in an investigation of the electronic properties of defects introduced in phosphorus doped n-type $\text{Si}_{1-x}\text{Ge}_x$ ($x=0$ to 0.25) during 1 keV argon and 0.75 keV helium ion-etching and those introduced by 0.75 keV argon-ion etching of boron doped p-type $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0$ to 0.20). The defects introduced during ion etching are compared to those detected after α -particle irradiation.

1 keV helium-ion etching (fluence = $1 \times 10^{12} \text{ cm}^{-2}$) introduces six electron defects (EHe1 - EHe6) in n-type material, prior to the deposition of gold Schottky barrier diodes (SBDs). The defects detected after etching are compared to those introduced by 5.4 MeV alpha-particle (α -) irradiation and, also, RF sputter-deposition of Au SBDs on material from the same wafer. Four of the electron defects (EHe1, EHe2, EHe4 and EHe6) are detected in Si. The remaining two defects (EHe3 and EHe5) are only detected in material containing germanium. It was noted that defects introduced during the He-ion etch process have the same DLTS "signatures" as defects after the sputter deposition process, but none were the same as those introduced during the α -particle irradiation.

0.75 keV Ar-ion etching and 5.4 MeV α -particle irradiation introduced the same prominent defects in strained p- $\text{Si}_{1-x}\text{Ge}_x$. The activation energies of the defects were found to decrease in the same fashion as the decrease in bandgap with increasing Ge concentration, suggesting that they are pinned to the conduction band. We have tentatively identified the defects to be structurally similar to the V_2^{+0} and a trap at $E_v + 0.50 \text{ eV}$, which are observed in p-Si after Ar-ion etching and α -particle irradiation. Due to the low concentrations of O and C in our samples, hole traps corresponding to the $\text{C}_i - \text{O}_i$ and $\text{C}_i - \text{C}_s$ (metastable) defects were not detected. We have also used DLTS to determine the depth distribution of the defects.

Ge CONTENT DEPENDENCE OF THE INFRARED SPECTRUM OF INTERSTITIAL OXYGEN IN CRYSTALLINE Si-Ge

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Key Words : silicon-germanium; silicon; oxygen; vibrational mode; infrared spectroscopy

The infrared vibrational mode absorption of interstitial oxygen (O_i) in bulk crystalline $Si_{1-x}Ge_x$ has been investigated as a function of the Ge content ($x = 0.03$ to 0.07). The Czochralski-grown crystals¹ contained oxygen in concentrations of $(5-6) \times 10^{17} \text{ cm}^{-3}$ as determined from the 1106 cm^{-1} room temperature absorption band.

Spectra at 5K reveal that this absorption band is more complex than in Si and consists of several components with maxima shifted towards lower wavenumbers with respect to the well-known 1136.4 cm^{-1} peak for $x = 0$. With increasing x the lower wavenumber components become gradually more important. Similar results have been obtained by Yamada-Kaneta et al.² for smaller x -values which may be regarded as complementary to the present data. The different components are attributed to oxygen interstitials perturbed by Ge neighbours at different positions with respect to the oxygen (second nearest neighbours and higher). Calculations show that the relative magnitude of the components as a function of x cannot be explained by a "chemically ordered" distribution of Ge atoms as assumed in ref.2. A fair agreement is however obtained when the occurrence of the different centres is calculated using a cell of 512 atoms into which the Ge atoms are distributed at random. This model also enables the incorporation of more distant neighbours in the calculations allowing to simulate the position of the least shifted components which are unresolved.

Raising the temperature towards 50K enables the observation of additional transitions starting from higher levels of the ground state multiplet (hot transitions). Decomposition and assignment of the spectra are made using experimental and calculated results obtained at 5K.

Other experiments concern the 1206 cm^{-1} band of O_i for which a decrease of the integrated absorption and a shift to higher wavenumbers are found with x increasing, in perfect continuation of the data of ref.2.

The relevance of the data with respect to theoretical models of interstitial oxygen in Si is discussed.

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ROLE OF NON-RADIATIVE DEFECTS IN THERMAL QUENCHING OF LUMINESCENCE IN SiGe/Si STRUCTURES GROWN BY MOLECULAR BEAM EPITAXY

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Key Words: non-radiative defects, SiGe, Si, MBE, luminescence, ODMR, thermal quenching

Recent rapid advances in modern epitaxial growth techniques have enabled the fabrication of high quality Si epilayers and Si-based low-dimensional artificial structures, and have awakened the long-sought desire for efficient Si-based light detectors and emitters, aiming at a monolithic integration of both optical and electronic devices based on the mature Si technology. To overcome the inherent low radiative efficiency of this indirect bandgap material system, both bandgap and doping engineering have been attempted. On the contrary, another important issue, i.e. important grown-in defects such as carrier lifetime limiting defects, has hardly been addressed so far in these systems. These lifetime limiting defects are known to be predominantly nonradiative in Si and SiGe, and have largely eluded from studies by various optical spectroscopies. They may undermine the progress of bandgap and doping engineering and will play a key role in determining the success of Si-based layered structures in potential applications in minority-carrier devices, in particular opto-electronic devices.

Most recently we have revealed [1], by the optical detection of magnetic resonance (ODMR) technique, several efficient grown-in non-radiative centers in undoped and B-doped Si epilayers and SiGe/Si heterostructures grown by molecular beam epitaxy (MBE). A dominant defect is proven to be the vacancy-oxygen (V-O) complex in Si. Experimental evidence on the formation mechanisms of these non-radiative defects has been provided as being due to a low surface adatom mobility and a lower desorption rate of O contamination from the growing surface during low temperature growth, and also due to ion bombardment as occurs e.g. during potential enhanced doping. In this work, we provide direct evidence that these non-radiative defects are largely responsible for a rapid thermal quenching of luminescence from SiGe quantum wells (QWs), impairing practical applications of these structures at room temperature. We show that the dominant mechanism responsible for a strong thermal quenching of SiGe QWs grown at low temperatures ($< 500^{\circ}\text{C}$) is due to a thermally activated, efficient non-radiative recombination channel, with a rather low activation energy of about 5 meV. This leads to a complete quenching of luminescence at a temperature as low as 30 °K. A post-growth hydrogen treatment is demonstrated to be only moderately effective in passivating the non-radiative defects and in reducing thermal quenching. Post-growth thermal annealing at high temperature (e.g. $> 500^{\circ}\text{C}$) is, on the other hand, shown to be highly effective and leads to a nearly complete removal of the non-radiative defects monitored in the ODMR experiments. By removing these non-radiative defects and thus the shunt pass for carrier recombination, a significant improvement in thermal quenching behavior of luminescence from the SiGe/Si structures has been achieved. The thermal quenching, in this case, is dominated by the intrinsic thermal activation of the holes from the QWs with an activation energy of about 80 meV when the Ge composition is around 20 %. These results correlate very well with effects of hydrogenation and thermal annealing of the non-radiative defects monitored in the ODMR experiments. Selective optical excitation above and below the bandgap of the Si barriers has been used to determine relative contributions of nonradiative recombination channels present in the SiGe QWs and the Si barriers.

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SCHOTTKY DIODES ON $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ ALLOYS : MEASUREMENT OF OFF-SET BANDS BY DLTS.

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Key words : SiGe/Si, SiGeC/Si, RTCVD, DLTS, Band offset

Adding substitutional carbon in SiGe alloy provides an additional parameter in strains manipulation and allows an increase of the critical thickness. However, the main electronic property features of this new ternary alloy are still unknown and in particular the value of the band offsets in the SiGeC/Si system. So, we propose to use electrical measurements to evaluate this parameter which is fundamental for devices modeling.

We have studied Schottky diodes tungsten (W) to p-type $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$ prepared by Rapid Thermal Chemical Vapor Deposition (RTCVD) with a Ge composition of 10% and C content varied from 0 to 0.74%. We have characterized them by Deep Level Transient Spectroscopy (DLTS) technique. We observed a deep level whose density decreases with C concentration ($5.37 \times 10^{14} \text{ cm}^{-3}$ for 0% and $1.42 \times 10^{13} \text{ cm}^{-3}$ for 0.74%) while its activation energy increases with C concentration (0.44 eV for 0% and 0.51 eV for 0.74%). This result shows that this level is probably due to the relaxations in the alloy.

Supposing that this level has a fixed binding energy referred to the vacuum state or to an internal energy level in SiGe and SiGeC, this study points out the possibility to use such a DLTS results to measure valence and conduction Band offset in SiGeC/Si system.

POSITRON LIFETIME STUDY OF ELECTRON-IRRADIATED SILICON-GERMANIUM BULK ALLOYS

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Key Words: SiGe, Positron lifetime, Electron irradiation, Vacancy-type defect

Positron lifetime measurement has been performed using Czochralski-grown $\text{Si}_x\text{Ge}_{1-x}$ bulk crystals ($x=0-0.82$) before and after the 3 MeV electron irradiation at room temperature. From the measurements before the irradiation, the positron lifetime in the bulk state (bulk lifetime) was determined. It was found that the bulk lifetime varied from those for Ge (235 ps) to Si (222 ps) with increasing x . The dependence of the bulk lifetime on x seems to be discontinuous at around $x=0.20$. This behavior is analogous with the abrupt change in the indirect band gap of $\text{Si}_x\text{Ge}_{1-x}$ crystal due to the switch of conduction band minima from Ge-like L-points to Si-like X-points. The discontinuous change in the positron lifetime at $x=0.20$ reflects the discontinuous change in the overlap integral of wavefunctions of positron and electron. Probably, the response of electrons to positrons is different in Ge-like ($x<0.20$) and Si-like ($x>0.20$) regions due to the different band structure in each region.

After the irradiation, the second lifetime component due to vacancy-type defects were detected for $x>0.20$, but not for $x<0.20$. The lifetime of the second component was 330 ps for $0.20<x<0.42$ and decreased to 280 ps for $x>0.63$. These results show that (i) the concentration of vacancies is under the detection limit for $x<0.20$, (ii) vacancy clusters such as tri- and quadri-vacancies are formed for $0.20<x<0.42$ and (iii) small vacancies such as mono- and di-vacancies are generated for $x>0.63$. Mono- and divacancies in Ge are known to be unstable at room temperature. Monovacancies in Si are also unstable at room temperature but survive as complexes with impurities. Divacancies in Si are known to be stable at room temperature. The above results reflect the fact that the thermal stability of vacancies changes from Ge-like one to Si-like one with x . It is interesting to note that vacancies start to survive at around $x=0.20$ (i.e., the thermal stability of vacancies abruptly changes at around $x=0.20$) where the conduction band minima switch from Ge-like L-points to Si-like X-points. The properties of vacancies in $\text{Si}_x\text{Ge}_{1-x}$ crystal may correlate with the band gap.

ACCUMULATION OF CARRIERS IN A SHALLOW DONOR EXCITED STATE OF GaP:Te

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Key Words: shallow donors, phonon assisted tunneling, recombination kinetics

Tellurium shallow donors in Gallium Phosphide have been ionized by means of phonon assisted tunneling in the electric field of pulsed far-infrared laser radiation [1]. In response to the laser pulse a photoconductive signal has been detected with a fast component reproducing the laser pulse and a slow component which rises after the irradiation has ceased and finally exponentially decays with a strongly temperature dependent time constant in the range of microseconds to several milliseconds.

This peculiar temporal structure of the signal is explained by a nanosecond timescale cascade capture mechanism in highly excited Coulomb states and subsequent accumulation of carriers in an excited state with vanishingly small direct recombination probability to the ground state, identified as the valley-orbit split $1s(E)$ -level of Tellurium.

Recombination from there is finally achieved by micro- to millisecond timescale thermal excitation into somewhat higher lying s- and p-states and subsequent radiative transitions into the ground state, which is proved by the observation of mid-infrared luminescence. The whole effect yields a possible application as infrared semiconductor impurity laser.

[1] S D Ganichev, I N Yassievich, W Prettl; *Semicond. Sci. Technol.* **11**, 679 (1996)

A SHARP DEFECT-ANNEALING STAGE NEAR 170K IN IRRADIATED N-TYPE INDIUM PHOSPHIDE

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Key Words: InP, irradiation, low temperature annealing, Frenkel pairs

Indium phosphide is of increasing interest for electronic and opto-electronic devices, and information is therefore needed on the properties and natures of lattice defects that may be produced in this semiconductor during crystal growth, ion-implantation processing etc. The defects present in the device material result from all the defect reactions that take place during the growth and processing, including those that can occur at room temperature itself. Irradiation of semiconductors at low temperature, as in the present work, is a controllable means of introducing and studying defects that are unstable at room temperature.

In this investigation we have introduced defects into n-InP by irradiation at 85K using 1.0 MeV protons. It is expected that in such irradiation most of the radiation-damage collisions produce rather simple lattice defects. For study of the electronic properties of the defects, we have used in-situ capacitance-voltage-temperature measurements and majority-carrier deep level transient spectroscopy, in association with post-irradiation heat treatments to determine the thermal stabilities and thermal annealing properties of the defects.

We find that the irradiation of the n-InP at 85K creates a DLTS peak near 120K that is removed by heat treatment to room temperature. By standard DLTS procedures we measure the thermal ionisation energy and electron-capture cross-section of the defect concerned as 0.20 eV and $2 \times 10^{-15} \text{ cm}^2$ respectively. Our isochronal heating experiments between 85K and 300K show that the defect is removed in a sharp annealing stage centred near 170K for 30-minute heatings, and that the annealing is consistent with first-order reaction kinetics of thermal activation energy 0.5 eV and pre-factor approximately $1 \times 10^{11} \text{ s}^{-1}$. This pre-factor value indicates that the defect annealing involves a rather small number of defect jumps, and therefore strongly suggests that the annealing stage near 170K is due to interstitial-vacancy combination within a Frenkel-pair defect of either indium or phosphorus. It seems very likely that this annealing process is the same as the one that occurs over the temperature range 150-200K in strongly n-type InP after high-dose irradiation by 2.0 MeV electrons at 20K, as observed in positron-annihilation experiments by Tornqvist et al. 1994 (ICDS-17: Materials Science Forum 143-147 347) and suggested by them to be associated with the annealing of indium vacancies. In such case, we deduce that the Tornqvist et al. defect has an electronic level in the upper half of the InP band gap and that its electron ionisation energy is 0.20eV.

ALPHA RADIATION INDUCED DEEP LEVELS IN P-InP

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Keywords: Radiation-induced defects, InP, DLTS, Defect reactions.

Deep level defects induced by alpha radiation in p-type InP crystals, grown by low pressure metalorganic chemical vapour deposition (LP-MOCVD) have been studied by deep-level transient spectroscopy (DLTS). Two prominent hole-emitting levels with thermal activation energies 0.34 eV and 0.39 eV to the valence band and three electron-emitting levels with activation energies 0.22 eV, 0.29 eV and 0.37 eV in the upper half-gap have been detected immediately after irradiation by 5.48 MeV alpha particles. These have been identified with the H3, H4 and E_C , E_A and E_D defects, respectively, hitherto observed as a result of electron and/or gamma irradiation. Another prominent hole level H5 at $E_v+0.58$ eV emerges as a result of minority carrier injection, following irradiation. Although both H4 and H5 are found to have temperature dependent capture cross-sections but the capture barrier for H5 is found to be significantly different than that reported in these earlier irradiation studies. Interesting transformations of the majority carrier deep levels are observed both with minority carrier injection and room temperature annealing. Our measurements provide new information on the changes observed in the deep level spectra as a result of minority carrier injection. In particular, no evidence is found for the recently proposed inter-conversion of the H5 and E_A defect.

INFLUENCE OF THE DISLOCATION LOOPS ON THE ANOMALOUS DIFFUSION OF THE Fe IMPLANTED INTO InP

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Key words : Fe-implantation, InP, anomalous diffusion, end of range loops

Semi-insulating layers in InP crystals can be obtained by implanting Fe. This paper reports on the study of the relationship between the anomalous diffusion of Fe implanted in undoped InP substrates and the dislocation loops left after annealing. To his aim, two types of samples were examined : 1) InP crystals with a room temperature single implant of 2 MeV Fe implantation at a dose of $5 \cdot 10^{13} \text{ cm}^{-2}$ at 200°C, followed by an implantation of P at 5 MeV a fluence of $2 \cdot 10^{14} \text{ cm}^{-2}$ at room temperature. Annealing was performed at 650 and 750°C for 1.5 hr. The dopant and defects distributions were measured by SIMS and TEM, respectively.

The as-implanted samples of type 1) were amorphous. After annealing the amorphous layer was replaced by a band of twins and a band of end of range (EOR) extrinsic loops, mostly of the Frank type, located at the former a/c interface. Loop coarsening was observed by increasing the annealing temperature. SIMS spectra of the annealed samples showed an anomalous distribution of Fe, evidenced by the presence of two very close peaks of Fe accumulation at two positions that correspond to the depths of the EOR loops and of the bottom edge of the twin band. This indicates that the anomalous diffusion of Fe is determined by Fe gettering at such defects.

In samples of type 2), no damage was introduced by Fe implanted at 200°C, whereas P implantation produced a buried amorphous layer. Upon annealing two bands of loops formed, i.e. a band of EOR loops at the bottom a/c interface of the buried layer and a band of loops at the depth where the two interfaces of the buried layer have met. These two bands lay far beyond the Ferich region, namely at a depth of $\sim 2.5 R_p$ and $\sim 2R_p$, respectively, R_p being the projected range of Fe implanted at 2 MeV. Even now an anomalous Fe diffusion occurred by annealing, as two Fe accumulation peaks were detected at positions corresponding to the two bands of loops confirming that Fe distribution is strongly affected by trapping of Fe at the dislocation loops, generated by the condensation of self-interstitials of the host matrix, rather than by formation of Fe precipitates. Fe gettering very likely took place at the partial dislocations bounding the loop. The correlation between the efficiency of Fe trapping by the EOR loops and the dynamics of loop coarsening has also been studied.

HOMOGENEITY OF Fe-DOPED InP WAFERS USING OPTICAL MICROPROBES

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Key Words: InP, Fe-doping, photocurrent, photoluminescence, homogeneity

Semi-insulating InP is used as a substrate for optoelectronic applications. Major requirements for these substrates are uniformity and low defect concentration. In order to get high resistivity doping with iron is required. The inhomogeneous distribution of iron produces fluctuations in the electrical and optical properties, which reduces the useful wafer surface.

The non uniformity of the electrical and optical properties in these wafers appears at both long and short range, since it is influenced by the dopant segregation and the presence of crystallographic defects (dislocations, microprecipitates, twins...). The study of the origin of these inhomogeneities is of great value in order to understand their formation mechanisms and the procedures to remove them. Therefore, experimental techniques that provide meaningful assessment of the inhomogeneities related to electrically active iron in Fe-doped InP wafers have a great interest for the improvement of the growth conditions and the treatments to be applied to the samples.

We present herein results concerning scanning photocurrent and scanning photoluminescence in semi-insulating Fe-doped InP wafers. Both, the photocurrent and the photoluminescence signals are related to the presence of electrically active iron. The photocurrent fluctuations are governed by the fluctuations in the $[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$ concentration ratio, while the photoluminescence efficiency is strongly limited by the electrically active iron concentration, which is a non radiative recombination center, limiting the minority carrier lifetime. A correlation between both techniques should allow to understand the origin of the $[\text{Fe}^{3+}] / [\text{Fe}^{2+}]$ fluctuations. Several examples are presented for illustrating the main issues regarding electrically active iron distribution in Fe-doped InP.

STUDY OF THE IRON-RELATED DEFECTS ON Si-InP CRYSTALS BY POSITRON ANNIHILATION SPECTROSCOPY

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Key Words: Indium Phosphide, Iron, Positron Annihilation

Semi-insulating InP is a basic material used in the fabrication of optoelectronic devices. The standard method to obtain high resistivities is doping with iron which acts as a deep acceptor and compensates the residual shallow donors. However, iron also introduces many problems which are not completely understood. For example, the charge compensation mechanism of iron has not yet been well explained: the total concentration of Fe atoms necessary to get an effective compensation and render the material semi-insulating has to be much higher than the concentration of the residual shallow donors. It is believed that the excess of iron atoms is forming part of microprecipitates (1).

Irradiation with thermal neutrons may be used for doping purposes in semiconductors. In InP a precise concentration of tin atoms are introduced from the transmutation of In. This doping method also introduces other defects, mainly indium vacancies (V_{In}), in amounts that increase with the neutron fluence (2).

The aim of this work is to investigate the effect of the iron when an increasing amount of defects is introduced in the InP matrix by thermal neutron irradiation. Information on the interaction between Fe and irradiation-related defects is derived from positron lifetime measurements. For this purpose, several samples of semi-insulating InP (Fe doped) obtained from the same ingot were irradiated with thermal neutrons at different fluences, yielding concentrations for the tin-transmuted atoms between 4×10^{15} and 10^{18} cm^{-3} . Before irradiation the positron lifetime spectra are fitted with a unique value of 247 ps. After neutron irradiation, it has been identified a new lifetime of 340 ps which nature has been explained in terms of a new complex defect consisting of an iron impurity and a neutron-induced-indium vacancy. The constant value obtained for the intensity of this lifetime component indicates that the ratio between the concentration of the two components of the complex (Fe: In-vacancy) remains constant which probably means that part of the iron comes from the dissociation of precipitates caused by the neutron irradiation. By comparing with the results obtained in unintentionally doped InP, it is clearly observed that iron inhibits the positron trapping into the V_{In} -related defects. The temperature dependence of the lifetime parameters has also been investigated in the range between 14K and 295K. It appears to confirm that the mentioned positron traps are neutral with a complex structure.

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(2) B. Mari, F.J. Navarro, M.A. Hernandez and J. Riera 1996 Nucl. Instr. And Meth. B 120 240

OSMIUM RELATED DEEP LEVELS IN INP AND THEIR INTERACTION WITH ALPHA RADIATION

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Keywords: Transition-metal impurities, InP, Defect complexes, Radiation effects.

Transition metals are known to create near-mid-gap deep levels leading to electrical compensation of semiconductors needed for producing semi-insulating material. Iron is one such dopant for InP, but suffers from the serious drawback of strong thermal instability associated with its high diffusion coefficient. Osmium has been tried for this purpose as part of our extensive programme to search for a possible alternative dopant from the 4d and 5d transition metals. Osmium doping has been carried out during growth of InP crystals by low pressure metalorganic chemical vapour deposition (LP-MOCVD). We report results of a combined electrical and optical DLTS study of Os-doped InP. Two prominent deep levels in the lower half-gap, labelled OsA and OsB, and one in the upper half-gap (OsC) have been detected. All of these have been found to show strongly field-dependent emission characteristics and activation energies. Detailed comparison of reduced-reverse bias, electrical injection and optical DLTS spectra yields important information on their relative capture cross-sections for the majority and minority carriers, necessary to ascertain their role in determining the electrical properties of the material.

Preliminary results of the investigations of the response of the Os-related deep-levels in p-InP to irradiation with alpha particles, carried out to probe their microscopic structure, are also reported. The minority carrier (electron) level OsC is found to show a strong enhancement while the majority carrier levels OsA and OsB show only a slight increase with irradiation. The strong enhancement of OsC indicates that this defect is either a complex of Os with the radiation-induced primary defects such as the two types of vacancies and interstitials or is electrically activated by the presence of these defects.

DEFECTS ANALYSIS IN InAlAs/InGaAs HETEROSTRUCTURES GROWN ON (111) INP SUBSTRATES.

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Nowadays, there are great interests in the optical and electronical properties of strained compounds grown on InP substrates. Depending on the crystallographic orientation, effects such as high electronic properties or Quantum Confined Stark Effect have already been demonstrated. In the past, a large quantity of works was devoted to the study of the defects present in heteroepitaxial mismatched layers of $\text{In}_x\text{Ga}_{1-x}\text{As}$ or $\text{In}_x\text{Al}_{1-x}\text{As}$ grown on (100) oriented InP substrates. Those studies showed that depending on the Indium composition and technological parameters, a network of misfit dislocations, the presence of islands due to the tridimensional growth, or composition inhomogeneities can contribute to the structure relaxation. Recently, technological efforts have been devoted to the obtention of strained InAlAs/InGaAs Quantum Well structures grown on (111) oriented InP substrates. Nevertheless, few work has been performed in order to understand the mechanisms of relaxation in this case. In this study, we present the characterization by Atomic Force Microscopy and Transmission Electron Microscopy InGaAs/InAlAs heterostructures grown by Molecular Beam Epitaxy on (111)B 1° off toward [-211] oriented InP substrates. The AFM observations have revealed stepped like surface morphology that is analysed not only taking into account the misorientation but also the possible influence of strain induced effects already observed on the (100) substrates. For the QW structures the combination of both techniques allows us to conclude that the most part of the observed defects are developed in the plane of growth and originate from both interfaces delimiting the QW.

CLUSTERING MECHANISM OF SELF INTERSTITIALS IN Si

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Key Words: silicon, self-interstitial, cluster, clustering mechanism

Self-interstitials play an important role in various phenomena in Si such as self-diffusion, dopant diffusion and their agglomeration. Nevertheless, an isolated self-interstitial has never been observed by any experimental techniques in a convincing manner.

We proposed a fully reconstructed cluster of four self-interstitials (I4) in Si, whose structure is in common with extended defects such as {113} defects, reconstructed surfaces and dislocations in Si. Our electronic computation has already shown that the I4 model is more stable than four isolated interstitials; 2.2 eV per interstitial. Also, neither floating bonds nor dangling bonds exist in the cluster. This result implies that self-interstitials tend to form clusters.

For understanding the clustering mechanism of self-interstitials, we have performed an energy calculation using Stillinger-Weber potential through lattice-relaxation procedure. A supercell of 444 cubic unit cells is assumed in which we insert one or more <100> split interstitials. A single [100] split interstitial generates dilatation in lattice on (100), while compression appears at the above and below of it along [100]. Therefore, whenever each interstitial locates in the dilatation side of the other interstitial, the elastic energy may be reduced. In addition, rebonding further reduce the energy. We have found by the computation that the energies of a single interstitial and its agglomerates containing two, three or four interstitials are 5.3, 3.9, 3.0 and 2.2 eV per interstitial, respectively. The agglomeration of four interstitials forms the I4 cluster with fully rebonding. Although the I4 cluster is four-coordinated, a defect localized state (0.37 eV) appears inside the minimum band gap, occupied by two electrons in the ground state. Thus, self-interstitials in the cluster forms are virtually impossible to be detected by EPR, TEM and other standard experimental techniques.

FRENKEL PAIRS AND IMPURITY-DEFECT INTERACTIONS IN P-TYPE SILICON IRRADIATED WITH FAST ELECTRONS AND Γ -RAYS AT LOW TEMPERATURES

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Key words: silicon, irradiation, defect interaction

There is a lot of experimental information about impurity-defect interactions in Si. As a matter of fact, this information has been extracted from radiation experiments mostly. On the other hand, the production of Frenkel pairs (primary defects), a key process in such experiments on Si, cannot be observed directly by any technique available. Because of this our knowledge of Frenkel pairs, their properties and behaviour is scarce, even the threshold energy for atomic displacement in Si is a matter of controversy. From a practical point of view, Si containing group-III impurities in high concentrations is a suitable object for radiation experiments, since Frenkel pairs, if separated during irradiation, can give rise to the formation of secondary defects whose properties have been studied in detail. The present work is concerned with production and annealing processes of defects in heavily doped p-Si following electron irradiation at $T \leq 5$ K. Commercial Czochralski-grown Si wafers doped with B and Ga were used. The dopant concentration is running from $7 \cdot 10^{17} \text{ cm}^{-3}$ to $3 \cdot 10^{19} \text{ cm}^{-3}$, thus covering under the same irradiation conditions an impurity range from moderately doped materials to degenerate ones. Electron irradiations (2.5 MeV) were carried out using beam currents ranging from $1 \mu\text{A/cm}^2$ to $15 \mu\text{A/cm}^2$. Electrical measurements (Hall effect and resistivity) were taken following irradiation and annealing. Additionally, we discuss how the separation of Frenkel pairs can be affected by high and low electronic excitation conditions during gamma-irradiation of non-degenerate p-Si. Important results of this work are summarized in the following:

The production rate of Frenkel pairs in degenerate p-Si (about 1 cm^{-1}) turned out to be independent of the beam current over the range studied. Our Hall effect measurements showed that this rate is constant even at high doses, up to $8 \cdot 10^{18} \text{ cm}^{-2}$, when the irradiated material becomes strongly compensated. Under the same irradiation conditions, the fraction of Frenkel pairs giving rise to the formation of secondary boron-related defects is decreased by nearly 30 percent with decreasing boron concentration from $3 \cdot 10^{19} \text{ cm}^{-3}$ to $8 \cdot 10^{17} \text{ cm}^{-3}$, thus reflecting partial loss of intrinsic defects to different reaction paths. The relationship between the production rates of primary and secondary defects is discussed. Boron-related defects start to anneal at around room temperature, as is expected for interstitial boron atoms and boron-vacancy complexes. In contrast, Ga-related defects were found to be more stable and can only be annealed out at elevated temperatures.

For non-degenerate p-Si, one can readily realize low and high electronic excitation conditions during low-temperature gamma-irradiation making use of Si:B, Si:Ga, and Si:In with different ionisation energies. In this way it has been shown that under high excitation conditions the production rate of secondary defects is greatly enhanced, at least by a factor of five, as compared to low excitation conditions. It means that the fraction of Frenkel pairs reacting with group-III-dopants during irradiation is strongly charge-state dependent.

IMPLANTATION OF REACTIVE AND UNREACTIVE IONS IN SILICON

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Key Words: Implantation, Silicon

We present the results of a series of experiments, performed in our laboratory, on the implantation of SIMEQ1 keV/amu reactive (H, C, N, O) and unreactive (He, Ar) ions into silicon. In particular we investigated on the possibility of producing chemical bonds between the projectile and the target atoms searching for the appearance of characteristic IR bands. When the impinging ions are reactive (H, C, N, O) they form bonds with the Si atoms in the target that are evidenced by IR spectroscopy. Implantation with argon rules out the possibility that the new bands are due to a damage into the crystalline structure of silicon.

IMPURITY-VACANCY COMPLEXES FORMED BY ELECTRON IRRADIATION OF CZOCHRALSKI SILICON.

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Keywords: Positron Annihilation, Silicon, Irradiation

A comprehensive study of electron irradiated Czochralski Si has been conducted using positron lifetime and Doppler broadening spectroscopies.

Eight samples, ranging from heavily doped n-type to heavily doped p-type, were irradiated simultaneously at room temperature to facilitate quantitative comparisons between the samples. The influence from the oxygen impurity was also investigated by comparison with oxygen-free Si. It is noteworthy that positron annihilation experiments can be conducted on highly conductive materials unlike the cases of infrared and electron paramagnetic resonance.

For lightly doped materials (dopant concentration less than $5 \times 10^{16}/\text{cm}^3$) the irradiation damage is dominated by free and negatively charged divacancies for the dose employed in this work ($1.2 \times 10^{18} \text{ e}^-/\text{cm}^2$). For the heavily doped materials (dopant concentrations larger than $5 \times 10^{17}/\text{cm}^3$) vacancy-dopant complexes dominate, some of which involve divacancies, and in these samples very high introduction rates of the vacancies (up to 2 cm^{-1}) could be estimated for n-type materials.

In $5 \times 10^{17} \text{ P}/\text{cm}^3$ doped samples neutral P-V_2 complexes dominate while in the case of $5 \times 10^{18} \text{ P}/\text{cm}^3$ P V complexes are found. Isochronal annealing of the latter sample indicates three annealing stages, one around 70°C , another around 200°C and a third around 350°C . In $5 \times 10^{17} \text{ B}/\text{cm}^3$ doped samples no vacancies could be detected, likely due to vacancies being positively charged, but in $5 \times 10^{18} \text{ B}/\text{cm}^3$ doped samples, positively charged defects (B V_2) could be detected due to their high concentration.

The high introduction rates observed in both n+ and p+ samples suggest a significant reduction in vacancy interstitial recombination during the irradiation. Association of divacancies with P, Sb and B dopants was found to modify significantly the Doppler S parameter relative to the value for free divacancies.

APPLICATION OF SPIN DEPENDENT RECOMBINATION FOR INVESTIGATION OF THE POINT DEFECTS IN IRRADIATED SILICON

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Key Words: electron paramagnetic resonance, spin dependent recombination, radiation defects

New methods of detection the electron paramagnetic resonance (EPR) spectra of point defects in silicon crystals based on the effects of spin dependent recombination (SDR) and resonance change of the microwave photoconductivity of samples were developed. Being four orders of magnitude more sensitive than traditional EPR technique these methods allow to detect EPR spectra of the paramagnetic recombination centers and spectra of their excited spin 1 states when the concentration of defects is low and not enough for detection by usual EPR.

We report the results of the investigation the radiation defects in low dose irradiated silicon crystals and in crystals irradiated by 1 MeV electrons at high temperatures of 150 - 450 °C.

The main attention is given to study the SDR-EPR spectra of the excited triplet state of carbon related centers in pure float-zone silicon crystals. The detection of SDR-EPR spectra was performed in the wide temperature range of 3.8 - 80 K. The change of symmetry of SDR-EPR spectra of the excited states due to the temperature activated motion of the carbon-interstitial - carbon-substitution complex was investigated.

Several new SDR-EPR spectra and spectra attributed to the excited spin 1 states of divacancy and complex phosphorus+vacancy were investigated in the wide temperature range. It was found that different SDR-EPR spectra are observed at different temperature range. These results show that the contribution of the defects of different types to the processes of spin dependent recombination depends on the temperature.

New SDR-EPR spectra were found also in silicon crystals irradiated by 1 MeV electrons at high temperatures.

ELECTRICAL AND OPTICAL CHARACTERISATION OF DEFECTS INDUCED IN EPITAXIALLY GROWN N-SI DURING 1 KEV NOBLE GAS ION BOMBARDMENT

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Key Words: DLTS, IV, CV, defects, dry etching, Schottky diodes, defect engineering

Low energy noble gas ions are routinely used during dry etching, such as ion beam etching (IBE) and reactive ion etching (RIE), of semiconductors to achieve anisotropic etches. During these processes, energetic ions impinge the substrate creating damage to its sub-surface region. This damage alters the electrical and optical properties of the semiconductor and hence the characteristics of the devices fabricated thereon. Defect engineering, which requires that defects are introduced in a reproducible and controlled fashion, has been successfully used to modify the lifetime of minority carriers and tailor the barrier heights of Schottky barrier diodes (SBDs). However, the physical nature of the defects and their introduction rates have to be known, together with their electronic properties and concentrations.

We have used deep level transient spectroscopy (DLTS) to determine the electronic properties, as well as the spatial distribution of the defects introduced in n-Si during 1 keV ion bombardment using He, Ne, Ar, Kr and Xe ions. To learn more about the nature of these defects, we have compared their electronic properties to those of the primary defects induced during MeV alpha-particle and electron irradiation (most of which have been structurally identified). Amongst other defects the C_i-C_s , VO- and VP-centres, and $V_2^{-/0}$ (after annealing at 180 °C for 30 min) have been observed in all bombarded samples.^{1,2} We have explained the non-detection of $V_2^{-/0}$ to be due to the presence of stress fields in our low energy bombarded samples. He- and Ne-ion bombardment were found to introduce a similar set of defects, with a higher concentration of defects being introduced by Ne ions. The heavier noble gas ions created a different set of defects in Si, which we have attributed to their higher rates of nuclear stopping. Some of the low energy defects could be due to vacancy clusters (larger than divacancies) and the incorporation of noble gas ions into these clusters.

The photoluminescence (PL) intensities of the C-line (789.4 meV) and G-line (969.5 meV)³ transitions corresponding to the C_i-O_i defect, with an energy level at $E_v + 0.36$ eV, and the metastable C_i-C_s defect,² respectively, were investigated as a function of incident ion mass, dose and energy. The PL intensities of both spectral lines were found to decrease with increasing bombarding ion mass. For Ne ion bombardment, their PL intensities reached maximum values at a fluence of $1 \times 10^{12} \text{ cm}^{-2}$ and, thereafter, decreased. We propose that the reductions in intensities of the spectral lines are due to the introduction of increased amounts of non-radiative recombination centres. DLTS measurements were used to validate our proposition. The energy dependence of the PL intensities of the G- and C-lines is described qualitatively by considering the integral sum of defects created by ions with energies in the range 1 - 150 keV over the excitation depth of our Ar-ion laser in Si. The energy deposited by the bombarding noble gas ions to energetic recoils is also considered.

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INTRINSIC POINT DEFECT ENGINEERING IN SILICON HIGH-VOLTAGE POWER DEVICE TECHNOLOGY

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Key Words: silicon, intrinsic point defects, defect formation

The field of Intrinsic Point Defect Engineering started in the 70's. It is based on the idea that non-equilibrium intrinsic point defects (IPDs) take part in forming the structural defects and electrically active centers as well as in the diffusion of impurity atoms. Those ideas led to the development of different methods of gettering and passivation of defects in silicon devices.

Difficulties in studying the process of generation and relaxation of IPDs during the heat treatment are related to two factors. Firstly, vacancies and self-interstitials cannot be observed as free single defects. They can be studied only relying on the indirect data of structural defects, their electrically active centers and the diffusion of doping impurities. Secondly, due to a low concentration of these defects their nature cannot be investigated by such methods as the electron paramagnetic resonance, the optical absorption, etc.

The study the effects of IPDs on the formation of oxidation stacking faults and on the doping impurity diffusion provided a basis for the development of intrinsic point defect engineering in microelectronic device technology. The purpose of our work is to overview the results of our investigations on the influence of IPDs generated under high temperature annealing (characteristic of high-voltage power devices) on the behavior of swirl-defects in dislocation-free FZ-Si, on the formation of electrically active centers in neutron transmutation doped silicon and high voltage p-n junctions and on the deep diffusion of aluminium in Si.

The type and concentration of generated IPDs was controlled by changing the medium in which the heat treatment took place. The heat treatment in the oxidizing atmosphere results in the generation of self-interstitials; the heat treatment in the inert atmosphere and in vacuum is accompanied by supersaturation of silicon with vacancies, while the heat treatment in the chlorine-containing atmosphere makes it possible to control the type of the dominating IPDs. X- and γ -ray diffraction, TEM, X-ray topography by Lang, DLTS, temperature dependence of minority carrier lifetime and reverse current volume component, microplasma spectroscopy techniques were used to study the properties of defects and structures.

In conclusion, list the some obtained results: (I) IPD parameters were determined from the study of the swirl-defect behavior during high temperature annealing and of the diffusion of aluminium; (ii) a diffuse scattering of γ -rays on the IPD-related defects was discovered; (iii) for the first time, the generation of vacancy defects was observed directly, after the heat treatment of Si in the chlorine-containing atmosphere; (iiii) deep level centers, whose appearance was related to IPDs, were identified.

ELECTRICAL CHARACTERIZATION OF NEUTRON IRRADIATED *PIN* OXYGENATED SILICON DETECTORS

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keywords: radiation damage, electrical properties, DLTS, detectors

Radiation damage is known to constitute a strict drawback to the application of Silicon as a particle detector, particularly in high energy physics experiments. Many questions are still open about the nature of defect centers introduced by the radiation. At present, Oxygen is under investigation as candidate center responsible of improving the radiation hardness of silicon detectors for what concerns leakage current and type-inversion behaviour.

We have evaluated the effect of neutron irradiation on both oxygenated and not oxygenated *pin* Silicon detectors. Current-voltage measurements as a function of the temperature and capacitance-voltage measurements at different frequencies have been performed to better understand the effect of the defects due to the neutron irradiation on the electrical properties.

Direct information about the trap parameters, as concentration and energy levels, has been deduced by DLTS measurements. For some traps, the capture-cross section has been calculated by using time variable filling pulses in DLTS measurements.

MODES OF VO₃ AND VO₄ DEFECTS IN NEUTRON IRRADIATED SILICON

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Key Words: Silicon, defects, neutron irradiation, annealing

The understanding of formation and evolution with temperature of defects in irradiated silicon is still incomplete especially in the high temperature range. Results gathering from various experimental techniques have given significant evidence about the structure of various multivacancy-multioxygen complexes in silicon. However, the picture is not finished yet in all its details. A variety of experimental signals exist which has not been definitely correlated with certain defect structures.

Using IR spectroscopy we have investigated the LVMs of various defects appearing in Cz-grown silicon ($[O_i]_0 = 10^{18} \text{ cm}^{-3}$) after fast neutron irradiation, in room temperature and subsequent thermal annealing, with special interest on VO₃ and VO₄ defects. A simple theoretical model employing semiempirical calculations has been used to calculate the vibrational frequencies of these defects. When the 883 cm^{-1} band of VO₂ defect anneals out at $\approx 450^\circ\text{C}$ three bands at 899 , 962 and 993 cm^{-1} attributed to VO₃ [VO₂+O_i] defect appear in the spectra. At a slightly higher temperature another peak at 978 cm^{-1} previously attributed in the literature to a modified VO₃ defect emerges. Our calculations favour attribution of this defect to a [VO₂+VO₂] structure. On further annealing, when the bands of VO₃ defect disappear from the spectra, two bands at 983 and 1004 cm^{-1} appear. They have been correlated with VO₄ [VO₂+2O_i] defect, in oxygen implanted Si. However in our studies, in neutron irradiated Si, the above bands are not present and another pair of bands at 1032 and 1043 cm^{-1} always appears which also have been related to [VO₂+2O_i] defect. Our theoretical analysis support correlation of 983 and 1004 cm^{-1} bands with VO₄ defect. Furthermore, the question concerning the identity of the structure related to 1032 and 1043 cm^{-1} bands is discussed and complexes like V₄O₂ or V₅O₂, which are known to exist at these temperatures, are considered as possible candidates.

PERFORMANCE DEGRADATION OF MICROCRYSTALLINE AND AMORPHOUS SILICON-BASED p-i-n DETECTORS UPON He^4 IRRADIATION

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Keywords: Radiation damage, microcrystalline silicon, infrared detector

Radiation damage in various crystalline semiconductor materials, in particular silicon, after irradiation with both electron or proton beams in the 1 to 10 MeV range has been studied in detail since a number of years (1). In this contribution we compare the degradation of amorphous and microcrystalline silicon thin films after exposure to a 1.6 MeV He^4 beam. In particular, we study the changes in the spectral response of infrared-sensitive fully microcrystalline p-i-n detector structures.

The samples were deposited on glass substrates coated with indium tin oxide as back contact, followed by p-type, intrinsic, and n-type silicon layers and a top metal contact. The total areal thickness was about 0.3 mg/cm^2 . The He^4 beam was focussed to about 1 mm in diameter. The fluences ranged from 10^{13} to 10^{17} cm^{-2} . We expect a homogenous profile of newly created defects since the energy loss is only 0.5 MeV/mg/cm^2 .

As an example, after a fluence of $2 \times 10^{15} \text{ cm}^{-2}$ the open-circuit voltage of the amorphous p-i-n structure drops by about 90 mV from the initial value of 750 mV measured under illumination with 633 nm light from a HeNe laser. The short-circuit current, however, is reduced by a factor of five. This is in accordance with previous results obtained from Schottky barrier type structures after irradiation with a proton beam (2). Under higher fluences the spectral response shifted from the red portion of the visible spectrum to the blue region.

Contrary to what one would expect from the inhomogenous nature of microcrystalline silicon thin films, the microcrystalline devices also showed a shift of the spectra, indicating a reduction of the internal electric field due to newly created charged defects.

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RAMAN SCATTERING MEASUREMENTS IN NEUTRON-IRRADIATED SILICON

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Key words: neutron irradiation, silicon, radiation damage, Raman scattering

Neutron transmutation doping is one of the well-known methods to produce high-quality n-type Si. Unfortunately, the thermal neutrons which induce the transmutation reaction $^{30}\text{Si}(n,\gamma)^{31}\text{Si} \rightarrow ^{31}\text{P}$, are always accompanied by fast neutrons. Due to this high-energy neutron irradiation, large regions of displaced atoms are created in the Si. These regions are highly disordered and may be amorphous. Because of this irradiation damage, the resistivity is drastically increased and annealing up to 800°C is necessary for a good electronic performance. Although the annealing procedures have been thoroughly investigated, 'perfect' annealing of the damage is never obtained. We aim to investigate the structure and influence of this damage as a function of the irradiation dose by i.e. ultrasonic methods [1,2]. Since the amount of damage that is introduced not only depends on the irradiation dose, but also on several irradiation conditions, an additional method to quantify the radiation damage is needed.

In this study we use Raman spectroscopy to investigate the damage caused by high-energy neutrons for a high dose. Measurements were carried out on single-crystalline CZ bulk Si samples which were irradiated with a fast-neutron dose of 1.7 and $3.2 \times 10^{21} \text{ n/cm}^2$ ($E > 0.1 \text{ MeV}$). We investigated the Raman scattering for frequencies around 500 cm^{-1} . While the linewidth and the ratio $(I_0 - I / I_0)$ of the crystalline band at 520 cm^{-1} give some information about the creation of disorder, the rise of the amorphous band with the maximum at 480 cm^{-1} characterizes the crystalline to amorphous transition (I_0 and I are the Raman intensities of the undisturbed resp. damaged crystal) [3]. The intensity of the 520 cm^{-1} band is determined for the unirradiated and the irradiated crystals. For the irradiated crystals a band at 480 cm^{-1} is observed indicating the presence of amorphous regions in the crystals due to the irradiation. These results will be discussed.

We also observed that at very low Raman frequencies a feature reminiscent of the so called Boson peak typical for amorphous solids is present. This is interesting in view of the fact that the origin of this Boson peak in amorphous solids is still under discussion [4].

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STUDY OF A Li- AND C-RELATED CENTER FORMED AT HIGH ANNEALING TEMPERATURES IN NEUTRON-IRRADIATED FLOATING ZONE SILICON DOPED WITH LI.

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This work investigates the formation and structure of a photoluminescent center thermally created from neutron-irradiated silicon. The interest for studying this new deep center is twofold. Firstly, the center is formed at high annealing temperatures (550-600 °C) in Li-doped silicon enriched with C during the last steps of the radiation damage release such as it is reflected in the photoluminescence spectra given in the figure. The spectrum consists of two main lines at 879.3 and 1093.2 meV related to the non-phonon line of the *new center*, and the emission from exciton bound to Li donor with one TO phonon creation, respectively [1]. This latter photoluminescence structure is also found either in the non-irradiated Li doped samples or in those annealed at 650 °C. Secondly, the center is passivated upon annealing at room temperature. This is evidenced through the continuous decay experienced by the photoluminescence intensity at 879.3 meV with time.

Uniaxial stress experiments show that the 879.3 meV center is monoclinic I with only small departures from the trigonal symmetry. The isotopic structure exhibited by the non-phonon lines when a fraction of ^7Li is replaced by ^6Li indicates that the center involves one Li atom. The isotopic shift, $\Delta E = E(^7\text{Li}) - E(^6\text{Li}) = 0.19$ meV, is similar to that observed for the Q center ($\text{Li}_4\text{-V}$) in silicon [2]. Based on the dependence of the non-phonon intensity with the C concentration together with the high annealing temperatures required to form this center, we tentatively propose a T-like structure for this center [3], but replacing H by Li. In such a case the axis of the C-C split interstitial would be nearly along the $\langle 111 \rangle$ direction instead of $\langle 100 \rangle$, according to the stress data. The saturation of the dangling bond associated with this structure presumably by Li atoms would explain the passivation process observed at room temperature.

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SELFINTERSTITIALS IN IRRADIATED SILICON

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Key words: silicon, defect, selfinterstitial, athermal

In this paper we review recent studies of selfinterstitial and selfinterstitial-related defects in H^+ and He^+ ions irradiated at 77 K Si using DLTS and EPR methods.

Combined DLTS and EPR studies revealed correlation between behavior of $E1=E_c-0.39$ eV DLTS state and new intensive isotropic spectrum (labeled Si-AA12). We have identified E1 state and Si-AA12 spectrum as a selfinterstitial complex because both of them show intrinsic interstitial-related properties. These states have appeared in all irradiated samples irrespective of the kind of acceptor impurities in Czochralski-grown or float zone crystals as well as in high purity Si. Injection enhanced low temperature migration of observed defects increases of interstitial carbon (C_i) and interstitial acceptor atoms as well as Si_i-O_i metastable complex (MC, EPR spectra A18, AA13 and AA14)[1] and oxygen-related H7 DLTS state. AA12 and E1 defect have the same electrical level position and temperature range of annealing. Temperature independent injection rate for annealing of E1 defect indicates athermal mechanism of migration as expected for selfinterstitial as well as cubic symmetry of AA12 center may be the result of motional average for predicted bonded paramagnetic state Si_i^+ [2].

Correlation of properties between B configuration of MC[1] and new $H7=E_v+0.13$ eV DLTS state is also found. The H7 defect may be associated with the energy level B (+/0). Interstitial-related character of the H7 defect is confirmed by the appearance of C_i after annealing of H7 defect. At last for both defects the same reversible transformation ($E1 \leftrightarrow H7$ and $AA12 \leftrightarrow MC$) are found. The observed correlation is additional evidence of interstitial nature of discussed defects.

We have observed a new H4 DLTS state. The kinetics for different stages of the H14 annealing are described by first, second and third orders. This kinetics is corresponded to diffusion controlled recombination of defects expected for vacancy-selfinterstitial pairs. We have identified the H4 defect as a vacancy-selfinterstitial pair related complex.

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STUDY OF IRRADIATION-INDUCED VACANCY-LIKE DEFECTS AND A-CENTER-RELATED COMPLEXES IN SILICON

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Keywords: Silicon, electron irradiation, A center, positron annihilation, IR spectroscopy

Undoped and differently doped silicon samples (B, P As and Sb) were irradiated with 2MeV electrons (10^{18} cm^{-2}) at low temperature (4K) to study the defect formation and transformation during the annealing in the range between 90 and 900 K. The annealing behavior depends on the dopant and on the oxygen concentration. Vacancies and divacancies are the dominating defects in undoped material. The E center (vacancy-dopant complex) is only detectable in highly doped n-type Si. Complexes containing oxygen are also observable by positrons and they influence strongly the annealing behavior. In addition, temperature-dependent positron lifetime measurements were performed after irradiation with different doses, at different temperatures (4 K and 300 K), and after different annealing steps. The positron lifetime behavior depends distinctly on sample temperature for all conductivity types of silicon and it is typical for the competitive trapping in vacancies and in shallow positron traps. The concentration of shallow traps correlates with the oxygen content in the material. A possible candidate is the A center (vacancy-oxygen complex). Combined IR investigations show that no A centers are present after low temperature irradiation up to a dose of 10^{18} cm^{-2} . However, A centers are detectable after room-temperature irradiation and, therefore, we conclude that shallow traps after 4 K irradiation are modified A centers, at least with the following properties: small open volume, containing oxygen, and negatively charged.

DEFECTS IN As-GROWN SILICON AND THEIR EVOLUTION DURING HEAT TREATMENTS

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grown-in defects, point defect reactions, crystal pulling, Cz silicon, FZ silicon

Commercial silicon materials are grown under pulling conditions resulting in vacancy-rich crystals. The high concentration of vacancies leads to the formation of so-called D-defects which have a detrimental impact on the electrical properties of thin gate oxides. Therefore D-defects have been studied intensively in previous years. Recently, it was established that as-grown Czochralski silicon contains 10^5 - 10^7 cm⁻³ octahedral voids with sizes ranging from 50 to 300 nm. The void density correlates well with the observed gate oxide and D-defect densities. As interstitial oxygen is present in high concentrations oxide precipitate nuclei are formed during crystal growth. Due to the slower diffusion of oxygen the size of these nuclei is much smaller than those of the D-defects while their density is a few orders of magnitude higher. As vacancy supersaturation facilitates the nucleation and growth of oxide precipitates, the precipitation of interstitial oxygen during further thermal processes is determined by the initial grown-in defect density which itself is determined by the crystal pulling conditions.

In the present paper results are reported of an experimental and numerical investigation of grown-in point defect clusters as a function of crystal pulling conditions. Infrared scattering and interference techniques are used to measure the defect size and density distributions in as-grown and heat treated Czochralski and Floating Zone wafers. A large fraction of the grown-in defects is smaller than the size detection limit of the available analytical tools and is therefore not observed in the as-grown material. Increasing the defect sizes by thermal anneals allows to shift the initial defect size distribution above the size detection limit and yields thus indirect information on the grown-in distribution.

The experimental observations can be reproduced with high accuracy by numerically simulating the whole pulling process including intrinsic point defect incorporation and homogenous nucleation and growth of voids and oxide nuclei during solidification and cooling of the crystal. Consistent estimates of the intrinsic point defect solubility and diffusivity can also be determined.

LUMINESCENCE CENTERS IN HIGH-ENERGY ION-IMPLANTED SILICON

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Key Words: photoluminescence, silicon, ion implantation, Cu contamination, point defect

In the recent Si ULSI technologies, high-energy (several hundreds keV) ion implantation has been used in the device fabrication processes. During the ion implantation and the following thermal annealing, various defects are induced in Si substrates and they might interact with other defects and impurities. However, fundamental properties of these process-induced defects have not been understood well. From this point of view, we have investigated the defects in Si induced by ion implantation and thermal annealing by using photoluminescence (PL) technique. In this study, we have examined the effects of annealing atmosphere and Cu contamination on the PL spectra and observed sharp luminescence lines at 0.992 eV and 1.097 eV in high-energy ion-implanted Si. We consider that these lines are due to the different types of the point defect clusters. The defect formation of the 0.992 eV center is strongly affected by the annealing atmosphere and the Cu contamination while that of the 1.097 eV center is not affected.

Samples were generated by implanting 300 keV B⁺ or 700 keV P⁺ to a dose of 2×10^{13} cm⁻² into (100) p-type Czochralski-grown Si wafers. Samples were annealed in a furnace at 200 - 700 °C for 60 minutes in vacuum or in N₂ atmosphere. In the case of the annealing in vacuum, samples were put in a sealed quartz ampoule and Cu contamination was carried out by putting a small Cu wire with samples in a ampoule. PL spectra were measured at 4.2 K. Samples were excited by the 488 nm line of an Ar ion laser. The emission from the samples were analyzed by a 50 cm single monochromator and detected by a cooled Ge detector.

In the PL spectra of the annealed samples, I1, I2, and I3 lines, which have been reported to originate from radiation damage, are observed as well as the band-edge emission due to bound excitons and electron hole droplets. Besides those lines, sharp PL lines appear at 0.992 eV and at 1.097 eV depending on the annealing condition.

The PL line at 0.992 eV appears only after the annealing in vacuum. In the case of the annealing in vacuum without Cu contamination, this line appears after the annealing at 500 - 600 °C. If the samples are annealed in vacuum with Cu contamination, the annealing temperature at which the 0.992 eV line is observed ranges 300 - 600 °C. As this line appears in both cases of B-implanted and P-implanted samples, the luminescence center of this line contains neither B nor P atoms. This center does not contain Cu atoms because the line also appears after the annealing in vacuum without Cu contamination. However, the dependence of the 0.992 eV line on the annealing temperature suggests that Cu atoms strongly enhance the formation of this center. Considering the annealing behavior and the dependence on the annealing atmosphere, we tentatively assign the 0.992 eV line to the vacancy-type of point defect clusters.

On the other hand, the 1.097 eV line is observed in the B-implanted and the P-implanted samples annealed at 300 - 400 °C and depends on neither the annealing atmosphere nor the Cu contamination. The energy position of the 1.097 eV line coincides with that of free exciton line of Si. However, in the high-resolution PL spectra, the 1.097 eV line is relatively strong in intensity and distinguished from the free exciton line. We consider that the origin of the 1.097 eV line is also the point defect clusters induced by ion implantation and thermal annealing. However, the annealing behavior indicates that the structure and the formation mechanism of the 1.097 eV defect are much different from those of the 0.992 eV defect.

THRESHOLD ENERGY FOR CREATION OF RADIATION DEFECTS IN SILICON

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Key Words: defect, irradiation, silicon, threshold

Defect production rate (DPR) as a function of temperature and defect-forming electron energy has been studied in silicon. It is shown that the value of electron energy, for which DPR goes to zero, is not always in accordance with the threshold energy (TE). In many cases DPR goes to zero in a result of formation of conditions for effective Frenkel pairs annihilation. These conditions may be connected with temperature, doping concentration and intensity of irradiation. It is obtained that the function $DPR=F(T)$ has the temperature point of minimum DPR (TPM). For 1.2 MeV electrons irradiation and low doped phosphorus silicon TPM is equal 118 K. Decrease of electron energy results in growth of TPM. Increase of doping concentration has an effect of lowering of TPM.

Analyses of such type experiments and the process of breaking in a crystal lattice of "hot" atoms give a result that the TE is reduced to 12.6 eV for most of published "threshold" experiments. The determined TE is equal to the minimum value of TE that it has been earlier received in experiments at a room temperature. It is also found the energy of silicon atom bonds (10.7 eV) and the energy barrier for migration of interstitials (1.5 eV).

A COMPARISON OF THE PHOTOLUMINESCENCE DUE TO GOLD AND PLATINUM IMPURITIES IN SILICON

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Key words: silicon, photoluminescence, Si:Pt, Si:Au

Photoluminescence measurements on a variety of silicon samples implanted with Au and Pt show that, whereas Au doping leads to one prominent spectrum already reported in the literature[1], three new vibronic bands are observed for Pt with principal zero-phonon lines at ~777, ~884, and ~1026 meV. In all cases, a strong in-band local phonon mode sideband occurs in addition to a broad sideband involving host crystal phonons. The local mode energy and Huang-Rhys parameter values for the centres lie in the ranges 8-11 meV and 4-5, respectively. All three centres have a manifold of excited state levels, with the observed transitions occurring into a single ground state. The defects are produced by rapidly quenching implanted samples to room temperature following an anneal at 900°C. The relative intensities of the three spectra depend on the starting material and on the details of the quench. Storage at room temperature also affects the relative intensities. Uniaxial stress measurements on the 1026 meV centre show that it is of trigonal symmetry; preliminary measurements on the other centres indicate that they are axial also, so that none of the spectra can be assigned to isolated substitutional Pt impurities. Likewise, no correspondence can be established between these photoluminescence spectra and published Pt acceptor absorption spectra, confirming that they cannot be assigned to transitions between Pt acceptor levels. Neither do they correspond to the positions of reported donor absorption transitions at Pt impurities[2,3]. The likelihood is that the luminescence is produced at centres involving Pt and one of the common trace impurities in silicon; a variety of such defects has been reported in EPR measurements[4,5]. There is some evidence that the 777meV centre is due to Pt-Fe pairs, with parallels to the 735meV centre believed to be due to Au-Fe pairs[6]. These details and their implications, and the results of additional uniaxial stress and Zeeman measurements, will be discussed.

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ANNEALING OF LOW-TEMPERATURE SUBSTITUTIONAL GOLD IN SILICON: RING-DIFFUSION OF SUBSTITUTIONAL GOLD IN SILICON

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Key words; impurity diffusion, Si:Au, ring mechanism, substitutional impurity

Gold atoms in silicon occupy interstitial and substitutional sites, and substitutional gold exists in three states due the thermal condition: high-temperature substitutional gold in the condition of supersaturation above 850° C or undersaturation, low-temperature substitutional gold in that of supersaturation below 850° C, and agglomerates of substitutional gold as a fraction of annealed one. High-temperature substitutional gold diffuses via Seeger's kick-out mechanism as confirmed by Gösele et. al. Morooka et. al. proposed a ring mechanism for the diffusion of low-temperature substitutional gold. Therefore, gold atoms in silicon diffuse by intricate processes due to the state of substitutional gold depending on the condition of heat treatment.

Ring-diffusion of low-temperature substitutional gold has investigated by a special annealing of supersaturated substitutional gold. Silicon specimens, in which gold had been diffused previously at 1000° C, was heat-treated again at 500° C-700° C, and the supersaturated low-temperature substitutional gold was reduced to a thermal equilibrium concentration by the annealing. An annealing-time dependence of the concentration of the substitutional gold was measured. The concentration decreased rapidly with a short time-constant at the first stage of annealing, and then decreased slowly with a log time-constant at subsequent stage. The first rapid annealing is caused by a ring-diffusion of low-temperature substitutional gold with a homogeneous agglomeration. The second slow annealing is caused by an out-diffusion of the gold to a specimen surface. Diffusion coefficient for the ring-diffusion of substitutional gold obtained from the results is

$$D=(10^{-5}-10^{-3})\exp(-(1.7\pm0.2)/kT) \quad [\text{cm}^2/\text{s}].$$

The activation energy for the ring-diffusion was 1.5-1.9 eV. The concentration profiles of low-temperature substitutional gold in the annealing, which were obtained by ICTS measurements, will be presented also discussed using above diffusion coefficient.

INVESTIGATION OF IMPURITY-INDUCTED MICROWAVE ABSORPTION IN Au-DOPED AND PURE SILICON .

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Key words: high resistivity silicon, low absorption in Si.

The problem of the millimeter wave gyrotrons for plasma heating systems with 1 MW output power at 100 - 200 GHz in continuous mode is the materials with ultra low absorption for output power windows. Silicon and other IV group semiconductors are considered to be the most perspective materials for this application. In this paper we report results of investigation of impurity-induced microwave absorption in high-pure and Au-doped silicon.

For the first time monocrystal silicon with high resistivity and superlow dielectric losses in microwave range was produced by doping with the gold ($\rho = 360 \text{ k}\Omega\text{-cm}$, $\text{tg}\delta = 3 \times 10^{-6}$ at $T = 290 \text{ K}$ and $f = 145 \text{ GHz}$). Resistivity and dielectric losses in Au-doped material are closed to those in intrinsic silicon .

The absorption in high-pure and doped silicon was studied in the millimeter wave range and the temperature interval 80 - 370 K. At cooling of silicon, doped by gold, down to temperature of freezing of gold radiation losses sharply fall. There is a region with minimum losses $T < 280 \text{ K}$. The coincidence of temperature dependence of losses and temperature dependence of resistivity for high purity and Au-doped silicon wafers in temperature interval 200-320K shows that the main contribution to total dielectric losses of far IR and microwave radiation is given by free charge carriers.

The work was supported by the Grant 96-03-32798 from the Russian Foundation for Fundamental Researches.

ISOLATED SUBSTITUTIONAL SILVER AND SILVER-INDUCED DEFECTS IN SILICON: AN ELECTRON PARAMAGNETIC RESONANCE INVESTIGATION

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Key Words: silver, copper, silicon, EPR, hyperfine interaction

Copper, silver and gold in the group 1B of the periodic table receive much interest as deep-level dopants in silicon. This is due to their technological relevance and interesting physical properties of transition metal impurities with a complete d^{10} electron shell. However, in spite of numerous experimental and theoretical studies, the microscopic structure of their isolated defect configurations have not been fully clarified. Therefore further experiments are required in this field in order to understand the chemical trend and to develop the theory for these impurities.

In this contribution three electron paramagnetic resonance spectra in silicon doped with silver in a water vapor atmosphere are reported. The observed centers, labelled Si-NL56, Si-NL57 and Si-NL58, show a symmetry lower than cubic and an effective electron spin $S=1/2$. Based on studies with enriched silver isotopes and analysis of the observed two-fold hyperfine splitting, the participation of one silver atom is established for the first two centers. The Si-NL56 center of the orthorhombic-I symmetry is identified as an isolated substitutional silver atom, and its electronic structure is shown to conform to the vacancy model. Together with the earlier observation of the isolated interstitial silver atom, Si-NL42, the microscopic picture of the isolated silver in silicon has become more complete. Due to the presence of an additional hyperfine interaction with a nuclear spin $I=5/2$ the Si-NL57 spectrum of the trigonal symmetry is assigned to a complex of silver with another impurity introduced during the diffusion process. Taking into account the sample preparation procedure, the Si-NL57 center is attributed to an Al_s-Ag_i pair in a negative charge state. This observation also indicates the diffusion enhancement of aluminum in silicon treated in the water vapor atmosphere. By analysis of the features of the tetragonal spectrum, Si-NL58, and the defect formation, it is identified as a copper-copper pair in a negatively charged state. The relation of this center and a well-known copper-copper pair observed at 1014.7 meV in photoluminescence is discussed.

The obtained results give an important impetus to the study of the d^{10} transition metals in silicon.

SILVER RELATED DONOR DEFECT IN SILICON

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Key Words: silicon, silver, photoluminescence, Zeeman effect, uniaxial stress

The silver donor centre in silicon produces the 6289 cm^{-1} , or ABC, photoluminescence system. Several sharp lines were observed, which have been described as due to transitions from the split effective-mass-like electronic states near conduction band to the ground state. It has been found that the centre has C_{2v} or lower symmetry. However, we still have very limited knowledge about this silver centre. Here we show for the first time, to the best of our knowledge, detailed studies of the centre under external fields and annealing treatment. We also show that a new level, which produces the 'forbidden' zero-phonon line reported in ref.[1], plays a key role in the sideband of this system.

From our further photoluminescence investigation of this system by Fourier transform spectroscopy, we find that the ionization energy of the bound exciton, about 30 meV, is very far from its spectroscopic binding energy of 389 meV. Since the electron in the exciton has been identified as an effective-mass particle, the hole is evidently tightly bound. Our low temperature spectra confirm the existence of a new zero-phonon line, located at about 6280 cm^{-1} . We believe that this line is a forbidden transition from a new level, lying $\sim 2\text{ cm}^{-1}$ below the previous lowest detectable excited level A, to the same ground state as the other zero-phonon line A, B, and C. The unusual temperature-dependent behaviour of the vibronic bandshape shows that the vibronic sideband is, in fact, caused by transitions between the 'forbidden' level and the ground state. Consequently there must be a strong coupling between this 'forbidden' level and the upper excited states. This is consistent with the results of our uniaxial stress and Zeeman investigations. Uniaxial stress splitting also shows that this donor centre has C_{1h} symmetry.

A complicated annealing behaviour has been obtained. The centre can be partly destroyed by heating at low temperature, around 250°C , or totally at higher temperature, above 500°C . Only the destruction at low temperature can be recovered by further heat treatment.

We also reported that another silver-related photoluminescence system, overlapping the ABC system of silver, which is observed in heavily silver-doped samples.

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RATE LIMITING MECHANISM OF TRANSITION METAL GETTERING IN MULTICRYSTALLINE SILICON

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keywords: transition metals, multicrystalline silicon, dislocations, gettering

Multicrystalline silicon is a very interesting material for terrestrial solar cells. Its low cost and respectable energy conversion efficiency (12-15%) makes it arguably the most cost competitive material for large-volume solar power generation. However, the multicrystalline silicon solar cell efficiency is severely degraded by regions of high minority carrier recombination which possess both dislocations and microdefects. These structural defects are known to increase in recombination activity with transition metal decoration, therefore, gettering of metal impurities from the material would be expected to greatly enhance solar cell performance. Contrary to this rationale, experiments using frontside phosphorus and/or backside aluminum treatments have been found to improve regions with low recombination activity while having little or no effect on the high recombination regions and in turn only slightly improving the overall cell performance. The goal of this research is to determine the mechanism by which gettering is ineffectual on these high recombination regions.

We have performed studies on integrated circuit (IC) quality single crystal and multicrystalline solar cell silicon in the as-grown state and after a variety of processing/gettering steps. With Surface Photovoltage measurements of the minority carrier diffusion length, we have seen that segregation-type external gettering is effective for improving IC quality material but ineffective for improving the high recombination regions in multicrystalline silicon. Using Deep Level Transient Spectroscopy, we have determined that in as-grown multicrystalline silicon metal impurities primarily dwell in regions of high dislocation density which have significant carrier recombination. Additionally, with the use of synchrotron-based x-ray fluorescence mapping and correlated structural analysis, we have concluded that metal impurities specifically reside at dislocations and grain boundaries in high recombination regions of as-grown material as well as after gettering treatments. Modeling results of the diffusion process during gettering clearly show that the gettering processes would be expected to drastically reduce metal impurity concentrations in the material, contrary to these experimental results. Based on these results one can conclude that external gettering as applied to multicrystalline silicon is limited by the *release* of the impurity from the structural defects while for single crystal silicon it is a *diffusion*-limited process. This fact suggests the metal could be in the form of a stable metal carbide or oxide which is not easily dissolved or possibly as a metal atom or metal silicide that is highly stabilized by the strain field of the structural defect. We are studying the chemical nature of the metal atom at these structural defects and the kinetics of dissolution to develop a better understanding of metal impurity behavior and improve multicrystalline silicon solar cell performance.

PRECIPITATION AND DISSOLUTION OF FE IN FLOAT ZONE SILICON

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Keywords: precipitation, dissolution, diffusion length

Gettering techniques used in both integrated circuit (I.C.) and photovoltaic (PV) silicon materials depend upon dissolution and precipitation of transition metals. Yet transition metal dissolution and precipitation kinetics in the presence of various structural defects have not been studied systematically. In order to better understand these processes, we have precipitated and dissolved iron in single crystal and multicrystalline float zone (FZ) silicon materials. Some FZ materials had intentional iron contamination during growth while others were intentionally iron contaminated at high temperatures. Samples were heated to 950°C and quenched. Precipitations were performed with short anneals at 700, 600, 475, 350 and 235 °C, and dissolutions were performed at short anneals at 950°C. In order to monitor the precipitation kinetics, dissolved iron concentrations were measured with deep level transient spectroscopy (DLTS). The product of precipitate radius and precipitation site density, nr_0 (Ham's law[1]) were determined from precipitation rates. It was observed that nr_0 products increase orders of magnitude with decreasing precipitation temperatures (i.e. increasing supersaturation). The dissolution kinetics of iron precipitates, and consequences for gettering, are discussed. Diffusion lengths during precipitation and dissolution were measured with surface photovoltage (SPV) and the recombination activity of the precipitates was observed with electron beam induced current (EBIC) techniques. Minority carrier diffusion lengths improved upon precipitation of iron, indicating a dependence of the recombination activity of the Fe on the configuration of the Fe precipitate.

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THE ORTHORHOMBIC FeIn COMPLEX IN SILICON

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Key Words: FeIn, uniaxial stress, Zeeman, Si

The excitation spectrum of the neutral orthorhombic FeIn center in silicon will be discussed in some detail. Recent results obtained by Fourier transform spectroscopy using perturbation techniques i.e. uniaxial stress and Zeeman spectroscopy will be presented. A model is proposed that perfectly accounts for the strong selection rules observed in a previous thermalization study[1] as well as the Zeeman splitting and polarization selection rules at different magnetic fields. The initial as well as the final state is derived from a $^4B_1$ term split by spin-orbit interaction with a nearby $^4B_2$ term. The spin-orbit and crystal-field parameters for both the initial and final states are almost identical and close to those obtained from a previous electron paramagnetic resonance study[2]. Surprisingly, no uniaxial-stress splitting of the excitation lines has been observed for this low-symmetry center. This observation together with the fact that both states are described by almost equal electronic parameters may implicate that both states have similar origin and the spectrum will be discussed in terms of intra-d² transitions at the Fe ion.

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THE Si:Au AND Si:Pt $1S_{3/2}(\Gamma_8)+\Gamma$ PHONON-ASSISTED FANO RESONANCE

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Key Words: Silicon, Au, Pt, Fano resonance, $2p'$, excitation spectrum

The excitation spectra for the Au and Pt acceptors in silicon have been studied by Fourier transform infrared spectroscopy including uniaxial-stress perturbations. The resonance-like doublet structure, previously attributed as the $2p'$ line Coulombic line, is interpreted as the $1S_{3/2}(\Gamma_8)$ phonon-assisted Fano resonance involving the Γ zone-center phonon. The acceptor deformation potentials b and d for the Au and Pt $1S_{3/2}(\Gamma_8)$ state are in close agreement with those previously determined for the shallow B acceptor. Stress-induced preferential alignment effects are revealed for both centers. The doublet structure is shown to be due to crystal-field splitting of the $1S_{3/2}(\Gamma_8)$ Coulomb state.

DETECTION OF TWO CONFIGURATIONS OF THE COPPER-PAIR RELATED CENTERS IN SILICON

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Keywords: copper, silicon, DLTS, photoluminescence

It is well known that copper in silicon precipitates almost completely during cooling from high temperatures. However, a certain fraction of copper can remain in an electrically or optically active state. Recently, Erzgräber and Schmalz¹ established a good quantitative correlation between the amplitude of the DLTS peak, corresponding to the deep level at $E_v+0.09$ eV, and the amplitude of a photoluminescence line at 1.015 eV, previously identified² as the luminescence of isoelectronic copper pairs.

In this paper, the results of deep level transient spectroscopy (DLTS) and photoluminescence (PL) studies of the thermal instability of the Cu-pair related center within several hours after rapid quench are reported. Copper was diffused in float zone p-Si samples at 600°C. DLTS studies revealed, that the concentration of Cu-pair level decreased with time after quench and stabilized at a level of 70-80% of the initial concentration. The remaining concentration of the center was quite stable up to temperatures of 150°C, as it was reported earlier³. The time dependence of the decay could be approximated by an exponential. The time constant of the decay depended both on the temperature and on electric field in the space charge region and was of the order of several hours at the room temperature. The activation energy of the process of thermal dissociation and the dependence of dissociation rate on electric field were studied.

The coexistence of stable and unstable components at room temperature was confirmed by PL measurements. When measured immediately after the quench, the Cu-pair related line in the PL spectra had a double structure with the energy difference between peaks of about 0.8 meV. After 24 h room temperature anneal, the double structure became far less pronounced, and the overall intensity of the PL line decreased. These experimental facts indicate, that at least two nonequivalent configurations of copper-pair related centers exist, which can not be resolved by standard DLTS, but are detectable by PL. The possible models of the center are discussed, including the pairing of substitutional and interstitial copper atoms and pairing with an unknown defect X with the formation of complexes CuCuX.

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ELECTRONIC PROPERTIES OF COPPER-3D TRANSITION METAL PAIR COMPLEXES IN SILICON

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Key words: copper, transition metal, silicon

Isolated interstitial 3d transition metals (TM) are very mobile in silicon, forming complexes with both shallow and deep acceptors. EPR experiments have shown that some of these pairs are aligned along the (111) direction, with a substitutional acceptor and a TM impurity in a nearby interstitial site. It has been suggested that an ionic model (in which the complex is formed by a positively charged TM ion at the nearest tetrahedral interstitial site (Td) to a substitutional negatively charged acceptor ion) may describe the EPR parameters of copper-TM centers in silicon, as it been suggested for gold-TM centers.

In this work, we report theoretical investigations of the chemical trends in the electronic properties of transition metal impurity pair complexes in a silicon. Self-consistent *spin-unrestricted* electronic state calculations have been carried out for the substitutional copper-3d interstitial transition metal pairs, using a cluster model.

The Fermi hyperfine contact fields at Cu, TM and silicon nuclei have been evaluated and compared with the experimental results, as well as the Mott-Hubbard energies. The analysis of the one-electron energy spectra of Cu_5Cr_i , Cu_5Mn_i and Cu_5Fe_i , lead to the conclusion that the stable pairs in trigonal symmetry are formed by a covalent mechanism which includes, besides copper and the TM impurities, also the silicon neighbors. Therefore, the electronic and magnetic properties of the pairs are related to molecular orbitals spread out over the entire cluster rather than being derived from the interactions between two localized magnetic centers.

PHOTOLUMINESCENCE ASSOCIATED WITH A TRICLINIC FORM OF Di-CARBON HYDROGEN CENTRE IN CRYSTALLINE SILICON.

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Keywords: carbon, hydrogen, silicon, photoluminescence.

It has been shown recently that interaction between interstitial carbon and hydrogen during the annealing of crystalline silicon at temperatures in the range 400-600°C leads to the formation of an unusually stable C-C-H complex, responsible for the T-line luminescence system [1]. One of the characteristic features of this centre is that it includes a split interstitial C-C structure which is totally different from the known configurations of the di-carbon centre and is expected not to be stable without the presence of a hydrogen atom. The work reported here is concerned with another stable form of di-carbon hydrogen centre which has a configuration different from the T-centre.

We present the results of photoluminescence investigations on the carbon-hydrogen centre, which is created in irradiated silicon after annealing at temperatures above 300°C, with a principal zero-phonon transition at 760.8 meV (M-line). Analysis of local vibrational modes and their C-isotope shifts suggests that this centre is created by the interaction between a hydrogen atom and the di-carbon centre responsible for the 969.5 meV (G-line) luminescence system. The two centres are shown to have similar carbon-related local mode associated with an atomic structure which is involved in both defects and remains unperturbed by hydrogen in the M-centre. Temperature-controlled measurements suggest that the M-form has higher total energy than the T-form. Uniaxial stress and magnetic field measurements show that the M-centre has triclinic symmetry, which is lower than the monoclinic I symmetry of the G-centre. The detailed analysis of external field perturbation measurements also suggests that the M-centre creates deep acceptor level (-/0) at $E_c - 0.37$ eV.

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FANO RESONANCE IN A VIBRONIC SIDEBAND IN SILICON

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Key Words: Fano resonance, silicon, uniaxial stress, Zeeman perturbations

Fano resonances occur when a discrete state interacts with a continuum. In silicon, Fano resonances are especially well known for the chalcogen donors, where the discrete state is an electronic state plus a well defined phonon, and the continuum is the electronic ionisation continuum. In this paper we report the existence of a novel Fano resonance in a luminescence band. The luminescence band has its zero phonon line at 991 meV, and a vibronic continuum produced by coupling to a broad spectrum of lattice modes. The resonance is observed at 980 meV, in the part of the vibronic band involving low energy acoustic modes. The band is created in hydrogenated Czochralski silicon which has been irradiated and annealed at temperatures greater than 500 C. The temperature dependence data show one weakly bound particle.

The considerable size of the resonance allowed us to examine the effects of uniaxial stress perturbations and Zeeman perturbations on the Fano resonance as well as the zero phonon line of the centre. The zero phonon line splits into 2, 3, and 4 components under 001, 111, and 110 stresses, possibly indicating trigonal symmetry. The resonance follows a very similar behaviour to the zero phonon line in both the uniaxial stress and Zeeman perturbations except, intriguingly, the lineshape of the resonance can be modulated by uniaxial stresses along the 110 axis.

FORMATION OF OXYGEN DIMERS IN SILICON DURING ELECTRON IRRADIATIONS ABOVE 200°C

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Key words: silicon, electron irradiation, vacancy oxygen complexes, oxygen dimers

Electron irradiation (2.5 MeV) of silicon Cz-crystals heated in the range 200-350°C during irradiation has been performed. Infrared absorption studies of the crystals reveal that besides the appearance of the well-known absorption bands related to different vacancy-oxygen complexes, bands at about 1012 and 1060 cm⁻¹ grow up. These bands have recently been assigned to the oxygen dimer. The dose and temperature-dependence of the growth of these bands will be presented as well as a kinetic model for dimer formation.

FORMATION OF ULTRASHALLOW DONORS IN SILICON BY LONG-TERM-ANNEALING AT 470°C

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Key Words: shallow thermal donors, oxygen clusters, electrical characterization

Czochralski-grown and phosphorus-doped ($\sim 2 \cdot 10^{14} \text{ cm}^{-3}$) silicon samples with concentrations of interstitial oxygen and substitutional carbon atoms of $\sim 7 \cdot 10^{17} \text{ cm}^{-3}$ and $\sim 2 \cdot 10^{16} \text{ cm}^{-3}$, respectively, have been annealed at 470 °C in inert ambients (nitrogen and argon) for durations between 1 h and 500 h. The samples were subsequently characterized by Fourier transform infrared absorption measurements, photothermal ionization spectroscopy, and various electrical techniques such as four point probe resistivity measurements, admittance spectroscopy (ADSPEC), thermally stimulated capacitance measurements (TSCAP), capacitance-voltage measurements and deep level transient spectroscopy. An increasing concentration of free carrier electrons is observed at room temperature with increasing anneal time, reaching an almost constant value of $\sim 8 \cdot 10^{15} \text{ cm}^{-3}$ after ~ 25 -50 h. ADSPEC and TSCAP measurements performed at frequencies from 10^3 to 10^6 Hz for temperatures between 14 and 300 K revealed the presence of ultrashallow donors with level positions gradually shifting from ~ 35 meV to ~ 25 meV below the conduction band edge as a function of annealing time. The data indicate that the donors are initially of double character and then become single ones at long enough anneal times. The samples were examined both in the near surface region ($\leq 1 \mu\text{m}$) and also at larger depths ($\sim 15 \mu\text{m}$) after chemical etching, and within the experimental accuracy no variations in the concentration and energy position of the donors were observed. The donor complexes are most likely oxygen-related but not of the same origin as the so-called shallow thermal donors (STD's) reported by Navarro et al [1].

endabstract

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INFLUENCE OF THE Li CONCENTRATION IN THE PHOTOLUMINESCENCE SPECTRA OF NEUTRON-IRRADIATED SILICON CRYSTALS: PASSIVATION OF RADIATION INDUCED CENTERS.

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Li-related defects in silicon have received considerably attention due to the ability of Li as passivator of defects and deep level impurities [1, 2]. Furthermore its high diffusiveness, even at room temperature, makes it an efficient impurity for being used in silicon devices [3]. In this work we investigate the passivation of centers formed by annealing in neutron-irradiated Li-doped silicon crystals through photoluminescence. The feasibility of this technique for detecting passivation processes is also analysed. In the present case quantitative estimates were done by comparing the luminescence intensity [4] of different centers some of which are not passivated by Li atoms.

The study has been performed on several neutron-irradiated (ndose= 10^{17} cm⁻²) floating zone and Czochralski silicon crystals with Li concentrations ranging from 10^{14} to 10^{17} cm⁻³. The centers were created by successive isochronal annealing from room temperature to 600 °C. The passivation processes as well as the formation of centers involving Li atoms were analysed through the dependence of the photoluminescence spectra with the Li concentration. As a result it is shown that the C center (789.6 meV) associated with carbon and oxygen interstitials [5] is efficiently passivated at room temperature by Li. However there are centers such as I1 (1018.2 meV) or I3 (1039.8 meV) [5] which are not passivated by Li, and thus they can be used as probes for quantitative analysis. Interestingly, other centers formed at higher annealing temperatures such as the M center (760.9 meV) [5] or that responsible for lines D1 and D2 at 1108 meV and related to the <111> split interstitial by Minaev et al. [6], are also passivated by Li. A survey of these results will be given at the Conference.

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OXYGEN-RELATED FAST-DIFFUSING SPECIES IN SILICON

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Key words: silicon, oxygen, clusters, enhanced diffusion, thermal donors

The nature of the fast-diffusing species (FDS_s) responsible for the enhanced oxygen in- and out-diffusion at $T < 700^\circ\text{C}$, formation of thermal double donors (TDD_s), etc. continues to be one of the main puzzles in the problem of oxygen diffusion and clustering in silicon at elevated temperatures [1]. Various kinds of FDS_s have been suggested including complexes of oxygen with an intrinsic defect or impurity (e.g. hydrogen), quasi-free or unbonded oxygen atoms, oxygen molecules or dimers. In present paper we have re-examined previous studies in this field. The limits for the possible quasi-equilibrium concentration and diffusivity of FDS_s are estimated. It is shown that none of the suggested models can explain consistently all the experimental findings.

We report also new information about some FDS characteristics. The data are obtained from the careful studies of the TDD generation kinetics in Si crystals with different oxygen and carbon content. An analysis of the data has led us to *the conclusion that not only dimers [2,3], but other small oxygen complexes (trimers and the first TDD species) are mobile* as well and they should contribute to the successive formation of thermal donors, enhanced oxygen mass-transport, formation of the TDD depleted layers, etc. It is argued that the high migration ability of trimers and the first TDD species can be associated with their bistability.

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PSEUDO OR DEEP DONOR EXCITATION SPECTRA IN SILICON.

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Key Words: Pseudo-donors, Deep-donors

The concept of pseudo-donors is occasionally used in conjunction with excitation spectra of deep centers in semiconductors. We will discuss the pseudo-donor model for deep-level spectra in silicon for which the transitions take place from a deep ground state to shallow-donor states. The pseudo-donor model originates from studies of bound excitons and in that case the hole is considerably more strongly bound than the electron a shallow donor like spectrum may be observed. In this case, the first manifold of excited states contains all six 1s states whereas for shallow donors, for which usually one of the 1s states is the ground state, only five or fewer 1s states are expected close to the 1s EMA position. The criteria for a center to be a pseudo-donor is then simply that transitions to all six 1s states are observed in, e.g., the excitation spectrum. Transitions to all six 1s states have been observed for several deep donors in silicon. It will be argued that it is due to their deep-ground states non-Coulombic origin and that the pseudo-donor model is not applicable for these centers.

SHALLOW THERMAL DONORS IN ANNEALED CZ SILICON AND LINKS TO THE NL10 EPR SPECTRUM: THE RELEVANCE OF H, AL AND N IMPURITIES

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Key Words: Si. oxygen. shallow thermal donors, IR electronic absorption, EPR

Heat treatment of CZ silicon at $T \sim 470^\circ\text{C}$ leads to the formation of shallow thermal donors (STDs) with ionisation energies of 36 meV that are detected by infrared (IR) absorption from their electronic transitions ($T \sim 10\text{ K}$). There is evidence that these centres give rise to an EPR spectrum labelled NL10. ENDOR measurements reveal 2-3 clustered oxygen (^{17}O) atoms in the defect core, together with an Al atom in some of the defects. Measurements show that a hydrogen (or deuterium) atom can be present instead of the Al atom, while there is circumstantial evidence that a nitrogen atom may be present instead of either H or Al: there is support for the latter proposal from ab initio theory. The upshot is that there is considerable confusion in the literature. We now show that three types of STD defects can form leading to a significant clarification.

We show first that IR STD spectra from annealed Al-doped samples are different from those obtained from hydrogenated boron, phosphorus or indium doped samples. Secondly, there are small shifts in the energies of the latter STD transitions when H is replaced by D. If hydrogen is introduced into Al-doped material, the two sets of centres STD(Al) and STD(H) are produced simultaneously (it should be noted that Al-doped crystals may inadvertently contain hydrogen). These observations therefore provide clear links to the NL10(Al) and NL10(H) ENDOR spectra. Boron-doped samples pre-heated (at 1300°C) in N_2 gas and then annealed at 550°C reveal a third IR STD spectrum (we label this spectra STD(N) for clarity). However STD(H) defects present in hydrogen contaminated samples dominate the IR spectra of nitrogen-treated samples annealed at lower temperatures (470°C) (we find that STD(H) centres are not stable for $T > 500^\circ\text{C}$). While no nitrogen ENDOR has been detected for the NL10 spectrum from nitrogen-treated samples, the ^{29}Si ENDOR transitions are not identical with those found for NL10(H) or NL10(Al).

In summary, IR spectra reveal three distinct families of STD centres. In the same samples, ENDOR measurements clearly distinguish two different types of EPR NL10 spectra, while a third spectrum shows differences in the ^{29}Si ENDOR spectrum.

THE INFLUENCE OF ISOVALENT DOPING ON THE OXYGEN DIFFUSION IN SILICON

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Key Words: silicon, isovalent impurity, oxygen, diffusion, deformation

The theoretical analysis of the influence of doping of Si with isovalent impurities (IVI) on the diffusion processes of oxygen was performed. The approach of elastic continuum was used at that. The deformative character of interaction between atoms of IVI and oxygen was shown to exist in silicon doped with IVI. In particular, this interaction leads to the decrease of potential barrier height for diffusion of interstitial oxygen in silicon doped with germanium. In consequence there is an additional diffusion of oxygen atoms in the direction of germanium atoms: Si_2O -quasimolecules dispose near by the atoms of germanium.

The influence of overlap of deformation fields created by atoms of Ge in Silicon on the oxygen diffusion was taken into account. The comparison of influence of doping with different IVI (carbon, tin and germanium) on the processes of oxygen diffusion in silicon was carried out.

The obtained results were used for description of influence of doping with germanium on the relaxation of dichroism of oxygen in Silicon.

DETERMINATION OF THE OXYGEN CONTENT IN PLATELIKE AND OCTAHEDRAL OXYGEN PRECIPITATES IN SILICON WITH FT-IR SPECTROSCOPY

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Key Words: silicon, oxygen, precipitation, infrared spectroscopy

Depending on the thermal treatment octahedral and/or platelike oxide precipitates are formed in Czochralski grown silicon wafers. Regarding the technological importance of the defect, experimental methods to determine the content of oxygen present in the respective precipitates are of great interest. In the present contribution a procedure is presented to determine the amount of precipitated oxygen from the infrared absorption spectrum. Other aspects of the study concern composition, density and microstructure of the precipitates.

p- and n-type Si wafers with interstitial oxygen (O_i) concentrations of $(9-11) \times 10^{17} \text{ cm}^{-3}$ were subjected to different kinds of thermal treatments. FT-IR measurements were made at 300K and 6K (the latter for the determination of O_i concentration when precipitate bands are present). Elimination of the contribution of O_i from the 300K spectrum resulted in the spectrum of the precipitates only. The latter consists of partially overlapping bands at about 1110 and 1225 cm^{-1} , generally attributed to octahedral and platelike precipitates respectively.

The absorption spectra can be reconstructed using the theory of absorption of light by small particles, only requiring the dielectric functions of medium and particles¹, together with the geometric shape of the latter. Octahedral precipitates were approximated by spheres. For platelike precipitates the radius and aspect ratio (the ratio of the axes of the spheroid) were calculated using Ham's diffusion theory² and the optimal aspect ratio relation from Hu³, respectively. Simulations of platelike particles were performed on a set of dielectric functions and the positions of the band maxima were compared with the experimental ones, resulting in only one acceptable candidate.

As a result an empirical relation was obtained between the amplitudes of the absorption bands and the oxygen content of each kind of precipitate. Agreement within 10% with the amount of oxygen lost during thermal treatment was obtained for an extended set of samples. It was concluded that in all the samples the majority of precipitated oxygen was found to be in the form of octahedral precipitates.

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DIFFUSION AND PRECIPITATION OF OXYGEN IN SILICON DOPED WITH GERMANIUM

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Key Words: silicon, germanium, oxygen, diffusion, thermal donor

The investigation of influence of doping of Si with germanium ($\leq 1\%$) on the processes of oxygen diffusion and precipitation at the thermal treatment $T=450^\circ\text{C}$ was performed. The relative loss of oxygen in the samples of SilangleGerangle was found to depend nonmonotonously on the concentration of Ge and to have a pronounced maximum at $N_{\text{Ge}} \approx 3 \cdot 10^{19} \text{ cm}^{-3}$.

For describing of the process of oxygen precipitation in SiGe the system of quasi-chemical equations has been formed. The possible channels of oxygen loss at the thermal treatment have been taken into consideration including both enhanced oxygen diffusion and the decrease of the capture radius of oxygen by the embryos at thermal donors formation. It was shown that enhanced diffusion of oxygen and the decrease of the capture radius at annealing lead to monotonous decrease of the oxygen clasterization rate.

Earlier it has been shown that there is a correlated distribution of Ge and O atoms in SiGe. In consequence a new type of thermal donor embryos may appear[1]. The numerical decision of the system of kinetic equations, composed in accordance with this channel of oxygen loss on formation of these thermal donor embryos, results in the nonmonotonous dependence of the relative oxygen loss and decrease of formation efficiency of thermal donors in SilangleGerangle at the thermal treatment.

The comparison of theoretical dependence of the relative loss of oxygen and thermal donor concentration at thermal treatment of SiGe with the experimental results has shown a satisfactory conformity.

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ELECTRIC-DIPOLE SPIN RESONANCE OF Be-DOPED SILICON

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Key Words: Si:Be, double acceptor, electric-dipole spin resonance

Doping silicon with Be introduces a number of defects which have been previously investigated by DLTS, infrared spectroscopy, photoluminescence and Raman technique. Spin resonance measurements in Be-doped Si have not been reported to the best of our knowledge. Two DLTS levels at E_V+190 meV and E_V+440 meV are ascribed to the double acceptor levels of isolated substitutional Be. In accordance with this an acceptor level at $E_V+191.9$ meV of tetrahedral symmetry is found by IR spectroscopy. The ground state of this centre is split by 0.51 meV. Another defect commonly found by IR spectroscopy in slowly cooled samples is a trigonal acceptor at $E_V+145.8$ meV. It is assigned to a Be-Be pair defect.

We report here on electric-dipole spin resonance (EDSR) measurements at 24 GHz, 33 GHz, and 60 GHz of Be-doped Si. This variant of conventional EPR has been recently used to investigate Si and GaAs doped with single acceptors and Si doped with the double acceptor Zn.

Be diffusion into silicon was performed at about 1200°C for 30 minutes using a sandwich structure of two Be-plated silicon samples. Si crucibles were used to minimize sample contamination. We find two trigonal spectra and a number of isotropic lines indicating cubic defect symmetry. One of the trigonal spectra shows a rather peculiar temperature dependence of line strength and line width: the lines increase and become narrower when the temperature is increased from below 2 K to about 2.8 K, where the maximum line strength is observed. Above this maximum a strong decrease and broadening is observed, which cannot be explained by thermalisation of the ground state levels alone. For this spectrum a reasonable fit is possible with effective g-values of $g_{\parallel}=2.59$ and $g_{\perp}=0$, so that it should not be easily detectable with conventional EPR. The origin of the spectra will be discussed, taking into account a possible participation of foreign atoms.

PHOTOLUMINESCENCE CENTERS ASSOCIATED WITH NOBLE-GAS IMPURITIES IN SI

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Keywords: theory, noble gas, silicon, photoluminescence, divacancies

The implantation of noble-gas (NG) ions in Si results in the formation of defects centers with unexpected properties. (1) A brief 300 °C anneal following the implant results the appearance of sharp, NG-dependent, photoluminescence (PL) bands. (2) The bands grow at the expense of a Ω defect-related PL center at 1018 meV. (3) The centers associated with the 1018 meV line as well as the He, Ne, Ar, and Kr defects have trigonal symmetry, but the Xe defect is tetragonal and behaves differently under stress. (4) After a 450 °C anneal, all the bands are replaced by a broad and NG-independent PL. (5) During the implant, the NG impurities diffuse into the bulk considerably deeper ($\sim 1 \mu\text{m}$) than predicted by implantation theory ($\sim 30 \text{ \AA}$).

Our calculations are performed in molecular clusters at the ab-initio and approximate ab-initio Hartree-Fock (HF) levels. The results explain at least qualitatively all the key features of NG-related centers and imply a unique identification for the 1018 meV band. The predictions are as follows.

- (1) Interstitial NG impurities are not associated with the PL. Their activation energies for diffusion are large.
- (2) NG atoms do not become substitutional but are strongly repelled by vacancies. This suggests an unusual vacancy-enhanced diffusion mechanism.
- (3) NG-divacancy complexes form with little or no activation energy and are very stable. Their calculated properties make them excellent candidates as the defects responsible for the observed PL.
- (4) In a reconstructed divacancy, the electron affinity of the 6 Si nearest neighbors to a NG results in its partial ionization. While this ionization is too small to result in covalent bonding for He, Ne, Ar, and Kr, the trends show that Xe is likely to bind, and therefore behave differently.
- (5) Vacancy aggregates larger than the divacancy cannot be responsible for the observed PL. However, the formation of a ring-hexavacancy-NG complex could nicely explain the disappearance of the PL at higher temperatures.
- (6) The 1018 meV PL band is associated with the neutral divacancy.

CADMIUM-RELATED DEFECTS IN SILICON: ELECTRON-PARAMAGNETIC-RESONANCE IDENTIFICATION

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Key Words: silicon, transition metals, magnetic resonance, ionic implantation

The group II impurities Zn and Cd in silicon have been extensively studied during the last years. The electronic properties have been determined from space charge and Hall measurements, and it has been concluded that both atoms occupy in their isolated form a regular substitutional site and, lacking two electrons to be isovalent impurities, they act as double acceptors. Both elements show a pronounced tendency to form complexes with other impurities. The spatial and electronic structure of isolated Zn and Cd is under discussion as the corresponding structure of the isolated Pt^- and Au^0 and there is no generally accepted model for the defect's electronic structure. The number of electrons in the 3d and 4d orbitals for the substitutional Zn/Cd (configuration of the free neutral atom $3d^{10}4s^2/4d^{10}5s^2$) is in competition with the sp^3 hybridized covalent bonds: $3d^8/4d^8$ (Ludwig-Woodbury model) or $3d^{10}/4d^{10}$ with two bound holes in the covalent bonds.

Very recently the deep level transient spectroscopy was applied to some radioactive impurities (DLTS-RI) in silicon. It could be demonstrated that the chemical nature as well as the number of probe atoms that participate in the considered defect centres can be identified by the time dependence concentration of the incorporated radioactive impurities and their daughter elements. The DLTS-RI method was also applied to radioactive $^{111}\text{In}^*$ atom, a standard probe atom for the PAC-technique, which are transmuted into stable cadmium atoms. Besides 2 Cd-induced centres that contain one Cd atom each and a FeCd-pair the singly and doubly charged state of the isolated double acceptor could be identified /1/. In spite of these studies, the microscopic structure of the Cd-induced centres, which is often revealed by means of electron paramagnetic resonance (EPR) spectroscopy, is not clear, because also the DLTS-RI method gives no direct information on the microscopic structure of the centres involved. For the charge state $\text{Zn}_s^-/\text{Cd}_s^-$ with one bound hole one might expect EPR or electric-dipole spin resonance (EDSR) spectra analogous to those observed for the single acceptors B, Al, Ga and In in Si /2/. However, so far only various transitions metal-Zn pairs have been identified by EPR in samples with corresponding co-doping /3/. Transition of isolated Zn_s^- were not found up to now /4/. EPR-results of Cd-related centres were not as yet published.

In this paper EPR investigations of Cd-diffused and Cd-implanted silicon samples are reported. Partly the same samples like in /1/ were used, so allowing a direct comparison of the EPR and DLTS-RI results. Two Cd-related centres labelled Cd(1) and Cd(2) were observed. The Cd(1) centre shows the typical cubic angular dependence of the fine and hyperfine structures of a G_8 -state. The chemical identification of the Cd(1)-defect is based on the observed hyperfine structure and natural abundance (n.a.) of the Cd-isotopes with non-zero nuclear spin ^{111}Cd (n.a. 12,75%, $I=1/2$) and ^{113}Cd (n.a. 12,26%, $I=1/2$). This centre Cd(1) has been attributed to a single cadmium atom in the negative charge state on a tetrahedral, probably substitutional, site. From the angular dependence of the spectrum arising from Cd(2) the symmetry is determined to be orthorhombic. In view of the detected hyperfine interaction with an intensity behaviour similar to the centre Cd(1) this spectrum is attributed to a single Cd-atom or a complex containing one cadmium atom. This centre is tentatively identified as a Cd-B pair.

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PERSISTENT EXCITED CONDUCTIVITY INDUCED BY PROTON IRRADIATION IN A-SI:H

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Keywords; persistent conductivity, a-Si:H, Staebler-Wronski effect, proton irradiation

Hydrogenated amorphous Si (a-Si:H) has been widely used for solar cells and optical sensors, etc., since hydrogen passivation has succeeded in attaining a high quantum efficiency. However, a-Si:H is subject to the so-called Staebler-Wronski (SW) effect, i.e., strong light illumination of band-to-band excitation deteriorates both photo- and dark conductivity. The SW effect is basically explained in terms of defect formation due to electronic excitation.

Recently, it has been proposed [1] that a-Si:H is potentially applicable for devices under strong radiation fields, e.g., for reactors, accelerators and spacecrafts. Higher radiation performance of photoconductivity than crystalline Si was observed for a-Si:H and was tentatively ascribed to structural flexibility of the amorphous structure. High energy ions ($E > 1$ MeV/amu), as injected into a semiconductor, deposit most of the incident energy via electronic excitation. Only a small amount of the energy is partitioned to atomic displacements. In this context, the SW-like effect could be also induced by high energy ions.

In this point of view, radiation-induced conductivity (RIC) of a-Si:H induced by a 17 MeV proton beam has been studied. The RIC is quite different from the SW effect, which is actually observed before the proton irradiation, under visible light illumination. During the proton irradiation, the electric conductivity shows a steep rise initially, followed by a gradual rise. After terminating the irradiation, the conductivity decays but keeps a 2-3 orders higher value than the unirradiated one. The persistent excited conductivity (PEC) continues longer, at the lower temperatures. At $T = 200$ K, the PEC sustains itself over 30 hours after proton irradiation for 1 minute. The PEC disappears after annealing at $T = 450$ K.

The PEC is different from the typical SW effect or persistent photoconductivity observed in GaAlAs. This phenomenon is supposed to be newly discovered for a-Si:H.

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PHONON SCATTERING IN HEAT—TREATED CZ—SILICON

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Key Words: phonon spectroscopy, oxide precipitates, Cz—silicon

Acoustic phonon spectroscopy with superconducting tunnelling junctions provides information on nanoscopic crystal defects with sizes corresponding to phonon wavelengths. This was first shown for Ca—colloids in electron—irradiated CaF_2 [1]. We have investigated time—and energy—resolved phonon scattering in heat—treated Cz—silicon with high and low carbon content. Long—term annealing around 750 °C was used for nucleation, short—term annealing above 1000 °C for growth of the precipitates.

Annealing for nucleation results in strong, broad—band and mainly elastic scattering. Distinct differences between the phonon spectra of carbon—rich and carbon—lean material indicate that there is a greater amount of inelastic scattering processes in the latter case, which could be caused by a difference in the structure of the oxygen precipitates or their related defects. After subsequent heat—treatment above 1000 °C we find resonant phonon scattering in the range between 1 meV and 4 meV in samples with high carbon content. In a sample that has undergone a typical “intrinsic gettering” thermal cycling with pre—annealings at 1100 °C+750 °C and three isothermal annealings at 1050 °C for intervals of 30 minutes the phonon transmission spectra show a series of rather narrow absorptions with line widths of about 0.6 meV. These resonances slightly change their positions and line form after the second anneal, whereas they appear to be unchanged after the third annealing. If these resonances are caused by the excitation of geometric eigenvibrations of oxygen aggregates, their size would be expected to be $\lambda_{\text{phon}}/2 \approx 3.9 \text{ nm}$ for the low—energetic line, which remains at 2.75 meV after annealing for 1.5 hours. According to TEM measurements this is the typical thickness of platelet precipitates, which occur in this temperature range.

We compare our phonon spectroscopic results to the precipitate—related infrared absorption measured at 3.5 K, which also allows the exact determination of oxygen and carbon contents. The oxygen concentration as determined by IR spectroscopy can be compared to the value obtained from the strength of the resonant phonon scattering by the low—energy vibrational—rotational transition of the interstitial oxygen.

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THE RESPONSE OF THE 889 CM⁻¹ OXYGEN MODE IN SI TO UNIAXIAL STRESS.

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Key Words: Oxygen, Silicon, Uniaxial Stress, Dichroism, VO₂

In previous studies of the early stages of oxygen agglomeration in silicon a local vibrational Si-O mode was observed at 889 cm⁻¹ in oxygen-rich material irradiated with electrons and in oxygen-implanted silicon. The intensity of the mode was found to increase with the square of the interstitial oxygen concentration and it was argued that the defect giving rise to this mode contains two oxygen atoms. However, coimplantation of ¹⁶O and ¹⁸O into overlapping profiles only produced the same modes as those observed after implantation of single isotopes. Therefore, if two oxygen atoms are involved, their dynamic coupling must be weak. The defect has tentatively been identified with VO₂, i.e. a vacancy in which two oxygen atoms saturate the four dangling bonds. This identification was supported by *ab initio* cluster calculations which showed that such a structure is stable and that the dynamical coupling between the oxygen atoms indeed is weak. No direct experimental information on the symmetry of the 889 cm⁻¹ center has been presented so far, and the microstructure remains unidentified.

In this work, the response of the 889 cm⁻¹ mode to uniaxial stress is studied. Silicon crystals with dimensions 2×2×10 mm³ were cut from float-zone or Czochralskii material. The float-zone samples were implanted with O³⁺ ions at several energies so that a uniform oxygen concentration of 1.5×10¹⁹ cm⁻³ was obtained in a 14 μm thick layer. The Czochralskii samples were irradiated with 5×10¹⁷ cm⁻² electrons at 2.5 MeV. Subsequently, all samples were annealed at 330 °C for 30 min. to produce the 889 cm⁻¹ center. The uniaxial stress measurements show that the 889 cm⁻¹ mode either is two-dimensional and originates from a tetragonal defect, or it is one-dimensional and belongs to an orthorhombic-I center. Additional information has been obtained by stress-induced dichroism. Uniaxial stress is applied at ~170 °C and subsequently the samples are cooled to room temperature where the stress is removed. Significant dichroism is observed for uniaxial stress along the [100] and [110] axes whereas stress along the [111] axis do not produce any dichroism. This is consistent with tetragonal symmetry (D_{2d}), but inconsistent with orthorhombic-I symmetry. These findings provide strong support to the assignment of the 889 cm⁻¹ mode to VO₂.

TEMPERATURE-DEPENDENT WIDTHS OF INFRARED AND FAR- INFRARED ABSORPTION LINES OF OXYGEN IN SILICON

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Key words: Infrared absorption, Line width, Impurity, Oxygen, Silicon

The bond-interstitial oxygen (O_i) in silicon causes the absorption bands at about 30 and 1100 cm⁻¹, which comprise four and three lines, respectively. Due to the coupling between the bond-perpendicular low-energy anharmonic excitation (LEAE) and the bond-parallel local vibration of the O_i, the energy level ladder of the LEAE occurs for each of the ground and the first excited states of the local vibration. This energy-level scheme well explained the energies and intensities measured for these absorption lines. However, the strong temperature dependence of the line widths characteristic of these absorptions has not yet been described theoretically.

Since available experimental data are insufficient for the present theoretical study, we first measured temperature dependence of the line widths for the range 4.2-70 K with a maximum resolution of 0.01 cm⁻¹. All absorption lines, having Lorentzian shape and overlapping each other at high temperatures, exhibited strong temperature dependence of the line width, e.g., the full width at half maximum of the 29.3-cm⁻¹ line was 0.09 cm⁻¹ at 4.2 K and 1.79 cm⁻¹ at 62 K. Below 20 K, this line was by far the narrowest of all lines.

We simplified our previous model for the local-vibration-coupled LEAE, and took into account the coupling of the LEAE to the host lattice phonons. Thus the total Hamiltonian is of the form

$$[\text{Local vibration}] + [\text{LEAE}] + [\text{Host lattice phonons}],$$

where + indicates the coupling terms. By means of the one-particle Green's function, we calculated how the coupling to the host lattice phonons causes finite width to the absorption lines of the [Local vibration] + [LEAE] system. For all lines in the 30- and 1100-cm⁻¹ bands, the observed temperature dependences of the widths were successfully fitted by the calculated theoretical curves that took into account the lowest-order effect of the phonon coupling. This revealed that, below 60 K, the line widths are caused by the direct process alone, i.e., the transitions by one-phonon emission and absorption in the lower and the upper energy-level ladders of the LEAE. The Raman process was turned out to be negligible.

In the present formulation of the coupling to the lattice phonons, the LEAE was assumed to interact with the displacements of the two adjacent Si atoms which are reduced to the A_{1g}, A_{2u}, E_g and E_u representations of the D_{3d} group. The theoretical fit to the experiment showed that the A_{1g}-phonon transitions have much higher probabilities than the others, dominating essential features of the temperature dependence. It turned out that the width of the low-temperature 29.3-cm⁻¹ line is caused by an E_u-phonon transition with very small probability. This explains the anomalous narrowness of this line. The residual width of the 1136-cm⁻¹ line, 0.6 cm⁻¹ at 4.2 K, was considered to be due to other temperature-insensitive origin.

COMPARISON OF MUONIUM (HYDROGEN) DYNAMICS IN GERMANIUM AND SILICON

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Key Words: Hydrogen, Dynamics, Diffusion, Germanium, Silicon

An investigation into the dynamics of transitions among muonium (Mu) states reveals distinct differences in the behaviour of Mu for Ge compared to Si. Since Mu represents an experimentally accessible analog of isolated atomic hydrogen defects in semiconductors these results provide a qualitative picture of hydrogen behaviour as well. At high temperatures rapid cyclic electron capture and ionization lead to muon spin depolarization from which the individual transition rates can be obtained and the active Mu^0 state identified. Comparison of the charge-cycle depolarization results with low-T rates for transitions out of initially formed Mu states is used to establish a consistent set of process assignments. The emerging picture of Mu (or H) in Ge is that Mu^0 has nearly the same energy in the bond-centered (BC) and tetrahedral (T) interstices with an extremely small barrier to site changes. In silicon Mu^0_{BC} is significantly more stable than Mu^0_{T} and the barrier is much larger. While bi-directional site changes begin near 100K for Ge, a small prefactor results in slow Mu^0 site changes above 200K compared to the charge-cycle rates. The high-temperature results for germanium are consistent with this, implying separate $\text{Mu}^0_{\text{BC}} \rightarrow \text{Mu}^+$ and $\text{Mu}^0_{\text{T}} \rightarrow \text{Mu}^+$ cycles. In contrast, for nearly intrinsic silicon the charge-cycle onset is near 400K and involves a more complicated three-step cycle with Mu^0 visiting both the T and BC locations during each cycle. This three-state cycle appears to dominate the high-temperature muon spin depolarization even in fairly heavily doped n-type silicon where other cycles may also occur. Since Mu^0_{T} is far more mobile at all temperatures than any of the other states, we conclude that hydrogen diffusion is controlled by transitions into and out of this mobile state for both Si and Ge, but that the details differ considerably. Possible assignments and formation processes are discussed for an additional diamagnetic Mu state in Ge with a binding energy of 0.75eV which is slowly formed.

EFFECTS OF HYDROGEN PLASMA ON DISLOCATION MOTION IN SILICON

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Key Words: dislocation , glide velocity, hydrogen plasma, silicon

Dislocations in semiconductors are electrically active and their motion is largely affected by their electronic states. The fact that hydrogen passivates electrically active centers in semiconductors is also well known. To study effects of hydrogen on dislocation motion, we have measured the velocity of dislocation glide motion in phosphorus-doped FZ-silicon during hydrogen plasma irradiation. Dislocations were introduced by four-point bending and the double etching method was used to measure dislocation velocity. The velocity was drastically promoted under hydrogen plasma by a factor of 10 to 100 in the temperature range of 663-753K, and the activation energy of dislocation motion was reduced to 1.2eV from the value, 2.3eV, in the dark. There are two possibilities responsible for such enhancement. One is so called radiation-enhanced dislocation glide induced by plasma light. The other is that hydrogen actually plays some roles to enhance dislocation motion. In order to distinguish both possibilities, we have done similar experiments under nitrogen plasma with the same light intensity as hydrogen plasma. No enhancement of dislocation motion was observed at all. Further, spreading resistance measurements have been done on boron-doped silicon samples that were exposed to hydrogen plasma at 393K in the bending apparatus. From the measured depth profile of resistivity, it was found that hydrogen atoms were incorporated up to about 10 μm beneath the surface to passivate boron. This assures us that hydrogen atoms were incorporated to enough depth at the temperatures where dislocation velocity was measured. These results clearly indicate that hydrogen enhances dislocation motion, possibly by passivating dangling bonds existing at kink sites on dislocation core to reduce the activation energies of kink formation and/or migration.

EPR EVIDENCE OF HYDROGEN-ENHANCED DIFFUSION OF ALUMINUM IN SILICON

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Key Words: silicon, aluminum pair, hydrogen, magnetic resonance

In this contribution we present the observation of low-temperature (<200 K) enhanced migration of aluminum atom in silicon implanted with hydrogen. The conclusion about long-range aluminum migration results from the detection of a new EPR spectrum (labelled Si-AA15) which is clearly identified as a defect containing Al-Al pair. The migration of Al atom occurred in our experiment at $T < 200$ K can not be a normal or recombination-enhanced migration and apparently is an atomic process catalysed by hydrogen.

For EPR study aluminum doped ($\sim 5 \times 10^{16} \text{ cm}^{-3}$) floating-zone-refined silicon samples were used as a starting material. Two ways for hydrogen introduction into samples were used: a proton implantation at 80 K by means of a cyclotron (~ 10 MeV) as well as a heat-treatment of sample at $T \sim 1200^\circ\text{C}$ (30 min) with presence of water vapour, quenched to room temperature and subsequent γ -particles irradiation at 80 K. The AA15 spectrum is appeared after annealing of sample at ~ 200 K and anneal out at 300 K for both way preparation of samples.

The AA15 spectrum can be described as arising from an anisotropic defect of C_{1h} symmetry with $S=1/2$. The ^{27}Al (100% abundant, $I=5/2$) hyperfine interaction clear reveals the presence of two nearly equivalent aluminum atoms in structure of AA15 defect. From analysis of the ^{27}Al hyperfine interaction we have deduced that $\sim 15\%$ resonant wave function accounted for on each of two aluminum atoms and it is definitely of a s-nature: 45 % 3S and 55 % 3P.

Second new EPR centre labelled Si-AA16 with $S=1/2$ containing only one Al atom was also obtained in the same samples. The AA16 centre have weakly anisotropic g- and A-tensors ($g=2.0035$ and $A_{||}=823 \text{ MHz}$; $A_{\perp}=834 \text{ MHz}$) and is stable up to ~ 200 K. We suggest that AA16 centre is a weakly binding aluminum-hydrogen pair in interstitial position (Al-H)_i.

The AA15 centre can be formed either under conditions of H-implantation at 80 K or during of thermal annealing up to 200 K. In the both cases it is necessary to conclude that long-range migration of aluminum atom at low temperature is required. It is also clearly that hydrogen plays an important role when the AA15 centre is formed, since this centre is absent in Al-doped (hydrogen free) samples after α -particle or electron irradiation. We suggest that aluminum migration takes place in form of (Al-H)_i complex, and hydrogen role may be in the decrease of thermal barrier for migration of Al_i, as well as in the case of hydrogen influence on the oxygen migration [2,3]. Tentative models including Al-Al interstitial pair as well as mechanism of hydrogen-enhanced migration will be discussed.

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INITIAL OXIDATION OF THE HYDROGENATED Si <111> SURFACE

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Key Words: surface defect, Si/SiO₂ interface, Oxygen in Si

We study the formation of a complex surface defect, the clustering of Oxygen atoms at the hydrogenated Si <111> surface. The system is relevant by itself, and also to the understanding of the Si/SiO₂ interface which is one of the most investigated in the field of semiconductors because of its fundamental role for device physics. Indeed, it is often speculated that the final interface structure may depend on the whole dynamics of the growth process, and thus the initial stages of surface oxidation are of special interest, and merited extensive experimental investigations. Theoretical studies for the incorporation of monolayers (or fractions of monolayers) can be handled in the usual first-principles supercell approaches. For the very initial stages, however, they are specially difficult because one must focus on isolated surface defects, which would demand unusually large supercells.

We present a study of the hydrogenated Si <111> surface, under exposure to atomic Oxygen. To be able to perform this investigation, we use a semiempirical Hartree-Fock technique, reparametrized to give a good description of structural and vibrational properties for bulk Si and quartz, for O-defects in Si, and for small relevant molecules (MNDO/Crystal). The technique allows us to obtain self-consistent charge rearrangements, total energies, and vibrational frequencies. We then simulate the surface through cluster models (with 50 and 134 atoms), including four Si layers, with the surface layer saturated by Hydrogen atoms, and terminated on the back side and lateral boundaries by Si pseudo-atoms. We allow relaxation of the three top layers, in the case of the free Si-H surface; the defect is then studied at the center of the surface, allowing relaxation of up to second neighbors.

We find that subsurface incorporation at the bond-interstitial site is preferred over a surface Si-OH configuration, and we simulate the incorporation of one up to three subsurface O-atoms, thus reaching the saturation limit of the back bonds of a Si-H unit. We obtain Si-H stretching frequencies within a few percent of the experimental values. Our results support the experimental assignments in that we find a mode localised at the surface defect, that shifts to higher energies with the number of subsurface O-atoms. We obtain a very definite trend in the total energy of the defect with increasing number of O-atoms in close interaction, which allows us to conclude that the initial stages of oxidation, for the H-Si <111> surface, proceed through island formation.

OPTICAL ABSORPTION DUE TO HYDROGEN BOUND TO INTERSTITIAL Si IN Si CRYSTAL GROWN IN HYDROGEN ATMOSPHERE

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Key Words: interstitial, hydrogen, localized vibration, optical absorption, Si

Various kinds of secondary defects, such as swirls and voids, were observed in as-grown Si. They were considered to be generated by the agglomeration of vacancies and interstitials. It is indispensable to know properties of vacancy and interstitial at high temperatures in order to understand the agglomeration process. Their properties at high temperatures such as

concentration at thermal equilibrium and formation energy, however, have not been determined yet. In the case of vacancies, positron annihilation method is applicable to determine their concentration at high temperature. Within our knowledge, experimental methods applicable to determine the concentration of interstitial have not been reported so far. We have reached to the conclusion that the optical absorption peak at 2223 cm^{-1} observed in proton-irradiated Si and Si grown in hydrogen atmosphere was related to vibration of hydrogen bound to interstitial. Hence we propose that properties of interstitial Si atom can be determined by monitoring the above absorption.

Si crystals were grown by floating-zone method in hydrogen atmosphere at about 1 atm. pressure. Velocities of crystal growth were between 0.1 to 3 mm/min. Two kinds of specimen holder were adopted, namely, a carbon holder and a metal holder. Their optical absorption spectra at 6 K were measured with the use of a FT-IR spectrometer.

In the case of crystals grown with the use of carbon holder, many optical absorption lines included 2223 cm^{-1} were observed. Those lines were in good agreement with those observed in proton-irradiated specimens. It means that those lines were related to vibration of hydrogen atoms bound to simple point defects like interstitial and vacancy. In the case of crystals grown with the use of metal holder, those lines were not observed. The difference between those two kinds of crystals was the concentration of carbon, being high in the former crystal. Those optical absorption lines were not observed even the concentration of carbon was high if tin was codoped around 10^{18} cm^{-3} . We propose that some optical absorption lines including 2223 cm^{-1} line are due to localized vibration of hydrogen bound to interstitial Si based on Abe's proposal. He proposed that interstitial Si and vacancy were prevalent when crystals were doped with impurities of smaller and larger covalent radius than that of Si, respectively, based on the observation that swirls of interstitial-type and vacancy-type were developed depending on the dopants of smaller and larger covalent radius, respectively.

THEORY OF GOLD-HYDROGEN DEFECTS IN SI

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Key Words: gold, hydrogen, silicon, *ab initio* theory.

The theoretical understanding of the interaction of H with TM impurities in Si is complicated by the existence of many possible sites for H with almost degenerate energies. Furthermore, the main experimental information on the defects in general has come from DLTS measurements which have not yielded either the composition of the defects or their structures. *Ab initio* local density functional theory is used to examine the structure of AuH_n , $n \leq 4$ defects in Si with both anti-bonding and bond-centred locations investigated. We use the Slater transition state method to investigate the donor and acceptor levels and these are compared with DLTS investigations. It is shown that in general the defects possess both deep donor and acceptor levels. However, AuH_3 does not possess any deep donor levels and only a shallow acceptor level. This defect may be identified with the the passivated Au-H complex previously reported.

CHARACTERISATION OF RECOMBINATION CENTRES IN SEMICONDUCTORS BY DLTS

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Key words: DLTS, recombination centres

Defects play a key role in the material properties of virtually all semiconductor devices. Among these, recombination centres, i. e. defects that can exchange charge carriers effectively with both the valence and conduction bands, are particularly important for the operation of solar cells. Despite its technological importance, the understanding of carrier kinetics at recombination centres is limited.

An experimental technique (a modified version of the Deep-Level Transient Spectroscopy, DLTS) has been developed which, by combining both the majority and minority carrier injection, allows deep levels to be filled by both types of carriers in a controlled manner and thus provides a convenient technique for the detection and characterisation of recombination centres [1].

This paper gives a theoretical description of this technique which agrees well with the experimental observations (Fig. 1). This theory, in turn, provides an accurate method for the determination of both minority and majority carrier cross sections for the same deep level. When input into the Shockley-Hall-Read statistics, these data make it possible to determine the minority carrier lifetime and predict the performance of semiconductor devices, in particular, the solar cells. It will be shown that an excellent agreement is obtained with the observed solar cell data.

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FREQUENCY DEPENDENCE OF DEEP IMPURITY TUNNEL IONIZATION IN TERAHERTZ-FIELDS

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Key Words: tunnel ionization, terahertz fields, deep impurities

The frequency dependence of phonon assisted tunnel ionisation [1] of deep impurities by terahertz radiation has been observed for the first time. The emission probability increases with increasing frequency and decreasing temperature. The dependence of the ionization probability of Hg in Ge on the intensity and radiation frequency has been investigated for wavelengths between 35 μm and 280 μm and temperatures between 20 and 90 K. At high temperatures the rate of carrier emission is independent of the radiation frequency whereas at low temperatures a strong dependence on the photon energy has been observed.

The nonlinear process of ionization of deep impurities in high-frequency electromagnetic fields shows different types of frequency dependences in two limiting cases: tunnel ionization at low frequencies and multiphoton ionization at high frequencies. In terahertz range, depending upon temperature, radiation frequency and intensity, both processes may take place. For high frequencies and low temperatures the approximation of a static electric field is no longer valid. So a new model for alternating electric fields has been developed. The experimental results have been analyzed in terms of this new model.

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CHARGE DISTRIBUTION AND OPTICAL PROPERTIES OF F^+ AND F CENTERS IN KNbO_3 FERROELECTRIC CRYSTALS

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Key words: point defects, theory, electronic structure, optical properties, perovskites

Perovskite-type KNbO_3 crystals have numerous electro-optic and non-linear optic applications. As the temperature lowers, KNbO_3 undergoes a sequence of phase transitions, from paraelectric cubic phase to ferroelectric tetragonal (at 708 K), then to the orthorhombic (at 498 K), and lastly to the rhombohedral (at 263 K) phase. It is well understood now that its properties are considerably affected by *defects and impurities*. The oxygen vacancy, V_O , is quite common defect in many oxide crystals. It produces two kinds of electron centers called F^+ and F (one and two electrons trapped by V_O , respectively).

We use quantum chemical version of the Hartree-Fock method known as the Intermediate Neglect of the Differential Overlap (*INDO*). This approach has been applied, and very successfully to calculations for many pure and defective oxide crystals, including MgO , Al_2O_3 , TiO_2 . To avoid a problem of the boundary conditions well-known for a cluster model, we use here the *supercell model* which is $2 \times 2 \times 2$ extension of the primitive unit cell, i.e. contains 40 atoms.

To simulate the F center, we remove one of O atoms. In the cubic phase all O atoms are equivalent and have the local symmetry C_{4v} whereas in the orthorhombic phase there are *two* kinds of non-equivalent O atoms whose symmetry is lower, C_{2v} or C_s . After the O atom is removed, the atomic configuration of surrounding atoms is re-optimized via search of the total energy minimum as a function of the atomic displacements from regular lattice sites. Calculation of the adiabatic energy curves for the ground and excited state permits to find the *optical absorption energy* (using the so-called ΔSCF procedure). To extend the basis set in the F -type center calculation, additional $1s$, $2p$ atomic orbitals were centered at the O vacancy. Their parameters were chosen close to those used by us in the F center calculations in MgO .

Because of the C_{4v} local symmetry of the F -type centers in the KNbO_3 cubic phase, its excited state splits into two levels, one of which remains two-fold degenerate. Our SCF calculations predict the two relevant absorption bands: at 2.34 eV and 2.66 eV for the F^+ center and 2.73 eV and 2.97 eV for the F center. Around room temperature, in the orthorhombic phase, there exist two kinds of F -type centers associated with two non-equivalent O atoms revealing the C_{4v} and C_s symmetry. Their absorption energies will be discussed. The electron defects similar to what we have calculated here differ strongly from the F center in MgO but are known in partly-covalent SiO_2 crystals (e.g., in the so-called E'_1 center an electron is also not localized inside V_O but sits on the sp^3 orbital of neighbouring Si atom).

EFFECT OF INTERCRYSTALLITE BOUNDARIES OF TWO TYPES IN SEMICONDUCTORS-FERROELECTRICS ON THEIR THERMOPHYSICAL PROPERTIES

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There is a widespread view that the nature of the posistor effect in semiconductors-ferroelectrics can be explained by the presence of a screening layer at intercrystallite boundaries. This is described fairly convincingly by the Heywang W. theory in which it is assumed that all intercrystallite boundaries are identical. In our earlier studies [1], two types of intercrystallite boundaries were detected in some ceramic materials. The present work was devoted to studying the effect which said boundaries of different type have on the thermophysical properties of posistor materials. The investigation was conducted on ceramic samples of semiconductive lead ferroniobate titanate [2] prepared by a special technique. In view of the fact that the difference in the type of boundaries is determined by concrete stages of sintering, the process of sintering of samples was interrupted at certain temperatures. The analysis of the thermophysical characteristics (thermal conductivity, temperature resistance coefficient and others) was carried out in the 300-600 K range.

The following dependences of the thermophysical parameters were studied:

- on conditions of the high-temperature formation of ceramic microstructure (development of intergrain boundaries of various types);
- on nonstoichiometry of the composition in regard to lead;
- on defectiveness of the starting oxides of titanium, niobium and iron.

Possibilities have been examined of varying the defectiveness of the ferroceramic structure and controlling its thermophysical properties by introducing small amounts of specially selected glass.

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PERIODICAL HETEROPHASE STRUCTURES AND AUTOSOLITONS IN PHOTOFERROELECTRICS

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Key Words: photostimulated phase transition; interphase boundary, autosoliton.

It is known that the periodical domain structure arises due to screening effects. In this report it is demonstrated that the domains of autosoliton kind arise in photoferroelectrics because of redistribution of electrons on trapping levels.

The properties of photostimulated ferroelectric phase transition are determined in many ways by the mutual effects of the electron and lattice subsystems. As a result, the width of the band gap is increased due to spontaneous polarization, and there is a shift in the Curie temperature because of a change in the population of trapping levels. Autosoliton arises when a single stationary state of a system became a metastable state. The task had been solved for one dimensional case. The existence of an autosoliton and the distribution of the order parameter in it are directly related to the spatial distribution of the concentration of electrons on trapping levels.

Evolution of one—dimensional autosolitons can give rise to the periodical domainstructure of para— and ferroelectric phases. This structure arises when a single stationary state of a system became a nonstable state. The period of this structure is determined by electron diffusion.

When there is the oscillations in uniform case, the autowave regime arises in one dimension. The autowave is a periodical domain structure of para— and ferroelectric phases moved with the constant velocity.

The behavior which arises is associated with the dynamics of the ferroelectric—semicon- ductor as a whole and is an example of synergistic behavior.

SELF ORGANIZATION PHENOMENA IN FERROELECTRIC— SEMICONDUCTORS

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Key Words: dynamic regimes; photostimulated phase transition; interphase boundary.

The properties of photostimulated ferroelectric phase transition are determined in many ways by the mutual effects of the electron and lattice subsystems. As a result, the width of the band gap is increased through the onset of a spontaneous polarization, and there is a shift in the Curie temperature because of a change in the population of trapping levels.

There is a closed region of an instability of the ferroelectric phase in the temperature - illumination intensity phase space of this system. In this region the self-excited oscillations of the polarization and of the number of electrons in trapping levels arise in uniform case. The mechanism for the self-excited oscillations can be described as follows: For a system in the ferroelectric phase, the pumping leads to an increase in the number of electrons in trapping levels. This increase lowers the phase transition temperature, and the system remains in the paraelectric phase. There is an increase in the probability for thermal scattering into the conduction band, and the trapping levels became emptied. this effect results in an increase in the phase transition temperature and a return to the ferroelectric phase. A similar picture with a periodic change in phase during illumination has been observed in proustite (Ag_3AsS_3).

In one dimension case the autowave regime arise in the instability region. The autowave is a periodical domain structure moved with the constant velocity. In one dimension case the autosolitons can arise in this system too. Within the scope of this model the experimental observation of oscillations of an interphase boundary in a system with a temperature gradient have been described.

CREATION OF DEFECTS "LOCALIZED IN VOLUME" AS A METHOD FOR STUDYING MULTIAXIAL FERROELECTRICS- SEMICONDUCTORS

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Key words : ferroelectric, semiconductor, defect, domain

The paper summarizes some results of experiments concerned with microindentation of single crystals. The complex form of the region strained under a local mechanical load leads to defects of the crystal structure "localized in the volume". They may be represented by microcracks, ferroelectric and ferroelastic domains, rosettes of dislocation. Deliberate creation of such defects can be employed as a specific method of studying ferroelectric, semiconductive and other properties of real crystals.

For example, an anomalously extensive growth of cracks in a-domain BaTiO₃ crystals and the inversion of this phenomenon depending on the carrier type allows one to analyze the screening of charged twin boundaries effected by the majority carriers of the crystal¹. When examining the e-domain BaTiO₃ single crystals, an "internal" 90° domain has been found in the area under a local mechanical load which does not reach the crystal's surface. The formation of such twin is characterized by the relaxation time τ depending exponentially on the load F . A change in the semiconductive properties of the crystal (such as concentration and type of carriers) and other alterations that affect its field of space charges produce a shift in the dependence $\tau(F)$ ². This fact indicates that a semiconductive subsystem takes in the process of the 90° switching. The size of the domain wedges formed on the surface of e-domain BaTiO₃ crystals under the action of remanent mechanical stresses increases exponentially with the time of illumination by photoactive light¹. Plastic processes characteristic of local deformations in a PbTiO₃ crystal go on in form of microcracking, twinning, generation and motion of dislocations¹. It has been detected that the illumination of e-domain crystals reduces the size of rosettes of dislocation and enhances the crack formation around the indenter impact; the polar character of this process has been ascertained.

Thus, the study of dynamics of the defects localized in the bulk, allows one to investigate more thoroughly the processes that occur in real crystals.

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MESOSCOPIC SIMULATIONS ON LASER ABLATION OF ZnO

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Key words : ZnO, Pulsed Laser Deposition, Theory

Pulsed laser Deposition is a technique that has a simple experimental setup but in which both microscopic and macroscopic complex phenomena happen. Therefore it is very difficult to develop a satisfactory theory for the technique which explains both type of phenomena. The solution may be in mesoscopic modeling, in which one can use results both from atomistic and macroscopic models.

Mesoscopic simulations were performed in order to simulate the interaction of laser radiation with a ZnO target with sub-band-gap energy. The target was assumed to be homogeneous except in places such as grain boundaries, where there is a great concentration of absorbing defects. The surface was also assumed to have a greater absorbing defects concentration. These preferential absorbing places accumulate electrons, which will also absorb the incident radiation, and the material start having a metal like behavior near the grain boundaries and the surface. They heat up much faster than the rest of the material, and evaporation starts at the grain boundary. Differences in the evaporation rate of electrons and the ionized defects generate a positive electric charge in the grain boundaries. This positive electric charge may drive electrons from the bulk of the material towards the grain boundaries.

The strong electric fields generated by the electric charges accumulated in the surface and at grain boundaries may generate large stresses by means of the piezoelectric effect. We will discuss the effect of such electric field on evaporation and piezoelectric of ZnO.

EVIDENCE FOR THE COUPLING BETWEEN THE LATTICE AND THE VIBRATION OF INTERSTITIAL O IN GERMANIUM

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Key Words: monoisotopic Ge, local modes, phonon coupling

A very small shift (of the order of 0.01 cm^{-1}) of the frequencies of the vibration-rotation local modes of $^{70}\text{Ge}_2^{16}\text{O}$ and $^{76}\text{Ge}_2^{16}\text{O}$ near 860 cm^{-1} has been systematically observed between quasi-monoisotopic ^{70}Ge and ^{76}Ge and natural Ge (72.6 amu) samples when measured at low temperature under high resolution. The shift is negative for ^{70}Ge and positive for ^{76}Ge and it can be detected only because the full width at half-maximum of the local modes is about 0.04 cm^{-1} .

This effect has been related to the shift of the phonon frequency spectra in natural Ge and qmi Ge and to the shape of the three-phonon density of states near 860 cm^{-1} . Spectroscopic data showing this effect are presented and a modeling of the interaction is discussed. It is predicted that the effect should not occur with ^{18}O .

IMPURITY EFFECT ON DISLOCATION DLTS SPECTRA

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The influence of transition metal on dislocation electrical activity in Si crystals was studied by many groups. It was shown that dislocation interaction with transition metals can essentially influence its electrical properties. But some results of such investigations are controversial. Besides, very small attention was paid to the dislocation electrical property formation due to its interaction with oxygen. In the present study the influence of different impurities on deep level spectrum associated with dislocations in Si has been studied by the DLTS method. It has been shown that the deep level center concentration in the same samples deformed at the same temperature using the deformation cell made from the steel is essentially higher than that after deformation in clean conditions. It seems that the difference observed depends on oxygen concentration in the samples under study being smaller in samples with the higher oxygen concentration. It has been shown that dislocation electrical activity depends on its pathway. On the clean dislocations obtained after very short deformation at 600°C no spectra have been revealed by the DLTS method. But the spectra can be observed after an increase of deformation duration or after subsequent annealing. It has been shown that oxygen presented in the samples as well as contamination by transition metal enhances the dislocation activity formation during its motion or subsequent annealing. This results show that the electrical properties of moving dislocation are formed mainly by gathering impurities during its motion. As our experiments have shown oxygen leads to the increase of dislocation related DLTS spectra only in the crystals with not very high oxygen concentration. In the crystals with oxygen concentration higher than 10^{18} cm^{-3} no DLTS spectra have been observed. In our opinion the absence of dislocation DLTS spectra in highly oxygen doped crystals can be explained by the increase of charge space region radius around dislocations in such crystals and by the influence of electrostatic barrier formed near charged dislocation on filling the dislocation related centers under the DLTS measurements.

LOCALIZATION OF NONDEGENERATE ELECTRONS AT RANDOM POTENTIAL OF CHARGED IMPURITIES

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Key Word: weak and strong localization, charged impurities, magnetoconductivity

The low temperatures mobility saturation and the negative magnetoconductivity in a nondegenerate 3D electron gas in compensated *Ge* were observed and shown to be due to strong and weak localization effects.

Ge crystals doped with deep multiply charged impurities and compensated with shallow donors were studied. The Fermi level in these crystals lies deep in the forbidden band and at low temperatures, T , the conductivity is controlled by light excitation of free electrons from deep centers. In this case the electron gas in the conduction band is nondegenerate. A mobility edge for conducting electrons should exist due to strong charged impurity scattering. Near the mobility edge energy the electron wavelength should be of order of mean free path. This strong-localization condition can be easily fulfilled in compensated material. In our crystals, the mobility edge energy can exceed mean thermal energy, kT , at rather high temperatures (up to 60 K) and moderate impurity concentration. Due to Boltzman distribution function, only exponentially small number of electrons in the narrow energy band of order of kT above the mobility edge should give the main contribution to the conductivity at low T . The electron-electron interaction is negligible because of small electron concentration.

The mobility edge existence is confirmed by the temperature dependence of mobility determined from classical magnetoresistance. The electron mobility turned out to be constant at T below some threshold value and to depend weakly on charged impurity concentration. The saturated mobility value appeared to be inversely proportional to the mobility edge energy but not to the impurity concentration.

The negative magnetoconductivity (NMC) observed in the range of classically weak magnetic fields was due to magnetic-field suppression of quantum corrections to the conductivity. The electron-wave dephasing time found from initial part of NMC curves coincided with the acoustic-phonon scattering time. The dephasing time values were of two orders of magnitude more than the mean free time due to impurity scattering. The saturated values of relative NMC depended on charged impurity concentration and did not exceed several per cents although NMC should be close to 1 for conducting electrons having energies near the mobility edge. The magnetic length at which the negative MC saturated was found to correspond to the radius of a random potential caused by space disorder of impurities. The existence of a minimum size of closed electron trajectories of order of mean distance between impurity centers was shown to be the cause of the small NMC magnitude.

NEW APPLICATION OF IR PHOTOCONDUCTIVITY METHOD FOR DETERMINATION OF ELECTRICALLY AND OPTICALLY ACTIVE IMPURITIES IN SEMICONDUCTORS

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Key words: IR spectroscopy, photoconductivity, absorption, Si, impurities

Absorption and photoconductivity IR spectroscopy is one of the primary methods for determination of optically and electrically active impurities in semiconductors with high sensitivity and resolution. It is known, that the impurity and lattice absorption change a photoconductivity continuum of electrically active centers in semiconductor [1,2]. The absorption in impurity transitions gives narrow dips in photoconductivity continuum of the investigated sample at low temperatures. In this paper we present a new method (the low temperature photoconductivity with absorption (PCAS)) for determination of the absorption coefficients and concentrations of all optically active impurities with spectral lines dipped in photoconductivity (PC) continuum spectrum of the investigated semiconductor sample. This method is the variant of absorption spectroscopy using the analysed samples as contactless photoconductivity IR detectors.

The relation between the absorption coefficient in the sharp spectral line α and experimentally determined value of sharp dip (U_2/U_1) in the smooth PC continuum at low temperature is given by

$$U_2/U_1 = (1 + \alpha l \gamma) \cdot (1 - \exp\{-\gamma l\}) / (1 - \exp\{(\alpha + \gamma) \cdot l\}),$$

where $U_{1,2}$ are the photoconductivity signals in center (1) and out of dip (2); γ is the absorption coefficient in PC continuum; l is the absorption path length.

The method was applied to determination of impurity concentrations N ($\alpha = \sigma \cdot N$, where σ is absorption cross section) in B-, P-, Al- and thermal double donors-doped silicon crystals. The PCAS spectra and "pure" absorption spectra (AS) were taken with high resolution FTIR spectrometers Bruker IFS-113 or 120HR using original contactless PC measurements [2].

The comparison of PCAS data with the data of other known methods of measurement of impurity absorption coefficients and concentrations shows good opportunities of the new method for quantitative determination of impurities. For example, the values of carbon absorption coefficients at 607 cm^{-1} determined from PCAS ($\alpha[C_s] = 9.6 \text{ cm}^{-1}$) and AS ($\alpha[C_s] = 8.7 \text{ cm}^{-1}$) for Ga-doped ($3.6 \cdot 10^{14} \text{ cm}^{-3}$) Si crystal agree. Concentrations of electrically active impurities of P, B, Al, carbon-acceptor complexes and thermal double donors determined with PCAS method in the interval $10^{12} - 10^{16} \text{ cm}^{-3}$ correspond with those determined from Hall measurements. Analytical possibilities and applications of this method will be discussed.

The work was supported by the Grant 96-03-32581 from the Russian Foundation for Fundamental Researches.

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MULTIPHONON-ASSISTED TUNNELING IONIZATION OF DEEP IMPURITIES IN A HIGH-FREQUENCY ELECTRIC FIELD

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Key words: multiphonon transition, tunneling, far infrared radiation, deep centers

A theory of multiphonon-assisted tunneling ionization under high-frequency electric field is presented.

Recently tunneling ionization of various types of deep centers in germanium and $\text{Al}_x\text{Ga}_{1-x}\text{Sb}$ by far infrared radiation was observed by Ganichev et al. (Phys.Rev.Lett., 71, 3882 (1993), 75, 1590 (1995); Semicond.Sci.Technol., 11, 679 (1996)) in a wide range of intensities and temperatures. The photon energies were by several tens smaller than the binding energies of the impurities. It was shown that the ionization is caused by a tunneling process in the electric field of the high-power radiation. The results obtained demonstrate that high-frequency far-infrared laser pulses may be used to study the elementary process of tunneling in extremely large electric field strengths, avoiding contact phenomena and avalanche breakdown.

In the framework of semiclassical approximation the dependence of probability of multiphonon-assisted tunneling ionization on the strength and frequency of the electric field and temperature is studied. It is shown that the tunneling probability increases with the frequency increase. The effect originates from the possibility for an electron to acquire additional energy from the high-frequency electric field in the process of tunneling.

As an example, results of numerical calculations of the probability of the multiphonon-assisted tunneling ionization for gold and mercury in germanium and gold in silicon are presented.

THE JAHN-TELLER EFFECT AND THE STRUCTURE OF MONOVACANCIES IN Si, SiC AND C

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Key words: Vacancies, Jahn-Teller effect, ab initio calculations

Vacancy surroundings can possess a local symmetry which is lower than the symmetry of the ideal lattice. For example, various experimental studies for Si vacancies suggest a local D_{2d} symmetry instead of a T_d symmetry. The basic mechanism for the symmetry breaking is the Jahn-Teller effect. For a local T_d symmetry the four dangling bonds left at the neighbouring atoms of a Si vacancy give rise to a completely filled non-degenerate and a partially filled threefold degenerate defect state in the fundamental gap, i.e., T_d symmetry gives rise to a degenerate ground state. According to the Jahn-Teller theorem, a degenerate ground state is usually expected to be unstable with respect to the formation of a non-degenerate ground state by means of a symmetry-breaking distortion. Consequently, not only for Si, but for all isoelectronic materials crystallizing in diamond or zincblende structure, e.g. also for cubic SiC or for C (diamond), vacancies should exhibit a lower local symmetry than T_d . The minimum requirement is to end up with at least two completely filled non-degenerate defect states and one empty twofold degenerate defect state. This can be achieved by a local rhombohedral C_{3v} or a local tetragonal D_{2d} symmetry. A further symmetry-reduction is not expected to result in an additional energy gain. Hence, it is sufficient to discuss these two local symmetries (besides T_d symmetry).

We present large-scale ab initio calculations for the atomic and electronic structure of vacancies in Si. First results for cubic SiC and diamond are presented too. The calculations have been performed within the framework of density functional theory in the local density approximation using ultrasoft Vanderbilt pseudopotentials and a plane-wave basis set. We discuss the dependence of the results with respect to the k-point sampling, the supercell size and the supercell shape. The local symmetry of the ground state, the energy differences between configurations of different local symmetry and the atomic displacements are found to be very sensitive with respect to the numerical details. For Si only a 128(127)-atom cell gives sufficiently converged results. We find a tendency for the stabilization of a ground state of the Si vacancy with D_{2d} symmetry with rising supercell size. However, the convergence of the results is still far from being perfect. Even for the largest supercells we find a relatively large dispersion of the induced defect bands. However, by means of a tight-binding description of the artificial vacancy-vacancy interaction arising in supercell calculations we are able to extract the "real" vacancy levels and Jahn-Teller splittings for an isolated vacancy from the calculated bands. The large dispersion of the defect bands leads to the common problem that for smaller cells and certain k-point samplings (e.g. Γ -point only sampling) an unphysical occupation of states around the conduction band minimum can occur. In the light of these findings it is easy to explain why different ground states have been found in previous ab initio work on Si vacancies using different k-point samplings and supercells.

NOVEL LUMINESCENT CENTRES IN CADMIUM DOPED SILICON

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Key words: silicon, photoluminescence, cadmium, Si: Cd

Samples of silicon doped with cadmium are found to produce a series of unusual and complex luminescence spectra. Three independent groups of lines are observed, for which the relative intensities depend on the annealing treatment. All three groups are multi-line spectra, with low energy in-band phonon modes. For the lowest energy group (minimum energy zero-phonon line at $1058.2 \pm 0.1 \text{ meV}$) transitions occur from an excited state manifold of five levels spread over 4.3 meV into a single ground state. The calculated infinite temperature relative intensities among the lines vary over a factor of thirty. For this group, the in-band phonon mode energy is 8 meV . Another group of lines (with the minimum energy zero-phonon line at $1066.8 \pm 0.15 \text{ meV}$) is broadly similar to the 1058 meV group, except that there are not less than eight lines within a range of only 2.4 meV . For this group, an in-band phonon mode is not detected; it may be obscured by the 1058 meV group of lines. The third group presents a simpler spectrum, consisting of only three zero-phonon lines spread over 5.2 meV , with the minimum energy component at $1083.3 \pm 0.05 \text{ meV}$; the in-band phonon mode energy is 4.8 meV . The thermal activation data in this case clearly show that both the excited and ground states are manifolds of three levels each, with very strong selection rules governing the transitions. All three groups are accompanied by broad sidebands and their intensities show a thermal deactivation energy of $\sim 12 \text{ meV}$. The spectra were first observed in samples which had been implanted with radioactive ^{111}In (which decays to Cd with a 2.8day half-life) several weeks after the In implantation indicating that a slowly diffusing impurity also present in the samples is involved in the defects. The spectra have been observed in both CZ and FZ starting materials and in samples prepared by diffusion and by ion-implantation. Annealing the samples in the temperature range $100\text{--}300^\circ\text{C}$ following a quench from high temperatures substantially enhances the luminescence intensity in addition to altering the relative intensities of the three groups. The fine structure in the spectra indicates similarities to the spectra produced by intra d-shell transitions on metal impurities in many semiconductors. Uniaxial stress and Zeeman measurements are currently in progress in order to fully characterise the transitions.

RECOMBINATION CENTERS IN ELECTRON IRRADIATED Si, GaAs AND GaInP.

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Keywords: Solar cells, recombination centers, lifetime, Si, GaAs, GaInP, space degradation.

Using the current-voltage characteristics of an abrupt Si n+p junction, we show how the minority carrier lifetimes (τ), the capture cross sections for electrons (σ_e) and holes (σ_h), and the energy level (E_T) of the corresponding recombination center can be determined independently, thus allowing to characterize completely this recombination center. This technique is applied to study the main recombination center in p-type, moderately doped (10^{16} cm^{-3}), Czochralski grown Si and to study the temperature dependence of σ_e , σ_h and τ . It is extended to GaAs and GaInP p+-n junctions to characterize the native recombination centers in the n regions, epitaxially grown by MOCVD. It is finally applied to characterize the recombination centers introduced by electron irradiation at various temperatures (80 to 300 K) in Si, GaAs and GaInP solar cells. In electron irradiated Si cells, we demonstrate that the main recombination center introduced by irradiation at 90 K is the vacancy. It becomes the divacancy for higher irradiation temperatures, when the vacancy becomes mobile. In irradiated GaAs the recombination center, presumably associated with the As vacancy, does not change with the temperature of irradiation in the range 80 - 300 K. This study is applied to the modelization of the degradation of space solar cells in conditions of deep space mission, i.e. low intensity of illumination and low temperature.

RESONANCE ACCEPTOR STATES AND THZ GENERATION IN UNIAXIALLY STRAINED p-Ge

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Key Word: resonance states, uniaxial compression, stimulated emission

The spectrum of stimulated THz emission from uniaxially compressed *p-Ge* is presented. The peaks corresponding to different optical transitions from resonance to ground and excited states of an acceptor were observed in the spectrum of the stimulated emission. These peaks were identified by means of a comparison of experimental data with calculated acceptor level positions in dependence on pressure. The mechanism of a population inversion due to free carrier accumulation near energies of resonance acceptor states based on the resonance scattering is proposed.

Uniaxial strain is known to split the degenerate at $k=0$ valence band of *Ge* as well as the acceptor state. The energy separation of the ground and split-off acceptor states increases with stress and at certain value of pressure P ($P \approx 4$ kbar for $P \parallel [111]$ and $P \approx 3$ kbar for $[100]$ crystallographic directions, respectively) the split-off state enters into the continuous valence band spectrum and creates the resonance state. Free holes having energies close to those of the resonance state undergoes the strong resonance scattering which can result in electric field induced population inversion with respect to optical transitions into acceptor states being in the forbidden band. The necessary conditions for such inversion are derived.

The spectrum of stimulated THz emission from uniaxially compressed *p-Ge* was found to contain the series of peaks. The energies of these peaks increased with pressure. The energy of the most intensive peak is varied from 8 to 42 meV by increasing pressure from 4 to 11 kbar for $P \parallel [111]$. The peak energies were compared to those found from calculated pressure dependence of the energies of localized and resonance acceptor states. The comparison allows us to identify the acceptor states which take part in stimulated optical transitions. In particular, the main peak is connected with the optical transition from the resonance $1s$ to $2p^0$ localized state (state classification corresponds to high pressure limit, when impurity states can be considered in approximation of independent valence subbands).

This work was made possible in part by Grant No 96-02-17352 from Russian Basic Research Foundation and Volkswagen Grant.

RESONANCE MODE PHONON REPLICA IN THE OPTICAL SPECTRA OF TRANSITION-METAL IMPURITIES IN GaP

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Key Words: GaP, Transition Metals, Ti, V, Cr, Mn, Fe, Co, Ni, Local Vibrations

The optical absorption and photoluminescence spectra of internal d-d transitions at transition-metal impurities (TM) in cubic GaP show sharp (linewidth $\approx 1 \text{ cm}^{-1}$) phonon replica of the zero-phonon lines. We found $\hbar \nu = (325 \pm 10) \text{ cm}^{-1}$ for the energy of the phonon at all of the TMs Ti, V, Cr, Mn, Fe, Co, Ni and no correlation with the impurity mass. To explain this, we used a method [1] based on the valence-force model of Keating and Kane to calculate the vibration frequencies and amplitudes of local vibrational modes (LVMs) at the impurity. The valence-force parameters and the effective charges for the perfect GaP crystal are obtained by fitting the phonon dispersion curves to neutron scattering data. We used the scaling factor approximation to determine the valence force parameters at the defect site. The validity of the model is tested by calculating LVMs for $^{11}\text{B}_{\text{Ga}}$ and $^{10}\text{B}_{\text{Ga}}$ impurities in GaP which gives excellent agreement with the experiment. As the next step we calculated the impurity induced phonon density of states for TM at Ga site in GaP. For a scaling factor of $S=-0.2$, corresponding to a softening of the interatomic forces at the impurity by 20%, an intensive LVM of T_2 symmetry appears at 325 cm^{-1} . We calculated the energy shift of this LVM with respect to different TM masses and found it to be smaller than the experimental linewidth of 1 cm^{-1} . This explains the absence of a correlation between the observed phonon energy and the TM mass. The phonon replica are therefore interpreted as resonance modes at the bottom of the optical phonon branch.

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LUMINESCENCE DUE TO ELECTRON-HOLE CONDENSATION IN SILICON-ON-INSULATOR AND ITS APPLICATION TO DEFECT AND INTERFACE CHARACTERIZATION

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Key Words: photoluminescence, silicon, SOI, electron-hole droplet, exciton

A silicon-on-insulator (SOI) is regarded as one of the most promising structures for the next generation devices. Recently various techniques have been reported for producing high quality ultrathin SOI layers, such as bond and etch-back SOI (BESOI) and separation by implanted oxygen (SIMOX). The thickness of the state-of-the-art SOI layers is a mere 100 nm. The characterization of such ultrathin SOI layers has so far been quite difficult. In this report we describe a characteristic luminescence from these SOI layers under ultraviolet (UV) light excitation. We demonstrate the applicability of the luminescence to the characterization of defects and interfaces of the SOI layers.

The samples used for the measurement were BESOI and low-dose SIMOX wafers. The sample structure consisted of a substrate, a buried oxide, an SOI and a surface oxide layer. For comparison we measured the samples whose oxide and SOI layers were removed by HF and alkaline solutions, respectively. Photoluminescence (PL) from the samples was measured at 4.2 - 295 K under the 351 and 364 nm lines of Ar⁺ laser and the 641 nm line of Kr⁺ laser. The excitation intensity was varied by three orders of magnitude.

When the samples were excited by the visible light, the light penetrated deep into the substrate (approximately 5 μ m). In all the samples, the emission due to excitons came out predominantly from the substrates; there was no substantial difference in the PL spectra among the samples. In contrast, a drastic change occurred under the UV light excitation: A characteristic PL band appeared if and only if the SOI layer was sandwiched by oxide layers. The characteristic band at 4.2 K had the same spectral shape as the emission band due to electron-hole droplet (EHD), although the excitation intensity was too low to generate EHD in conventional Si wafers. The spectral shape of the band changed systematically with the excitation intensity and with temperature.

We believe that the characteristic band originates from the electron-hole condensation in the SOI layer. The UV light can excite only the SOI layer because of the very small penetration depth (approximately 50 nm), and the excited carriers are confined within this layer by the presence of the diffusion barrier. If the SOI layer is sandwiched by the oxide layers, the recombination velocity at the interfaces becomes very low. This makes the density of electrons and holes extremely high even under a weak excitation condition. Electrons and holes form free exciton (FE), electron-hole plasma (EHP) and/or EHD depending on their density and temperature. The systematic spectral dependence on the excitation intensity and temperature can be understood in terms of the phase transition among these three states. The generation of the EHP/EHD is strongly dependent on the recombination in the SOI layer and at the interfaces. Therefore, analysis of the EHP/EHD signal as a function of temperature and excitation intensity allows us to characterize defects in the SOI layer and the interfacial quality.

The authors would like to thank E. Otsuka and H. Nakata for valuable comments and discussions on EHD and EHP

MORPHOLOGY FEATURES AND ETCHING BEHAVIOR OF THE NEW TYPE OF EXTENDED MICRODEFECTS IN SI

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Discovered recently the new type of extended microdefects in Si was supposed to have $\{113\}$ habit planes and unusual indices of the defect axis [1]. The defects are revealed as narrow ridges of enough large length up to 10-15 micrometers on different crystal surfaces. However, many elements of the defects morphology revealed by orthodox etching experiments are unclear. In this paper new results of the defects morphology analysis are presented.

Photoetching (PE) of Si in Sirtle-like solutions was used for the first time for analysis of the defects morphology and estimation some properties of the defects. Irradiation of He-Ne laser was used in PE and surface structures were examined with interference microscopy.

It is found, that both normal and PE give rise to formation of etch hillocks on the defects sites. It was shown by photoetching that normal treatment in Sirtle (S) etchant reveals defects structure which can be interpreted as "memory" effects. The images of the defects after PE are wider than images after S etching and show very high sensitivity of the defects to such etching process. The features of the PE figures show, that the variations of impurity concentration or increased recombination rate of photocarriers near by the defect core are responsible for ridges formation along the defects line. It was found from analysis of etch figures on (112) plane, that defect axis can be $[110]$, similarly to (113) RLD's and $[112]$.

It is important, that the defects lie directly in (111) slip plane or in the crystal volume adjacent to slip plane. Thus, the dynamic reconstructions in dislocation core may be responsible for the defects nucleation. Possible mechanisms of the defects formation based on generation of self-interstitials by moving dislocation and nature of the defects impurity atmosphere are discussed.

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SILICON SURFACE DEFECTS: THE ROLES OF PASSIVATION AND SURFACE CONTAMINATION

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Key words: surface defect, passivation, dangling bond, lifetime, sticking coefficient

Passivation of the silicon surface is essential to prevent contamination by physisorption and chemisorption. A bare silicon surface is highly reactive, and therefore easily attracts oxygen, metal ions and small particles that lead to significant surface contamination. An HF last treatment has provided the standard method to passivate the silicon surface. However, more stringent requirements on the surface cleanliness and atomic flatness, and a concern regarding HF use because of safety and environmental issues have generated the need for effective alternative passivation chemistries.

We show that the degree of surface passivation of a silicon wafer is easily detected by monitoring the surface recombination velocity. Dangling surface bonds introduce deep states in the gap that act as recombination centers for minority carriers. The method is sensitive to 10^{-7} ML (10^8 cm^{-2}) surface defect concentrations. A brief survey of applications to surface roughness, metal deposition and oxidation will be given.

We have studied in detail the surface passivation of silicon in different atmospheres and by using alternative passivation chemistries. Exposure of a hydrogen terminated passivated surface to oxygen results in an instantaneous degradation of the surface as non-polar Si-H bonds are replaced by Si-OH and Si-O-Si structures. The rate of surface defect generation corresponds to the rate of oxidation measured by FTIR absorption. We determine a sticking coefficient of oxygen of 3.5×10^{-18} at room temperature.

By comparing alternative passivation chemistries, halogens reach and even exceed the passivation degree, attained by hydrogen. Halogen passivated surfaces show the first order Langmuir adsorption behavior from methanol solution and a high resistance to oxidation. Both steric and enthalpic factors lead to a higher energy barrier for the chemisorption reaction of O_2 on halogen terminated silicon than for hydrogen terminated silicon (1.2 eV).

UV ENHANCED AND SOLAR BLIND PHOTODETECTORS BASED ON LARGE-BAND-GAP MATERIALS.

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There are many applications (biomedical, astronomy, flame safeguard systems and others) that require the measurement of blue or UV radiation in presence of visible light. The spectral selectivity of photodiodes depends on a band-gap of semiconductor which is shown on Figure 1.

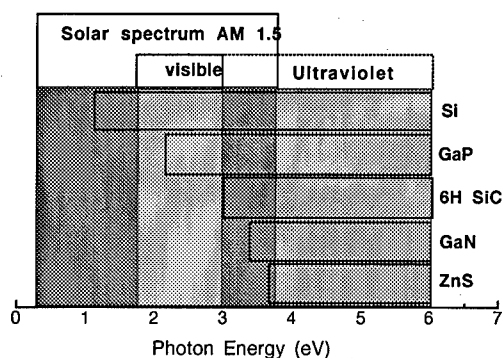


Figure 1. Semiconductors of interest as visible, UV and solar blind photodetectors, including the above spectral ranges.

In this direction, researchers are giving attention to large-band-gap semiconductor compounds such as GaP[1], SiC[2] and GaN[3] in contrast to Si-based photodiodes in which the selectivity can be provided with additional blocking filters or dielectric coating to fit them with the spectral region of interest.

The large-band-gap (3.6 eV) zinc sulphide (ZnS) greatly reduces the sensitivity to photons in the terrestrial solar radiation [4] and it is an attractive material for developing the solar blind photodetectors.

The purpose of this work is to introduce characteristics of improved UV-enhanced GaP surface-barrier detectors and solar blind ZnS-based photodetectors with F-doped tin oxide transparent and conductive electrode as high temperature devices with excellent electro-optical characteristics. The UV efficiency, selectivity and specific detectivity of new photodetectors are compared with those obtained from devices based on SiC and GaN semiconductor compounds.

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DEEP LEVEL DEFECTS IN RTA p^+np STRUCTURES

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Key Words: DEFECTS, p^+np STRUCTURES ION IMPLANTATION, RTA. DLTS

The defect formation in silicon layers, which were ion implanted and annealed by rapid thermal annealing (RTA) techniques, has been investigated. The two terminal p^+np structure was used as test structure (vehicle) for the present investigation. This structure has a fully depleted base (for $V=0V$). Current control is achieved by an internal potential barrier, whose energy height may be controlled by the ion implantation energy and dose of the base. As such this p^+np structure is an excellent device for investigating the behavior of trap states and defects, after ion implantation and rapid thermal annealing or furnace annealing. The present paper reports on results obtained from the investigation of deep levels in such structures which were doubly ion implanted with 150KeV phosphorous ions, at a dose of $1 \times 10^{13} \text{ cm}^{-2}$ or $3 \times 10^{12} \text{ cm}^{-2}$ and subsequently with 28KeV boron ions at a dose of $1 \times 10^{14} \text{ cm}^{-2}$. After ion implantation, the samples were RTA annealed at 850°C for up to 90sec, or furnace annealed at 1000°C for 10min.

The defect structure was investigated using deep level transient spectroscopy (DLTS). The predominant traps identified in unannealed p^+np samples were majority carrier traps at 0.34, 0.56 and 0.62eV, their exact position depending on the p^+np bias conditions. This bias sensitivity indicates that the traps are probably due to the fine structure of dislocations near interfaces. The density of these defects is found to be dramatically lower in the RTA p^+np samples compared with that in the furnace annealed samples. It is also important to note that the defect structure varies when the implant dose of phosphorous increases to 10^{13} cm^{-2} . The presence of microtwins, along with dislocations, becomes a possibility. The results of this investigation on the important stability factor of deep levels introduced by ion implantation and the effect of RTA and furnace annealing on their density will be presented and discussed. The sensitivity to p^+np bias conditions and its connection with traps near the layer interfaces will also be discussed.

CRYSTAL-FIELD TRANSITIONS OF Nd^{3+} AND Er^{3+} IN PEROVSKITE-TYPE CRYSTALS

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Keywords: rare earth, erbium, neodymium, perovskites, photoluminescence, Raman effect

The crystal-field levels of the 4f electrons of rare-earth ions introduced as dopants in a solid matrix have been extensively studied. These electronic wavefunctions are very localized, but nevertheless influenced by the electric and magnetic order in the host crystal.

Their study in high- T_C superconductors, where the rare-earth ion is a part of the crystallographic unit cell, has become of increasing interest [1]. The aim of this paper is to study compounds which have a crystal structure and similar composition to that of high- T_C superconductors and determine the environment and the properties of the rare-earth element.

R_2BaZnO_5 (R denotes a rare-earth element) crystallizes in two different structures depending on the rare-earth ionic radius. One of them, (R denotes Sm, Eu, Tm, Y) is orthorhombic with space group Pnma. The second family (R denotes La and Nd) is tetragonal, the space group is $I4/mcm$. The latter structure contains Nd-O layers separated by slabs consisting of isolated ZnO_4 tetrahedral units and Ba atoms between them. Most of the components with the composition R_2BaZnO_5 have an orthorhombic structure described by the space group Pbnm. All of these components are insulators. For energies larger than 1000 cm^{-1} , the interaction of these materials is dominated by the electrons of the 4f shell of the rare-earth element.

We report on a study on Nd^{3+} and Er^{3+} in $\text{Nd}_2\text{Ba}(\text{Zn,Cu})\text{O}_5$ and $\text{Er}_2\text{Ba}(\text{Ni,Cu})\text{O}_5$ by means of photoluminescence, absorption, and Raman spectroscopy in magnetic fields up to 15 T. The crystal field levels of Nd^{3+} and Er^{3+} were determined in the range $0\text{--}30000 \text{ cm}^{-1}$ applying the optical techniques mentioned above at different temperatures. The photoluminescence of the $\text{Nd}_2\text{Ba}(\text{Zn,Cu})\text{O}_5$ compound is dominated by the emission from the $^4\text{F}_{3/2}$ state to the $^4\text{I}_{15/2}$, $^4\text{I}_{13/2}$, $^4\text{I}_{11/2}$ and $^4\text{I}_{9/2}$ multiplet. For the $\text{Er}_2\text{Ba}(\text{Ni,Cu})\text{O}_5$ material, the $^4\text{I}_{13/2}\text{--}^4\text{I}_{15/2}$ transition with the well known $1.54 \mu\text{m}$ luminescence is strongest. However more zero-phonon lines (ZPL) are observed than expected in the simple crystal-field picture. This indicates that either other phases are present in the crystal or that the rare-earth is also incorporated on other sites.

All degeneracies of the states are lifted except for the Kramers degeneracy because of the C_{2v} symmetry around the rare earth. The $\text{Nd}_2\text{BaZnO}_5$ compound shows the usual Zeeman-behavior, whereas extraordinary large shifts ($g_{\text{eff}}=8.2$) of the ZPLs in magnetic fields have been evaluated for the Er compounds.

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DEFECTS SPECTROSCOPY IN β -Ga₂O₃

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Key words: β -Ga₂O₃, magnetic resonance, vacancy, transition metals

Gallium oxide β -Ga₂O₃ is a wide band gap semiconductor with a room temperature band gap of 4.7 eV. It exhibits interesting intrinsic properties with applications in dielectrics and as gaseous sensors. Its n-type conduction is thought to be controlled by oxygen vacancies according to the earliest reports. We studied bulk crystals, transparent and conducting at room temperature, by electron paramagnetic and electron nuclear double resonance (EPR, ENDOR) investigations and time integrated photoluminescence. As trace impurities we identify iron and chromium in the 3+ charge states. In addition a slightly anisotropic signals is seen by EPR around $g=1.95$ which shows partially resolved ligand hyperfine (lhf) structure. From ENDOR we can demonstrate that the lhf arises from nearest neighbor Gallium nuclei in distorted tetrahedral and octahedral coordination (the crystal structure is monoclinic C2/m). The defect with $S=1/2$ hence resides on the oxygen sublattice and the absence of any central hyperfine interaction supports the model of the oxygen vacancy as responsible defect. Annealing experiments under oxidizing and reducing atmospheres were performed to study the thermal stability of the defect. Under oxidizing conditions the conductivity drastically decreases (the sample became high resistive) whereas the defects properties hardly changed. The control of the conductivity by intrinsic defects such as the oxygen vacancy has to be questioned and the role of shallow extrinsic donors also seen by EPR has to be taken into consideration.

DX-CENTERS IN IONIC SEMICONDUCTOR CdF_2 : PHYSICS AND APPLICATIONS

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Metastable center, deep state, lattice relaxation, photochromic effect, holography

Besides covalent and ionic-covalent semiconductors, the metastable DX-like centers occur in the wide-gap, predominantly ionic CdF_2 crystals doped with some tri-valent Me impurities ($\text{Me} = \text{In, Ga, Al}$) and reduced in the hydrogen or metal vapors to convert the crystals into the semiconductor state. The studies of photo- and thermo-transformation of these centers show that a change of the center state is induced by a change in its charge. The bimolecular kinetics of the thermodestruction of the shallow center and the quantum yield 2 of the photochemical reaction of the deep-shallow center transformation testify clearly to participation of two shallow centers in formation of one deep and vice versa [1]. Direct evidence of the negative-U nature of the deep state of the center was found in the experimental measurements of magnetic moment J of $\text{CdF}_2:\text{In}$ which showed the absence of magnetic moment in this state and its appearance with $J = \frac{1}{2}$ for the shallow state [2]. Two types of deep centers were discovered for Ga- and Al-doped crystals; these centers differ strongly in the lattice relaxation accompanying their formation. It is concluded that Me centers in CdF_2 are not DX-like ones, as was initially supposed, but the true DX centers with all their typical features, though it is rather strange for such ionic compound as CdF_2 . One can conclude that a strong hybridization of states occurs in this compound. Parameters of the configuration-coordinate models for the Me centers are determined and their microscopic models are proposed [3]. Results of the experimental study of center structure are considered. An explanation is given why the non-transition Me impurities in CdF_2 form the metastable centers whereas the transition-metal (of the column III) and rare-earth ones produce the shallow donors only [4].

The giant photochromic effect in $\text{CdF}_2:\text{Me}$ was recently used for the writing the holographic gratings in these crystals [5,6]. Their diffraction efficiency and the sensitivity of crystals are evaluated on the basis of the analysis of the photochemical transformations and compared with the experimental values of these parameters [7]. Possible using of these media for writing both static and dynamic gratings are discussed.

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EFFECT OF NEUTRON IRRADIATION ON Ga-BASED SEMICONDUCTORS

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Key Words: NTD, Positron Annihilation

Positron annihilation technique (PAT) has demonstrated its capability to detect defects in semiconductor materials. However it seems that PAT has been scarcely applied to III-VI layered semiconductor. These compounds have attracted much attention in the last years due to their electronic transport properties and non-linear optical coefficients. They have a structure formed by layers containing monoatomic planes, which are bonding by Van der Waals forces. Within a layer the bonding between atoms is covalent. The GaSe and GaS compounds belong to this group, and they have not been as extensively studied by PAT as InSe (the most representative of the III-VI group). It may be expected that this two-dimensional bonding scheme yields similar positron annihilation characteristics in all these III-VI semiconductors.

Neutron-transmutation doping (NTD) is a convenient method for semiconductor doping purpose when a precise amount and a homogeneous distribution of the impurities are required. The process depends on the capture cross-sections and the natural abundance of each isotope. During the NTD process some lattice defects are created due to the β^- and γ^- particles produced in the nuclear reactions and also due to the fast neutrons which unavoidable accompany the thermal neutrons flux and cannot be completely eliminated. In this situation, the recoil energy transmitted to the involved atom through the β^- and γ^- decay can displace the resultant Ge-atoms from their initial Ga sites to interstitial positions. PAT as a technique sensitive to vacancies, can be useful to investigate the nature and charge state of those vacancy related defects created after irradiation.

We present here positron lifetime and Doppler broadening measurements performed on NTD-GaS and GaSe single crystals. The samples were irradiated at different fluences yielding estimated concentrations for Ge-transmuted atoms between 2.5×10^{15} and $2 \times 10^{16} \text{ cm}^{-3}$. The as-grown materials are well described by only one lifetime component: 287 ps for GaSe and 291 ps for GaS. For the irradiated specimens the positron lifetime spectra reveal a new second component: 335 and 330 ps for GaSe and GaS, respectively. The average lifetime τ_m and S-parameter have shown a saturation effect with increasing radiation dose. The nature of these radiation induced defects are discussed in terms of the well-known trapping model.

ELECTRON SPIN RESONANCE FEATURES OF THE P_{b1} INTERFACE DEFECT IN THERMAL (100)Si/SiO₂

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Key words: Si/SiO₂ structure; interface defects; point defects; electron spin resonance

The thermal growth of the Si/SiO₂ structure is known to be attendant with the natural incorporation of coordination defects at the Si/SiO₂ interface as a result of network-lattice mismatch. Over the recent decades, these have been the subject of intense research, mainly driven by their adverse electrical effect on Si-based devices. This has evoked ceaseless electrical characterization. However, as to atomic identification, the key information so far came from electron spin resonance (ESR) analysis - a tool with atomic level physicochemical sensitivity.[1]

As detected by ESR, the Si/SiO₂ interface defects are generically referred to as P_b centers, their appearance being dependent on the Si substrate surface orientation. At the (111) Si/SiO₂ interface, ESR has so far detected only one type of defect, specifically called P_b . It has been convincingly identified as the interfacial $\text{oSi} \equiv \text{Si}_3$ defect. The center exhibits C_{3v} ([111] axial) symmetry with principal g values $g_{\parallel} = 2.0014$ and $g_{\perp} \sim 2.0086$.

At the (100) Si/SiO₂ interface, by contrast, ESR has isolated two spectroscopically different types of defects, called P_{b0} and P_{b1} . [2] Both were initially also pictured as interfacial single dangling Si-bond type of defects, where P_{b1} was modeled as an interfacial $\text{oSi} \equiv \text{Si}_2\text{O}$ entity, the center thus purported to be of different chemical structure than P_b . However, this assignment was subsequently countered both experimentally and theoretically. This leaves the atomic structure still obscure, mainly because ESR analysis has so far failed to provide an as convincing set of data as for P_b . Reasons for this are the inherently smaller defect density (3 times) in (100) Si/SiO₂ and spectral overlap. Particularly in the case of P_{b1} , this has obstructed an accurate g matrix and hyperfine interaction evaluation. The present work regards the former part. During recent extended analysis of intrinsic interface defect generation as a function of oxidation conditions, fabrication parameters could be delineated predominantly leading to P_b , incorporation ($[P_{b1}]/[P_{b0}] \sim 20$). This allowed accurate P_{b1} signal characterization. The element of inclusiveness inherent to inferring ESR parameters from entangled weak P_{b0} and P_{b1} spectra has thus been alleviated.

Main results on P_{b1} include: (1) accurate g matrix calibration confirming the P_{b1} point symmetry as monoclinic-I; (2) principal g values $g_1 = 2.0058$, $g_2 = 2.00735 \pm 0.00010$, and $g_3 = 2.0022$, where the g_2 (admittedly about the unpaired Si hybrid direction) direction is at $3 \pm 1^\circ$ (towards the interface) with a $\langle 111 \rangle$ direction at 35.3° with the interface plane. Only the four crystallographic defect orientations (ESR) equivalent through the 4 [100] face symmetry occur; (3) The linewidth is found weakly dependent on magnet angle, ascribed to a strain induced spread $\sigma_{g_{\perp}} \sim 0.00035$ in $g_{\perp}$, about 2-3 times less than typical for P_b in (111)Si/SiO₂.

A detailed analysis of the P_{b1} ESR characteristics is presented. The nature of the defect, that is its atomic structure, is addressed within the context of the salient ESR data combined with previously established experimental facts. The key part appears reconcilable with a dangling Si orbital located slightly sub-interface in the substrate.

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ELECTRONIC PROPERTIES OF DOPED HALIDES USING THE AB INITIO PERTURBED CLUSTER METHOD

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Key Words: *ab initio*, wide-band-gap, ammonium halides

We are interested to study the electronic properties of thallium-doped ammonium halide crystals. This system, potentially for wavelength tunable blue/green solid state lasers, presents absorption bands in the 200-300 nm ultraviolet range, and the emission bands cover the blue or blue/green range, depending on the host. We have developed a self-consistent *ab initio* method based on cluster interactions. It consists of an iterative procedure with a Hartree-Fock calculation for an "active cluster" in the field of the rest of the crystal represented by a set of frozen-orbital precalculated clusters. The active and frozen clusters are exchanged until the system has converged. Each step in the iteration consists of a molecular calculation of the "active cluster" with the passive orbitals frozen. This procedure is able, in principle, to handle very large systems of clusters to simulate solids.

Using this method we compute ground and excited state properties of pure and doped alkali halides and ammonium halides.

EVIDENCE OF METASTABLE DEEP ACCEPTORS IN AgGaS_2 FROM TIME-RESOLVED EMISSION

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Key words: chalcopyrite semiconductors, metastability

Donor-acceptor pair emission from chalcopyrite semiconductors such as AgGaS_2 and CuGaS_2 have been reported by various authors in the past. Recently we have demonstrated via hydrostatic pressure measurements that some of these transitions involve deep acceptors since they have pressure coefficients larger than the bandgap[1,2]. We have now found interesting time-dependent behaviors in this emission. Under steady state illumination at low temperatures the emission intensity decays exponentially with time constants between 60-140s. The decay time depends on the excitation laser intensity (see Fig. 1) and on sample temperature. While the decay time decreases monotonically with increasing laser intensity, the dependence on temperature is more complicated. It increases at first with temperature but reaches a minimum and starts to rise as the temperature is increased towards room temperature (see Fig. 2). We have developed a model which reproduces all the observed experimental results based on the existence of a metastable state of the deep acceptors involved. Under optical illumination the acceptors are excited into the optically-inactive metastable state. We shall discuss the possibility that these acceptors are related to the AX centers proposed by Park and Chadi[3].

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GROWTH SURFACE DEPENDENCE OF CATHODOLUMINESCENCE OF CUBIC BORON NITRIDE

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Key words: Cubic Boron Nitride, Cathodoluminescence

Optical properties of cubic boron nitride (cBN) has not been well investigated compared with those of diamond, and we have started studying on luminescence of cBN. A type of commercially available cBN grain (SBN-M, SHOWA DENKO KK, Japan) was found to exhibit intense cathodoluminescence, which was clearly dependent on growth surfaces.

The crystals, 200 μm in diameter, have octahedral habit truncated with small {100} and exhibit amber color. Cathodoluminescence was examined with a scanning electron microscope fitted with an attachment for cathodoluminescence spectroscopy and topography. Spectra were measured between 250 and 500 nm at a liquid nitrogen temperature with an accelerating voltage of 25kV.

Four luminescence centers were detected on one crystal. Three of them, which have been reported, are T, O and US-I centers with zero phonon lines at 258, 390 and 351 nm, respectively^{1,2}. The other was an undocumented broad band with a peak around 350 nm. Each center clearly depends on growth surfaces: (1) The T center and the broad band were seen on boron terminated {111}, (2) the O center on nitrogen terminated {111} and (3) the US-I was on {100}.

The T and O centers have been reported to be found in crystals grown with doping Si¹, and they may be related to Si impurities. The present result that these are seen on {111} is consistent with the report, because it is reasonably assumed that Si is easily incorporated into {111} by analogy with well known facts that impurities such as Ni and boron are easily incorporated into {111} growth sectors of synthetic diamonds.

On the other hand, the US-I center is commonly seen in a variety of crystals² and has been suggested to be produced by some defects without incorporation of impurities². Therefore, the presence of the center on {100} does not necessarily indicate that specific impurities are trapped on the surfaces.

Both the T center and the broad band were seen on a boron terminated {111} surface, but their distributions were different. There may be some correlation between the distribution of the centers and surface morphology. More detailed investigation is needed.

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INITIAL STAGES OF InP/GaP (100) AND (111) GROWTH BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION (MOCVD)

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Key Words : InP/GaP, Heteroepitaxy, Monolayer, Quantum Dot, AFM, TEM, RBS

The initial stages of the three dimensional metal organic vapor phase epitaxy growth of InP/GaP (100) and (111) have been studied by Atomic Force Microscopy (AFM), Rutherford Back Scattering (RBS) and Transmission Electron Microscopy (TEM).

We have shown that the heteroepitaxial growth takes place under Stranski-Krastinov mode (layer by layer and dislocation free island growth) and we have determined the 2D→3D transition in the InP/GaP system at $1.5 \text{ ML} \pm 0.2 \text{ ML}$.

On the other hand, we show by AFM and TEM techniques that the shape and the size distribution of the InP/GaP self-assembled nanostructures depend on the substrate orientation. Thus we have performed the epitaxy to obtain quantum dots and quantum wires structures coherently strained to the substrate.

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LATTICE RELAXATION OF IN DONORS IN CdF2

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Key Words: bistable donors, CdF2:In, photostriction, large lattice relaxation

It has been already well established that the large lattice relaxation (LLR) is a major mechanism responsible for defect metastability in semiconductors. In more covalent host (AIII-BV and very likely AII-BVI semiconductors) relaxation is due to a change of the atomic site (interstitial - substitutional). This mechanism leads to the formation of the DX states and there exists ample amount of data testifying its validity. In the case of more ionic hosts one should consider a symmetric collapse (or expansion). Expected lattice relaxation should be close to the difference ionic radii of the impurity in the two charge states. The total relaxation is large about 1 - 2 eV.

For both types of relaxation one expects a macroscopic dilatation of the crystal. Its amount depends on the type of relaxation and the number of phototransformed defects. However, if the metastability is accompanied by the generation of free carriers, their presence may also lead to macroscopic dilatation.

Indium in CdF2 crystals is well-known bistable center. At low temperatures (below 100 K) illumination transforms all localized In donors into hydrogenic states with a Bohr radius of about 0.7 nm. It is expected that the lattice relaxation is centrosymmetric. The magnitude of the local lattice collapse upon ionization of indium is about the difference of ionic radii r_{3+} of In (3+ and 2+). Therefore the relative change of the crystal length, $\Delta l/l_0$, is expected to be:

where d_{ca} is the Cd-F distance, N_{In}^* and N_{cation} are the concentrations of indium and cation ions in CdF2 crystal, respectively. Substituting to this formula the data for CdF2 one can obtain the expected relaxation about $2.5 \cdot 10^{-5}$ for $N_{In}^* = 8 \cdot 10^{18} \text{ cm}^{-3}$ phototransformed centers. There is no contribution of the free elections to the effect since the ionization energy of shallow donors in CdF2 is about 100 meV and at low temperatures their concentration is negligible.

We used for measuring such a small relaxation a scanning tunneling microscope (STM). The CdF2:In sample of $l_0 = 5 \text{ mm}$ length with concentration of In equal to $8 \cdot 10^{18} \text{ cm}^{-3}$ (estimated from the Hall measurements) was placed in STM. Shrinkage of the crystal was observed upon illumination. The effect is linear in the accumulated light dose and it is metastable at liquid helium temperature. Maximum observed change of the crystal length was about 9 nm, i.e., the relative changes where in the order $1.8 \cdot 10^{-6}$. Although the sign of the observed changes agrees with the theoretical expectations, the magnitude of the effect is smaller more than 10 times than expected from the theoretical first principle computations, performed by Song et al. (1995). Possible explanation of this discrepancy is associated with negative U behavior of the bistable dopants in CdF2 crystals.

MAGNETO-OPTICAL CHARACTERISATION OF $\text{CuIn}(\text{Ga})\text{Se}_2$

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Key Words: photovoltaic, $\text{CuIn}(\text{Ga})\text{Se}_2$, magneto-optic

Polycrystalline $\text{CuIn}(\text{Ga})\text{Se}_2$ -layers used in thin film solar cells were analysed with optical and magneto-optical methods. The samples were synthesized by the two-step rapid thermal processing (RTP) method. After the deposition of the elements on the substrate by sputtering and evaporation, the precursors were annealed in a furnace with high heating rates up to 550 °C. In absorption and photoluminescence excitation (PLE) the free exciton is seen at 1.04 eV in the copper-rich layers ($\text{Cu}/\text{In} > 1$) but not in layers with excess of indium. With Magnetic Circular Dichroism (MCD) the free exciton can be detected in Cu-rich as well as in In-rich samples. The energy position of the exciton is practically constant over a wide range of compositions. Between 1.5 K and 300 K the temperature dependence of the exciton-bandgap was determined with MCD. In Cu-rich $\text{CuIn}(\text{Ga})\text{Se}_2$ two luminescence transitions with phonon replicas appear at 0.91 eV and 0.96 eV. The high energy emission is assigned to a band-acceptor transition, since the energy position shifts blue with $1.1k_B T$ and $\text{CuIn}(\text{Ga})\text{Se}_2$ is p-type. At high excitation powers the shift of energy and intensity saturates. This confirms a recombination process between discrete energy levels. In contrast the luminescence transitions in In-rich films are severely influenced by fluctuating potentials caused by the high concentration and compensation of defects. The nature of the defects will be discussed.

MISFIT DISLOCATIONS IN MULTISTRUCTURE SEMICONDUCTOR PARTICLES

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This paper reports our studies of the correlation between charge carrier transport properties of small multistructure silver halide (AgHal) particles and the misfit dislocations presenting in the surface structural layer. The particles under consideration possess so-called core-shell structure consisting of a crystal AgBr core of around 1.2 μm in size covered with around 50 nm thick $\text{AgBr}_{(1-x)}\text{I}_x$ (where $x = 0.01-0.05$) layer. The mentioned structural configuration was characterized using SEM microscopy and X-ray spectroscopy.

In our previous studies it was shown that 3 lattice parameters between core and shell crystalline structures gives rise to misfit dislocations in the surface crystalline layer of AgBr/AgBrI particle [1]. The theoretical simulation of charge transfer mechanism predicted the increase of surface layer conductivity due to the presence of misfit dislocations.

In this contribution we present the experimental results for core and shell conductivities in AgHal semiconductor particles calculated from Maxwell-Wagner effect measurements accomplished in the frequency range between 30 Hz and 100 MHz. We analyzed the imaginary part of dielectric loss curve versus frequency for twin AgHal particles embedded in isolating medium. It was found that the dispersion curve of the interface polarization gave two maximums while its frequency values were proportional respectively to the core and the shell crystalline structure conductivities in AgBr/AgBrI particle. The dispersion curve maximum standing for the surface crystal layer was observed under much higher frequency than from our point of view may confirm the influence of conductivity mechanism ruled by the presented misfit dislocations.

We have also analyzed the dislocation mechanism of ionic charge transfer process for silver halide crystal and compared its efficiency with the one for common mechanism taking into account only the mobility of the interstitial Ag ions.

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STRUCTURAL CHANGE AND RELAXATION PROCESSES OF TETRAHEDRAL POINT DEFECTS

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Keywords: point defect, structural change, metastability, electron correlation, defect reaction.

Most of the electronic and atomic processes in semiconductors are governed by the properties of point defects. Recently, large lattice relaxation phenomena have attracted much attention such as the negative- U effect and the off-centre instability found at substitutional impurities in covalent semiconductors.

We have performed a comprehensive theoretical study on the structural change and relaxation process of a tetrahedral (T_d) four-site model, which is the most conceivable simple model for various point defects in covalent semiconductors (vacancies, substitutional and interstitial impurities). The present model consists of four sites and is characterized by the electronic transfer energy $-T$, the on-site Coulomb repulsion energy U , the lattice relaxation energy S induced by the lattice distortion Q_i at the site i ($i=1\sim 4$) and the number of electrons n ($=0\sim 8$). The system has the electron-hole symmetry: the character of the ground state of n electrons corresponds to that of the $8-n$ electrons.

The stable configurations in the adiabatic potential surface are calculated exactly for the electronic ground and excited states which are classified by the total electron spin. Some of the results are as follow:

For $n=0$ (8), there is only one possible state which has the T_d symmetry.

For $n=1$ (7), the stable state is either symmetric F (an electron is delocalized), where $\bar{Q}_1 = \bar{Q}_2 = \bar{Q}_3 = \bar{Q}_4$ (T_d symmetry) or asymmetric S (an electron is self trapped such that $\bar{Q}_1 > \bar{Q}_2 = \bar{Q}_3 = \bar{Q}_4$, C_{3v}), and it changes as a first-order transition at $S/T=6.0$.

For $n=2$ (6), the spin triplet states always show an asymmetric distortion, such that $\bar{Q}_1 = \bar{Q}_2 > \bar{Q}_3 = \bar{Q}_4$ (C_{2v}) except for $S=0$. For the singlet states, if T is large enough the symmetric state ($Sym., T_d$) is stable, where two electrons have equal amplitudes at each site. With increasing U and/or S , structural changes take place. If $U>S>>T$, two electrons are localized at different sites repelling each other such that $\bar{Q}_1 = \bar{Q}_2 > \bar{Q}_3 = \bar{Q}_4$, (**Dimer.**, C_{2v}). If $U\sim S>>T$, the charge transfer state (1) (**C.T.1**, C_{3v}) becomes stable, where two electrons are weakly localized around one site (such that $\bar{Q}_1 > \bar{Q}_2 = \bar{Q}_3 = \bar{Q}_4$). If $S>U>>T$, the charge transfer state (2) (**C.T.2**, C_{3v}) becomes stable, where two electrons are strongly localized at one site (such that $\bar{Q}_1 \gg \bar{Q}_2 = \bar{Q}_3 = \bar{Q}_4$).

We also discuss the structural changes and relaxation processes of the defect induced by an intra-defect excitation ($n=\text{constant}$, ground/excited) or a carrier trapping ($n \rightarrow n \pm 1$).

THE INFLUENCE OF DEFECTS ON THE LATERAL SPREAD OF IMPLANTED IONS

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key word: high-fluence implantation, nanoscale-device, dynamical relaxation

The technology of minimizing electric devices has demanded much finer prediction for the three dimensional distribution of dopants implanted into crystals. Conventionally the three dimensional ion distribution is examined in terms of longitudinal or lateral spread. For predicting longitudinal distribution, reliable measures have been well established. For example, SIMS and RBS from experimental viewpoint, LSS from theoretical one, and MALROWE and TRIM from computational one. On the contrary only a few experiments allow to measure lateral distribution. Tomography technique by Fink et al., SEM by Gong et al., and micro-RBS by Takai et al. provided contour maps showing equi-concentration lines on vertical cross section in the bulk as well as simulations.

The distribution function for the lateral spread has been supposed to be a gaussian. In the case of amorphous targets, Lorentz et al. showed [1] that the standard deviation or the lateral straggling of the gaussian function is not invariant but depend on depth, using Monte-Carlo simulation. This work clarified the importance of the microscopic lateral straggling which depends on depth, while the macroscopic one being a constant. In the case of crystalline targets [2], we derived an expression for the microscopic lateral straggling as a function of depth, with parameters depending both on incident energy and incident angle. In principle, this function could reproduce the two dimensional distribution of dopants in a masked target, using error functions related to the window size.

The estimation of the edge effect is performed by integrating the concentration of dopants under mask. However, this assumption becomes unrealistic with increasing the fluence, because the mathematical integration implies to superpose the local concentration of ions regardless the influence of defects produced by previously implanted dopants. In fact a high-density area might be locally allowed. In order to calibrate our results obtained by low-fluence simulation, we refer the result of the TRIDYN code [3] including high-fluence effect. Although TRIDYN itself is originally used for one dimensional analysis, it considers the dynamical relaxation process during sequential ion bombardment. The key of discussion is thus to what extent the dynamical relaxation should be considered.

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SHALLOW ELECTRON CENTRES IN $\text{CdF}_2:\text{M}^{3+}$ AND SILVER HALIDES

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Key Words: excited electron centres

Shallow electron centres are associated with interesting properties in $\text{CdF}_2:\text{M}^{3+}$ ($\text{M} = \text{Ga}, \text{In}$) and silver halides. The trivalent centres in CdF_2 exhibit shallow-deep metastability and have potentials for optical data storage[1]. The shallow electrons associated with certain impurities (e.g. Cd) or interstitial silver in AgBr and AgCl are believed to play key roles in the photo-induced processes[2].

We have studied these systems using a method developed earlier for excited electron centers in insulators[3]. In CdF_2 we found that the deep level (compact state) is separated from the shallow level (diffuse state) by a small potential barrier and the estimated changes of the optical refractive index between the deep and shallow states are in qualitative agreement with experiment.

We also report on our preliminary work of the shallow electron centres in silver chloride and silver bromide. The systems considered are the electrons trapped at an interstitial silver, the normal as well as the so-called split, and at a substitutional Cd^{2+} centre. The electron is in a diffuse state and the surrounding lattice is substantially relaxed. Possible mechanisms for the observed anomalous heat generation in photo-excited silver halides[2] are investigated.

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THEORETICAL CALCULATIONS OF NATIVE DEFECTS IN c-BN

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Key words: wide band gap, BN, defects, semiconductors

Cubic Boron Nitrate (c-BN) is a large band-gap material (~ 6.4 eV) with several physical properties similar to those of diamond, but can be n- and p-type doped, while diamond is only p-type. It could be an important material for devices at high temperature and high pressure.

The aim of this work is to obtain a comprehensive explanation for the behavior of native defects in c-BN. Particularly, we are interested in the structural and electronic properties of N-vacancy, B-antisite, C-interstitial and O-substitutional. We have performed an ab-initio all electron Hartree-Fock calculation, not using an effective potential for the core electrons. The crystal was simulated by a molecular cluster with 71 atoms.

We found for the neutral isolated boron-antisite a Jahn-Teller distortion in the $\langle 111 \rangle$ direction. The fully occupied e-level, with ligand character (π -type), is located 4.81 eV above the top of the valence band.

For the N-vacancy we discuss in detail the formation of the F-center in c-BN and compare with the same center in wurzite-BN. We also discuss the role played by carbon atoms in the formation of F-centers.

TRANSITION FROM TUNNELING TO POOLE-FRENKEL TYPE TRANSPORT IN ALUMINUM-NITRIDE

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Keywords: AlN, tunneling transport, charged defects

Aluminum nitride (AlN) films in the thickness range between 15 Å to 2 µm were tested for different transport models and for the possible role of deep defects.

The films were deposited by reactive sputtering in an Ar/N₂ plasma of an Al (with 1% Si, and 0.5% Cu) target at room temperature. Usually the AlN insulator films were sandwiched between ferromagnetic layers to study magnetoresistance effects in tunnel junctions. The small amount of Cu serves as barrier against electromigration. For the purpose of testing transport models we also used glass substrates that were coated with a semitransparent Co bottom layer. The sandwich structure was terminated with a Cr top contact layer deposited by electron beam evaporation.

From optical transmission measurements in the UV and visible spectral range and from highly sensitive photothermal deflection spectroscopy we deduced a broad absorption band in the visible that could be due to intrinsic or copper-related defects in the insulator.

I-V characteristics were measured in perpendicular direction from room temperature down to 20 K, while limiting the current to some ten mA/cm². I-V curves of thin films with thicknesses below about 30 Å nominal thickness are well described by the tunneling model with an effective barrier height varying between 1.5 and 3.5 eV. The fit value for the thickness, however, was systematically smaller than the nominal value, indicating some interface roughness. The temperature dependence was very weak, confirming tunneling transport as a main transport mechanism.

Thicker AlN layers could be more easily fitted to a Poole-Frenkel process that is based on reemission of deeply trapped carriers. We suppose that a large number of defects of yet unknown nature is responsible for the particular voltage and temperature dependence observed in thick films.

A confirmation of these hypotheses of defect related transport through the AlN films comes from the results of sweep-out experiments. In this technique defects are charged (discharged) by applying short voltage pulses and emptied (filled) by reversing the bias. From the observed current transients we estimated the energy depth of the defects involved to lie more than 0.8 eV below the transport path.

TRANSIENT LATTICE VIBRATION INDUCED BY SUCCESSIVE CARRIER CAPTURES BY A DEEP-LEVEL DEFECT AND THE EFFECT ON DEFECT REACTIONS

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Keywords: deep-level, recombination, lattice relaxation, multiphonon process, defect reaction.

The nonradiative multiphonon recombination at deep-defects in semiconductors, which consists of successive captures of an electron and a hole, can be described consistently only by using a proper configuration coordinate diagram (CCD) with many electron representation [1]. During the lattice relaxation after an electron (hole) capture, an energy equal to the thermal depth E_{th} of an electron (hole) is converted to phonons. It has been suggested that these transient vibrations enhance the following capture and also defect reactions [1, 2].

We study theoretically the dynamics of the transient lattice vibration induced by successive carrier captures by a deep-level defect. The time evolution of the normal phonon modes $\{q_k(t)\}$ are calculated exactly: each $q_k(t)$ oscillates harmonically around $q_k=0$ or $\bar{q}_k$ depending on which type of carrier has been captured. The interaction mode, Q (the abscissa of the CCD in Fig.1), is not a normal mode but a linear combination of many normal modes $\{q_k\}$ of different frequencies $\{\omega_k\}$. Then, after each capture, $Q(t)$ shows a damped oscillation around $Q=0$ or $\bar{Q}$ in a period $\sim 2\pi/\Delta\omega$, where $\Delta\omega$ is the width of the frequency distribution. An electron (hole) can be athermally captured just when $Q(t)$ crosses Q_e (Q_h), the intersection of two adiabatic potentials. Thus the carrier captures and the transient lattice vibration are highly correlated processes (capture enhanced capture), which depend on the carrier densities n_e and n_h , the capture cross sections σ_e and σ_h , the activation energies E_{act}^e and E_{act}^h , and the frequency distribution $\Delta\omega$ of phonons.

If several pairs of electrons and holes are captured within a short period $\sim 2\pi/\Delta\omega$, the amplitude of the interaction mode $Q(t)$ increases remarkably, and it may overcome the potential barrier for a defect reaction [2]. More than the band gap energy $E_g=E_{th}^e + E_{th}^h$ can be used for this phonon kick mechanism.

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PHOTOLUMINESCENCE, OPTICAL ABSORPTION, AND EPR STUDIES OF THE $\text{Co}^{2+}\text{-S}_\text{p}$ PAIR DEFECT IN GaP

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Key Words: GaP:Co:S, EPR, PL

The optical spectra of GaP:Co in the spectral region of the lowest d-d transitions are dominated by the zero-phonon line (zpl) at 4509.2 cm^{-1} measured in photoluminescence (PL) and optical absorption. This zpl is due to the $^4\text{A}_2 \leftrightarrow ^4\text{T}_2$ transition of substitutional isolated Co^{2+} . On GaP:Co samples containing about $1\text{ to }3 \times 10^{16}\text{ cm}^{-3}$ sulphur, additionally two zpls have been found at 3976.3 cm^{-1} and 3966.4 cm^{-1} in PL. The first one is measured in optical absorption also. The splittings and shifts of the PL line at 3976 cm^{-1} under uniaxial stress reveal that it belongs to a centre with trigonal symmetry. In the electron paramagnetic resonance (EPR) spectrum of such samples besides the intense and slightly anisotropic resonance line at $g = 2.164$ due to isolated $\text{Co}^{2+}_{\text{Ga}}$, a less intense angular dependent spectrum is detected. This spectrum is caused by a Co^{2+} -centre with trigonal symmetry. From the angular dependence the spin-Hamiltonian parameters $g_{\parallel} = 2.162$, $g_{\perp} = 2.164$, and $|D| = 5.0\text{ cm}^{-1}$ are derived. The splitting of the $^4\text{A}_2$ ground state of Co^{2+} by the trigonal crystal field component together with spin-orbit coupling amounts to $2D = 10\text{ cm}^{-1}$. This value coincides with the distance of the two PL lines, which can be assigned to the cold lines originating from the lowest level of the excited $^4\text{T}_2$ state and terminating in the two ground state levels. Therefore, both optical and EPR results can be consistently interpreted as caused by a $\text{Co}^{2+}_{\text{Ga}}\text{-S}_\text{p}$ nearest neighbour pair defect.

ELECTRICALLY DETECTED MAGNETIC RESONANCE: AN INVESTIGATION INTO THE PHYSICS UNDERLYING SPIN-DEPENDENT RECOMBINATION

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Key Words: Electrically detected magnetic resonance, a-Si:H, GaAs, GaN

For many years, spin-dependent transport measurements have been limited to elemental semiconductors, mostly silicon, with only a few reports on applications to compound materials. Recently, the technique has been successfully extended by several groups to the investigation of III-V materials, most notably GaAs and GaN. However, the studies have concentrated on the identification of specific recombination channels, making use of the significantly increased sensitivity of this method as compared to conventional ESR. Little work has been performed to understand the physics of this technique, with the ultimate goal of extracting spin densities from measurements of electrically detected magnetic resonance.

Several theoretical descriptions of spin-dependent recombination exist. The two extreme cases among them are the Kaplan, Solomon and Mott model invoking the formation of a spin pair and the Lepine model, which assumes interaction solely via the polarisation of the ensembles of the reaction partners. Both models make predictions on temperature and microwave frequency dependence of the resonant conductivity change $\Delta\sigma/\sigma$. Varying the temperature over an extended range to test the predictions, however, can result in changes of the dominant transport processes which can mask the relevant behaviour of the spin-dependent recombination. The extension of EDMR to III-V materials and the realisation of EDMR at frequencies other than 9 GHz allows such more fundamental studies.

We will present comparative experiments on the dependence of EDMR on the microwave frequency used for the experiments (434 MHz, 9 and 34 GHz). To be able to properly take into account saturation effects, the measurements have been performed over up to 5 orders of magnitude in microwave power. By comparing the results obtained on C₆₀, a-Si:H, GaN and GaAs, the effect of spin-orbit coupling on the mechanism of EDMR will be discussed in detail.

BEHAVIOUR OF INTRINSIC DEFECTS AND IMPURITY IN III-V COMPOUNDS AT INITIAL STAGE OF DIFFUSION PROCESS

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Key Words: defects, diffusion

A role of intrinsic defects in the semiconductor technology is well known. Their influence on the matter properties was clearly demonstrated in the silicon technology, while the defect behaviour in III-V compound was not received the adequate study. The diffusion is one of the most suitable process for a study of the defect behaviour. We believe that the initial diffusion stage (IDS), establishment stage at which temperature of the system rises from room temperature to final temperature corresponded to temperature of steady-state diffusion, being the most non-equilibrium diffusion stage, is responsible for the defect behaviour. It should be noticed that IDS has been as yet little studied.

Our investigations on the InP, GaAs, and InGaAs layers doped with zinc showed that the Zn diffusion at IDS was accompanied by a very intense defect formation with a large depth of defect penetration. Moreover, this process stimulated a very deep penetration of the part of the electrically active Zn even at IDS. This penetration was found to begin at a low temperature. For example, the Zn atoms with a concentration of $\sim 10^{17} \text{ cm}^{-3}$ were introduced in InP in a depth of $\sim 1 \text{ mm}$ at IDS in several seconds at a temperature of about 375°C , while a concentration of the electrically inactive Zn was $10^{18}\text{-}10^{19} \text{ cm}^{-3}$ in the near-surface region. At the same time, a fast relaxation of the created defects was taking place as the temperature rose.

Moreover, the comparative investigations of the Zn atoms and defect distribution profiles after IDS and the steady state diffusion allowed the temporal evolution of the intrinsic defects to be tracked during the diffusion process. The importance of IDS was demonstrated to understand the defect and impurity behaviour.

LOW TEMPERATURE IMPURITY DIFFUSION INTO LARGE-BAND-GAP SEMICONDUCTORS

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Key Words: low temperature diffusion, diamond, 6H-SiC, electroluminescence

We present the first findings of the electroluminescence from ultra-shallow p-n junctions which have been prepared using low temperature (900°C-1100°C) phosphorus/ boron diffusion into diamond and 6H-SiC wafers.

Dopant diffusion in semiconductors is known to be amenable to control by adjusting the fluxes of self-interstitials and vacancies emerging from the monocrystalline surface. Use of thin oxide overlayers deposited on semiconductor wafers in combination with high diffusion temperatures has been found to result predominantly in the generation of self-interstitials by the oxidized surface, and hence, in increased rates of impurity diffusion by the kick-out, while vacancy diffusion mechanisms are associated with thick oxide overlayer or polycrystalline silicon layers and low diffusion temperatures. Therefore, the present work was aimed at the realization of the diamond and SiC planar p-n junctions using thick oxide overlayers and polycrystalline layers in combination with phosphorus/boron low temperature diffusion which are responsible for the domination of vacancy diffusion mechanisms.

The diffusion experiments involving phosphorus and boron diffusion were performed from gas phase at 1100°C and 900°C into p-type diamond and n-type 6H-SiC wafers. Thick oxide overlayer on the working and back sides of the 6H-SiC wafer were previously prepared using the pyrolysis of silane, whereas the diamond wafer was covered by a thick polycrystalline silicon layer. Diffusion profiles obtained were controlled using the SIMS technique.

The use of thick oxide overlayers and polycrystalline layers is demonstrated to make it possible the formation of both p^+n and n^+p junctions in large-band-gap semiconductors. The direct I-V characteristics exhibit classical type of the 6H-SiC and diamond p-n junctions and reveal lateral quantum wells and crystallographically-oriented quantum wires inside both p^+ and n^+ - ultra-shallow diffusion profiles. These large-band-gap nanostructures are shown to cause high electroluminescence efficiency of p-n junctions obtained, which is also exhibited for silicon nanostructures prepared using the same technological techniques at 800°C.

HEAT-TREATMENT INDUCED MODIFICATIONS OF POROUS SILICON.

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Keywords: Porous Silicon, Positron Annihilation

Recently, positron annihilation has been applied to the investigation of porous silicon [1]. A new observation is that vacancy clusters exist in the SiO_x layer covering the Si nanocrystallites as deduced from the presence of a 400-500 ps lifetime. The vacancy clusters in turn affect the amount of positrons which can escape into the pores where they form positronium whose annihilation is very sensitive to surface defects and adsorbed gases.

Heat treatments in argon up to 1170°C led to the following modifications: A mass increase of the film of 17% takes place between 300 and 500°C (as determined by the positron experiments) and the vacancy cluster concentration increases by a factor of three. Both these observations are interpreted to arise from incorporation of oxygen during H effusion.

Above 500°C no further oxygen uptake can be found but between 600°C and 1170°C the vacancy cluster concentration decreases steadily which, above 900°C, involves vacancy migration. At 1170°C only a third of the originally present vacancy clusters remain. Positronium is located predominantly in the pores up to ≈900°C, indicating very few surface traps, but above this temperature traps are formed and positronium becomes located at the surface. Structural disintegration of the porous film is observed above 900°C.

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PHOTOLUMINESCENCE VIBRATIONAL SPECTROSCOPY OF DEFECTS CONTAINING LIGHT IMPURITIES (C, H, O) IN SILICON

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Keywords: silicon, carbon, hydrogen, oxygen, photoluminescence

Knowledge about the vibrational properties of centres containing light impurities like H, C and O in Si provides a powerful tool for investigating their atomic structures. Information about defect vibrational modes can be obtained in several ways, and the one most extensively used for this purpose has been mid-infrared absorption spectroscopy. Alternatively, the vibronic properties of defects can be explored by photoluminescence spectroscopy which in many cases has several advantages in comparison with absorption spectroscopy. For example, often it provides much higher sensitivity in terms of defect concentration, especially for the centres having local modes with energies located within the intensive lattice absorption band. Also, it provides a more effective way for identifying different modes belonging to the same centre and for establishing defect symmetry by applying external field perturbations on electronic transitions.

The results of recent photoluminescence investigations will be reported which demonstrate the above advantages in the case of several carbon, C-H and C-H-O related centres, created in irradiated silicon after annealing at temperatures up to 600°C. New vibrational features have been observed for several defects, including the well known double carbon (G-line) and carbon-oxygen (C-line) centres. It has been found that many complexes appearing at different temperatures exhibit similar or, in some case, almost the same local mode vibrations, which suggests that some parts of their structures have similar atomic compositions. This reveals the links between relatively simple and more complex centres and allows their transformations to be monitored at different stages of the thermal treatments.