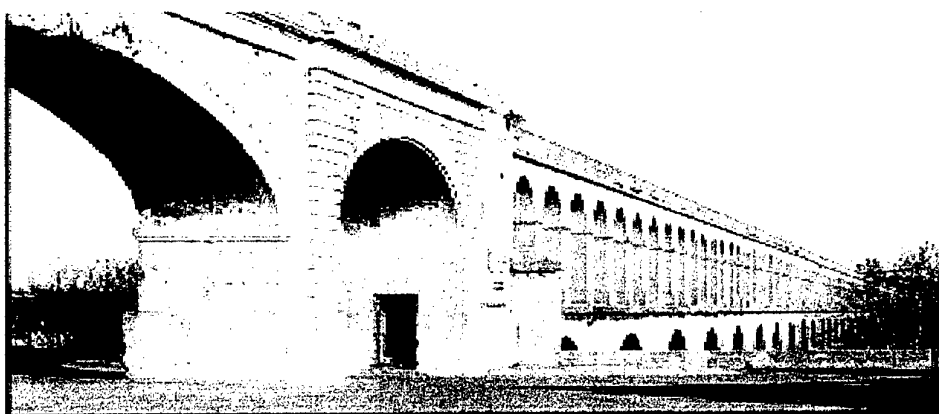




PROGRAMME and ABSTRACTS

8th International Conference on SHALLOW-LEVEL CENTERS IN SEMICONDUCTORS

SLCS - 98
Montpellier
France
July 27-30, 1998

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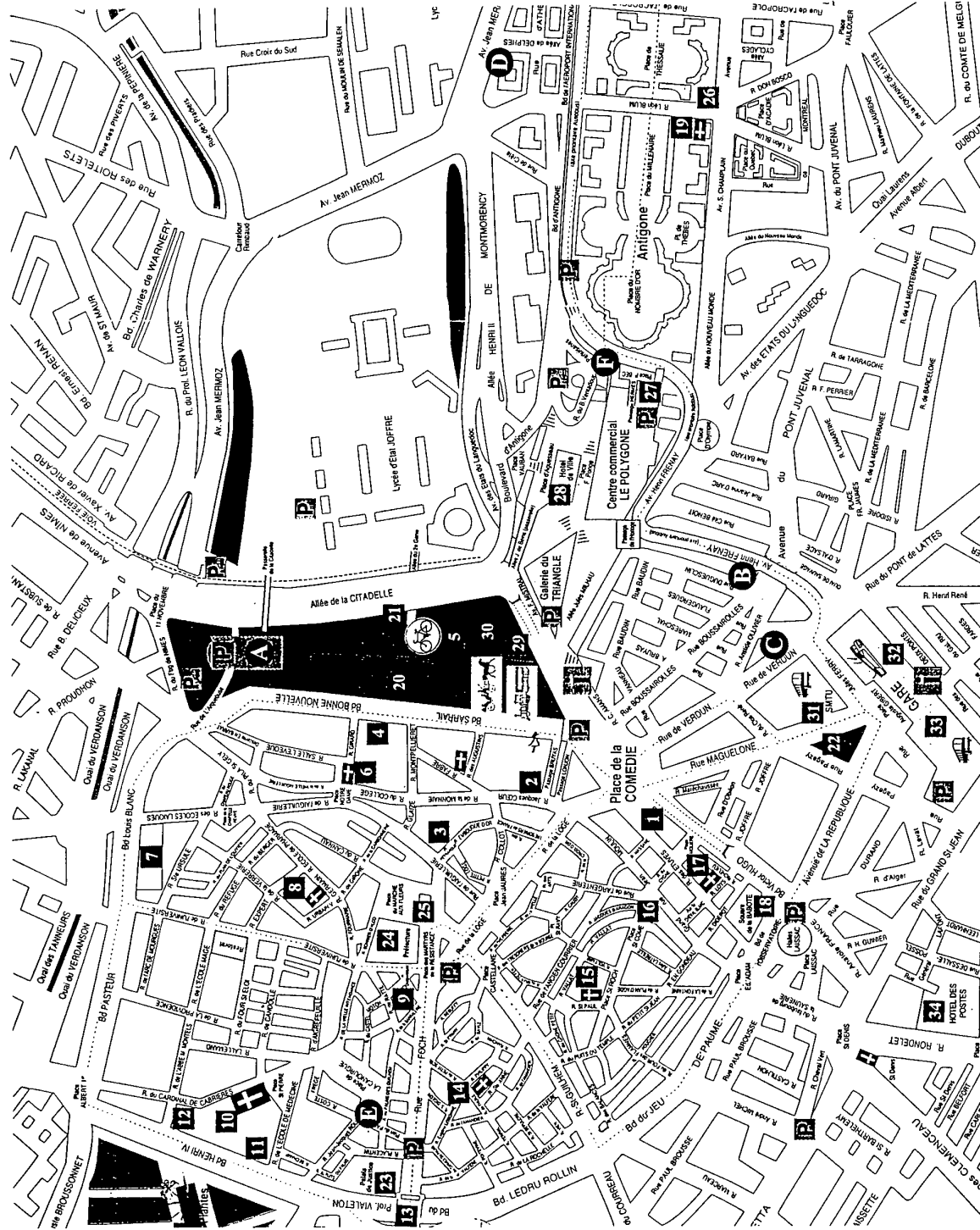
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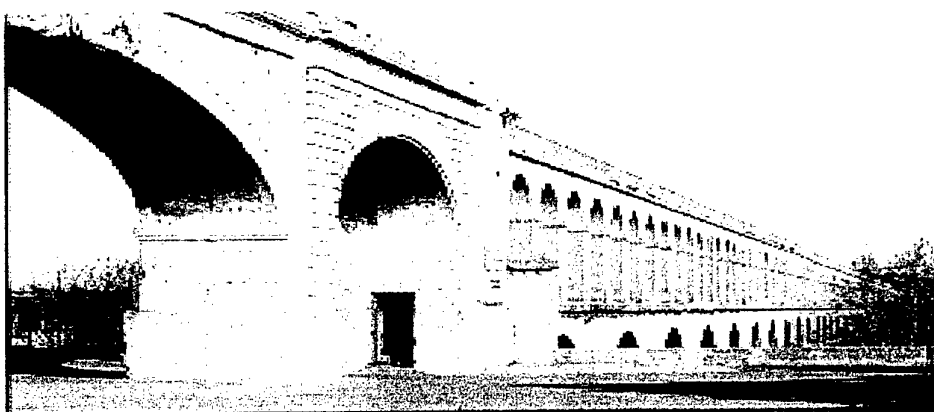
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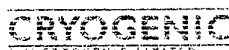


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The 8th International Conference on
SHALLOW-LEVEL CENTERS
IN SEMICONDUCTORS

Montpellier, 27-30 July 1998

WELCOME From The Organizing Committee

The 8th International Conference on Shallow-Level Centers in Semiconductors. SLCS-98 is a satellite of the 24th International Conference on the Physics of Semiconductors (ICPS 1998, Jerusalem, Israel).

This conference is part of a series initiated in Berkeley (1984) and continued in Trieste (1986), Linköping (1988), London (1990), Kobe (1992), Berkeley (1994) and Amsterdam (1996).

This year the Program Committee and the Organizing Committee selected over 150 submissions in order to compose the comprehensive and up-to-date program that is included in this booklet.

The booklet includes the program of invited talks and the abstracts of all conference contributions.

Scientific Secretariat

SLCS98. GES -Université Montpellier II
Place Eugène Bataillon - C.C. 074
34095 Montpellier Cedex 5 - France
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Fax : +33.4.67.14.37.91
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Scientific Program

Oral Presentations

All invited talks are scheduled for 30 minutes, including 5 minutes for discussion. All oral communications are scheduled for 15 minutes, including 3 minutes for discussion.

We kindly request all speakers and the session chairpersons to keep strictly in time because of the narrow shekel of the conference!

Poster Presentations

Posters may be hung on the morning of the presentation day. They must be removed at the end of the poster sessions. Authors are expected to be present at their poster during the session, in which their poster is scheduled for presentation and discussion.

The material put at your disposal is a grey veltonyl board (width= 0.9 m - height 1.20 m). Please note that it is strictly forbidden to use staples, nails or glue to hang up the posters. The use of self-adhesive velcro bands or special hooks is compulsory. This material will be provided to you.

Proceedings

Manuscript preparation instructions

The manuscript should reach the SLCS-98 scientific secretariat before July 6th, 1998.

After a review, all accepted contributions will be published in a regular issue of *Physica Status Solidi (b)*.

Instructions for authors:

Accepted papers are considered as regular submissions to *Physica Status Solidi (b)*, published by WILEY-VCH Verlag Berlin.

Manuscripts (written in English) should be printed (or typed) double spaced on one side of paper only and submitted in three copies.

Classification of the manuscripts (PACS numbers and substance classification), the author's name, institution, address, FAX/telephone number and electronic-mail address should be given. The classification scheme is printed in the January issues and in the Index Volume of *Physica Status Solidi*.

Please, mark the corresponding author!

An abstract of about ten lines (in English) is required.

Equations should be typewritten and numbered sequentially. Separate lines for equations should be used. Special care should be taken to distinguish subscripts, superscripts, and certain symbols. SI-units should be used throughout.

References should be numbered [in square brackets] and listed in the order of appearance on a separate sheet, in the format used in *Physica Status Solidi*.

Carefully prepared, photo-reproducible figures are required. They should be enclosed on separate sheets of paper. The lettering and symbols should be large and clear enough for reduction. Avoid small open symbols, small dots and small decimal points. Photographs should be submitted on white paper. Duplicates for all figures are desirable. Figure captions should be printed on a separate sheet of paper (with special instructions concerning the size of illustrations, if applicable).

Authors who prepare their paper in LATEX (TEX), WORD, WORD PERFECT or WINWORD should submit a floppy disk together with their manuscript. All textual material of the paper (including tables, captions, etc.) should be in a single file. Please ensure that the text is identical in the hard-copy and in the floppy disk.

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Please notice that three pages of a manuscript (80 characters/line; 30 lines/page) give two printed pages and three figures give one printed page.

Refereeing will be finished during the meeting.

In case revision is necessary please resubmit your revised manuscript both as hard-copy and as a disk file.

AT THE LATEST BY **August 31th, 1998**

To

Scientific Secretariat

SLCS98. GES -Université Montpellier II

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34095 Montpellier Cedex 5 - France

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MANUSCRIPTS THAT ARE RECEIVED LATER WILL NOT BE INCLUDED IN THE PROCEEDINGS.

GENERAL PROGRAMME

Monday, July 27th

- 17.00 - 19.30 Registration
18.30 Welcome Aperitif, place: Espace Einstein (Registration Hall)

Tuesday, July 28th

- 7.45 - 8.15 Registration
8.15 - 8.45 Opening session
8.45 - 10.30 Session A: *"Metal-insulator transitions and defect interactions"*
10.30 - 11.00 Coffee break
11.00 - 12.30 Session B: *"Bound excitons and Raman scattering at shallow centers"*
12.30 - 14.00 Lunch
14.00 - 15.30 Session C: *"Wide-gap I"*
15.30 - 16.00 Coffee Break
16.00 - 17.00 Session D: *"Wide-gap II - SiC"*
17.00 - 18.30 Poster Session: P1

Wednesday, July 29th

- 8.15 - 10.30 Session E: *"Hydrogen passivation and related topics, thermal donors"*
10.30 - 11.00 Coffee break
11.00 - 12.30 Session F: *"Low-D systems I"*
12.30 - 14.00 Lunch
14.00 - 16.00 Session G: *"Shallow excited states of deep level impurities and shallow-deep crossover"*
16.00 - 17.30 Poster Session: P2

Excursion & Conference Dinner

- 17.45 Departure by bus for the Excursion & Conference Dinner
Meeting Place: Convention Center Le Corum 0-level, side Lyceé Joffre
18.30 Visit to Aigues-Mortes ramparts
19.30 Boarding on the houseboat « Isles de Stel » for conference dinner
23.30 Return to Montpellier

Thursday, July 30th

- 8.15 - 10.30 Session H: *"New methods in experiment. New methods in theory."*
10.30 - 11.00 Coffee break
11.00 - 12.30 Session J: *"Low-D systems II"*
12.30 - 14.00 Lunch
14.00 - 15.30 Session K: *"Wide-gap III"*
15.30 - 16.00 Closing Session

Tuesday, July 28th

SESSION A : Chairman: V. Perel

8.45 - 10.30

Metal-insulator transitions and defect interactions

- A1: INVITED : W. Walukiewicz, O. D. Dubon, H.H. Silvestri, E.E. Haller
Hole transport in the upper Hubbard band in copper doped germanium under uniaxial pressure
- A2 J.F. Sampaio, H.S. Moreira, E.S. Alves, A.G. de Oliveira
The Coulomb gap in the shallow band of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}:\text{Si}$
- A3 A. Fujimoto, H. Kobori, T. Ohyama, S. Ishida
The drastic change of magnetoresistance by the rise of electron temperature in Sb doped Si
- A4 Y.T. Rebane
Topological interaction of shallow-level centers with dislocations in semiconductors
- A5 J. Yamauchi, N. Aoki, I. Mizushima
Dynamical properties of impurity clusters in silicon
- A6 A. Amore Bonapasta, M. Capizzi, P. Giannozzi
Near-edge states induced by hydrogen inclusion in gallium arsenide

Tuesday, July 28th

SESSION B: Chairman: G. Martinez

11.00 - 12.30

Bound excitons and Raman scattering at shallow centers

- B1: INVITED A. Hoffmann, V. Kutzer, A. Göldner
Bound excitons in wide gap II-VI and nitrides semiconductors - comparison of optical studies of shallow dopants in these materials
- B2 A.A. Rogachev
Excitonic molecules captured by quantum dots and isoelectronic impurities in multivalley semiconductors
- B3 T. Egilsson, J.P. Bergman, I.G. Ivanov, A. Henry, E. Janzén
The D_1 exciton in 4H-SiC
- B4 H.A. Nickel, G.S. Herold, T. Yeo, G. Kioseoglou, Z.X. Jiang, B.D. McCombe, A. Petrou, D. Broido
Internal transitions of neutral and charged magneto-excitons in AlGaAs/GaAs quantum wells
- B5 G. Irmer, M. Wenzel, J. Monecke
Raman scattering at shallow acceptors in InP

Tuesday, July 28th

SESSION C: Chairman: M. Stutzmann

14.00 - 15.30

Wide-gap I

- C1: INVITED R. Stepniewski, A. Wyszomolek, M. Potemski, J. Lusakowski, K. Korona, K. Pakula, J.M. Baranowski, G. Martinez, I. Grzegory, S. Porowski
Impurity related luminescence of homoepitaxial GaN studied with high magnetic fields

-
- | | |
|----|--|
| C2 | <u>A.M. Witowski, M.L. Sadowski, K. Pakula, P. Wyder</u>
Far infrared magnetospectroscopy of shallow donors in GaN |
| C3 | <u>M.W. Bayerl, M.S. Brandt, M. Stutzmann</u>
Spin dependent processes and Mg acceptors in GaN single quantum well diodes and p-type GaN films |
| C4 | <u>N. Achtziger, C. Hülsen, W. Witthuhn, M.K. Linnarsson, M. Janson, B.G. Svensson</u>
Mobility, passivating effect and thermal stability of hydrogen in silicon carbide |
| C5 | <u>J.L.P. Castineira, J.R. Leite, J.L.F. da Silva, L.M.R. Scolfaro</u>
Electronic structure and stability of Be impurity in cubic boron nitride |
-

Tuesday, July 28th

SESSION D: Chairman: M. Suezawa

16.00 - 17.00

Wide-gap II - SiC

- | | |
|-------------|--|
| D1: INVITED | <u>J.P. Bergman, E. Janzén, W.J. Choyke</u>
Multiple bound excitons associated with shallow donors in different polytypes of silicon carbide |
| D2: INVITED | <u>S. Greulich-Weber</u>
The microscopic and electronic structure of shallow donors in silicon carbide |
-

Wednesday, July 29th

SESSION E: Chairman: C.A.J. Ammerlaan

8.15 - 10.30

Hydrogen passivation and related topics, thermal donors

- | | |
|-------------|---|
| E1: INVITED | <u>B. Clerjaud</u>
Acceptor neutralization by hydrogen in GaN and wide band gap II-VI materials |
| E2 | <u>M. Suezawa, R. Mori</u>
Optical absorption study of the interaction between group II acceptors and hydrogen in Si |
| E3 | <u>J. Hamann, L. Worschech, D. Blaß, C.Y. Hu, T. Filz, W. Ossau, V. Ostheimer, C. Schmitz, H. Wolf, Th. Wichert</u>
Microscopic structure of hydrogen-related defects in CdTe |
| E4: INVITED | <u>R.C. Newman</u>
Shallow thermal donors in silicon: the roles of Al, H, N and point defects |
| E5 | <u>D. Aberg, T. Hallberg, B.G. Svensson, J.L. Lindström</u>
Formation of ultra shallow donors in silicon by annealing in nitrogen at 470 °C |
| E6 | <u>D. Karg, A. Voigt, G. Pensl, M. Schulz, H.P. Strunk, W. Zulehner</u>
Annihilation studies of oxygen-related new donors in Cz-Si |
| E7 | <u>R. Dirksen, T. Gregorkiewicz, C.A.J. Ammerlaan</u>
Individual thermal donor species studied with high-frequency magnetic resonance spectroscopy |

Wednesday, July 29th

SESSION F: Chairman: M. Grynberg

11.00 -12.30

Low-D systems I

- F1: INVITED B.D. McCombe, Z.X. Jiang, P. Hawrylak
Spectroscopy of neutral and charged donors in semiconductor quantum wells: many body effects
- F2 C. Riva, V.A. Schweigert, F.M. Peeters
Angular momentum transitions and magnetic evaporation in off-center D⁻ centers in a quantum well
- F3 I.D. Mikhailov, F.J. Betancur, J.H. Marin, L.E. Oliveira
Model structure for D⁻ states in GaAs-(Ga,Al)As quantum wells
- F4 L. Calmels, A. Ghazali, A. Gold
Many-body effects for bound states in low-dimensional electron gases
- F5 S. Wongmanerod, P.O. Holtz, K. Reginski, M. Bugajski, M. Godlewski, B. Sernelius, O. Mauritz, Q.X. Zhao, J.P. Bergman, B. Monemar
Optical properties of p-type modulation doped GaAs/AlGaAs quantum wells

Wednesday, July 29th

SESSION G: Chairman: W. Jantsch

14.00 -16.00

Shallow excited states of deep-level impurities and shallow-deep crossover

- G1: INVITED T. Gregorkiewicz, J.M. Langer
The role of shallow bound states in the excitation and de-excitation of rare-earth ions in semiconductors
- G2 H. Schroth, K. Laßmann, Chr. Borgmann, H. Bracht
Nonlinear Zeeman-splitting of the Si:Be_s⁻ acceptor ground state: influence of the p_{1/2} split-off valence band?
- G3 A. Näser, W. Gehlhoff, H. Overhof, R.A. Yankov
EPR identification of a shallow donor state of cadmium in silicon
- G4 A. Baraldi, S. Franchi, C. Ghezzi, R. Magnanini, A. Parisini, L. Tarricone
A shallow state coexisting with the DX center in Te-doped AlGaSb
- G5 C. Skierbiszewski, Z. Wilamowski
The universal behaviour of shallow-deep level instabilities in semiconductors
- G6 J.C. Bourgoin
Role of excited states in the metastability of donors in III-V alloys
- G7 S. Voß, N.A. Stolwijk, H. Bracht, P. Kringhøj, A. Nylandsted Larsen
Electronic properties of Zn in Si_{1-x}Ge_x alloys: the change-over from highly localized deep states to shallow-level centers.

Thursday, July 30th

SESSION H: *Chairman: M. Dyakonov*

8.15 - 10.30

New methods in experiment. New methods in theory

- H1: INVITED M. Morgenstern, R. Dombrowski, Ch. Wittneven, R. Wiesendanger
Scanning tunneling spectroscopy on InAs(110): scattering of electron waves at ionized dopants
- H2 N.T. Bagraev, V.E. Gasumyants, W. Gehlhoff, L.E. Klyachkin, A.M. Malyarenko, A. Näser, V.V. Romanov, S.A. Rykov, E.V. Vladimirskaia
Pair charge correlations localized on shallow-level centres inside self-assembly silicon quantum wells
- H3 M.O. Henry, E. Alves, C.A.J. Ammerlaan, J. Bollmann, A. Burchard, G. Correia, M. Deicher, M. Fanciulli, D. Forkel-Wirth, M.H. Knopf, S. Lindner, R. Magerle, E. McGlynn, J.C. Soares, A. Stotzler, G. Weyer
Radioactive isotope identifications of Au and Pt photoluminescence centres in silicon
- H4 E.E. Orlova, R. Ch. Zhukavin, V.N. Shastin
Far infrared active media based on the shallow impurity states transitions in silicon
- H5 A.V. Malyshev, I.A. Merkulov, A.V. Rodina
Effective mass calculation of the shallow acceptor ground state g-factor for A_3B_5 semiconductors
- H6 C.D. Latham, R. Jones, J. Wagner, B.R. Davidson, R.C. Newman, C.C. Button, P.R. Briddon, S. Öberg
Di-carbon defects in AlAs and GaAs
- H7 M.A. Odnoblyudov, V.M. Chistakov, I.N. Yassievich, M.S. Kagan
Resonant states in strained semiconductors
- H8 E.P. Pokatilov, V.M. Fomin, J.T. Devreese, S.N. Balaban, S.N. Klimin
Impurity-bound hole polaron in a cylindrical quantum wire

Thursday, July 30th

SESSION J: *Chairman: B.D. McCombe*

11.00 - 12.30

Low-D systems II

- J1: INVITED R.N. Bhargava
Transformation of deep-impurities to shallow-impurities by quantum confinement
- J2 B.J. Pawlak, T. Gregorkiewicz, C.A.J. Ammerlaan
Confinement effects on phosphorus donors embedded in silicon microcrystals
- J3 A. Raymond, B. Couzinet, M.I. Elmezouar, W. Zawadzki, M. Kubisa, B. Etienne
Magneto-donors and donor-bound excitons in GaAs/Ga_{0.67}Al_{0.33}As heterostructures in the quantum Hall regime
- J4 W. Jantsch, Z. Wilamowski, F. Schaffler
ESR investigations of modulation doped Si/SiGe quantum wells

-
- J5 V.Ya. Aleshkin, V.I. Gavrilenko, I.V. Erofeeva, A.L. Korotkov,
D.V. Kozlov, O.A. Kuznetsov, M.D. Moldavskaya
**Far infrared spectroscopy of shallow acceptors in strained Ge/GeSi
quatum well heterostructures**
-

Thursday, July 30th

SESSION K: Chairman: P. Fisher

14.00 -15.30

Wide-gap III

- K1: INVITED H. Katayama-Yoshida, T. Nishimatsu, T. Yamamoto, N. Orita
**Comparison between the theoretical prediction of codoping and the
recent experimental evidences in p-type GaN, AlN, ZnSe, CuInS₂, and
n-type diamond**
- K2 P. Prystawko, M. Leszczynski, B. Beaumont, P. Gibart, E. Frayssinet,
P. Wisniewski, A. Sliwinski, M. Bockowski, T. Suski, S. Porowski
Si-doping of homoepitaxial GaN layers
- K3 D.J. As
**Electrical properties of Mg doped and undoped MBE grown cubic
GaN epilayers**
- K4: INVITED A.K. Ramdas,
**Infrared and Raman spectroscopy of acceptor bound holes: boron
acceptors in isotopically controlled 'blue' diamonds**

Tuesday, July 28th

POSTER SESSION P1

17.00 -18.30

Effects of external fields and pressure:.....67-79

- P1-1 N.S. Averkiev, A.A. Dukin, V.G. Golubev
**Shallow donor resonant state width narrowing near crossing with
underlying Landau subband bottom in GaAs**
- P1-2 R.A. Lewis, T.S. Cheng, M. Henini
Magneto-spectroscopy of beryllium impurity in gallium arsenide
- P1-3 P. Fisher, C.A. Freeth, R.E.M. Vickers
High field Zeeman spectroscopy of singly ionised zinc in germanium
- P1-4 P.C. Jobe Prabakar, R.E.M. Vickers, P. Fisher
Zeeman spectroscopy of Zn-H complex in germanium
- P1-5 E.P. Skipetrov, N.A Chernova, E.I. Slyn'ko, Yu.K. Vygranenko
**Ytterbium-induced impurity states and insulator-metal transition under
pressure in Pb_{1-x}Ge_xTe alloys**
- P1-6 A. Dargys, N. Zurauskiene
Dissipative tunneling of charge carriers from shallow impurities
- P1-7 S.I. Budzulyak, J.P. Dotsenko, V.M. Ermakov, V.V. Kolomoets, V.F. Machulin,
I.V. Prokopenko, E.F. Venger, E. Liarokapis, D.P. Tunstall
**Impact ionization of shallow donor states related to different minima-type
of the germanium C-band**

- P1-8 J.P. Dotsenkol, A.E. Gorin, V.V. Kolomoets, V.F. Machulin, E.F. Venger, E. Liarokapis, D.P. Tunstall
Localization and impact ionization of shallow donor states in Si and Ge under strain-induced MI transition
- P1-9 A.Yu. Mollaev, S.M. Salikhov, R.R. Bashirov, S.F. Gabibov
Research of a shallow donor centres in a strong magnetic field
- P1-10 E.M. Kazaryan, A.A. Sarkisyan, A.A. Avetisyan, A.P. Djotyan
Impurity states in narrow band semiconductor in a high magnetic field
- P1-11 R.E.M. Vickers, P. Fisher, C.A. Freeth
Anomalies and Zeeman spectra of the Lyman series of neutral zinc in germanium
- P1-12 A. Latgé, N. Porras-Montenegro, M. de Dios-Leyva, L.E. Oliveira
Effects of in-plane magnetic fields in the acceptor-related photoluminescence spectra of p-doped coupled-well superlattices
- P1-13 B.S. Monozon, J.L. Dunn, C.A. Bates
Resonance effect in an impurity quantum well subject to electric and strong magnetic fields

Doping limits and control over impurities.....80-86

- P1-14 M. Wienecke, B. Reinhold, F. Henneberger, A. Burchardt
Shallow doping of wide-band gap II-VI compounds
- P1-15 M. Koizuka, H. Yamada-Kaneta
Gap states caused by oxygen precipitates in Czochralski silicon wafers
- P1-16 A.Yu. Kuznetsov, D. Aberg, B.G. Svensson
Shallow donors in silicon crystallized from amorphous phase via a silicide mediated epitaxy
- P1-17 Z.N. Adamian, V.M. Aroutiounian, A.P. Hakhoyan, R.S. Barseghian
Magnesium implantation in silicon by means of laser radiation
- P1-18 S.F. Marenkin, V.A. Morozova, O.G. Koshelev, G. Biskupski
Lattice defects in undoped CdAs₂ monocrystals
- P1-19 O. Paetzold, K. Sonnenberg, G. Irmer
Effect of melt stoichiometry on shallow acceptor formation in heavily doped GaAs
- P1-20 S.N. Mustafaeva, E.M. Kerimova, S.I. Mekhtieva,
Ag and CuAs shallow dopants in TlInSe₂ single crystals

Defect interactions and metal-insulator transitions.....87-97

- P1-21 V. Yu. Ivanov, A.R. Omelchuk, Yu.G. Semenov, M. Godlewski
Electronic processes related to donor-acceptor pair blue anti-Stokes luminescence in ZnSe crystals
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SESSION A

Metal-insulator transitions and defect interactions

Chairman: V. Perel

TUESDAY JULY 28th

8.45-10.30

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HOLE TRANSPORT IN THE UPPER HUBBARD BAND IN COPPER DOPED GERMANIUM UNDER UNIAXIAL PRESSURE

W. Walukiewicz^a, O. D. Dubon^a, H. H. Silvestri^{a,b} and E. E. Haller^{a,b}

Materials Sciences Division, Lawrence Berkeley National Laboratory^a and
Department of Materials Science and Mineral Engineering, University of California at Berkeley^b

Substitutional copper in Ge forms a unique triple acceptor system with all three holes occupying a four-fold degenerate, highly localized 1s ground state. Uniaxial pressure lifts the degeneracy and splits the ground state into a pair of double degenerate states. At pressures higher than about 4.2 kbar the ground state is transformed from $1s^3$ to $1s^2 2s^1$ configuration. Under such transformation two holes remain in the 1s state and the third hole is transferred to a much more extended 2s state. We have reported recently that the uniaxial stress induced transformation of the Cu ground state leads to a gigantic enhancement of the low temperature conductivity¹. The conductivity is due to hole transport in the upper Hubbard band formed by overcharged $1s^2 2s^2$ states. The Hubbard band is well separated from the valence band allowing for a systematic study of the impurity band transport in a wide range of temperatures and Cu concentrations. This is in contrast to standard hydrogenic impurities where a close proximity of the overcharged states to the conduction or the valence band edge requires measurements at extremely low temperatures and makes a reliable separation of the impurity from the band conduction difficult.

We have studied both experimentally and theoretically hole transport in the upper Hubbard band of Ge crystals with the Cu concentrations ranging from $3 \times 10^{14} \text{ cm}^{-3}$ to $1.6 \times 10^{16} \text{ cm}^{-3}$. In this Cu concentration range the temperature dependence of the hole concentration changes from thermally activated semiconductor-like behavior with the full Hubbard gap of 3.7 meV to a temperature independent semimetallic behavior corresponding to overlapping Hubbard bands. The highly delocalized nature of the overcharged 2s Cu states and a large overlap of the hole wavefunctions on adjacent Cu sites leads to formation of an impurity band with exceptionally large hole mobilities. Low temperature hole mobilities approaching $10^6 \text{ cm}^2/\text{Vs}$ are observed for low Cu concentrations.

Theoretical calculations show that this high mobility is well described by scattering of low effective mass holes from ionized and neutral copper centers. The scattering cross section of the neutral centers depends on the size of the Cu wavefunction. At high pressures all the neutral Cu centers are quite efficient scattering centers because of the large spatial extent of the $1s^2 2s^1$ ground state configuration. At intermediate stresses some of the Cu centers remain in the highly localized $1s^3$ configuration leading to a drastic reduction of the neutral center scattering and a large enhancement of the hole mobility. Mobilities in mid $10^6 \text{ cm}^2/\text{Vs}$ were found in the sample with Cu concentration of $3 \times 10^{14} \text{ cm}^{-3}$ at intermediate stresses. This is higher than electron or hole mobilities ever observed for such a high impurity concentration.

At Cu concentrations higher than about $3 \times 10^{15} \text{ cm}^{-3}$ we observe an onset of Anderson localization that manifests itself in a thermally activated low temperature mobility. We attribute this effect to a disorder and a spatial variation of the Hubbard gap resulting from the random distribution of Cu atoms in the crystal lattice.

This work was supported by US DOE under Contract No. DE-AC03-76SF00098.

[1] O. D. Dubon et. al., Phys Rev Lett. 78, 3519, (1997)

THE COULOMB GAP IN THE SHALLOW BAND OF $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As} : \text{Si}$

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30123-970, Belo Horizonte, M.G., Brazil.

We studied hopping^{1,2} of electrons in the shallow impurity band of Si dopants in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ alloy, for several different concentrations of these electrons, in a single sample. The shallow state of the dopant in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ is an excited state with lifetime, at temperatures bellow 100K, long enough to allow experiments lasting several days. The fundamental state, the so called DX center, is a deep level of the dopant atom with an extra electron. It's formation requires one dopant atom with its own electron and one more taken from another atom.³ It works as a compensating center for the second atom, which will be an ionized donor with an empty state in the shallow impurity band. The creation of DX centers, besides decreasing the shallow donor concentration (N_d) leads to an increase in its ionized part. So the DX center plays two roles: it changes the donor concentration and also behaves as a compensating defect. Hence, disregarding any unintentional acceptor dopants, one has $N_d = (N_{\text{Si}} + n)/2$; $N_{\text{DX}} = (N_{\text{Si}} - n)/2$; $K = N_d/N_{\text{DX}}$, where N_{Si} is the silicon concentration and N_{DX} is the DX center concentration. By shining light on the sample DX center are converted into shallow donors, changing n , N_d and K .

Our sample had $N_{\text{Si}} = 68 \times 10^{16} \text{cm}^{-3}$, and with infrared radiation we obtained n values between $1.2 \times 10^{16} \text{cm}^{-3}$ and $16.6 \times 10^{16} \text{cm}^{-3}$, corresponding to compensation ratios from 0.6 to 0.97, respectively. The donor concentration changed from $34 \times 10^{16} \text{cm}^{-3}$ to $42.4 \times 10^{16} \text{cm}^{-3}$. The temperature dependence of the sample's resistivity (ρ), for each n value, was measured in the range of 0.32K to 60K. Bellow 20K the data present Mott's transport regime, $\rho \propto \exp(-(T/T_{1/4})^{1/4})$, which, at lower temperatures, turns to the Efros-Shklovskii regime $\rho \propto \exp(-(T/T_{1/2})^{1/2})$. The data corresponding to $n = 16.6 \times 10^{16} \text{cm}^{-3}$ can be fit to a diffusive rather than hopping regimes. This means that the metal-insulator transition occurs for n between $13.6 \times 10^{16} \text{cm}^{-3}$ and $16.6 \times 10^{16} \text{cm}^{-3}$. These values are much higher than the value $5 \times 10^{16} \text{cm}^{-3}$ obtained from the Mott's criterion, confirming the compensating character⁴ of the DX center and so its negative charge. This was a matter of big challenge some years ago, and even now there are researchers who doubt it. With the $T_{1/2}$ and $T_{1/4}$ parameters, obtained from the fitting, we calculated the width Δ of the soft Coulomb gap developed in the impurity band by the relation²

$\Delta = k_B T_{1/2} \sqrt{T_{1/2}/T_{1/4}}$. The dependence of this gap width on the electron concentration n and on the compensation ratio K is shown in the figure⁵. Our results indicate that the Coulomb gap has a maximum at K between 0.94 and 0.97. This maximum is expected because at $K \approx 0.6$ the sample is in the metallic regime where the gap does not exist; and when $K \rightarrow 1$ the electron concentration goes to zero and the gap vanishes. Theoretical predictions for the maximum point and the K behavior of this gap are still lacking in the literature.

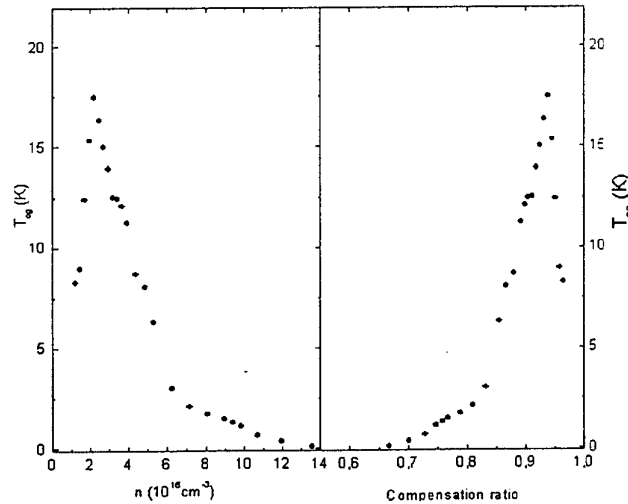


Figure 1: The Coulomb Gap width Δ/k_B versus electron concentration n (left) and compensation ratio K (right).

¹ N. F. Mott, "Metal-Insulator Transitions", 2nd Ed., (Taylor & Francis, 1990).

² B. I. Shklovskii, and A. L. Efros, "Electronic Properties of Doped Semiconductors" (Springer-Verlag, Berlin, 1984).

³ Chadi and Chang, Phys. Rev. Lett., **61**, 873 (1988); P. Mooney, J. Appl. Phys. **67**, R1 (1990).

⁴ H. Fritzsche, Phil. Mag.B **42**, 835 (1980); N. F. Mott, and J. H. Davies, Phil. Mag.B **42**, 845 (1980).

⁵ H. S. Moreira, J. F. Sampaio, E. S. Alves, and A. G. de Oliveira, Phys. Rev. Lett., **80**, 1706 (1998).

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THE DRASTIC CHANGE OF MAGNETORESISTANCE BY THE RISE OF ELECTRON TEMPERATURE IN Sb DOPED Si

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DC electrical measurements have been performed on Si:Sb near the metal-insulator transition for five kinds of sample. Temperature, electric current and magnetic field dependence have been examined for these samples. We found that for samples with the concentration below the critical one of the metal-insulator transition the resistivity, Hall coefficient and magnetoresistance depend on the electric current. In this concentration region the electric field can excite electrons from the strong localized states of the impurity band to the weak localized states above them. Therefore electron temperature rises and the resistivity, Hall coefficient and magnetoresistance change.

As an example, we show some experimental data for a sample whose donor concentration is $0.80N_c$, where $N_c (\approx 3 \times 10^{18} \text{ cm}^{-3})$ is a critical concentration.^{1,2} Electric current dependence of the resistivity is shown in Fig.1. In the low electric current region the resistivity is followed by Ohm's law, but as electric current increases the resistivity decreases. Owing to the electric field effect electrons are excited into higher energy states and the electron distribution and electron mobility change. The electric current dependence of the resistivity and Hall coefficient have been analyzed based on the two-band model.³ Two bands correspond to the impurity and conduction bands. This analysis yields $n_c \approx 10^{16} \text{ cm}^{-3}$ and $n_i \approx 10^{18} \text{ cm}^{-3}$ in the low electric current region, where n_c and n_i is the concentration in the respective band and the subscript c and i denote the conduction and the impurity bands, respectively. But below N_c the impurity band consists of two Hubbard bands and may be split into upper and lower Hubbard bands. Therefore, the conventional two-band model should be modified. Electric current dependence of the magnetoresistance are shown in Fig.2. A positive magnetoresistance is observed in the low electric current region. The positive magnetoresistance $\rho(B)$ in Variable-Range Hopping conduction is reported to behave as $\ln(\rho(B)/\rho(0)) \propto B^2$, where B is the magnetic field.⁴ As the electric current increases, the positive magnetoresistance diminishes and the negative one becomes notable. It is concluded that these phenomena originate in a rise in the electron temperature and the transfer of electrons from strong to weak localized states.

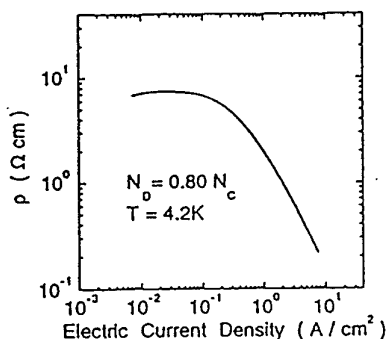


Fig.1 Electric current density dependence of the resistivity

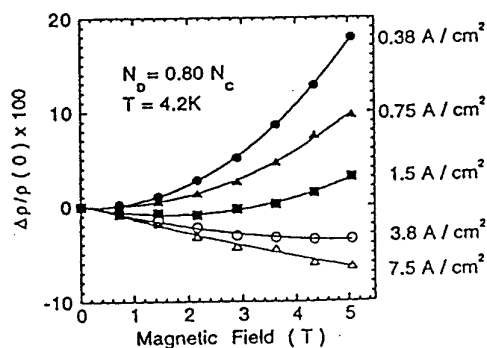


Fig.2 Electric current density dependence of the magnetoresistance

1. A. P. Long et al. : J. Phys. C : Solid State Phys. 17 425 (1984).
2. T. G. Castner et al. : Phys. Rev. Lett. 34 1627 (1975).
3. H. Miyazawa et al. : J. Phys. Soc. Jpn. 23 290 (1967).
4. A. N. Ionov et al. : Sov. Phys. JETP. Lett. 42 406 (1985).

TOPOLOGICAL INTERACTION OF SHALLOW-LEVEL CENTERS WITH DISLOCATIONS IN SEMICONDUCTORS

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A novel interaction of shallow-level centers with dislocations is studied. The interaction results from the violation of the topological structure of the crystal lattice by dislocations. To investigate the interaction the recently developed theory of gauge-invariant k - p -Hamiltonians for crystals with topological defects is applied [1,2]. According to this theory the k - p -Hamiltonian for strained crystal with non-trivial topology contains in addition to usual deformation potential a topological gauge potential corresponding to a non-Abelian group $E(3)$ of the proper Euclidean transformations of three-dimensional space.

The topological gauge field corresponding to this gauge potential is confined inside the dislocation cores but it influences the shallow impurity states in vicinity of dislocations via an Aharonov-Bohm effect-like interaction. This may affect the energy levels and the wave functions of shallow centers in vicinity of dislocations to high extent. For example, the binding energies of shallow donors at screw dislocations are reduced by the factor of 2.25 in the case of isotropic non-central valleys and by the factor of 4.0 in the case of highly anisotropic valleys. Besides, the topological interaction may convert some deep-level centers in the vicinity of dislocations into shallow-level ones those can be described in the effective mass approximation.

For split dislocations the interaction of shallow-level centers with the stacking faults existing between partials becomes important and it is taken into account on the base of the recently developed δ -quantum well model of the stacking faults [3].

The effects of these interactions on donor-acceptor recombination spectra in crystals with dislocations are discussed.

[1] Y T Rebane Phys.Rev. B 52, 1590 (1995)

[2] Y.T.Rebane and J.W.Steeds Phys.Rev.Lett. 75, 3716 (1995)

[3] Y.T.Rebane, Y.G.Shreter, and M.Albrecht phys.stat.sol (a) 164 ,141 (1997)

DYNAMICAL PROPERTIES OF IMPURITY CLUSTERS IN SILICON

J. Yamauchi, N. Aoki* and I. Mizushima*

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We investigated Raman and infrared absorption(IR) frequencies of several boron(B) clusters in Si based on the first-principles calculation and have found that *icosahedral*(ICO) B_{12} clusters exist in Si. Throughout systematic experiments, we found that holes are generated in high concentration without any post-annealing after B ion implantation into Si with the high-dose of more than $1 \times 10^{16} \text{cm}^{-2}$. It implies that these holes originate from the B_{12} ICO clusters[1]. Our first-principles calculation confirmed that the ICO cluster generates two holes per cluster in consistent with these experimental results[2]. Since dopant impurities in Si are mostly activated at substitutional sites through thermal annealing and excess dopants above a solid solubility limit form electrically *inactive* clusters, the generation of holes from the clustered B atoms may be called as an anomalous behavior. We have been therefore devoted to clarify the real structure of the B clusters and the mechanism of these activation.

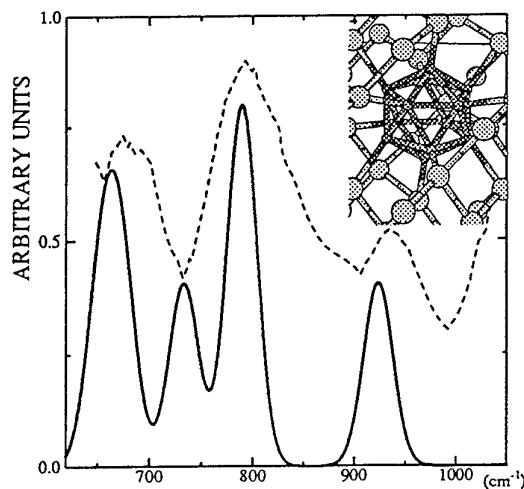
It is not an easy task to identify the atomic structure of clustered B solely through experiments. This is because there is no method to observe directly an atomic structure inside a bulk crystal, although a scanning tunneling microscope may be helpful to obtain atomic scale information near a surface region. On the other hand, Raman and IR spectra are most sensitive to the local structure, although it is very difficult to correlate the atomic structure with the vibrational frequency. In this paper, we show successful one-to-one correspondence of the local atomic structure with the experimental IR spectra.

We carried out the systematic calculation of the dynamical matrix obtained from the second derivatives of total energy with respect to displacement vectors. We obtained the derivatives within the framework of the local density approximation. For the sake of the accuracy of the present method, we calculated the vibrational modes for several simple cases; Si crystal, and substitutional B in Si. Results shows that the calculated values indicate reasonable agreements with those of experiments, namely the calculated (experimental) value 517cm^{-1} (520cm^{-1}) for Si crystal and 612cm^{-1} (620cm^{-1}) for the substitutional B in Si. We investigated the vibrational modes of several cluster configurations, which are expected to exist in Si, and found that the ICO B_{12} most naturally reproduce the experimental spectra as shown in Fig. 1. It should be noted that the cubo-octahedral cluster, which exists in the compounds MB_{12} ($M = \text{Sc, Y, Zr, and U}$), is found to be unstable against infinitesimal displacement.

Another important key issue in modern LSI technology is the clustering of arsenic atoms in the heavily doped region. Structures involving a Si vacancy are recently suggested for the arsenic clusters[3,4]. We are extending the above mentioned analysis to this problem. We will also report the analysis of the vibrational modes of arsenic clusters in Si.

- [1] I. Mizushima, *et al.*, Appl. Phys. Lett. **63** 373 (1993).
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Fig. 1 The calculated density of states of IR active vibrational modes of the icosahedral B_{12} cluster(solid) and the experimental IR spectrum(broken). The calculated line is broadened with the Gaussian, whose width corresponds to 300K. The experimental spectra more than 1000cm^{-1} are due to the oxygen impurities in Si. The inset is the perspective view of the icosahedral cluster in Si.



NEAR-EDGE STATES INDUCED BY HYDROGEN INCLUSION IN GALLIUM ARSENIDE

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It is well known that lattice deformations affect the optical response of semiconductors. In particular, these deformations may give rise to energy levels near the valence- and conduction-band edges, which are related to states localized in real space. In amorphous materials these states have a continuum distribution of energy levels which leads to an exponential absorption edge, the Urbach's tail. A similar behavior is expected in crystalline materials when local lattice deformations are produced by defects or impurities. As a matter of fact, a structured band has been reported to appear a few tens of meV below the energy band gap in the photoluminescence spectra of hydrogenated, nominally undoped GaAs and of hydrogenated InGaAs/GaAs quantum wells. These bands have tentatively been attributed to transitions involving localized levels due to lattice deformations.[1]

In the present study, we look for a possible link between the lattice deformations induced by atomic hydrogen in GaAs and the appearance of energy levels near the band edges. No theoretical study of these H effects has been performed yet, at least to our knowledge. Equilibrium geometries, electronic charge distributions, and electronic eigenvalues have been evaluated by first-principle local-density-functional methods for different locations of neutral and charged H atoms in the GaAs lattice. Atomic arrangements identical to those found for different equilibrium geometries of the H atom, *but that the H atom is removed*, have also been considered in order to separate the effects of the lattice deformation from those produced by the formation of H-host-atom bonds. Present results show that *discrete electronic levels near the conduction- and valence-band edges are induced by atomic H*. These near-edge levels have been accounted for by the different effects of the H interaction with the GaAs lattice, which have been described in terms of: (i) the distortion of the Ga-As bonds nearest neighbor of H; (ii) "simple" chemical arguments based on a LCAO (linear combination of atomic orbitals) model involving molecular orbitals centered on the H or on the Ga and As atoms; (iii) the influence of the charge of H ions on the local electronic charge distribution. Finally, the main features of the emission bands observed in the photoluminescence spectra of hydrogenated III-V compounds are well explained by radiative transitions between the near-edge levels calculated in the present LDA approach.

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SESSION B

Bound excitons and Raman scattering at shallow centers

Chairman: G. Martinez

TUESDAY JULY 28th

11.00-12.30

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Bound excitons in wide-gap II-VI and nitrides semiconductors - comparison of optical studies of shallow dopants in these materials.

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For growth of semiconductor devices like laser diodes and transistors a reproducible control of doping levels for shallow acceptors and donors in the range from 10^{16} to 10^{19} cm⁻³ is the crucial precondition. Beside the electrical characterization optical spectroscopy delivers an important access to investigate the chemical nature of impurities, their concentrations and the compensation effects involved. In wide band-gap semiconductors like II-VI compounds and nitride based semiconductor shallow dopands influence strongly the excitonic processes in the band edge regime. To distinguish doping effects from intrinsic properties like biexcitons or electron hole plasmas a detailed knowledge about the observed free and bound excitonic systems in the investigated crystal structure is mandatory. In this paper recent results obtained using photoluminescence (PL), resonant excitation spectroscopy, magneto-optics and time-resolved analysis are surveyed.

In the first part the development of luminescence and resonance excitation of bound exciton systems is treated under various excitation densities. The specific properties observable when using heteroepitaxial II-VI and nitride heterostructures instead of conventional bulk samples are discussed. Here especially, latest results about self-compensation mechanisms will be presented. Magneto-optical data were presented to characterize the chemical nature of the incorporated shallow impurities.

In the second part the dynamical characteristics of excitonic transitions are evaluated for various impurities, dopands and dopands concentrations, and excitation via particular resonant excitation channels. Relaxation and conversion channels between excitonic systems are analyzed, in particular in strained heteroepitaxial systems which show splitting effects of the bands from which the carriers stem. The dynamical behavior of excitons in wide gap material gives evidence of nonradiative decay channels. Calorimetric spectroscopy at mK temperatures was used to investigate the nonradiative processes and to determine quantum efficiencies.

In the last part latest results of transient four-wave mixing experiment at bound exciton complexes will be shown to demonstrate that shallow defects influence the dephasing in the investigated systems which gives information about the homogeneous and inhomogeneous broadening mechanisms.

EXCITONIC MOLECULES CAPTURED BY QUANTUM DOTS AND ISOELECTRONIC IMPURITIES IN MULTIVALLEY SEMICONDUCTORS

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Excitons in many-valley semiconductors form molecules consisting of four and more excitons. The degeneracy factor g of the conduction band in germanium is 8, and in silicon and gallium phosphide $g=12$. As in acceptors, the hole ground state in excitons is fourfold degenerate. The same is valid for exciton molecules, because they are quantum objects with spherical symmetry. The exciton binding energy in molecules is close to that in exciton-liquid droplets. Experimental evidence is considered for the existence, besides biexcitons, of stable exciton molecules consisting of three and four, and, possibly, 11 and 12 excitons. Molecules containing from five to ten excitons are apparently unstable. Many isoelectronic impurities like as *Bi* in *GaP* may be treated as quantum dots. In pure silicon, luminescence spectra of free exciton molecules exhibit six lines. Six lines were found also in the luminescence of exciton complexes (molecules) bound to shallow donors in silicon. These six lines were also observed in *GaP:Bi*. Electrons and holes can be captured by small size quantum wells, i.e. by quantum dots, and by isoelectronic impurities. Dots are also capable to capture excitons and biexcitons. In the present work for the first time theoretical and experimental consideration is given to the formation of exciton molecules containing three or four excitons in one dot. Existence of such exciton molecules is possible only in multivalley semiconductors [1,2]. The conduction and valence bands of such semiconductors as *GaP*, *AlAs*, *AlSb*, *Ge* and *Si* have several energy minima. The Coulomb interaction of electrons and holes in multivalley semiconductors results in formation of exciton molecules, i.e. not only of biexcitons, but also of essentially stronger bound triexcitons and tetraexcitons. Both free and bound on dots excitons can be strongly binded because in multivalley semiconductors up to four holes can be located in ground state (*s*-state). The number of electrons in ground state can be significantly larger, for example, in *GaP* there can be 6 electrons, in *Ge*- 8 and in *Si*- 12 electrons. We recently showed experimentally and theoretically that while the dot depth increases, first, the captured exciton molecule radius essentially decreases and only after, with the dot depth still increasing, the electron energy level rises. At further increase of the dot depth electrons and holes are captured independently and the Coulomb interaction of electrons and holes may be considered as a small correction. Kinetics of the formation of free and bound on quantum dots exciton molecules was studied. The capture by dots of electrons, holes, excitons and free exciton molecules was considered. An important feature of formation of exciton molecules captured by dots is the presence of tunnel transitions of electrons and holes between dots. It is shown that for *GaP:Bi* the tunnel transitions between isoelectronic impurities of *Bi* of the concentration higher than 10^{17}cm^{-3} determine distribution of dots with respect to the number of captured excitons, which does not depend on the excitation level in a wide range of excitation. Both the experimental and the theoretical results show that these molecule produce in the luminescence spectrum two lines each. One of the lines is due to radiative recombination, i.e. annihilation of an $n=2$ hole with an $n=1$ electron. Thus this recombination leaves the molecule in ground state and generates a narrow line. The second line is actually the long-wavelength tail of the luminescence line discussed earlier. The width of this line is determined by the lifetime of the empty state in the $n=1$ hole shell.

Supported by Russian Federal Scientific Program "Integration", grant N 326.37.

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THE D₁ EXCITON IN 4H-SiC

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The physical properties of silicon carbide (SiC) make the material well suited for high temperature, high power and high frequency electronics. The recent progress in crystal growth of SiC has lead to an increased interest in its development. SiC exists in several different polytypes of which the 3C-, 4H-, 6H- and 15R-polytypes are the most common. Of these, the 4H-polytype is considered to be the most appropriate for high power applications, as it has the widest band gap and an almost isotropic electron mobility. Very high temperatures (>1800 °C) are needed for diffusion doping of SiC, making the method impractical. Therefore, doping by ion implantation is of major importance. The main problem concerning ion implantation is the damage it causes to the lattice. This gives rise to unwanted defects, some of which persist even after annealing at temperatures up to 2000 °C. The best known of these is the D₁ centre. Its fingerprint is an efficient photoluminescence (PL) of energy 0.35-0.45 eV below the excitonic band gap, composed of sharp no-phonon lines followed by a characteristic phonon assisted structure. The D₁ centre can also be observed in electron and neutron irradiated material, and in some cases directly after growth.

The D₁ PL exhibits a complicated temperature dependence. Depending on the SiC polytype, the spectra are composed of either two or three superimposed spectra. The sub-spectra consist of a polytype dependent number (n) of no-phonon lines, each accompanied by the characteristic D₁ phonon structure. At the lowest temperatures, the lowest energy sub-spectrum dominates, but as the temperature increases the higher energy sub-spectra take over. The letters L, M, and H (low, medium and high temperature) are used to label the different sub-spectra. The no-phonon lines are denoted by L_i, M_i and H_i where i runs from 1 to n. The current model of the D₁ PL is excitonic recombination at an isoelectronic native defect [1].

Until now, most investigations of the D₁ exciton have been carried out for the 3C- and 6H- polytypes, whereas information is very scarce in the case of 4H-SiC. In this paper we report an extensive study of the properties of the D₁ PL observed in electron irradiated 4H-SiC. We have investigated the temperature dependence of the PL, its time decay and excitation properties. At low temperatures the D₁ PL in 4H-SiC consists of one no-phonon line L₁ (4272.6 Å) followed by a phonon assisted structure. As the temperature is raised, two higher energy no-phonon lines, M₁ (4261.3 Å) and H₁ (4257.0 Å), appear and the L₁ intensity rapidly decreases. At sufficiently high temperatures (T>100 K) the D₁ PL is quenched. The activation energy is found to be around 57 meV. At high temperatures the time decay of the three no-phonon lines L₁, M₁ and H₁ is identical, which shows that they are thermalized. The lifetime at 1.3 K is around 450 µs but decreases to a few µs at 70 K. PL excitation (PLE) spectra of phonon replicas of the L₁ line at low temperature reveal a weak peak corresponding to the L₁ no-phonon line and two strong peaks corresponding to the M₁ and H₁ lines. Furthermore, there is a series of sharp lines at higher energies in the PLE spectra. The energy positions of the lines fit well a hydrogenic series of excited states. The fitting gives a binding energy of 53 meV and an associated effective mass $m^* = 0.37m_0$. Our investigation gives important new information concerning the structure of the D₁ exciton. The low activation energy of the quenching of the D₁ PL, and the excited states observed in the PLE spectra, show that one of the excitonic particles is weakly bound. The effective mass of the secondary particle, obtained by fitting the PLE results to a simple hydrogenic model, is similar to the electron effective mass in 4H-SiC.

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INTERNAL TRANSITIONS OF NEUTRAL AND CHARGED MAGNETO-EXCITONS IN AlGaAs/GaAs QUANTUM WELLS

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Optically Detected Resonance (ODR) spectroscopy has been used to study electron and hole cyclotron resonance (CR) and various internal excitonic transitions (IETs) in undoped and barrier-doped $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}/\text{GaAs}$ multiple-quantum-well (MQW) samples (well widths between 8 nm and 20 nm) in magnetic fields up to 17 T at low temperatures. With this highly sensitive technique resonant magnetoabsorption of far infrared laser radiation is monitored through changes in the photoluminescence simultaneously excited by visible laser excitation. Internal transitions of neutral "heavy"-hole excitons (hhX) have recently been observed by ODR spectroscopy.¹ Further studies of an undoped 12.5 nm well-width sample have verified directly predictions² related to the cylindrical and time-reversal symmetries of the Hamiltonian for this system: the energy difference between electron and hole CR equals the energy difference between any pair of $1s \Rightarrow np(m)$ IETs (here the 3D hydrogen atom notation has been used to label the states). The two principal "heavy"-hole CR transitions (associated with the $3/2$ and $-3/2$ spin projections) were identified from comparison with theoretical calculations. In addition to the nearly degenerate $1s \Rightarrow 2p(+1)$ IET(s), two well-separated $1s \Rightarrow 2p(-1)$ transitions resulting from the two distinct heavy hole magneto-excitons were observed. The near degeneracy of the $1s \Rightarrow 2p(+1)$ IETs and the large splitting of the $1s \Rightarrow 2p(-1)$ are shown to result from the very small spin-splitting of the electron Landau levels and the large splitting of the hole levels, respectively.

Negatively (X^-) and positively (X^+) charged excitons in quantum wells have become of increasing interest since the initial observation of X^- in the CdTe system several years ago.³ We have extended our ODR studies of excitons to negatively charged (a photoinjected hole binding two electrons) excitons in nominally undoped and barrier-doped (Si at $2 \times 10^{10} \text{ cm}^{-2}$) 20 nm well-width $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ MQW samples. Both samples showed neutral "heavy"-hole and negatively charged exciton photoluminescence lines. The hhX recombination is strongest in the nominally undoped sample with a weaker X^- (singlet) line observed about 11 cm^{-1} below the hhX peak at zero magnetic field. In the modulation-doped sample the X^- PL dominates, with only a weak shoulder at higher energies giving evidence of the hhX recombination. The ODR measurements on these samples are dominated in both cases by internal transitions of the (singlet) X^- complex. These results represent the first experimental evidence of internal transitions of X^- . Both $1S \Rightarrow 2P(M = +1)$ and $1S \Rightarrow 2P(M = -1)$ lines are observed; here M is the quantum number for the total projection of angular momentum along the field (the sum of m_1 and m_2 for the two electrons). The role of symmetry in the two-electron system in understanding the complex spectra will be discussed. There is also evidence of internal triplet transitions of X^- and electron cyclotron resonance in the spectra, but no evidence of IETs corresponding to (neutral) hhX in either sample, the absence of which in the nominally undoped sample is surprising and presently not understood. While PL, PL excitation, and interband absorption or reflectance measurements can probe the ground states (and possibly s-like excited states) of these electron-hole complexes, IETs of hhX or X^- are inaccessible by these techniques. The present experiments demonstrate the power of ODR spectroscopy for studying the internal states of excitonic complexes, and its promise for elucidating the role of many body effects in mediating the transition from neutral- to charged-excitonic- to band-like behavior of the electronic states in a magnetic field.

Supported in part by NSF grants DMR 9722625 and DMR 9624029.

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³ K. Kheng *et al.*, Phys. Rev. Lett. 71, 1752 (1993).

RAMAN SCATTERING AT SHALLOW ACCEPTORS IN INP

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Electronic Raman scattering was used for the first time to investigate excited states of the shallow acceptors in Zn-doped and Cd-doped p-type semiconducting InP in dependence on impurity concentration in the temperature range between 10K and 160K. The acceptor concentrations of the samples investigated were in the range between $2 \cdot 10^{16} \text{ cm}^{-3}$ and $9 \cdot 10^{17} \text{ cm}^{-3}$. The Raman spectra were excited with a Ti: sapphire laser below the band gap at the wavelength 950 nm, the measurements were performed with a Jobin-Yvon T 64000 triple monochromator and the signal analyzed by multichannel detection with a cooled CCD.

The strongest Raman lines observed could be assigned to the transitions $1S_{3/2} \rightarrow 2S_{3/2}$ (E - line) , $1S_{3/2} \rightarrow 2P_{3/2}$ (G - line) and $1S_{3/2} \rightarrow 2P_{3/2}$ (C,D - lines) , some weaker lines were assigned to the transitions $1S_{3/2} \rightarrow nS_{3/2}$, tentatively. Some of the well resolved Zn-acceptor states, measured at low impurity concentration and low temperature, could be compared with results of earlier published photoluminescence studies and a good agreement was found.

The electronic Raman spectra show a similar behaviour in dependence on the impurity concentration and on temperature as observed in other p-type semiconductors, the spectra broaden with increasing acceptor concentration and temperature. In Zn-doped InP up to a concentration of about 10^{17} cm^{-3} excitations to discrete levels were observed, whereas in the case of Zn-doped GaAs the levels merge into broad bands already at acceptor concentrations of 10^{16} cm^{-3} , as shown by measurements performed for comparison. A linear relationship between the Raman intensity and the acceptor concentration was obtained, using optical phonon lines for calibration. At higher impurity concentrations an asymmetric tail on the high energy side of the electronic spectra was found, which extends beyond the acceptor activation energy up to the valence band continuum.

For the interpretation of optical and transport measurements in InP an accurate knowledge of the dispersion of the valence band top and the effective masses is important. However, for InP these data are not yet known with the desired accuracy. The energy spectrum of shallow acceptors is very sensitive to the hole effective masses. We used the measured acceptor energy levels in order to prove which sets of published Luttinger inverse hole masses γ_1 , γ_2 and γ_3 are compatible with our results.

SESSION C

Wide-gap I

Chairman: M. Stutzmann

TUESDAY JULY 28th

14.00-15.30

- C1: INVITED R. Stepniewski, A. Wyszomolek, M. Potemski, J. Lusakowski,
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I. Grzegory, S. Porowski
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- C2 A.M. Witowski, M.L. Sadowski, K. Pakula, P. Wyder
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- C3 M.W. Bayerl, M.S. Brandt, M. Stutzmann
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- C4 N. Ahtziger, C. Hülsen, W. Witthuhn, M.K. Linnarsson,
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Scolfaro
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IMPURITY RELATED LUMINESCENCE OF HOMOEPITAXIAL GAN STUDIED WITH HIGH MAGNETIC FIELDS

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An industrial need for opto-electronic devices operating in the blue part of the spectral range has recently attracted a lot of interest in the physical properties of Gallium Nitride (GaN). As a large-band-gap, big-effective-mass compound, GaN is quite distinct from the other III/V semiconductors. The physics of impurity states in GaN is attractive since the standard effective mass approach to impurity states might be limited due to the large values of the effective masses involved and the high amplitude of electron-phonon interaction. In spite of the technological success in producing both *p* and *n* type material, the understanding of the physical properties of shallow impurities in GaN is in many aspects not satisfactory. Valuable information about donors and acceptors can be obtained from the analysis of impurity related emission, especially if sharp lines (bound excitons, donor-acceptor pair spectra) due to the transitions involving donors and acceptors are observed. Such fine structures are observed in homoepitaxial GaN layers grown on GaN single crystals.

This paper presents the results of measurements of neutral impurities bound exciton and donor-acceptor pair emission lines in magnetic field up to 27 T. Low temperature luminescence spectra were measured with the magnetic field parallel and perpendicular to the *c* - axis of the GaN layers. The magnetic field splits the emission spectra. The splitting at highest magnetic fields is in the range of few meV.

The luminescence spectrum measured without a magnetic field shows two dominant narrow lines XA and XD. When a sufficiently high magnetic field is applied, both lines split, and the behaviour of the observed components depends on the magnetic field orientation with respect to the *c*-axis of the investigated wurtzite type crystal. These lines, on the basis of previously observed properties, have been assigned to the exciton bound to the neutral acceptor and neutral donor, respectively. In case of the exciton bound to the neutral donor, the observed splitting pattern is well understood on the basis of the conventional analysis of the band structure of the wurtzite-type symmetry. This relatively simple analysis, applied to the experimental data for different orientations of the magnetic field, allows us to determine the values of the effective Landé *g*-factors, separately for electrons and holes (weakly bound to the donor centre). A similar approach applied to the XA transition allows us to understand only the dominant spin-split components. Other satellite transitions, weakly pronounced but clearly resolved in a magnetic field, show a more subtle structure of the XA exciton the description of which is beyond the standard model.

In the case of the donor-acceptor pair spectra, surprisingly, the line splitting is very similar for both magnetic field configurations. The oscillator strengths of the split components depend on the magnetic field orientation. In addition to the structures observed for zero field, new lines appear which are forbidden without a magnetic field. These results are quite different from those observed for donor-acceptor pair spectra in CdS, where both the splitting pattern and the intensity changes of split components are very sensitive to the orientation of the magnetic field. Thus it is not possible to explain the magnetic field behaviour of the pair spectra in GaN basing on the present theory developed for pair spectra involving simple donors and acceptors in CdS. In order to describe properly the behaviour of the pair lines in magnetic field, we propose a model which takes into account the exchange interaction of shallow donor electrons with acceptor holes and the complex structure of the acceptor. The splitting pattern analysis based on this model enables us to determine the electron-hole exchange constant *A* and effective *g*-factors for electrons and holes bound to donors and acceptors. The dependence of constant *A* on the donor-acceptor separation is discussed.

The fine structure of the neutral acceptor bound exciton recombination and donor-acceptor pair spectra observed in the magneto-optical data is tentatively attributed to the internal structure of the acceptor and reflects the specific nature of acceptor states in GaN.

FAR INFRARED MAGNETOSPECTROSCOPY OF SHALLOW DONORS IN GaN

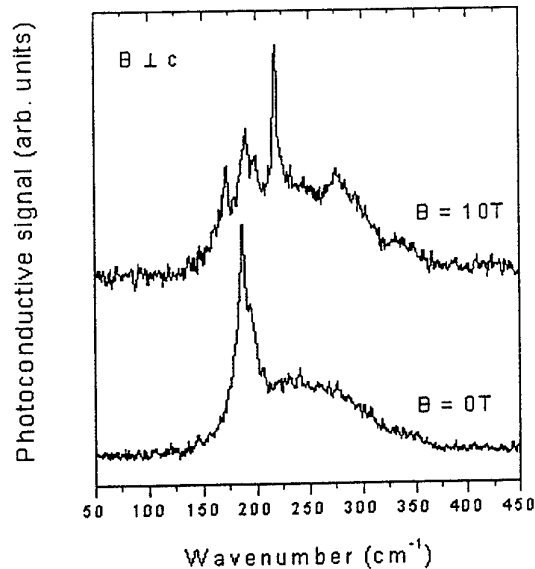
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Numerous attempts at investigating the properties of shallow donor states in GaN have been reported so far, but the quality of the available samples has usually resulted in a large scatter of the obtained parameters. The subject therefore still remains of interest. Here we present a complete far-infrared spectroscopic investigation of shallow donors in high-quality layers of GaN grown by MOCVD on a sapphire substrate. Measurements of transmission as well as photoconductivity were performed by Fourier transform spectrometry in magnetic fields up to 13T. The quality of the obtained spectra allows an unambiguous and detailed analysis of the results. GaN is a wurtzite type material, with the c -axis perpendicular to the substrate. Therefore two different configurations, namely B parallel to c and B perpendicular to c , are possible. Measurements performed in both configurations clearly show the effect of reduced symmetry on the shallow donor states.

Very clear and sharp lines were observed in the spectra for both configurations, which may unambiguously be assigned to transitions from the $1s$ state of a shallow impurity to all split components of the $2p$ state at different magnetic fields. The line at zero magnetic field is observed at an energy of 23.2 meV, and its subsequent splitting and the evolution of the components is well described using a simple model of a hydrogen-like centre in a slightly anisotropic crystal in a magnetic field. The splitting of the $2p_{-1}$ and $2p_{+1}$ states is directly related to the cyclotron energy, so that it is also possible to establish the effective mass as $0.22 m_0$. A strong diamagnetic shift was observed for all transitions and has to be included in the description. The ionisation energy of the impurity, i.e. the energy of the $1s$ state in a zero magnetic field, is found to be 30.5 meV. In configuration $B \parallel c$ mainly the lines due to the $1s \rightarrow 2p_{-1}$ and $1s \rightarrow 2p_{+1}$ transitions are observed.



In the $B \perp c$ configuration more lines appear when a magnetic field is applied, which are interpreted as being due to other components of state 2.

The figure shows examples of photoconductivity spectra for a sample in the $B \perp c$ configuration. The spectrum at 10T has been rescaled and shifted upward for clarity.

SPIN DEPENDENT PROCESSES AND MG ACCEPTORS IN GAN SINGLE QUANTUM WELL DIODES
AND P-TYPE GAN FILMS

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Despite the rapid advance in the GaN material system the performance of LEDs and other optoelectronic devices is still limited by the quality of the p-type injecting layers and ohmic contacts. We have performed electrically detected magnetic resonance (EDMR) measurements to reveal rate limiting transport processes in commercial blue and green InGaN single quantum well light emitting diodes. These experiments were performed at 34 GHz, which enables the resolution of two centers, one enhancing and one quenching, which could not be separated in earlier 9 GHz experiments [1]. The enhancing resonance has a g-factor of $g \approx 2.008$ and a linewidth of $\Delta B \approx 140$ G. Current level and degradation state influence both g-factor and signal intensity of this resonance. With respect to g-factor and linewidth the behavior of this signal is nearly identical in both LEDs, indicating that the resonance is not influenced by the different In-concentrations in the active quantum well.

Spin dependent dark conductivity (hopping) in p-type GaN has been observed also in Mg-doped MBE-grown thin films ($[Mg] = 5 \times 10^{19} / \text{cm}^3$). Thermopower experiments on this sample have shown a change in the sign of the Seebeck-voltage characteristic for hopping in a shallow impurity band. The EDMR signature observed is similar to that reported for earlier ODMR experiments [2]. An entirely new, very broad resonance ($\Delta B \approx 800$ G) is also found in the GaN:Mg films, which has a more pronounced anisotropy ($g_{\perp} = 2.6$; $g_{\parallel} = 1.9$).

The second, quenching line observed in the quantum well diodes has $g \approx 2.002$ and $\Delta B \approx 180$ G and could only be observed at high forward biases and under reverse breakthrough conditions. Similar resonances have been found in other GaN diode structures (pn-homojunction [3], minn⁺-structures [4]). These resonances are characteristic for EDMR experiments and are generally not observed in ODMR. The microscopic origin of the different EDMR signals and their relation to the Mg acceptors will be discussed.

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MOBILITY, PASSIVATING EFFECT AND THERMAL STABILITY OF HYDROGEN IN SILICON CARBIDE

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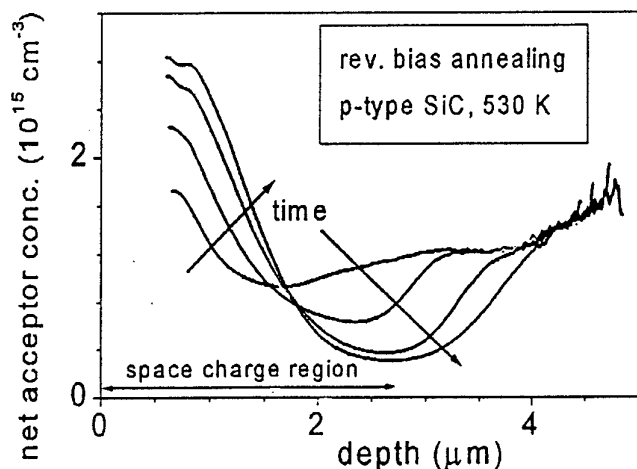
M. K. Linnarsson, M. Janson, B. G. Svensson

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In contrast to several other semiconductors, the present knowledge about hydrogen and its passivating effect in SiC is rather limited. This is partly due to difficulties to incorporate it intentionally by conventional means, e.g. plasma treatment. Incorporation during CVD growth is known [1]. In the present work, we are using ion implantation with unusually low energy to avoid, as far as possible, the hydrogen being trapped at its own implantation damage. Both the diffusion and the release of hydrogen from passivated acceptors are observed at unexpectedly low temperatures for the first time.

Samples of epitaxial n- and p-type SiC (4H and 6H) were implanted with 600 eV ions from a deuterium plasma, mainly consisting of $^2\text{H}_2^+$. The electrically active dopants (B and Al in p-type, N in n-type) were characterized by CV profiling and admittance spectroscopy on Schottky diodes. The atomic profile of ^2H was measured by SIMS.

In p-type SiC, hydrogen diffusion on a micrometer scale occurs in the whole temperature range investigated (300...680 K). An acceptor passivation up to 90 % is detected and the atomic ^2H profile and the profiles of passivated acceptors are overlapping well [2]. In n-type SiC, the amount of incorporated ^2H is much smaller and no donor passivation is detectable by CV profiling.



Low energy implantation is a rather efficient tool to incorporate hydrogen. Compared to high-energy implantation [3], hydrogen is mobile at unexpectedly low temperatures. Check experiments with a higher implantation energy (6 keV) reveal a reduced fraction of hydrogen diffusing on a micrometer scale and, consequently, no acceptor passivation is detectable in the temperature range used.

The stability of the acceptor passivation is studied by annealing under reverse bias conditions in a Schottky diode. Already at 530 K, an increase of the active acceptor concentration in the

space charge region and a reduction at greater depth is clearly visible in the CV depth profiles (Fig). This finding is well described by the drift of a positively charged passivating species (interpreted to be H^+) in an electric field. Subsequent annealing without electric field restores the initial, spatially homogenous passivation. The relative contribution of the acceptors boron and aluminum to the observed effects is discussed.

References:

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ELECTRONIC STRUCTURE AND STABILITY OF Be IMPURITY IN CUBIC BORON NITRIDE

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Since the first preparation of the zinc-blende boron nitride (c-BN) from the BN hexagonal phase in 1957; this material has been synthesized as small single crystals, polycrystals and thin films. Like diamond, c-BN is a wide gap material ($> 6\text{eV}$) with interesting mechanical, thermal, electronic and optical properties. However, c-BN is more promising for electronic and optoelectronic applications because, unlike diamond, it can be doped both p and n-type. As it has already been demonstrated with a p-n junction diode made from single crystals, c-BN will play an important role in the high-temperature electronic device technology. Owing to its interesting properties, suitable for several applications, c-BN has attracted increased interest under both, theoretical and experimental points of view. Regarding theory, however, only recently attempts have been undertaken to address the shallow or deep impurity level problems in this material in a more systematic way.

In this paper the full-potential linear-augmented-plane-wave (LAPW) method within the local density (LDA) and large unit cell approximations is used to perform self-consistent electronic structure calculations of substitutional and interstitial Be impurity in c-BN. The aim of the work is to use the calculations to explain experimental results which have been ascribed to this impurity in c-BN single crystals and polycrystals. It is well known that the addition of small amounts (0.01 to 1 percent by weight) of Be as metal or salt to the single crystal growth mixture induces p-type carriers in the material with activation energy for conduction ranging from 0.19 to 0.23 eV. Recently Be-doped c-BN polycrystals have been found to be p-type semiconductors with activation energy depending on the Be concentrations.

Our results show that Be replacing B at the c-BN lattice induces a shallow acceptor level in the band gap, placed at about 0.1 eV above the top of the valence band. This finding associated to the fact that Be at the B site has very low formation energy allow us to conclude that this impurity is a natural p-type dopant in c-BN. We found that Be at the N site leads to deep levels in the crystal band gap as does the impurity at the tetrahedral interstitial sites. The formation energies of these centers are much higher than that of the Be impurity replacing B, thus they occur in much lower concentrations in the c-BN crystals.

SESSION D

Wide-gap II - SiC

Chairman: M. Suezawa

TUESDAY JULY 28th

16.00-17.00

- D1: INVITED S. Bergman, E. Janzén, W.J. Choyke
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- D2: INVITED S. Greulich-Weber
The microscopic and electronic structure of shallow donors in
silicon carbide..... 22

**Multiple bound excitons associated with shallow donors in
different polytypes of silicon carbide**

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The low temperature photoluminescence (PL) spectrum from most semiconductor materials are usually dominated by recombination of excitons bound at different defects. This means that an electron-hole pair is bound to an usually neutral defect, which form an excited state of the crystal. In the case of a bound exciton to a neutral donor the excited state consist of three particles, two electron and one hole. During recombination one of the electrons recombine with the hole, leaving one electron at the donor in the final state. In some cases more than one electron-hole pair can bind to the defect. This is called a multiple bound exciton complex (MBEC) and is usually described within the so called shell model (SM) [1]. The complex consists, in the case of donors, of m holes and $(m+1)$ electrons. During recombination one electron recombines with one hole, leaving the complex with n holes and $n+1$ ($n=m-1$) electrons in the final state. MBEC has previously been observed in Si [see e.g. 2-3], CdSe [4] and in 3C SiC [5-6]. We have recently studied the MBEC bound to the nitrogen donor, in specially the 3C SiC polytype, using time resolved optical spectroscopy. The pulsed excitation enhances the MBEC emission and gives additional information about the recombination, as compared to previous PL and magneto optical measurements.

With the pulsed excitation we observe the recombinations of up to five ($m=5$) MBEC with both no-phonon and phonon assisted emission. The decay time of each MBEC recombination have successively shorter decay times of 160 ns, 64 ns, 42 ns, 35 ns, and 19 ns, with increasing number of excitons ($m=1,2,3,4,5$). The decrease of the decay time is expected to be due to the larger and more unstable complex formed with increasing the number of excitons. The decay of each MBEC level can be simulated with a set of coupled non-linear rate equations, which includes both recombination and generation from higher level MBEC. We have also observed a large number of additional emission lines, during the pulsed excitation, with a much faster decay. These can be explained as recombinations from excited states of the MBEC, as described based on the proposed electronic structure for the MBEC in 3C SiC [6].

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THE MICROSCOPIC AND ELECTRONIC STRUCTURE OF SHALLOW DONORS IN SILICON CARBIDE

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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 15R-, 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 donors in 6H- and 4H-SiC have an unexpectedly small isotropic hf interaction constant and a significant anisotropic hf interaction constant. Moreover, the hf interaction of the cubic site donor in 3C-SiC shows a 10 times smaller hf interaction than the quasi-cubic site donors in 4H- and 6H-SiC.

In this work we present ^{14}N hyperfine (hf) interactions and ^{29}Si and ^{13}C superhyperfine (shf) interactions observed with ENDOR for the polytypes 3C-, 4H- and 6H-SiC. 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 [4]. It turned out that the central-cell correction is not as simple as in Si where it is mainly due to the chemical nature of the donor, but that the valley-orbit interaction plays a major role. Taking this into account the assumption of the central-cell corrections in Si and SiC is re-visited. However, a theory explaining all the new experimental results is not yet available. There remains a challenge for further theoretical work.

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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SESSION E

Hydrogen passivation and related topics, thermal donors

Chairman: C.A.J. Ammerlaan

WEDNESDAY JULY 29th

8.15-10.30

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- E3 J. Hamann, L. Worschech, D. Blaß, C.Y. Hu, T. Filz,
 W. Ossau, V. Ostheimer, C. Schmitz, H. Wolf, Th. Wichert
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- E5 D. Aberg, T. Hallberg, B.G. Svensson, J.L. Lindström
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- E6 D. Karg, A. Voigt, G. Pensl, M. Schulz, H.P. Strunk, W.
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- E7 R. Dirksen, T. Gregorkiewicz, C.A.J. Ammerlaan
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ACCEPTOR NEUTRALISATION BY HYDROGEN IN GaN AND WIDE BAND GAP II-VI MATERIALS

B. Clerjaud

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One of the major problems encountered for the elaboration of blue light emitting devices processed with either nitrides or II-VI compounds is the difficulty for p-type doping of the materials. It will be shown that the unintentional introduction of hydrogen, issued for instance from the organo metallic precursors, during the process is responsible for at least part of the problem.

One of the best experimental techniques for investigating hydrogen in solids is local vibrational spectroscopy. The results obtained will be reviewed ; they show unambiguously that hydrogen forms complexes with the acceptors and neutralises them. The microscopic structure of the complexes will be discussed.

The processes which allow to reactivate the neutralised acceptors will be discussed ; their limitations will be outlined.

OPTICAL ABSORPTION STUDY OF THE INTERACTION BETWEEN GROUP II ACCEPTORS AND HYDROGEN IN Si

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Many studies have been shown on the interaction between group III acceptors and hydrogen (H) in Si by the measurement of electrical resistivity (H-passivation) and optical absorption spectrum (the vibration of H bound to them). However, there seems no paper on the interaction of group II acceptors and H in Si studied by means of optical absorption technique. The aim of our research is to study H-passivation of group II acceptors and to investigate vibrational state of H bound to those acceptors by means of optical absorption technique.

Zn was doped with the vapour method. Namely, specimens were sealed in evacuated quartz capsules together with a piece of Zn foil. They were annealed at 1200°C for 20 to 72 hours followed by quenching in water. Then H and/or deuterium (D) were doped in specimens by annealing them in H₂ and/or D₂ atmosphere followed by quenching. Be was doped with the dipping method. In this method, we first dipped specimens in an aqueous solution contained Be. Heat-treatment for doping of Be and H (and/or D) were the same to the above cases. We measured optical absorption spectra of above specimens with FT-IR equipment at about 6K with a resolution of 0.25 cm⁻¹.

In Zn doped Si, we observed two kinds of optical absorption, namely, electronic and vibrational origins. Three optical absorption lines were observed when only Zn was doped. They are due to electronic transition of acceptor Zn and agree well with those reported by Doernen et al.[1]. Their intensities are much decreased due to H doping. It clearly shows that hydrogen passivates Zn.

As the vibrational origin, we observed 3 absorption lines at about 2130, 2171 and 2173 cm⁻¹ in Zn-doped Si. Above three lines are due to vibration of hydrogen bound to Zn. This conclusion is based on the isotope effect on the optical absorption peaks. When we doped ⁶⁴Zn and ⁶⁸Zn, peak positions depended on the isotopes; namely, the difference of peak positions was about 0.9 cm⁻¹ for the above three lines. When we co-doped H and D in Zn-doped Si, the 2130 cm⁻¹ peak split into three peaks, namely, 2142.5, 2130.4 and 1608 cm⁻¹ peaks. The last one was also observed when D was doped in Zn-doped Si. This clearly indicates that two hydrogen atoms are bound to Zn. Namely, three peaks correspond to complexes of Zn-2H, Zn-H,D and Zn-2D.

The intensity of the 2130 cm⁻¹ peak is stronger than those of the 2171 and 2173 cm⁻¹ peaks. The line shape and absorption intensity of the 2171 and 2173 cm⁻¹ peaks were similar. Hence we think that these two peaks are due to the same complex. Zn in Si is known to diffuse with the kick-out mechanism. We therefore think that the 2130 cm⁻¹ peak is due to a complex of substitutional Zn and two hydrogen atoms, and the 2171 and 2173 cm⁻¹ peaks are due to a complex of interstitial Zn and two hydrogen atoms. The latter probably has low symmetry and has two peaks due to removal of degeneracy.

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MICROSCOPIC STRUCTURE OF HYDROGEN-RELATED DEFECTS IN CdTe

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The passivation of both donors and acceptors by pairing with hydrogen has been proposed as a mechanism that limits the carrier concentrations in II-VI semiconductors. In case of CdTe, several publications report a reduced carrier concentration after hydrogen doping for both p-type and n-type material. Using Local Vibrational Mode spectroscopy, the formation of close pairs, however, has only been confirmed for As-H and possibly N-H pairs.

Hydrogen-related photoluminescence (PL) lines are observed in nominally undoped, Bridgman-grown CdTe crystals. After treatment in a hydrogen plasma, the PL spectrum of the crystals differs from the spectrum of non-hydrogenated crystals by seven new lines in the excitonic region. The same seven lines are observed after implantation of 200 eV H⁺-ions at a sample temperature of 90 °C. Since the new lines appear after both doping in a hydrogen plasma and after H⁺ implantation, the lines are assigned to the presence of hydrogen in CdTe [1].

In order to obtain more information about the microscopic structure of the defects causing these lines, the dependence of the lines on the presence of high magnetic fields was investigated. The observed Zeeman splittings are explained in terms of group theoretical considerations. Analysing the Zeeman splittings of the lines as a function of the applied magnetic field, the g-factors of the electrons and holes were determined. The diamagnetic shifts of the centers of gravity of the split lines show that the associated defects are predominantly attractive to holes and point to an association with bound-exciton states. The symmetry of the defects was determined by Zeeman measurements for different crystal orientations. The anisotropy of the Zeeman splittings reveals a strong coupling to the axes of the non-isotropic defects. In addition, an influence of local strain is observed.

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SHALLOW THERMAL DONORS IN SILICON: THE ROLES OF Al, H, N AND POINT DEFECTS.

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Heat treatment of Czochralski silicon at temperatures below about 500° C leads to the formation of a series of double thermal donors (TDs) that are usually associated with aggregates of up to some 15 grown-in oxygen atoms. Series of single shallow thermal donors (STDs), with lower concentrations, also form and give rise to electronic transitions in the spectral range 200-300 cm⁻¹ that can be detected either by photo-thermal ionization spectroscopy (PITS) or by direct infrared (IR) absorption.

Recent high resolution IR measurements have distinguished at least three series of centres incorporating aluminium, hydrogen or some other unidentified impurity, commonly assumed to be nitrogen. The presence of Al and H (or D) leads to the observation of ENDOR transitions, while H atoms can be detected indirectly in IR spectra since the substitution of H by D gives rise to small shifts (0.1 cm⁻¹) in the energies of the electronic transitions. The shifts are due to the changes in the zero point energy and/or anharmonicity. However, N is not detected by ENDOR and other structures involving the incorporation of a lattice defect have been proposed to account for the third IR electronic spectrum. There has been confusion in the published literature concerning the identity of measured spectra since the small differences for the three types of centre were not known.

The stability of the STDs will be discussed with respect to increases in the anneal temperature. STD(H) is stable up to T > 500°C, although Si-H bonds are expected to dissociate at a lower temperature. It is therefore difficult to identify STDs with hydrogen-passivated TD centres, but this interpretation has been proposed to explain published DLTS measurements for the bistable TD1 and TD2 centres.

It is important to note that additional types of STDs are observed in irradiated silicon after a subsequent anneal, especially if hydrogen impurities are present.

These various measurements will be reviewed to determine the current state of knowledge concerning the atomic structure of the STDs. It is clear that an overall understanding has still not been achieved. Even after more than 40 years of study, this is also the case for the TD defects.

FORMATION OF ULTRA SHALLOW DONORS IN SILICON BY ANNEALING IN NITROGEN AT 470 °C

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Czochralski-grown phosphorus doped ($\sim 2 \cdot 10^{14} \text{ cm}^{-3}$) silicon wafers 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 in nitrogen, argon and vacuum ambients at 470 °C for times up to 500h. Sample characterization was made with capacitance-voltage, four point probe, deep level transient spectroscopy, thermally stimulated capacitance, admittance spectroscopy, and fourier transform infra-red spectroscopy. Secondary ion-mass spectrometry measurements are performed to determine nitrogen concentration versus depth profiles in the samples. Annealings in this temperature range for a few hours are known to produce shallow thermal donors[1]. It has previously been shown that after prolonged annealing of $\gtrsim 50\text{h}$ in nitrogen at 470 °C ultra shallow thermal donors (USTD's) are formed[2]. These have an energy position of $\sim 25 \text{ meV}$ below the conduction band. The present study shows that the net concentration of thermally formed donors is independent on annealing ambient within the experimental accuracy, and the concentration is seen to continually increase up until 100h at which values of $\sim 10^{16} \text{ cm}^{-3}$ are measured. Following this, a concentration decrease is noted, but with a slower rate for the nitrogen ambient than for the others. The majority of donors are shown to be due to the shallow single donors STD's and USTD's for long time anneals. Further, in this study it is also shown that nitrogen annealing ambient is indispensable for forming USTD's, and under vacuum and argon ambient the same concentrations of single donors are produced but of STD character. The samples were examined both near the surface and at depths of $15\mu\text{m}$, showing that the net donor production is not a surface effect but that the USTD formation depends on the sample depth.

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ANNIHILATION STUDIES OF OXYGEN-RELATED NEW DONORS IN CZ-SI

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New Donors (ND's) are generated in oxygen rich Czochralski-grown silicon (Cz-Si) during heat treatments at temperatures in the range of $550^{\circ}\text{C} \leq T \leq 850^{\circ}\text{C}$. The concentration of ND's can be increased by preannealing at $T=350^{\circ}\text{C}$ to $T=550^{\circ}\text{C}$ and by a high concentration of substitutional carbon. The energy levels of ND's ($20\text{meV} \leq E_C - E_T \leq 550\text{meV}$), determined in the upper half of the band gap, are continuously distributed. The distribution of ND states is explained in the framework of the 'SiO_x-Interface Model' [1]. According to Fukuoka [2], the formation energy of ND's in Cz-Si is equal to 1.7eV. However, no data are available in the literature about the annihilation of ND's. It is, therefore, the aim of this paper to study the annihilation behavior of ND's in Cz-Si.

Two different sets of samples (A, B) with slightly differing interstitial oxygen concentration (set A: $[\text{O}_i]=1.0 \times 10^{18}\text{cm}^{-3}$, set B: $[\text{O}_i]=1.3 \times 10^{18}\text{cm}^{-3}$) used in this investigation have been supplied by Wacker Siltronic. Set A samples (thickness=2.0mm) are unintentionally doped and set B samples (thickness=0.5mm) are phosphorus-doped ($[\text{P}]=8 \times 10^{14}\text{cm}^{-3}$). The concentration of substitutional carbon is approx. $5 \times 10^{15}\text{cm}^{-3}$ in both sets of Si samples. In order to form a high concentration of ND's in samples (A, B), we conducted successive heat treatments at $T=500^{\circ}\text{C}/t=100\text{h}$, $T=650^{\circ}\text{C}/t=100\text{h}$ and $T=800^{\circ}\text{C}/t=16\text{h}$ in a standard furnace. Hall effect, Deep Level Transient Spectroscopy (DLTS), Transmission Electron Microscopy (TEM), IR spectroscopy, four-point method and C-V measurements have been used to characterize the annealed samples. In both sets of samples (A, B), the generated concentration of ND's is approx. $1.5 \times 10^{15}\text{cm}^{-3}$; the ND energy levels are continuously distributed ($20\text{meV} \leq E_C - E_T \leq 550\text{meV}$) and the concentration of interstitial oxygen is reduced to approx. $1.5 \times 10^{17}\text{cm}^{-3}$.

For the annihilation studies of ND's, pairs of samples (A, B) are exposed to various heat treatments in the temperature range from $T=875^{\circ}\text{C}$ to $T=1100^{\circ}\text{C}$ in a Rapid Isothermal Annealing (RIA) system. The dependence of ND concentration, interstitial oxygen concentration and energy distribution of ND's is observed for stepwise isothermal annealing from $t=2\text{s}$ up to $t=10000\text{s}$. The main results are summarized in the following:

- The thermal activation energy for annihilation of energetically shallow ND's ($E_C - E_T \leq 100\text{meV}$) is equal to $(2.9 \pm 0.1)\text{eV}$ assuming first order kinetics.
- Energetically shallow ND's ($E_C - E_T \leq 100\text{meV}$) can be annihilated faster than energetically deep ND's ($E_C - E_T \geq 100\text{meV}$).
- Energetically deep ND's ($E_C - E_T \geq 100\text{meV}$) cannot completely be annihilated by heat treatments ranging from $T=875^{\circ}\text{C}$ to $T=1100^{\circ}\text{C}$. The concentration of residual energetically deep ND's decreases with increasing annealing temperature.
- The concentration of interstitial oxygen simultaneously increases with decreasing ND concentration and reaches an equilibrium concentration depending on the annealing temperature.

The activation energy of oxygen diffusion in the temperature range $T=550^{\circ}\text{C}$ to $T=1250^{\circ}\text{C}$ has been determined by several authors (e.g. [3]) to $(2.5 \pm 0.1)\text{eV}$. The value is close to the value determined for the annihilation process of ND's in this work. Consequently, it is difficult to meet a decision whether the thermal dissociation of oxygen clusters or the oxygen diffusion is the limiting process for the annihilation. The different mechanisms, which are involved in the annihilation process, are discussed.

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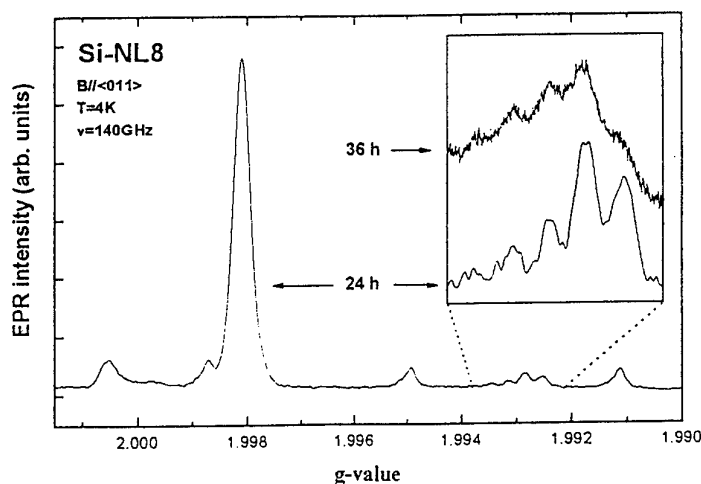
INDIVIDUAL THERMAL DONOR SPECIES STUDIED WITH HIGH-FREQUENCY MAGNETIC RESONANCE SPECTROSCOPY

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Thermal annealing of oxygen-rich silicon is known to generate shallow centers of double-donor character known as thermal donors (TDs). These are generally identified as oxygen aggregates whose ionization energies are determined by the size of a cluster which, in turn, is a function of the heat-treatment time ($T \approx 450^\circ\text{C}$). The microscopic structure of TDs is therefore usually assumed to comprise an electrically active core decorated with (peripheral) oxygen atoms whose number gradually increases for longer annealing. Following such a model TDs form a family of very similar yet structurally different impurity aggregates. In view of the similarity of the individual TD species extreme experimental resolution is required for their separation.

In the past individual TD species have been resolved by infrared absorption and electron-nuclear double resonance techniques. Also a small number of (the most abundant) species have been identified by a variation of deep level transient spectroscopy. The results obtained from these experiments proved, however, insufficient to establish the microscopic model of TD core or to unambiguously identify the TD growth/transformation mechanism.

In the present study we apply high-frequency electron paramagnetic resonance spectroscopy (EPR) to identify individual TD species generated by 450°C annealing of Czochralski-grown boron-doped silicon. TDs are observed in their singly ionized charge state TD^+ which is known to give rise to an EPR spectrum of an overall orthorhombic-I symmetry, known as Si-NL8. In contrast to the standard (low frequency) EPR in the current experiment conducted at a frequency of approximately 140 GHz (D-band) individual TD species could be resolved. This is illustrated in the figure where the EPR spectra obtained with the magnetic field along the $\langle 011 \rangle$ crystallographic direction for two differently annealed samples are compared. A different "composition" of the total TD family can be concluded indicating different generation kinetics of individual TD species. In the contribution also the symmetry of various TD species is discussed elucidating the thermal donor transformation mechanism.



High-frequency EPR spectrum of the Si-NL8 center recorded for magnetic field parallel to $\langle 011 \rangle$. In the inserted graph an enlargement of the resolved individual species is shown. In the longer treated sample (upper trace) the most anisotropic species is almost annealed out.

SESSION F

Low-D systems I

Chairman: M. Grynberg

WEDNESDAY JULY 29th

11.00-12.30

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F3	I.D. Mikhailov, F.J. Betancur, J.H. Marin, <u>L.E. Oliveira</u> Model structure for D⁺ states in GaAs-(Ga,Al)As quantum wells.....	33
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SPECTROSCOPY OF NEUTRAL AND CHARGED DONORS IN SEMICONDUCTOR QUANTUM WELLS: MANY BODY EFFECTS

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The ability to produce and selectively dope confining structures in semiconductors has permitted detailed investigation of the effects of confinement and impurity placement on shallow neutral donor and acceptor states. Experimental (optical spectroscopy) and theoretical efforts over the past few years have focused on identification of stable negative donor ions (D^-) in quantum-well structures [1] and on understanding the various two-electron energy states in high magnetic fields. [2,3] Recent experiments, in which the electron densities in the wells are much larger than the donor density, in effect utilize the donor ions in the wells to probe many-electron states of the electrons in the wells, which generally cannot be studied by direct means (cyclotron resonance) due to translational invariance (Kohn's Theorem).

This talk will review work on isolated neutral and negatively charged donors in quantum wells, point out interesting similarities to neutral and negatively charged excitons, emphasizing some recent work on internal transitions of these excitons, and then concentrate on far infrared (FIR) magneto-optical studies of a series of GaAs/Al_{0.3}Ga_{0.7}As multiple-quantum-well samples with Si donors-doped both in the 200Å well-centers ($2 \times 10^{10} \text{ cm}^{-2}$) and in the 600Å barrier-centers ($3.5\text{-}28 \times 10^{10} \text{ cm}^{-2}$). These FIR experiments reveal interesting many-electron and localization effects.[4] With increasing excess electron densities in the wells the two-electron D^- -singlet and -triplet (T^-) transitions evolve continuously into blue-shifted many-electron singlet-like and triplet-like transitions, the collective excitations of the many-electron system in the presence of a positively charged impurity ion. Results for the blue shifts are in reasonable agreement with recent many-body calculations at integral filling factors (FFs).[5] Anomalies are also observed near fractional FFs 1/3, 2/5, 1/2 and 4/3. In addition, for all samples studied the blueshift of the many-electron singlet-like transition decreases with increasing magnetic field for $FF < 1$, approaching from above the transition energy of the two-electron D^- -singlet, even though there are as many as 16 electrons/donor.

Concomitantly, the many-electron triplet-like transition loses strength. These results can be understood in the context of a model which invokes weak long-range disorder potential fluctuation in the quantum-well plane. When the characteristic magnetic length, $(c/eB)^{1/2}$, becomes significantly smaller than the correlation length of the fluctuating potential, electrons tend to localize in the lowest potential minima of the fluctuating potential landscape; statistically, a significant number of these potential minima are located laterally close to a positive donor ion in the well. Detailed numerical calculations for a nine electron system confined by a weak parabolic potential with a positive charge at the center show that two electrons are always bound in a spin-singlet configuration near the positive charge, and the remaining electrons tend to move to larger (outer) orbits within the parabolic confining potential as they become available at higher magnetic fields. Physically, excess electrons in the potential minimum maintain the maximum possible separation from the positive charge to decrease the electron-electron repulsion and to minimize the total energy. Thus at high fields a positive charge binding two spin-singlet electrons becomes spatially isolated from the remaining electrons with increasing field for $FF < 1$, and the optical properties of the many-electron system approach those of a two-electron D^- -singlet configuration. For a closely related system, a dense 2DEG in the presence of photoexcited holes, localization effects have also been invoked to explain observation of optical signatures of negatively charged and neutral excitons at $FF < 1$. [6].

* Work supported in part by ONR (N00014-97-10858) and NSF (DMR-9722625)

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ANGULAR MOMENTUM TRANSITIONS AND MAGNETIC EVAPORATION IN OFF-CENTER D^- CENTERS IN A QUANTUM WELL

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A D^- center is a shallow donor with two electrons bound to it. We have investigated the effect of the position of the donor in the quantum well on the energy spectrum and the oscillator strength of the D^- system in the presence of a perpendicular magnetic field. The D^- center is investigated theoretically within the effective mass approximation. The Hamiltonian is solved numerically. This allows, in the quasi-2D approximation, and we obtain the spectra of the D^- system for different donor position and for different well width.

As a function of the magnetic field we find that, when the D^- center is placed sufficiently off-center, it undergoes spin-singlet $\leftrightarrow$ spin-triplet transitions which are similar to those found in many-electron parabolic quantum dots. We investigate the origin of those transitions. The main difference, with respect to quantum dots, is that the number of transitions depends on the position of the donor and only a finite number of such singlet-triplet transitions are found as function of the strength of the magnetic field. For sufficiently large magnetic fields the two electron system becomes unbound. For the near center D^- system no singlet-triplet transitions and no unbinding of the D^- is found with increasing magnetic field. The magnetic field vs. donor position phase diagram is presented in Fig. 1 for a well width of $100\text{\AA}$ where ζ is the distance of the donor measured from the center of the quantum well and $\gamma_c = 0.148 B (T)$, and $a_B = 98.7\text{\AA}$ is the effective Bohr radius of the D^0 in a $GaAs/Al_{0.25}Ga_{0.75}As$ quantum well.

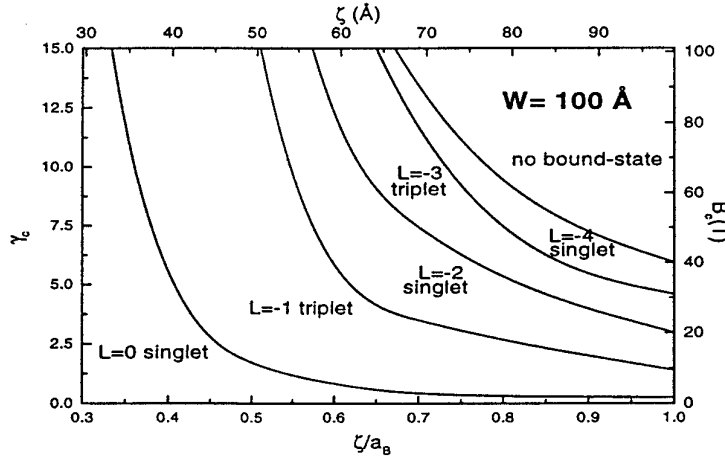


Figure 1: The spin-triplet spin-singlet phase diagram for a D^- in a $100\text{\AA}$ quantum well, for different values of L .

The oscillator strength for the off-center D^- was also calculated. Our results for the transition energies and the oscillator strength of a $200\text{\AA}$ quantum well are compared with the experimental data reported by Jiang *et al.* Phys. Rev. B 56, R1692 (1997) in the range $5 - 15 T$ and a good agreement was found.

MODEL STRUCTURE FOR D^- STATES IN GaAs-(Ga,Al)As QUANTUM WELLS

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A simple model in which both electrons of the D^- state are instantaneously localized approximately at the same distance with respect to the ion nucleus is considered. Within this model, the D^- Hamiltonian becomes separable, and the effect of the electron-electron interaction is essentially taken into account by the interaction of each of the electrons with a renormalized-nucleus effective charge which depends on the angle between the two electron vector positions. The trial function is taken as a product of two three-parameter one-particle wave functions in order to calculate the D^- ground-state energy as a function of the angle. Theoretical results for the D^- energy, including zero-point energy corrections within the harmonic approximation, are obtained for D^- centers centered in GaAs-(Ga,Al)As quantum wells as a function of the well width, and for different values of the magnetic field, applied perpendicular to the interfaces. Our results are in good agreement with the experimental data by Huant et al¹, the variational calculations by Szwacka et al² and the Quantum Monte Carlo values of Pang and Louie³.

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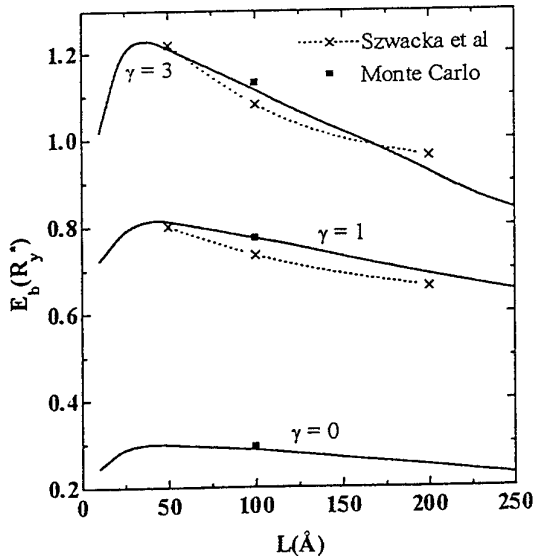


Figure 1. Ground-state binding energy for a negatively charged D^- centered in a GaAs-Ga_{0.75}Al_{0.25}As QW as a function of the well width L , and for different values of the magnetic field γ , calculated by using our model (solid curves) within a variational procedure, and including zero-point energy corrections. Also shown are the $\gamma = 1$ and $\gamma = 3$ variational results by Szwacka et al² (dotted curve is a guide to the eye), and Monte Carlo³ values for $L = 100$ Å.

MANY-BODY EFFECTS FOR BOUND STATES IN LOW-DIMENSIONAL ELECTRON GASES

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Abstract:

We study many-body effects of charged impurities in the low-dimensional electron gas. Many-body effects, introduced via the local-field correction[1-2], reduce the screening properties of the electron gas and increase the binding energy of Coulomb impurities.

In detail we describe many-body effects in the two-dimensional electron gas and in the quasi-one-dimensional electron gas. An oscillator potential is used for the confinement potential of one-dimensional systems. The effect of a valley degeneracy is discussed. Bound-states energies for the ground-state and for the Wigner-Seitz parameter between 1 and 10 are studied in detail and excited bound-states energies are also discussed.

Our results are relevant for bound-states of positively charged impurities but also for the binding energy of excitons. The screening is calculated for the test charge-electron interaction and we discuss the differences with the screening function for the test charge-test charge interaction [3]. We also present some results on bound states for negatively charged impurities.

References:

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OPTICAL PROPERTIES OF p-TYPE MODULATION DOPED GaAs/AlGaAs QUANTUM WELLS

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The collective behavior of charge carriers in semiconductors is an attractive topic both from applications and fundamental physics points of views. Due to the manifold applications of n-type modulation doped quantum structures, caused by their high electron mobility, in e.g. a High Electron Mobility Transistor (HEMT), the properties of the two dimensional electron gas (2DEG) in such structures have been thoroughly investigated. For the case of p-type modulation doped quantum structures, the corresponding level of knowledge is considerably lower. In particular, many-body effects, such as screening, the Fermi edge singularity (FES), exchange and correlation effects are considerably less studied for the p-type case.

In this work, the optical properties of modulation doped GaAs/AlGaAs quantum wells (QWs) have been investigated for a varying acceptor concentration in the barrier and are compared with a reference sample without doping. The samples studied have been grown by the Molecular Beam Epitaxy (MBE) technique. The stationary optical investigations have been performed by means of photoluminescence (PL) and PL excitation (PLE).

Several novel appearances in the spectra are observed as the hole concentration increases:

- The PL spectrum is dominated by an emission, which is interpreted as being due to the recombination between 2D holes from the bottom of the Fermi sea, i.e. with $k=0$ and free electrons. This predominant PL emission exhibits a significant red-shift, which is associated mainly with the bandgap renormalization (BGR) caused by many body effects. The observed BGR effect is compared with theoretical predictions of the effective bandgap shrinkage, based on self-consistent calculations with the Schrödinger and Poisson equations.

- The exciton quenching, preferably monitored in PLE, is investigated. The derived results are compared with exciton quenching in p-type bulk material as well as in QW structures with p-type doping in the center of the well. The acceptor doping level required to quench the excitons is found to be significantly lower than for the case with acceptor doping inside the well, but on the other hand, considerably higher than the one in the bulk case, due to the inefficiency of screening in a 2D system.

- One of the most interesting observations in this study is the appearance of a new feature on the high energy side of the predominant PL emission at higher hole concentrations. This feature is first observed as a weak shoulder of the predominant emission described above, but develops then into a separate peak with an increasing intensity and blue shifted with respect to the predominant PL peak, as the hole concentration increases. This new feature is interpreted as the FES, i.e. recombination between 2D holes at the Fermi edge (with $k=k_F$) and free electrons. The FES emission is well documented for the case of n-type modulation doped wells, but remains almost alien for p-type structures due to the complicated valence band structure involved. Additionally the dynamical behavior of the FES has been investigated by means of time-resolved PL. A relatively short decay time, as well as a short rise time has been measured for the FES emission. The observation of the FES also provides information on the sub-band filling in the QW, which works in the other direction compared to the BGR. Accordingly, the absorption (PLE) edge does not exhibit a similar red shift, as the acceptor concentration increases.

The results achieved on band filling as a function of doping level are compared with theoretical predictions. The simplest way to include many-body effects would be to add an exchange-correlation potential to the Hamiltonian in the self-consistent calculation. We have used another approach. The starting point for our many-body calculations is the self-consistent Hartree results with non-parabolicity caused by valence-band mixing. We make a quasi-2D calculation of the many-body self-energy shifts for the different states. In this approach, states at the Fermi-level, at the valence-band maximum and at the bottom of the conduction band are all shifted different amounts.

SESSION G

Shallow excited states of deep-level impurities and shallow-deep crossover

Chairman: W. Jantsch

WEDNESDAY JULY 29th

14.00-16.00

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THE ROLE OF SHALLOW BOUND STATES IN THE EXCITATION
AND DE-EXCITATION OF RARE-EARTH IONS IN SEMICONDUCTORS

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Key Words: energy transfer, RE-doping, photoluminescence, free-electron laser

Doping of semiconducting crystals with rare-earth (RE) ions offers a unique possibility of creating optical systems whose emission is characterized by sharp, atomic-like spectra with temperature independent, predictable wavelength. This is a consequence of the atomic character of the $4f$ -electron shell - the key configuration participating in the light emission. The screening of the $4f$ -shell by outer electrons imposes, however, the need of efficient energy transfer from the host-like (electron-hole pairs, hot electrons, etc.) excited states to the $4f$ -electronic configuration. A more than decade-long studies of RE ions in semiconductors showed that only the shallow bound states in a close vicinity (even on-site) of RE centers are capable of surpassing the isolation of the $4f$ -electrons. Characterization, and then control and optimization, of these states is of utmost importance if the efficient optoelectronic RE-based devices are to be developed.

From the practical point of view the Si:Er emerges as a system where the most advanced and successful silicon technology can be applied to manufacture optical elements whose emission coincides with the absorption minimum of silica fibers commonly used in telecommunications. However, the success the silicon photonics based on erbium doping is crucially dependent on the progress in increasing the efficiency of light generation. The same applies to other RE-doped systems, like Yb- and Er-doped III-V semiconductors. Although certain aspects of the energy transfer are common for all these systems, the indirect gap of Si and different valency than III-V semiconductors, in which RE ions may form isovalent bound states, makes the Si:Er system particularly challenging.

Based upon our recent extensive measurements of the excitation dynamics in Si:Er crystals we present a summary of the current understanding and characterization of the shallow levels (defects and bound excitons) and excitation/relaxation paths active in the process of Er emission. We will specially focus on the important role of the formation of donor level for the energy transfer mechanism. To this end we will report on recent investigation of the Er-bound exciton system as obtained by a double beam optical spectroscopy. In this experiment the Er PL, excited by a pulsed Nd:YAG laser, has been studied under influence of an intense infrared beam of variable wavelength generated by a free-electron laser. We shall also discuss Auger processes that may limit future application of Si:Er system. Our results and findings will be put in a broader context of the recent studies of Si:Er and III-V semiconductors doped with Er done by other groups. We will address also an outlook for the possible developments in the field of RE doping of semiconductors in the nearest future and give prospects of device applications.

NONLINEAR ZEEMAN-SPLITTING OF THE Si:Be_s⁻ ACCEPTOR GROUND STATE: INFLUENCE OF THE p_{1/2} SPLIT-OFF VALENCE BAND ?

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The ground state of group III acceptors in silicon is a Γ_8^+ quadruplet according to the fourfold degeneracy of the p_{3/2} valence band. Since the hole binding energy is of the same order as or even larger than the spin-orbit splitting of the valence band, a considerable mixing with the Γ_7^+ ground state of the p_{1/2} split-off valence band may be expected. In fact, the separation of the Γ_8^+ state from the Γ_7^+ state for Si:B is only 23 meV [1,2] and thus much smaller than the spin-orbit splitting of the valence band (44 meV). To our knowledge no data are available for deeper acceptors. The Γ_8^+/Γ_7^+ separation may there be even smaller corresponding to an increased interaction. An indication of such an increased interaction could be a small quadratic contribution to the Zeeman-splitting of group III acceptors that was found to increase with the depth of the acceptor species [3].

To continue this series to much deeper ground states we chose the singly ionized group II double acceptor Be_s⁻. The remaining hole of this centre is bound with approximately 440 meV as compared to 156 meV for Si:In, the deepest of the previously investigated acceptors [3]. Samples of FZ-silicon were doped with Be by diffusion at temperatures between 945°C and 1180°C. Some of them were predoped with P to partly compensate the Be double acceptor. The Zeeman-splitting of the ground state was then investigated by Electric-Dipole Spin Resonance (EDSR) at about 1.8 K in magnetic fields of up to 7 T and at frequencies near 24 GHz, 34 GHz, and 60 GHz. Additionally, FTIR measurements were performed to determine the defect content and the Fermi level position in our samples.

In appropriately compensated samples six EDSR lines are visible that can be attributed to transitions between the four sub-levels of the Γ_8^+ ground state of Be_s⁻. The whole spectrum is quite similar to that of group III acceptors, the angular dependence of the line strength and the thermalization of the lines being as expected for a Γ_8^+ state. In some of the uncompensated samples the lines appeared after strong illumination changing the charge state of Be_s⁰ to Be_s⁻. The Zeeman-splitting of the four levels in the range from about 0.7 T to about 4.3 T, where we observe transitions, is considerably nonlinear and only crudely described by a Hamiltonian containing terms up to second order in the magnetic field as used for group III acceptors [3]. We get $|g'_1| = 0.70 \pm 0.01$, no discernible anisotropy, i.e. $|g'_2| < 0.005$, and a strong quadratic coupling $|q_2+q_3| = (0.50 \pm 0.05)$ GHz/T². As an alternative approach we have taken into account the interaction with the Γ_7^+ state. In an isotropic approximation we can well describe the Zeeman-splitting if we assume a distance of only about 0.25 meV between the Γ_8^+ and Γ_7^+ levels.

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EPR IDENTIFICATION OF A SHALLOW DONOR STATE OF CADMIUM IN SILICON

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During the last years the electronic properties of the group II impurities Zn and Cd in Si have been extensively studied with Deep Level Transient Spectroscopy (DLTS) and Hall effect techniques. For both isolated dopants a substitutional site was concluded from the experiments for which one expects the singly and doubly charged acceptor levels to be positioned deep in the gap of silicon.

In recent DLTS investigations of Si doped with stable Cd and with radioactive ^{111}In transmuting into stable ^{111}Cd the two acceptor levels could be confirmed as well as two levels of Cd-induced centers and in addition a level tentatively ascribed to be due to a Fe-Cd pair /1/. The time dependence of the concentration of the radioactive impurities proved the chemical nature of the defect as well as the number of radioactive atoms incorporated into a given center. Some Cd-induced centers have been measured by means of Perturbed Angular Correlation (PAC) using the radioactive standard probe atom ^{111}In as well /2/. As none of the above methods gives direct information about the microscopic structure of the centers, there is still no generally accepted model. Electron Paramagnetic Resonance (EPR) can provide this information and at least in the Cd^+ and Cd^0 charge states the centers should be paramagnetic.

For first EPR investigations of Cd-doped silicon, we used Cd-diffused and Cd-implanted samples, originally prepared for DLTS-measurements. After partly passivation of the background B doping in these samples a center called Cd(1) was identified, which shows the typical cubic angular dependence of the fine structure and hyperfine structure splittings of a Γ_8 state /3/. The spectra are described using a spin-Hamiltonian including the linear and cubic Zeeman- and hyperfine-interactions with the fitted parameter set

$$\begin{array}{lll} |g| = 1.9462 \pm 0.0005 & |f| = 0.0024 \pm 0.0005 & \text{with } g \cdot f > 0, \\ |A| = (21.6 \pm 0.2) \cdot 10^{-4} \text{cm}^{-1} & |F| = (2.42 \pm 0.02) \cdot 10^{-4} \text{cm}^{-1} & \text{with } A \cdot F < 0. \end{array}$$

The first tentative interpretation of these spectra as due to a Cd^+ charge state with $J = 3/2$ in agreement with the DLTS data was not quite satisfactory in view of the magnitude of the g-factors g and f as well as the hyperfine constants A and F. In order to explore the nature of Cd(1) we have performed high-energy implantations of stable Cd into Si samples with different background B doping levels, followed by a high-temperature anneal at 1200°C. We do not find the Cd(1) spectra except for samples with a B level of more than $6 \cdot 10^{13} \text{cm}^{-3}$. These spectra were perfectly identical to the Cd(1) spectra observed previously. We therefore conclude that the Cd(1) spectra arise from the isolated Cd^+ donor state with an $S=3/2$ orbital singlet ground state. This defect should have a shallow level above the valence band.

These experimental findings are corroborated by electronic structure calculations based on the Local Density Approximation of the Density Functional Theory using the LMTO-ASA scheme. For the tetrahedral interstitial Cd there is one paramagnetic state, a $^2A_1$ state of Cd^+ with a contact hyperfine interaction of some 3 GHz and $S = 1/2$, in contrast to the experimental data observed for Cd(1). The gap state of isolated substitutional Cd transform according to t_2 and is fully occupied for Cd^{2+} . In the singly negative charge state we obtain a $(t_2)^5$ orbital triplet state which would not be in agreement with the observed g-factor. The positive charge state, Cd^+ , is a $S=3/2$ orbital singlet state in the absence of a Jahn-Teller distortion with a donor level just above the valence band edge. This electronic state does not show an isotropic hyperfine interaction other than by a core polarization effect (which is known for d-like magnetic moments only). The calculated value is an order of magnitude smaller than the value observed experimentally.

Although the t_2 -like gap state found for Cd^+ is in general agreement with the vacancy model applied to transition metal impurities at the end of the 4dⁿ (5dⁿ) period /4/, the high-spin orbital singlet ground state for Cd^+ is a surprise, in particular as the gap state of Cd^+ is even more vacancy-like than the Au^0 and Pd^+ gap states.

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A SHALLOW STATE COEXISTING WITH THE DX CENTER IN Te-DOPED AlGaSb

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The Te impurity is known to exhibit a DX-center behavior in AlGaSb (1,2). The metastable DX state coexists, however, with non-metastable shallow states of the same impurity as it was demonstrated in the more widely investigated AlGaAs alloy (3).

In this work the energy relationship between the DX level, the E_c conduction band edge and a non metastable D level of the Te impurity is investigated in $Al_xGa_{1-x}Sb$ through an extensive analysis of Hall density and mobility data. The experiments were performed in MBE samples in a wide range of temperature (10-300 K), alloy composition (from $x=0$ to $x=0.5$) and Te-doping (10^{16} - 10^{18} cm $^{-3}$).

The main conclusions can be summarized as follows.

(i)- For $x \geq 0.25$ the DX level is in the forbidden energy gap and the D level is revealed at low temperature when the electron capture rate of the DX center is vanishingly small. Under this condition the D state is related to a semiconductor-to-metal transition which can be easily induced by rising the free electron density up to the critical value of $\approx 1 \times 10^{17}$ cm $^{-3}$ through the well known effect of persistent photoconductivity.

(ii)- For $x \leq 0.10$ both the DX level and the non metastable D state are degenerate in energy with the conduction band. This is demonstrated by the absence of carrier freezing even at low doping densities.

(iii)- At $x=0.20$ the DX level is within the conduction band and the D level is in the forbidden gap. In this peculiar case and only for lightly doped samples (a few 10^{16} cm $^{-3}$) a strong freezing of carriers at the D state has been observed. The analysis shows that the D level is ≈ 14 meV below the E_c absolute conduction band edge.

(iv)- The above observations, together with inspection of the x -dependence of the Γ , L and X conduction band minima, indicate that the D state is linked to the L-valley. Inspection of mobility data suggest that the Γ -minimum is lower in energy than the L-minima at $x=0.20$: thus the electron binding energy at the D state is higher than the above quoted value in that sample.

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THE UNIVERSAL BEHAVIOUR OF SHALLOW-DEEP LEVEL INSTABILITIES IN SEMICONDUCTORS

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There is a wide class of donors with a tendency for metastability in various III-V and II-VI compounds. Here we present a universal approach that allows to describe the rich variety of phenomena related to shallow-deep donor instabilities in terms of a few parameters.

In order to account for the extraordinarily complex behaviour of presumptive shallow donor dopants, two deep states are considered in addition to the ionized D^+ - and the shallow effective mass (Γ , X, L- type) D_s^0 - state, and the very shallow D_s^- state. These localized states are: i) the two electron bonding, metastable DX^- state, stabilized upon broken bond C_{3v} symmetry, and ii) the one electron bonding A_1 state, which does not exhibit sizable effects related to the lattice relaxation.

We present a new universal configuration coordinate diagram (CCD) including the DX^- state, the neutral A_1 state and shallow states. This CCD describes two different orthogonal lattice relaxation modes: (i) along one of the $\langle 111 \rangle$ directions of the crystal for DX^- state and (ii) a breathing mode of T_d symmetry for A_1 - leading to an extremely small capture cross section of the A_1 state. We show that this approach allows to describe all known situations in III-V and II-VI compounds and to explain metastabilities, capture kinetics, and their pressure and temperature dependencies.

The germanium donor in GaAs and AlGaAs is chosen as an outstanding example where the behaviour of a complex system can be studied. Application of hydrostatic pressure to GaAs:Ge and AlGaAs:Ge changes the position of the DX^- state relative to the A_1 state, its capture barrier. Pressure is thus an unique tool to investigate *e.g.*, a) the coexistence of the two localized states of the donor, the DX^- and A_1 states, b) the anticrossing of the shallow and the deep A_1 level, c) the metal-insulation transition, d) the change in character of the capture barrier of the DX^- state. The Ge may thus be considered as a model donor for the rich variety of effects resulting from DX^- behaviour.

We present a critical survey through different theoretical models describing electron-phonon interaction and we compare results with accessible experimental data for other donor dopants III-V.

Finally, we discuss also our recent experimental results of instabilities of Si donor in AlGaIn.

ROLE OF EXCITED STATES IN THE METASTABILITY OF DONORS IN III-V ALLOYS.

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Depending on the relative energies of the conduction bands, variable with the alloy composition, there are cases where the shallow effective mass states (d) linked to a band higher in energy than the lowest conduction band can be deeper than that associated with the lowest band. This can occur for instance when the L band is above the Γ band because intervalley mixing induces a deepening of the associated effective mass state d_L . The energy of the d_L state is lower than that of the d_Γ one when the energy difference Δ between the L and Γ bands is smaller than $e_L - e_\Gamma$ where $e_{L,\Gamma}$ are the energies of the $d_{L,\Gamma}$ in states below their respective bands.

This situation is characterized by an apparent metastability of the excited impurity configuration for the following reason. Free electrons can be captured either directly, i.e. from the Γ band or indirectly *via* the L band. At relatively high temperature, direct capture cannot occur by a cascade (Lax) process because the excited states linked to the Γ band, too shallow, cannot be filled. Hence the capture takes place using a multiphonon emission process characterized by a capture cross section exponentially activated: $\sigma_p = \sigma_0 \exp(-B/kT)$. Indirect capture is characterized by a giant cross section σ_L since it occurs *via* a cascade process, the L excited states being deeper than the Γ ones, and the apparent cross section is $\sigma_L \exp(-\Delta/kT)$. Both types of process being thermally activated, ionized electrons remain metastable in the conduction band at low temperature. We shall demonstrate that this explanation allows to understand the existence of a metastability for various donor defects and impurities in III-V alloys. Several tests, including the correspondence between the band structure and the activation energies associated with capture and emission, will be described, thus demonstrating the validity of the proposed explanation.

ELECTRONIC PROPERTIES OF Zn IN $\text{Si}_{1-X}\text{Ge}_X$ ALLOYS: THE CHANGE-OVER FROM HIGHLY LOCALIZED DEEP STATES TO SHALLOW-LEVEL CENTERS

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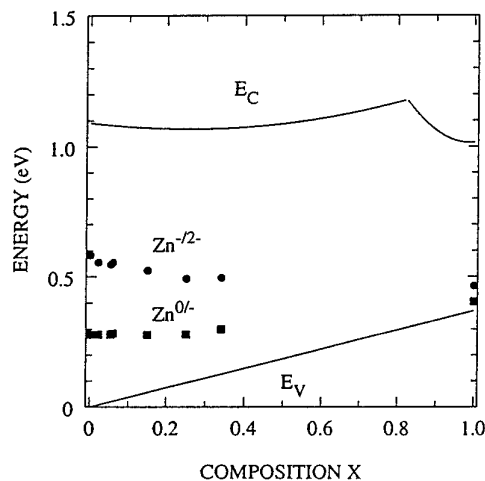
The potential application of SiGe for electronic and opto-electronic devices inspired us to investigate electronic properties of impurities incorporated in this material system. On one hand, knowledge of these impurity properties is basic to control device performance, while on the other hand, it may give new insights into the nature of defects in both Si and Ge. In this case we will focus on the electronic properties of Zn in $\text{Si}_{1-X}\text{Ge}_X$ with varying X .

Numerous studies on Zn in Si revealed the existence of two deep acceptor states. The associated energy levels obtained by different methods and authors scatter around the mean values of $E_V+0.3\text{ eV}$ and $E_V+0.6\text{ eV}$. It is generally accepted that these deep levels are associated with isolated Zn atoms incorporated on substitutional sites. In contrast to Si, substitutional Zn in Ge introduces two shallow acceptor states with energy levels of 0.035 eV and 0.095 eV above the valence-band edge.

We performed deep level transient spectroscopy (DLTS) measurements on Zn-doped $\text{Si}_{1-X}\text{Ge}_X$ with X between 0 and 34 at%. In the present study increasing deviations from exponential transient behavior were observed for increasing Ge concentrations. Such behavior is explained by the fact that in the SiGe alloys the Si and Ge atoms are statistically distributed. Random incorporation of Zn on substitutional sites leads to different surroundings of the Zn atoms. In general, carrier emission processes depend on the local environment of the emitting defect state.

Specifically, emission of holes by substitutional Zn is much faster in Ge than in Si. For these reasons we are dealing in a random SiGe:Zn alloy with a superposition of emission processes of different rate. To account for the statistical variation in the local environment of the Zn atoms a gaussian distribution of the ionization enthalpy around a mean value ΔH_0 is assumed. Within this model measured transients and spectra can be excellently fitted.

Our investigations reveal two deep hole traps which are attributed to the acceptor states $\text{Zn}^{0/-}$ and $\text{Zn}^{-/2-}$ of substitutional Zn. Taking into account band-offset data for $\text{Si}_{1-X}\text{Ge}_X$, we have found that the energy level related to $\text{Zn}^{0/-}$ is horizontally aligned across the composition-dependent bandgap (see figure) which gives evidence for a highly localized defect state. The defect level related to the second hole trap decreases with increasing Ge content. This finding is attributed to an electrostatic contribution to the energy of the $\text{Zn}^{-/2-}$ charge state. Current experiments should reveal the variation of the Zn levels with Ge concentrations higher than 34 at %.



SESSION H

New methods in experiment. New methods in theory

Chairman: M. Dyakonov

THURSDAY JULY 30th
8.15-10.30

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SCANNING TUNNELING SPECTROSCOPY ON INAS(110): SCATTERING OF ELECTRON WAVES AT IONIZED DOPANTS

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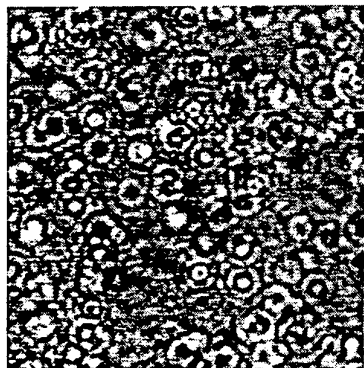


*Fig.1: dI/dV-image at 50 mV,
300 pA, 500 nm $\times$ 500 nm*

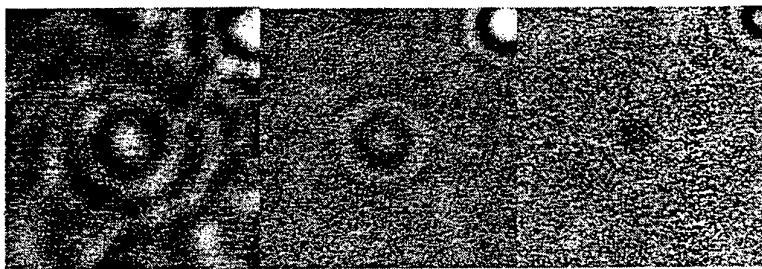


*Fig.2: dI/dV-images at 50/100/175 mV, 300 pA,
100 nm $\times$ 100 nm*

Scanning tunneling spectroscopy at low temperatures (8 K) allows the investigation of the electronic structure of surfaces with high spatial and spectroscopic resolution allowing to investigate the scattering of energy selected electron waves at individual ionized dopants.

In this study, we present dI/dV-images of n-InAs(110) ($N_D = 3 \times 10^{16} / \text{cm}^3$) at positive sample bias (50 mV- 200 mV), which exhibit circular symmetric corrugations around dopants lying up to 20 nm below the surface (Fig. 1). The diameter of the corrugations shrinks with increasing voltage (Fig. 2). The measured corrugations are ascribed to the scattering states of ionized dopants. Normalizing the images in an appropriate way gives direct access to the local distribution of the density of states at the surface, which is compared quantitatively with a WKB-calculation of the shape of the scattering states. The tip induced band bending has to be included to get agreement between model and experiment. However, the model has only one parameter to fit size, energy dependence and intensity relations of the corrugations: the depth of the dopant below the surface. The resulting depth distribution of dopants is in reasonable agreement with the measured dopant concentration.

In external magnetic fields the dI/dV-curves above the conduction band minimum exhibit oscillations due to the Landau level quantization of the conduction band. The energetic distance between neighbouring Landau levels is not uniform indicating that the effective mass of the sample depends on energy (non-parabolicity of the InAs-conduction band). The dI/dV-images obtained with an applied external magnetic field exhibit changes in the circular corrugations around dopants and additional large scale corrugations. These effects are discussed with respect to the Landau level quantization and potential shifts at the surface, respectively.

PAIR CHARGE CORRELATIONS LOCALIZED ON SHALLOW-LEVEL CENTRES INSIDE SELF-ASSEMBLY SILICON QUANTUM WELLS

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We present the findings of single-hole and pair-hole tunneling into the negative-U centres created by the reconstruction of shallow impurities at the edges of self-assembly longitudinal silicon quantum wells (SLQW). The quantum wells of this art are naturally formed inside ultra-shallow p⁺-diffusion profiles prepared using non-equilibrium boron diffusion into n-type silicon (100)-wafers. The p⁺-diffusion profile obtained at 900°C and thin oxide overlayer is the shallowest because of parity between the kick-out and dissociative vacancy diffusion mechanisms. The cyclotron resonance studies show that such p⁺-diffusion profiles consist predominantly of the SLQW. Using the quantized conductance (QC), EPR-EDEPR and NMR techniques, the dynamic quantum wires and dots have been revealed at the edges of SLQW, which are created by the electrostatic ordering of the dipole negative-U centres. These C_{3v} symmetry dipole boron (B⁺ - B⁻) centres that are caused by the negative-U reconstruction of the shallow boron acceptors (2B⁰ → B⁺ - B⁻) in the non-equilibrium diffusion process are regularly arranged along the SLQW edges.

The thermo-emf, CV and STM point contact measurements demonstrate the possibility of single electron/hole tunneling into silicon nanostructures thereby identifying a correlation gap in the DOS of degenerate hole gas, which is the result of the pair charge correlations localized on the negative-U centres. The value of the correlation gap obtained, Δ=0.022 eV, corresponds of the coherent length (ξ) equal to ~ 25 nm that is in good agreement with the data derived from the temperature and magnetic field dependencies of the magnetic susceptibility $\xi = (\Phi_0/2\pi H_{C2})^{1/2}$, which show a strong diamagnetism and confirm the model of pair charge correlations. The SLQW with homogeneous distribution of the negative-U centres are found to exhibit only single fluctuations in the correlation gap value, which can be present as natural quantum-size contacts favourable to pair charge tunneling. The presence of natural quantum-size contacts in the silicon nanostructure's system studied is shown to be revealed by the temperature dependence of the resistance due to the thermal excitation of pair charges $R \sim R_0 \cdot \exp(-\Delta/kT + \Delta/kT_c)$ as well as using the CV and STM point contact techniques. The double step in the current plateau and corresponding changes in the period of the current oscillations vs the gate voltage applied to the natural quantum-size contacts demonstrate also pair-hole and single-hole tunneling processes at 77 K and 300 K, respectively ($e=C \cdot \Delta U_g$; $2e=C \cdot 2\Delta U_g$). The presence of the natural quantum-size contacts in the silicon nanostructures based on the electrostatic ordering of the dipole negative-U centres is demonstrated to induce the sinusoidally varying critical current quenching at the external magnetic field: $I \sim I_0 \sin(\pi\Phi/\Phi_0)/(\pi\Phi/\Phi_0)$, where $\Phi_0=h/2e$; $\Phi=\Delta B \cdot S$; $S \equiv d(d+\lambda)$; d is the width of the quantum wire. The parallel quantum-size contacts are also formed inside silicon nanostructures during impurity dipole ordering, which are responsible for the current enhancement in a weak magnetic field as a result of the natural SQUID structure creation: $I_{\max} = 2I_0 \cdot |\cos(\pi\Phi/\Phi_0)|$.

Finally, the correlation gap and natural quantum-size contacts have been shown to be revealed by the single-hole and pair-hole tunneling into the silicon nanostructures created by the electrostatic ordering of dipole negative-U boron (B⁺ - B⁻) centres. The effects found seem to be related to the tunnelling of conduction electrons into the negative-U centres is favourable to the increase of the superconductor transition temperature T_c of metal-silicon eutectic alloys [1,2].

This work has been supported by the PhTNS-program (grant 97-1040), RBRF-program (grant 96-02-17197) and Federal Program «Integratsiya» (project 75:2.1).

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**RADIOACTIVE ISOTOPE IDENTIFICATIONS OF
Au AND Pt PHOTOLUMINESCENCE CENTRES IN SILICON**

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Photoluminescence (PL) measurements on silicon samples implanted with various radioactive Hg isotopes which decay fully or partly through the series Au/Pt/Ir/Os are reported. The majority of the data for Au-related defects were obtained using samples implanted with ¹⁹³Hg which decays through the series ¹⁹³Hg→¹⁹³Au→¹⁹³Pt, where the ¹⁹³Au half-life is 17hours. The results confirm earlier work concerning the involvement of Au in the 735meV centre observed in Fe-diffused silicon/1/. In this work we show first that a PL spectrum consisting of a series of doublets originating at 780/782meV is Au-related. A particularly important new result concerns the 1066meV trigonal centre, commonly attributed to Fe-B pairs, which we find to involve Au atoms. This supports the view that the 1066meV PL band could not be identified with the trigonal Fe-B centres observed in EPR/2/.

For Pt-related centres, ¹⁹¹Pt isotopes (half-life 2.9days) produced in the decay chain ¹⁹¹Hg→¹⁹¹Au→¹⁹¹Pt→¹⁹¹Ir provided conclusive proof of Pt involvement in three PL centres with zero-phonon lines at 1023, 884 and 777meV. Of these three Pt bands, only the 777meV intensity is observed to increase as Au→Pt transformations proceed. This centre is highly unstable in p-type material, a feature shared by the 735meV centre. The energy separation of the 735 and 777meV zero-phonon lines, 42meV, is close to the separation of the Au and Pt deep donor levels in silicon (~50meV), with Pt being the deeper. On this basis, and on the basis of energy level fine structure differences in the two cases, we suspect that the 735 and 777meV PL centres are Au and Pt counterparts of a defect formed with iron.

The PL results for both Au and Pt will be supported by DLTS data recorded for samples implanted with radioactive isotopes and treated in an identical manner to the PL samples.

Finally, we note that there is not sufficient evidence from the changes observed in the spectra as the transformations progressed to make any conclusive deductions concerning the occurrence of Ir or Os related PL spectra in our samples.

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FAR INFRARED ACTIVE MEDIA BASED ON THE SHALLOW IMPURITY STATES TRANSITIONS IN SILICON.

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The interest to far infrared active media based on the shallow impurity states in silicon is caused by two reasons. The first one is the low level of lattice absorption of FIR radiation in silicon. The second is the cascade character of acoustic phonon assisted relaxation along the excited coulombic impurity states¹ allowing to expect high efficiency of pumping of impurity excited states population, that is important for reaching continuous lasing. On the other hand the fast acoustic phonon assisted relaxation causes the main complication in obtaining the inverse population on impurity transitions, since it tends to form the equilibrium distribution with the lattice temperature. Thus the inverse population of impurity states implies the conditions in which the distribution is formed by the processes with threshold character (interaction with optical phonons, optical pumping) and faster, than acoustic phonon assisted and Auger processes, or the conditions, when the latter are suppressed for particular states. The other complication originates from the fact that absorption on impurity transitions lies in the same frequency region, that possible amplification and can prevent it. Hence the possibility of amplifications depends on the details of nonequilibrium distributions on excited impurity states.

The nonequilibrium excited impurity states carrier distribution was calculated using the procedure allowing to reduce the number of required matrix elements of transitions, based on the analysis of the probabilities of the different routs of the excited carrier through the ladder of excited states. This analysis gives the ratio of populations of the first excited states and the border conditions for the quasiclassical treatment of the higher excited states population². Such approach allows to account the overlap of orbits, essential for cascade capture, and the influence of the discrete character of the first excited impurity states spectrum on the carrier distribution. Two mechanisms of the inverse population of shallow impurity states in silicon have been proposed and analyzed. The first is based on the resonance interaction of the $2p_0$ state in Si:Bi with optic phonons (life time about 1 picosec)³. It is shown that the population inversion is realized under the conditions of optical pumping on the transitions ending the $2p_0$ Bi donor states from higher excited impurity states and cotinuum states with energies $E \leq kT$ as well, for the lattice temperatures $kT \leq E_{op}/\ln(\nu_{op}/\nu_{oi})$, where E_{op} is the energy of optical phonon, ν_{op} and ν_{oi} are the rates of transition from $2p_0$ state due to optic phonon spontaneous emission and optical ionization from the ground state correspondingly. The amplification up to 2 cm^{-1} is expected in the frequency range of $25 - 100\text{ cm}^{-1}$ for pumping intensities of CO_2 laser $I \geq 100\text{ W/cm}^2$, concentration of Bi donor centers $N_d \simeq 10^{16}\text{ cm}^{-3}$ and lattice temperatures $kT \leq 60\text{ K}$. The other mechanism of excited states overpopulation is based on the suppression of the acoustic phonon assisted relaxation from deep impurity states due to the momentum conservation law. In the case of Si : P the inversion population of $2p_0$ state is expected under the photoionization by CO_2 laser radiation and far-infrared ($168 - 180\text{ cm}^{-1}$) amplification ($0.5 \div 1\text{ cm}^{-1}$) on $1S(E) \rightarrow 2p_0$ and $1S(T2) \rightarrow 2p_0$ optical transitions can be reached for doping concentration $N_D \simeq 10^{15}\text{ cm}^{-3}$ for cryogenic temperatures ($kT \leq 10\text{ K}$) under 10 W/cm^2 CO_2 laser radiation density. The spontaneous emission was registered from the shallow donors in silicon (Si:P) under photoionization by CO_2 laser ($\lambda = 10.6\mu\text{m}$), using Ge:Ga and GaAs photodetectors. The filters inserted (GaAs, InSb, black poliethilen) extract the frequency range corresponding to the transitions mentioned above. The dependence of the spontaneous emission intensity on the intensity of pumping radiation confirms the possibility of amplification on impurity transitions.

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EFFECTIVE MASS CALCULATION OF THE SHALLOW ACCEPTOR GROUND STATE g -FACTOR FOR A3B5 SEMICONDUCTORS.

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One of the most important parameters of an impurity center in a semiconductor is the g -factor. The tensors $\hat{g}$ for the acceptor ground states in various semiconductors differ both quantitatively and qualitatively. The structure of the g -value tensor is defined not only by the symmetry of the crystal lattice but by other factors e.g. spontaneous local deformation (the Jahn-Teller effect), which may be very important for strongly localized states. This leads to the fact that g -factor calculations for acceptor states in crystals with the complex valence band structure is complex even in the effective mass approximation. We have carried out such calculations of the g -value dependencies on the acceptor binding energy for diamond-like[6] (such as GaAs) and wurtzite[7] (such as GaN) semiconductors.

The ground state wave function was calculated in the effective mass approximation by the method described in Ref. [5]. The acceptor binding potential was taken as the superposition of the Coulomb and short-range potential, which allowed us to consider acceptors with different binding energies. The only parameter of the short-range potential was calculated from the experimental value of the acceptor ground state energy.

A simple analytical expression for the g -value was obtained within the framework of the zero-radius potential model. This expression is independent of the binding energy and depends on the ratio of the light hole to heavy hole masses. This result is in good agreement with the numerically calculated one which is more accurate. Both the analytical and the numerical results agree well with the theoretical calculations[3] and the experimental data[2] for GaAs.

The low symmetry of the wurtzite crystal lattice leads to strong anisotropy of the g -factor of the localized hole. However, the structure of the tensor $\hat{g}$ is strongly dependent on the local deformation which may be caused by the Jahn-Teller effect. Such deformation lowers the symmetry in the vicinity of the impurity center and may lead to the total isotropization of the g -value of the localized state. This effect is observed in experiments (see for example Ref. [4]). To analyze this effect we obtained analytical expressions for the tensor $\hat{g}$ for strained wide-bandgap semiconductors (such as GaN). These expressions were derived for different ratios among spin-orbit, crystal-field, and strain-induced splittings. This simple analytical result may be used for qualitative analysis of experimental data obtained in the ODMR and the ESR experiments.

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DI-CARBON DEFECTS IN AlAs AND GaAs

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Heat treatment of heavily carbon doped AlAs and GaAs results in a drastic loss of C_{As} shallow acceptors. In Raman scattering experiments on annealed CBE grown GaAs and AlAs doped with ^{12}C and ^{13}C isotopes, it is found that the loss of carriers is accompanied by the appearance of two high frequency lines. These lie near to the stretch mode of an isolated C_2 molecule (1855 cm^{-1}). This is consistent with the formation of two types of di-carbon defects in these materials where the C atoms are bonded together and one or both of which act as a donor.

Using a local density functional method to investigate the structure and dynamics of several di-carbon defects, we find that the dimer at an As site is bistable and aligned approximately in a [100] direction in the neutral charge state, and in a [110] direction when positively ionised. The calculated frequencies lie within 10% of the measured values in both materials. Other defects are investigated too with a view of determining the structures giving rise to the modes.

RESONANT STATES IN STRAINED SEMICONDUCTORS

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Theoretical study of resonant states in strained semiconductor is presented.

In uniaxially stressed semiconductors the four-fold degeneracy of the valence band top is removed. Correspondingly, one series of acceptor states is splitted into two series of states and, correspondingly, the ground state of shallow acceptor is splitted into two doubly degenerate levels. Under certain pressure (≈ 4 kbar for Ge), one of these levels occurs in the valence band continuum and lowest resonant state appears. Thus, there are two series of acceptor levels in stressed semiconductors: local and resonant.

The presence of two series of acceptor states manifests itself via the intracenter optical transition between resonant and local states. The creation of the far-infrared lasers operating on these transitions has stimulated interest to the detailed theoretical study of resonant states.

In the present work we have calculated the wave functions, energy position and lifetime of resonant states in two limits i) in the framework of zero-radius-potential model and ii) in the case of Coulomb potential of an acceptor impurity. By using the zero-radius-potential model, we have investigated the conditions of the appearance of resonant states and found energy position, lifetime of resonant states as a function of pressure applied. This result can be directly applied to A^+ - states. In the case of Coulomb potential, we have calculated wave functions and energy position of resonant states in the limit of high pressure by using the variational approach. We have also applied the Dirac's method of consideration of resonant scattering to the case of the matrix Luttinger Hamiltonian and found the wave functions of resonant states, the amplitude of resonant scattering, the lifetime and the corrections to the energy positions, taking into account the interaction between discrete and continuum states. In the case of Coulomb potential, we have found the corrections to the energy positions induced by the short range potential of the central cell, too.

To understand the peculiarities associated with the intracenter optical transitions between resonant and local states, we have calculated the probabilities of these transitions and compared them with the probabilities of optical transitions from unperturbed states of continuum to the local one. The results of theoretical consideration are in good agreement with the experimental data on Ge:Ga where the stimulated intracenter transitions have been observed.

We also have applied our treatment of resonant states to the consideration of excited Coulomb states of deep acceptor which may also become resonant under stress and to the resonant states induced by shallow donor in stressed many valley semiconductors. The calculations are carried on for Si and Ge.

IMPURITY-BOUND HOLE POLARON IN A CYLINDRICAL QUANTUM WIRE

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The problem of a polaron bound to a charged impurity has been of primary importance for understanding the experimental observations of the optical absorption spectra in semiconductors [1]. Here, we investigate the energies of a hole polaron bound on an acceptor in a cylindrical quantum wire with a finite-barrier well.

Energies of the ground state and of the excited states of an acceptor in a wire-like cylindrical quantum-well heterostructure are calculated as a function of the cylinder radius R and of the displacement of the acceptor from the axis. The hole Hamiltonian is deduced for a confinement potential of the cylindrical symmetry. It is shown that in the quantum wire of a finite radius, the four-fold degenerate (in the Γ point) hole level is split into 2 two-fold degenerate levels. When deriving the acceptor energy spectrum in a quantum wire, the correct form of the electrostatic potential of an acceptor impurity placed inside a cylinder with dielectric constant ϵ_1 surrounded by a medium with dielectric constant ϵ_2 is used. If the inequality $R < a_b$ holds true, where a_b is the Bohr radius for an acceptor in the bulk, then the force lines of the electric field between an acceptor and a hole pass partially outside the cylinder (through a medium with another dielectric constant ϵ_2). Therefore, in this case the spherical approximation for the hole-acceptor interaction potential is not valid. A correct form of this potential allows us to obtain adequate results for the whole range of values of R . Besides that, we take into consideration the interaction between a hole and all kinds of phonon modes present in the structure: (i) cylindrical bulk-in, (ii) bulk-out and (iii) cylindrical interface modes [2].

We calculate the energies of a bound hole polaron by two methods, namely, within the framework of a variational approach and by means of perturbation theory. It is shown that at small radii of a quantum wire $R \leq a_b$ the above-mentioned factors influence significantly the acceptor energy spectrum. The polaron-acceptor binding energy is studied as a function of a distance between the impurity and the axis of a quantum wire. Resonant states of the bound polaron (for which the difference between ground and excited state energies is close to the phonon energy) are studied. The energy spectrum is analyzed for the heterostructures GaAs/Al_xGa_{1-x}As and for CdSe/glass. At small radii R , comparable to the polaron radius, the main part of the polaron contribution originates from the interaction of a hole with interface phonon modes, for both the ground state and the excited states. Under this condition the interface phonon modes can be expected to play the main role not only for a bound polaron formation but also for other phenomena due to the hole-phonon interaction. In conclusion, we show that a comparison of the obtained results with the experimental data provides information about the phonon modes, the hole-phonon interaction of quantum wires as well as about the spatial distribution of impurities.

We thank V. N. Gladilin for useful discussions. This work has been supported by the F.W.O.-V. projects No. G.0287.95 and W.O.G. 0073.94N (Belgium), partly by Interuniversitaire Attractiepolen (IUAP, Belgium) and by the PHANTOMS Research Network.

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SESSION J

Low-D systems II

Chairman: B.D. McCombe

THURSDAY JULY 30th

11.00-12.30

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- J3 A. Raymond, B. Couzinet, M.I. Elmezouar, W. Zawadzki, M. Kubisa, B. Etienne .
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TRANSFORMATION OF DEEP-IMPURITIES TO SHALLOW-IMPURITIES BY QUANTUM CONFINEMENT

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Nanocrystals Technology

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The modulation of the internal optical-transition matrix-elements involving tightly bound d or f shells of a localized impurity is rather difficult. For example, in visible line-emitting phosphors, the impurities are transition or rare-earth metals which possess d or f localized outer-shell electrons. In these *deep-impurities* the optical transition is atomic-like and highly localized. This strong localization leads to slow transfer of carriers from the host to the activator, preventing high efficiency and ultrafast optoelectronic devices.

To overcome this, we have confined a localized activator atom in a quantum dot. In these systems of quantum confined atoms (QCA), the intermixing of s - p electrons of the quantum confining host and d - f electrons of the activator atom occurs efficiently. This hybridization leads to enhanced transfer rates to the activator and simultaneously shortens the luminescent life time [1]. In $Y_2O_3:Tb$ nanocrystalline particles in the range of 30 -40Å, we observe enhanced absorption in the $4f^7 - 5d$ transition of the Tb^{3+} ion. This is brought about by the modulation of the 'extended' excited states by quantum confinement. *This is the first observation of the quantum confined modulation of the excited states of a localized atom.* This modulation of the excited states is a direct result of the enhanced overlap of the wavefunctions of the excited states of the impurity with the photo-excited electron-hole wavefunctions in the host. As the particle size decreases, this modulation increases, resulting in increased efficiency. *The photoluminescent efficiency of $Y_2O_3:Tb$ nanocrystalline particles is comparable to the best Tb^{3+} -based phosphors.*

The flow of energy in QCA could be visualized as a quantum mechanical funnel (QMF) where large energy is absorbed in the host quantum dot and rapidly transferred to a few localized atoms. The effective absorption cross section for such QCA is significantly enhanced because of the large overlap among the excited states and the boundary of the quantum dot. Thus, localized QCA functionally borrows the density of states from the host and thereby improves the efficiency and the recombination rate. *In QCA, the optical properties of deep states behave more like shallow states except that the atomic signature of the deep-localized states is retained.* The effectiveness of the atomic funnel will depend on the quantum confinement as well as the choice of the atom. Higher the degree of the localization (e.g. rare-earth and transition metals) larger would be the modulation factor in QCA..

Changes in the oscillator strength in an internal transition of an atom brought about by the quantum confinement can be exploited to develop new class of sensors, lasers, phosphors, high speed optoelectronic and integrated circuits. The potential applications of these quantum confined modulated atoms (QCMA) in science and technology will be discussed.

[#] Collaborators: V. Bhargava, V. Chhabra, B. Kulkarni and J.V.Veliadis

[1]. R.N.Bhargava et.al. Phys. Rev. Letts 72, 416 (1994); R.N.Bhargava J.Lum 70, 85 (1996).

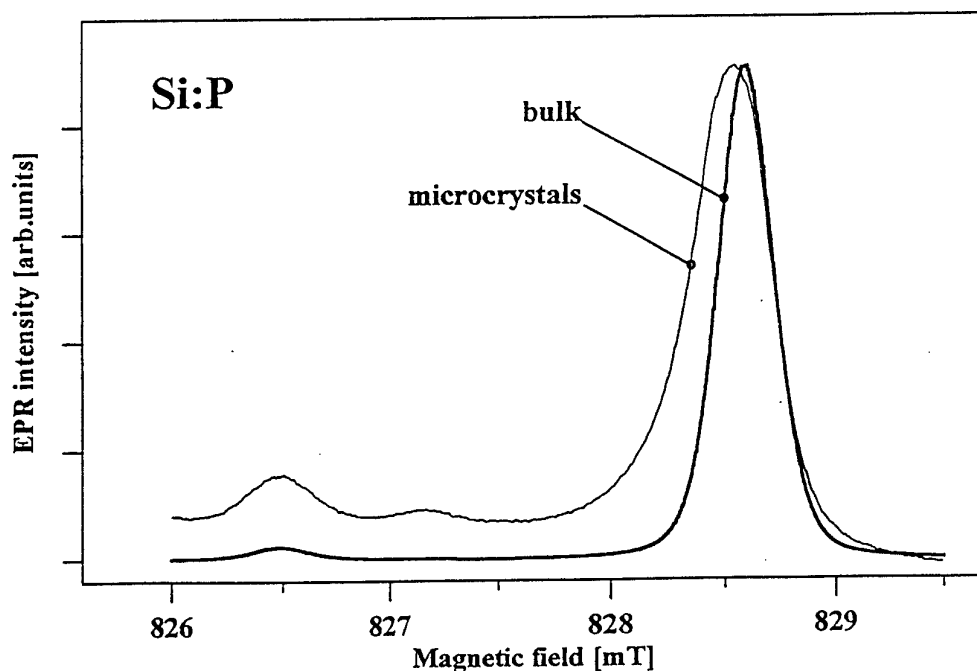
CONFINEMENT EFFECTS ON PHOSPHORUS DONORS EMBEDDED IN SILICON MICROCRYSTALS

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Due to their extended electronic structure shallow donor centers in semiconductors are especially sensitive to confinement effects. In the current experiment microcrystals prepared by mechanical ball milling of crystalline silicon doped with phosphorus were investigated by magnetic resonance spectroscopy. In the sample preparation procedure ball milling was followed by a sedimentation step. Crystallinity of the obtained grains was confirmed by X-ray diffraction. The actual size of microcrystals determined by Scanning Electron Microscopy (SEM) varied from 0.25 to 4 micrometers. Further reduction of grains was achieved by oxidation. Confinement effects were detected by their influence on the Electron Paramagnetic Resonance (EPR) spectrum of the phosphorus donor.

In the experiment lowering of the hyperfine interaction as a function of diminishing crystallite size has been observed. From asymmetry of the phosphorus-related EPR line appearing for small grains inhomogeneity of phosphorus centers distribution has been concluded. Both effects are tentatively ascribed to the growing surface-to-volume ratio of the microstructures. Also an increase of mutual overlap of electronic wave functions of individual donors upon diminished grain size has been noted by the appearance in the spectrum of hyperfine lines from donor pairs and triplets. The mentioned effects are illustrated in the figure. The EPR measurements were further paralleled by investigation of the photoluminescence emission of the microcrystals. A clear correlation between results obtained by both techniques has been established.

Implications of the experimental findings on the behavior of the electronic structure of shallow (donor) centers in a confinement environment are discussed.



*A part of the EPR spectrum of phosphorus in bulk silicon and in microcrystals,
temperature $T=4.2$ K, microwave frequency $\nu=23.12$ Ghz.*

MAGNETO-DONORS AND DONOR-BOUND EXCITONS IN GAAS/GA_{0.67}AL_{0.33}AS HETEROSTRUCTURES IN THE QUANTUM HALL REGIME

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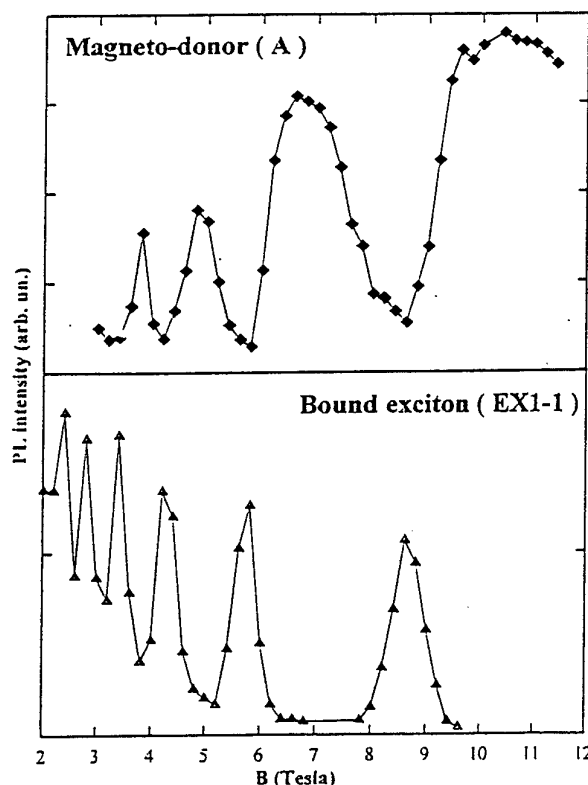
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Interband photoluminescence (PL) is studied as a function of magnetic field in modulation doped GaAs/Ga_{0.67}Al_{0.33}As heterostructures in the Quantum Hall regime. The oscillatory PL data exhibit free electron and donor (ground electric subband) to free hole transitions, as well as free and bound excitons (first excited subband) transitions. Pronounced intensity oscillations of all transitions are observed as the magnetic field varies between 0 and 11T. In particular, we observe, for the first time, strong intensity oscillations of donor-hole and bound exciton transitions with exactly opposite phase (Fig.1), from which we conclude that the observed bound excitons are bound to the donors at the GaAs/Ga_{0.67}Al_{0.33}As interface. Similarly, the intensities of free electron-hole and free exciton transitions oscillate with exactly opposite phase. Various mechanisms of the intensity oscillations are discussed, taking into account the available parallel behavior of the free and bound carrier excitations. We exclude an oscillatory screening by 2DEG to be the cause of the intensity oscillations as claimed by some authors. We conclude that the intensity transfer between the electron-hole and the free exciton transitions occurs when, as a function of magnetic field, the interband electron-hole energy becomes larger than the corresponding exciton energy, so that it is advantageous for the pair to form an excitonic state. Similar mechanism is responsible for the intensity transfer between the donor-hole and the bound exciton transitions.

Figure 1.

Intensities of magneto-donor transition A (upper trace) and the bound exciton transition EX1-1 (lower trace) versus magnetic field. The exact coincidence of minima for A and maxima for EX1-1 indicates that the exciton is bound to the donor.



ESR INVESTIGATIONS OF MODULATION DOPED Si/SiGe QUANTUM WELLS

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In this paper, we demonstrate that standard electron spin resonance (ESR) measurements can provide a contactless means to investigate charge transfer and metastability in modulation doped low dimensional structures.

We investigate MBE grown samples containing a single Si quantum well embedded between Si_{1-x}Ge_x barriers on top of a step graded buffer. For n-type modulation doping, a highly Sb doped layer is placed at a distance of 12 nm from the well. We observe four types of signals:

- (i) an ESR due to the shallow donors in SiGe with a width of $\Delta H \approx 2$ G,
- (ii) another extremely sharp resonance, with g-factor slightly smaller than that of the shallow donor and a line width of $\Delta H = 0.03$ G,
- (iii) a rather wide signal, whose width varies like $(\cos \Theta)^{-1}$, where Θ is the inclination of the magnetic field relative to the growth direction, and
- (iv) under illumination all the cyclotron resonances CR due to electrons and holes in the substrate which are identified from their typical angular dependence.

From the angular dependence of signal (iii) it is clear that it comes from the two-dimensional (2d) electron gas in the quantum well. A comparison of the amplitude and the temperature dependence to signal (iv) indicates also cyclotron resonance of the free electrons in the quantum well as its origin.

Both the resonance (ii) and the 2d CR increase persistently due to illumination after cooling in darkness. In particular, the cyclotron resonance (iii) of the 2d electron gas also becomes sharper after illumination, which is analogous to the mobility enhancement seen in transport experiments: after cooling in darkness, the Fermi level is close to the bottom of the quantum well states and carriers are more or less localised due to potential fluctuations. After illumination, the Fermi level increases and extended paths exist with higher mobility.

It is tempting thus to attribute resonance (iv) to that of the free carriers, CESR. Its linewidth indicates an outstandingly long spin-lattice relaxation time of the order of μsec s. Both the linewidth of the CESR and its amplitude show anisotropy which can be explained in detail by the fluctuating Rashba field - the crucial parameter for weak localisation in this system. The Rashba field arises from the asymmetric potential due to surface states and the one-sided modulation doping and can be determined thus. The consistency proves the CESR origin of this resonance.

We see thus in one experiment clearly separate signals from shallow donors and from all free (2d and 3d) carriers in the sample. We investigate the influence of illumination on the amplitude to the 2d CR. We find a clear threshold behaviour at the energy gap of Si_{1-x}Ge_x. This result demonstrates that charge transfer to the 2d channel is by orders of magnitude more efficient at interband excitation than by photo-ionisation of the shallow donors: their ESR signal (i) practically remains constant. Obviously the photo-generated holes are driven out of the region containing the quantum well and trapped at deep states in the 2 μm thick SiGe buffer.

FAR INFRARED SPECTROSCOPY OF SHALLOW ACCEPTORS IN STRAINED Ge/GeSi QUANTUM WELL HETEROSTRUCTURES

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The paper deals with shallow acceptors in strained multi-quantum-well (MQW) Ge/Ge_{1-x}Si_x heterostructures ($n = 80-160$, $x \approx 0.1$, $d_{Ge} = 200-800$ Å, $d_{GeSi} = 200$ Å) grown by CVD method on Ge(111) substrates. The quantum wells (QWs) are realized in Ge layers, the deformation being equivalent to the uniaxial tension along growth direction thus resulting in the splitting of degenerate valence band and in reducing of the binding energy of acceptor if compared with unstrained Ge. Shallow acceptors in both undoped (with residual impurities) and well-doped heterostructures were probed by far IR photoconductivity at $T = 4.2$ K using BOMEM DA3.36 FT spectrometer.

In relatively wide QWs (with respect to a typical Bohr radius of the acceptor) shallow acceptor are affected mainly by the strain rather than by the quantum confinement. Therefore at zero approximation the shallow acceptors in Ge/GeSi heterostructures can be treated as impurities in bulk Ge subjected to the uniaxial tension. In order to interpret the experimental results on far IR photoconductivity of Ge/GeSi heterostructures spectra of shallow acceptors in uniaxially stretched Ge were calculated using effective mass approximation. Eigenvalues for envelope function were found by variational approach. Trial wave functions were chosen similar to those for unstrained Ge [1], the strain induced anisotropy being taken into account by introducing of additional variational parameter. Binding energies of ground and few lowest excited p-like states (for which dipole optical transitions from the ground state are allowed) were found for a broad range of strains values. Typical extension of the wave function (Bohr radius) for the ground state along deformation was found to be of 40 Å.

Theoretical and experimental results proved to be in a good agreement for the sample with wide ($d_{Ge} = 800$ Å) QWs. In this sample the transition between ground and the lowest excited states at $\nu \approx 43$ cm⁻¹ and a broad band at $\nu = 60$ to 80 cm⁻¹ corresponding to transitions into higher excited states and to the energy continuum were revealed. The spectra of the samples with narrower QWs (200 Å) can be interpreted by introducing the "effective" deformation allowing for the additional valence band splitting resulting from the quantum confinement. In this case the valence band splitting is high enough to use the "anisotropic donor model" [2] to classify the excited states of the acceptors. In these samples the observed line centered at $\nu \approx 56$ cm⁻¹ can be attributed to the transitions to $3P_{\pm}$ and higher excited states and to the continuum. There is also powerful photoconductivity band observed at $\nu = 20$ to 40 cm⁻¹, the short wavelength part of the band being reproduced in all the sample investigated. It is related to the transitions into $2P_{\pm}$ states of the acceptors. In the samples made from the only chip (undoped, with residual acceptors) the strong long wavelength part of the band was observed that is probably attributed to the ionization of A⁺-centers formed due to the capture of additional holes from the barrier situated impurities by neutral acceptors in QWs. Such classification of the spectral lines in the samples with QW width of 200 Å is confirmed by the investigations in strong magnetic fields up to 5 T. The splitting of the spectral line in the magnetic fields over 2 T was discovered. The short wave length component of the split line exhibits the linear shift to the high frequency region with the increase of the magnetic field. At the same time the long wavelength component position practically does not depend on the field. Such behavior is typical to the transitions to P_{+} and P_{-} states correspondingly.

Direct measurements of the responsivity of the sample with QW width 200 Å gave the figure $S \approx 10^4$ V/W (NEP $\approx 10^{-11}$ W/Hz^{1/2}). This opens the possibility to use Ge/GeSi heterostructures as photoelectric detectors for the long wavelength end of far IR range.

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SESSION K

Wide-gap III

Chairman: P. Fisher

THURSDAY JULY 30th

14.00-15.30

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Comparison between the Theoretical Prediction of Codoping and the Recent Experimental Evidences in p-type GaN, AlN, ZnSe, CuInS₂ and n-type Diamond

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We propose a new valence control method, the "codoping method (using both n- and p-type dopants at the same time)", for the fabrication of low-resistivity p-type CuInS₂, ZnSe, GaN and low-resistivity n-type diamond crystals based on the ab initio electronic structure calculations. Based upon the calculation, we find the the codoping method (doping acceptor and donor at the same time) (i) reduce the formation energy of the donor with reducing the lattice-relaxation and Madelung energies, and (ii) increase the carrier mobility due to the short-range dipole scattering (long-range Coulomb interaction is dominated in the case of simple doping), and (iii) reduce the acceptor and donor energy levels because of the formation of donor and acceptor complexes (a donor level is raised and an acceptor levels is lowered with making donor-acceptor complexes).

In order to fabricate the low-resistivity p-type wide band-gap semiconductors, we proposed the following codoping (doping p- and n-type dopants at the same time); CuInS₂: V(Cu vacancy) + In (at Cu site) + 2P (at S site), ZnSe: In + 2Ne, or Cl + 2N, or Li + Cl (or I), or Te + 2N, and GaN: Si + 2Mg (or Be), or O + 2Mg (or Be), and AlN: O + 2C, and Diamond: B + 2N, or H + 2P.

We compare our prediction with the recent successful experiments of the fabrication of low-resistivity p-type and n-type wide band-gap semiconductors; for example, such as the highly conductive diamond film prepared by gas source MBE with methane and tri-n-butylphosphine [4], the carrier concentration enhancement of p-type ZnSe and ZnS by codoping with active nitrogen and tellurium [5], the O and Be codoping in GaN [6], and available new experimental data.

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Si-doping of homoepitaxial GaN layers

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The (Al,Ga,In)N compounds are regarded as those which will make a "blue revolution" by being used for constructing green/blue/UV diodes, lasers and detectors. However, despite a large research efforts, many of basic properties of these compounds are still not known. One of the reason of this situation is, that most of the nitrides are grown in a form of heteroepitaxial layers grown on highly mismatched substrates as sapphire or silicon carbide. The mismatch causes lattice relaxation by a very high density of misfit dislocations (10⁸-10¹⁰ cm⁻²). The single crystals of GaN, which would be the most ideal substrates, are difficult to be grown. The most successful way to grow single crystals of GaN is to use high-pressure, high temperature method (about 15 kbar and 1800K) [1].

In this work we present the results on Si-doping of homoepitaxial GaN layers. Gallium nitride epitaxial layers doped with silicon were grown by metalorganic chemical vapor deposition. Conductive single crystals of GaN-grown at high hydrostatic pressure were used as substrates. The layers were examined using X-ray diffraction, photoluminescence and far infrared reflectivity. *It was found that the incorporation of silicon depends on the side used for deposition.* For the two layers grown in the same run, the one grown on the (00.1) side (gallium-terminated) had always smaller free electron concentration with respect to the (00.1) side (nitrogen-terminated). This conclusion could be drawn from the lattice expansion by free electrons, the photoluminescence peak shift by Burstein-Moss effect and the position of plasma edge.

The difference in the mechanism of Silicon and Oxygen incorporation during layer growth on gallium and nitrogen terminated sides is discussed.

ELECTRICAL PROPERTIES OF Mg DOPED AND UNDOPED MBE GROWN CUBIC GaN EPILAYERS

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The electronic properties of undoped MBE grown cubic GaN (c-GaN) layers [1] reveal outstanding features of this material. In contrast to hexagonal GaN (h-GaN) the type of conduction in c-GaN can be influenced by the growth conditions and both p- and n-type GaN layers with low carrier concentrations are obtained. At stoichiometric growth conditions, exactly controlled in-situ by Reflection High Energy Electron Diffraction (RHEED) [2], photoluminescence (PL) show an unidentified shallow acceptor with an activation energy of about 100 meV [3]. This is within the lowest acceptor activation energy ever reported for GaN and demonstrates the existence of shallow acceptors longly looked for in this material. As possible origin of the shallow acceptor already present in nominally undoped c-GaN layers Gallium vacancy V_{Ga} , defect complex containing V_{Ga} , and isoelectronic traps, recently proposed [4], are discussed. Measurements of gain [5] in this material reveal gain values which are comparable to that of h-GaN. In addition optically excited stimulated emission from cleaved cavities has been observed [6] demonstrating the potential of c-GaN for the realization of blue emitting laser diodes.

In this paper we summarize recent doping experiments with Mg and explain the experimental data on the basis of theoretical calculations of defect levels both of intrinsic and extrinsic (shallow) impurities. Cubic GaN films are grown by rf-plasma assisted MBE on semi-insulating GaAs (001) substrates at a substrate temperature of 720°C. The growth rate is about 0.07 $\mu\text{m/h}$ and the thickness of the layers is about 1 μm , respectively. Elemental Mg is evaporated from a commercial available effusions cell at source temperatures between 300°C and 450°C. Secondary ion mass spectroscopy (SIMS), low temperature photoluminescence (PL) and temperature dependent Hall-effect measurements are used to study the incorporation, optical and electrical properties of these samples.

A Mg related donor-acceptor transition at 3.04 eV with an acceptor activation energy of $E_A = 0.230$ eV is observed by low temperature photoluminescence measurements. This energy level is in excellent agreement with recent theoretical calculations of Mg_{Ga} [7] and is somewhat lower than that for the corresponding value of 0.265 eV for h-GaN [8]. At Mg concentrations higher than 10^{18} cm^{-3} at least 3 additional deeper transitions at 2.95 eV, 2.65 eV and 2.3 eV are observed, indicating that also in c-GaN Mg is incorporated at different lattice sites or forms complexes at high Mg flux. Therefore, selfcompensation is a severe problem for high Mg doping in both c-GaN and h-GaN [9].

SIMS measurements show that at a growth temperature of 720°C the amount of incorporated Mg is limited to about $5 \cdot 10^{18} \text{ cm}^{-3}$ due to the high volatility of Mg. They further show an accumulation of Mg at the GaN/GaAs interface and suggests the effect of Mg diffusion towards the GaAs substrate.

Temperature dependent Hall effect measurements demonstrates that the cubic epilayers are p-type with hole concentration in the range of some 10^{16} cm^{-3} at 300 K. This rather low carrier concentration is expected due to the high thermal activation energy of the Mg acceptor. At low Mg-fluxes Mg forms a shallow acceptor and at high fluxes Mg is incorporated either as Mg_i , Mg_N or as complexes forming deeper acceptor or donor levels. The nature of the additional deeper defects observed in PL are further discussed in view of recently observed Mg-related deep donor [10] and acceptor [11] levels measured in h-GaN by deep level transient spectroscopy (DLTS). These Mg-related deep defects may also be responsible for the electrical compensation of the cubic GaN epilayers at high Mg concentrations.

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**Infrared and Raman Spectroscopy of Acceptor Bound Holes:
Boron Acceptors in Isotopically Controlled "Blue" Diamonds**

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The extremely rare, nitrogen-free, boron-doped diamonds exhibit *p*-type conductivity and resistivities as low as a few ohm-cm. As expected, they display a Lyman spectrum in the infrared associated with substitutional group III acceptors; the photoionization continuum extending well into the red endows such diamonds with the distinct blue color. The Lyman spectrum of boron acceptors in diamonds with natural carbon composition compared to that in boron doped ^{13}C diamond, reveals a remarkable example of "central cell" corrections to the effective mass theory for *the same substitutional acceptor but located in a host differing merely in its isotopic composition*.¹ The Lyman spectrum observed as a function of temperature, shows the existence of a close pair of $1s$ ground states separated by ~ 2 meV. The Raman spectrum,² of the blue diamonds discloses an electronic transition at 2.07(1) meV in natural and 2.01(1) meV in ^{13}C diamonds. The polarization characteristics of the Raman line clearly establish the transition to be between the spin-orbit split $1s(p_{3/2})$ and $1s(p_{1/2})$ ground states of the boron acceptors, with intensities theoretically predicted in terms of the so-called Luttinger parameters of the valence band; its Zeeman and piezospectroscopic effects fully support the assignment. The measured absolute cross section of the Raman line yields the acceptor concentration.

*In collaboration with Hyunjung Kim, R. Vogelgesang, S. Rodriguez, M. Grimsditch, and T. R. Anthony.

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POSTER SESSION P1

Effects of external fields and pressure

P1-1./ P1-13

SHALLOW DONOR RESONANT STATE WIDTH NARROWING
NEAR CROSSING WITH UNDERLYING LANDAU SUBBAND BOTTOM IN GaAs

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Shallow donor resonant states appear in a magnetic field under each $N > 0$ Landau subband. They are determined by three quantum labels: (N, M, k) . Here, N denotes the number of the Landau subband, from which this resonant state originated, M determines the angular momentum projection along the magnetic field, and k designates the states with fixed N and M as the energy of the state increases. The resonant states decay spontaneously into underlying Landau subbands. Due to this decay they possess a width called an autoionization width. As the magnetic field decreases, the resonant states approach the bottom of the closest underlying Landau subband and cross it. Theoretical calculation [1] of the autoionization width for some resonant states based on the time-independent scattering theory predicts that this width will monotonically increase up to the crossing between the resonant state and the Landau subband bottom, as the magnetic field is reduced.

To determine the state width, a linewidth of the transition from the ground state to this resonant state is measured. The linewidth is practically equal to the width of the resonant state, in which the transition takes place, because the width of the ground state is negligibly small as compared with the width of the final resonant state. The main contribution to the transition linewidths is made by the autoionization width rather than other broadenings (inhomogeneous- and stimulated by solid state interactions broadenings [2]). It follows from the above that the linewidth should have the maximum value at the crossing point.

In the present work we experimentally observed that the linewidth of transitions to resonant states initially increased, as the magnetic field is reduced, and reached a maximum magnitude, and then the linewidth began to decrease dramatically in the vicinity of crossing with the bottom of the closest underlying Landau subband. The transitions from the $(0, 0, 0)$ shallow donor ground state to the $(1, -1, 0)$, $(2, 0, 0)$ and $(2, -1, 0)$ resonant states were investigated. Measurements were made using the photoelectric spectroscopy technique with a submillimeter laser magnetospectrometer at $T = 4.2$ K. It was chosen the GaAs ($N_d + N_a < 10^{14} \text{ cm}^{-3}$) samples with a concentration of one dominant donor an order of magnitude larger than the overall concentration of all other donors. The narrowing of linewidth corresponding to transition to the $(1, -1, 0)$ state was observed near the crossing with the bottom of the $N=0$ Landau subband. The linewidth narrowing was also observed for the transitions to the $(2, -1, 0)$ and $(2, 0, 0)$ resonant states. For the last two transitions, the linewidth narrowing was studied near the crossing with the bottom of the $N=1$ subband. For all these lines, the narrowing began when the difference between the resonant state energy and the bottom of the corresponding Landau subband became approximately equal to the energy width of the lines. The linewidth narrowing near the crossing point ranged from 20 to 50% of the maximum magnitudes observed.

We developed a model which describes a resonant state as a spreading wave packet. It explains the observed decrease of the autoionization width near the crossing with the bottom of the Landau subband as being due to the reduction of the wave packet spreading rate when the average energy of the wave packet decreases. It was theoretically shown that the narrowing should occur for all resonant states when they approach the bottom of each underlying Landau subband by the energy difference comparable with resonant state width.

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MAGNETO-SPECTROSCOPY OF BERYLLIUM IMPURITY IN GALLIUM ARSENIDE

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Far-infrared absorption due to Lyman transitions of the Be acceptor, which substitutes for gallium in gallium arsenide, has recently been reported in "bulk" samples grown by molecular-beam epitaxy [1]. Sharp transitions corresponding to the G, D and C lines, i.e. from the ground state, $1s_{3/2}(\Gamma_8^+)$, to the first three excited odd-parity states, $2p_{3/2}(\Gamma_8^-)$, $2p_{5/2}(\Gamma_8^-)$ and $2p_{5/2}(\Gamma_7^-)$, are observed. The line widths and integrated intensities have been studied as a function of temperature. Photoconductivity of GaAs:Be and photoluminescence excited by above-gap radiation (sensitive to Be in the epitaxial layer) and by below-gap radiation (sensitive to C and Zn in the substrate) have also recently been described [2].

Further detailed information on this impurity system has now been obtained by carrying out far-infrared spectroscopy in a magnetic field on the same and higher-quality samples. Both absorption and photoconductivity measurements have been employed. In all cases the direction of light propagation, k , is parallel to $\langle 100 \rangle$. The direction of the magnetic field, B , is either $B \parallel \langle 010 \rangle$ or $B \perp \langle 011 \rangle$. The electric-field vector of the radiation is oriented either $E \parallel B$ or $E \perp B$. Depopulation effects which result from changing magnetic field ($0 < B < 6$ T) or temperature ($2 \text{ K} < T < 7 \text{ K}$) have assisted in identifying the various initial states involved in the observed transitions. This information is important since not all the allowed transitions are observed at a given magnetic field and temperature.

The data is of higher quality than that previously available for acceptors in GaAs. The g -factors determined for the $1s_{3/2}(\Gamma_8^+)$ state, $g_1' = 0.30$ and $g_2' = 0.07$, are in good agreement with the values of $g_1' = 0.30$ and $g_2' = 0.09$ reported in an experimental study of carbon impurity in liquid-encapsulated Czochralski grown GaAs [3] and in fair agreement with the values determined in a theoretical study for a generic acceptor in GaAs of $g_1' = 0.21$ and $g_2' = 0.11$ [4]. Similar remarks may be made regarding the g -factors of the $2p_{5/2}(\Gamma_8^-)$ state. The data for the $2p_{5/2}(\Gamma_7^-)$ state are less easy to interpret and there is insufficient data for the $2p_{3/2}(\Gamma_8^-)$ state to determine the g -factors.

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HIGH FIELD ZEEMAN SPECTROSCOPY OF SINGLY IONISED ZINC IN GERMANIUM

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The spectra of singly ionised zinc (Zn^-) in Ge have been studied extensively [1-4] but, until now, high field Zeeman measurements have not been made. Since the spacings of the energy states are ~ 4 times larger than are those of neutral acceptors, the interactions between states which produce some complex effects in the Zeeman spectra of neutral acceptors such as, for example, the group III impurities [5,6], occur at larger fields for Zn^- . This should permit more precision to be obtained for the measured g factors but is offset by the Stark broadening of the states, and hence line widths, intrinsic to ionised impurities. In the present measurements, samples with low concentrations of Zn^- have been chosen to minimise this broadening. Results will be presented with the magnetic field parallel to both $\langle 100 \rangle$ and $\langle 111 \rangle$ crystallographic directions for field strengths up to 6.5 T. During these studies of Zn^- , we have observed 'side-bands' associated with the D and C lines. For both lines, in the unperturbed spectra, these bands appear in pairs, symmetrically disposed about the 'parent' acceptor line, while the energy spacing of the members of the pairs is the same for both the C and D lines. An interesting feature of the strongest low-energy side bands is that they have an antiresonance or emission-like characteristic. This feature has been observed previously for the D lines of the neutral acceptors Cu, CuX [7] and Zn. However, since the energy spacing of the C and D lines of neutral acceptors is close to that of the side-band to 'parent' line spacing, both the low-energy side-band of the C line and the high-energy side-band of the D-line would be obscured by the other's 'parent' and thus explain why these have not been observed for the above neutral acceptors.

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ZEEMAN SPECTROSCOPY OF ZN-H COMPLEX IN GERMANIUM

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A divalent substitutional zinc atom in germanium complexed with an interstitial hydrogen atom gives rise to a monovalent acceptor of trigonal symmetry [1]. The axial nature of this complex splits the four-fold degenerate states associated with substitutional point defects into two two-fold degenerate states. Zeeman spectra of the Zn-H complex have been observed for **B** along $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ crystallographic directions in the Voigt configuration using linearly polarised radiation. Spectra of the C and D lines [2] for $B \leq 2$ Tesla are essentially identical to those of these lines of group III impurities [3]; here **B** is the field strength. At all fields, splitting of the excited state of the D lines is identical to that for group III acceptors in germanium [3,4]. The magnetic field dependence of the D components for both $E_{II}B$ and $E_{I}B$, and the selection rules, demand that only one of the two two-fold 1s-like energy levels is occupied at the temperatures used instead of both. The results confirm piezospectroscopic studies [1] which demonstrated that the axes of the complexes are along the four $\langle 111 \rangle$ covalent bond directions of the host.

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YTTERBIUM-INDUCED IMPURITY STATES AND INSULATOR-METAL TRANSITION UNDER PRESSURE IN $Pb_{1-x}Ge_xTe$ ALLOYS

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Temperature dependences of resistivity ρ and Hall constant R_H ($4.2 \leq T \leq 300K$, $B \leq 0.1$ T) of $Pb_{1-x}Ge_xTe$ ($x \leq 0.04$) alloys doped with Yb have been investigated under atmospheric pressure and under hydrostatic compression ($P \leq 12$ kbar).

The temperature dependences of ρ and R_H measured under atmospheric pressure revealed the low temperature activation regions of impurity conductivity (Fig.1). From the slope of the activation region the activation energy of Yb-induced level situated close to the valence band edge was determined. It is shown that in $Pb_{1-x}Ge_xTe$ ($x=0.038$) the activation energy of Yb impurity level $\Delta E_{Yb} = E_{Yb} - E_v \approx 22$ meV. With the decrease of Ge content the Yb level goes to the valence band edge with the rate $d(\Delta E_{Yb})/dx \approx 7$ meV/at.%, at $x \approx 0.01$ intersects it and goes into the valence band.

Under pressure the activation energy of Yb-induced level decreases monotonically (Fig.1). At some pressure P^* the activation region in the $\rho(1/T)$ dependences vanishes and $\rho(1/T)$ dependences assume a metallic character. At pressures $P > P^*$ the oscillations of transverse magnetoresistance of the investigated samples were observed. With the increase of pressure the frequency of the oscillations increases indicating the increase of the free hole concentration in the alloy. Thus one can conclude that under pressure Yb level moves to the valence band edge (Fig.2). At pressure P^* the impurity level intersects the top of the valence band, inducing the insulator-metal transition and the increase of free hole concentration due to the flow of electrons from the valence band to the impurity level. Upon the further increase of pressure Yb level goes deep into the valence band and the further increase of the free hole concentration takes place until all of the impurity states will be occupied with electrons. In the frame of the obtained model of the energy spectrum of $Pb_{1-x}Ge_xTe<Yb>$ alloys (Fig.2) the comparison of experimental and theoretical dependences of free hole concentration on pressure was performed and the main parameters of Yb impurity level were determined. It was found that the rate of impurity level movement under pressure $d(\Delta E_{Yb})/dP \approx 5$ meV/kbar, the Yb-induced level has a finit width (≈ 5 meV) and the total capacity of the level $N_{Yb} \approx 10^{20} \text{ cm}^{-3}$.

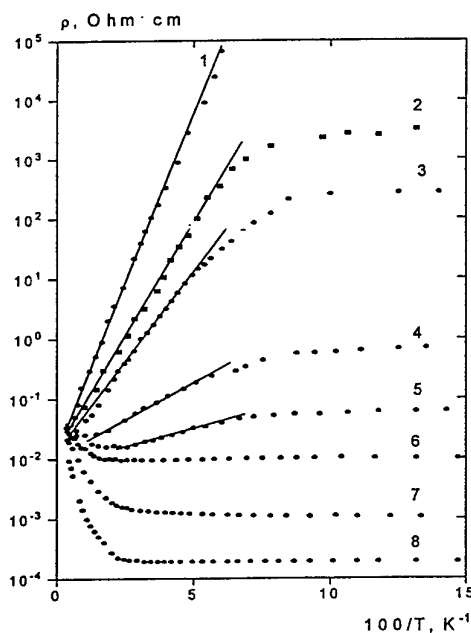


Fig.1. Temperature dependence of resistivity in $Pb_{1-x}Ge_xTe<Yb>$ ($x=0.038$). P, kbar: 1-0; 2-1.6; 3-2.3; 4-3.2; 5-4.5; 6-6.8; 7-8.7; 8-12.0.

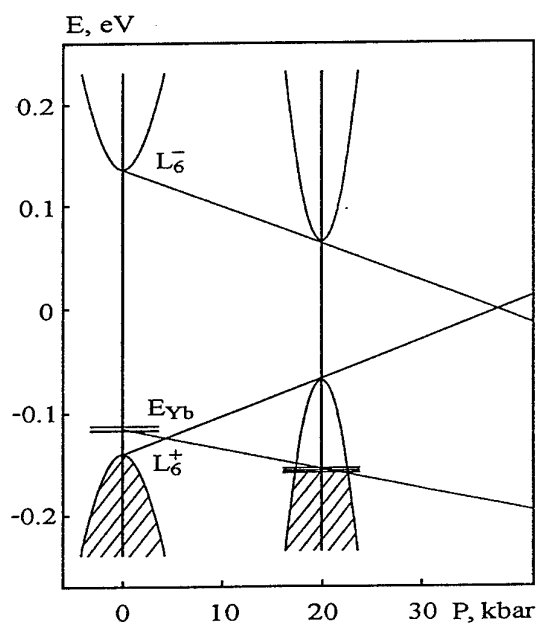


Fig.2. Reconstruction of the energy spectrum of $Pb_{1-x}Ge_xTe<Yb>$ ($x=0.038$) under pressure at 4.2 K.

DISSIPATIVE TUNNELLING OF CHARGE CARRIERS FROM SHALLOW IMPURITIES

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The effect of lattice vibrations on the field ionization of shallow impurities at low lattice temperature, when only acoustic phonons are active in the ionization process, is investigated by impurity transient tunnelling spectroscopy. The experimental results obtained on Ge:Sb,P and GaAs:Be are presented. The increase of tunnelling rate of bound charge carriers when lattice temperature was raised was observed at electric fields higher than 1 kV/cm and 5 kV/cm respectively for Ge:Sb,P and GaAs:Be. In both cases the lattice temperature was kept low enough, $T=4.2-6.5$ K for Ge:Sb,P and $T=4.2-17$ K for GaAs:Be, so that all charge carriers were on impurity sites before application of ramped ionizing electric field. In general, an increase of the bound-free tunnelling rate was observed when lattice temperature was increased.

The temperature dependence of the tunnelling rate is explained by using two dissipative tunnelling mechanisms. The importance of a particular mechanism depends on energy spectrum structure of the impurity atom. In Ge:Sb,P case the first excited energy levels of Sb- and P-donors are close to the ground level, while in GaAs:Be case Be-acceptor excited levels are relatively far away from the ground level, and thus have no influence on charge carrier tunnelling, even at high lattice temperature. In latter case the experimental results can be explained by acoustic phonon assisted tunnelling only. The activated tunnelling was found to be important in Ge:Sb, P. In this semiconductor the donor excited states are active in the tunnelling process: the electron starts from the ground donor level, appears in an intermediate excited level and then tunnels through a more transparent impurity barrier.

In addition, in case of beryllium acceptor we shall consider the role played by heavy and light valence band masses in the tunnelling dynamics. Using a simple hydrogenic model it will be shown that both at liquid helium temperature when pure (phononless) tunnelling predominates as well as at higher temperatures when acoustic phonon assisted tunneling predominates, the experimental results are in a better agreement with the theory when light hole mass is used in calculating the tunnelling probability.

IMPACT IONIZATION OF SHALLOW DONOR STATES RELATED TO DIFFERENT MINIMA-TYPE OF THE GERMANIUM C-BAND

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We analyse here the dependencies of breakdown electric field on uniaxial pressure for two various orientations of uniaxial deformation axis ($\vec{X} // [111] // \vec{E}$ and $\vec{X} // [001] // \vec{E}$) in Ge under the condition of impact ionization of the shallow donors states. We demonstrate that all main peculiarities of measured dependencies $E_{br}=f(\vec{X})$ can be explained by taking into account the absolute difference of conduction band transformations in highly strained crystals for two orientations mentioned above.

In the case $\vec{X} // [001]$, L_1 - Δ_1 -inversion of c-band minima-type in Ge takes place at pressure $X > 2.1$ GPa. It was demonstrated, that due to the L_1 - Δ_1 -inversion of the minima-type, the c-band of germanium becomes similar to silicon c-band. The effective mass of electron increases essentially, and the ionization energy of the ground state of shallow donors related to the Ge Δ_1 -minima approaches the corresponding values of these parameters determined for silicon: $E_i^\Delta(\text{Sb})=(36 \pm 2)\text{meV}$, $E_i^\Delta(\text{P})=(41 \pm 2)\text{meV}$, $E_i^\Delta(\text{As})=(45 \pm 2)\text{meV}$. Thus, direct confirmation of the main approaches of the effective mass theory was obtained.

Taking into account the relationship between the following energies $E_i^\Delta(\text{As}) > E_i^\Delta(\text{P}) > E_{opt} > E_i^\Delta(\text{Sb})$, we explain the nonmonotonous behaviour of the measured dependencies $E_{br}=f(\vec{X})$ for impurities As and P in Ge. So, if the energy of ionizing electrons exceeds the optical phonons energy the distribution function of electrons acquires the oscillatory form. The deformation potential constants of the c-band Δ_1 -minima in Ge were determined: $\Xi_d^\Delta=(10.4 \pm 1)\text{ eV}$, $\Xi_a^\Delta=(0.53 \pm 0.06)\text{ eV}$. Measured value of the electron mobility anisotropy for Δ_1 -valleys in pure Ge crystals is $K_\mu^\Delta = K_m^\Delta / K_\tau^\Delta = 4.4 \pm 0.15$. Since in both Ge and Si pure crystals $K_\tau \approx 1$, the value of the electron effective mass anisotropy in the Δ_1 -minima of Ge can also be estimated as $K_m^\Delta \approx 4.4$.

In the case $\vec{X} // [111]$, behaviour of the $E_{br}=f(\vec{X})$ dependencies for different donors (Sb, P, As) in Ge can be explained by both hot electric field induced and strain induced redistribution of electrons between equivalent (at $\vec{X} = 0$) L_1 -minima.

In general case the ratio of electron concentration in the high-energy valley (n_2) to the low-energy one (n_1) can be presented for non-degenerate distribution as $n_2/n_1 = \exp[(-\Delta\epsilon(X) \pm \delta\epsilon(E)) \times (kT_e)^{-1}]$. Here $\Delta\epsilon(X)$ is the strain-induced valley splitting, $\delta\epsilon(E)$ is the difference in the electron energy at "hot" and "cold" valleys, T_e - electron temperature for "cold" valley. The sign "-" should be choose for equivalent action of both electric field and uniaxial strain on electron repopulation between the minima; the sign "+" corresponds to the opposite action.

In pure Ge crystals the scattering-free acceleration of electrons in electric field, the total loss of their energy via impact ionization and return of electrons to the c-band bottom define the streaming nature of carriers motion since this process must occur again at the condition of electrons multiplication.

The developed methods of findings of some Δ_1 -minima parameters in Ge is discussed, as well.

LOCALIZATION AND IMPACT IONIZATION OF SHALLOW DONOR STATES IN Si AND Ge UNDER STRAIN-INDUCED MI TRANSITION

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Analyzing the both temperature dependencies of resistivity at different values of uniaxial pressure X and current-voltage characteristics (CVC) we studied the stress dependencies of the activation energy E_a and dependencies of the breakdown field on activation energy in the range of strain-induced MI transition in Si and Ge doped with shallow donors Sb and P.

The transition from the metallic-type conductivity to the activation-type one caused by a strain-induced change of the conduction band structure was examined earlier for degenerately doped Si:Sb and Ge:Sb crystals in the range of high uniaxial pressure [1]. Analysis of an energy band structure transformation under extremely high uniaxial pressure allows to choose a specific orientation of uniaxial pressure which must initiate the transition from the metallic-type conductivity to the activation-type one for both silicon and germanium. For $\vec{X} // [111]$ the strain-induced non-parabolicity of Δ_1 -minima arises in Si. In Ge, for $\vec{X} // [001]$ the germanium-like conduction band (L_1 -minima) transforms into the silicon-like c-band (Δ_1 -minima) at $\vec{X} > 2.1$ GPa. In both cases an essential increase of the transverse component of electron effective mass takes place. Therefore, the energy of ground state of shallow donors remarkably increases and the wave function overlapping substantially decreases, since it is known that the Bohr radius of the valence electron is determined as $a_B = \hbar^2 / m_e^2$.

Since on the insulating side of strain-induced MI transition free electrons can be generated, in particularly, by impact ionization of localized states, features of CVC's directly reflect the characteristic properties of strain-tuned localization of electrons and their multiplication under breakdown condition at low temperature and in the range of high uniaxial pressure. So, the CVC's measurements in both the c.current and pulse regimes show the transformation of linear CVC's on metallic side into s-shape ones in the range of strain-tuned electrons localization and breakdown of localized states under transition to the activation-type conductivity in both n-Si ($\vec{X} // [111]$) and n-Ge ($\vec{X} // [001]$) crystals. Because the E_2 -conductivity in unstrained crystals with intermediate level of doping is characterized by s-shape of CVC's the strain-induced MI transition for both n-Si and n-Ge degenerately doped with shallow donors can be identified just as the transition to the E_2 -conductivity. For impact ionization of electrons localized on the shallow donors under transition to the E_2 -conductivity we obtained both linear and non-linear dependencies $E_{br} = f(E_a)$ for different levels of doping in the range $N_c < N_d < 3N_c$. We speculate that the linear dependencies $E_{br} = f(E_a)$ can be explain by small distance between impurity atoms in degenerately doped crystals and by low value of the activation energy. Therefore, in spite of electron mobility in impurity band is less as compared with that in the c-band, the mobility of free electrons accelerated in impurity band can be high enough for scattering-free acquirement of energy which is sufficient for impact ionization of localized states on the insulating side of the strain-induced MI transition. The measured values of activation energy E_a of shallow donors localized states for both n-Si ($\vec{X} // [111]$) and n-Ge ($\vec{X} // [001]$) are in the range (1-5) meV. Taking into account any of scattering mechanisms of accelerated ionizing electrons one obtains non-linear dependencies $E_{br} = f(E_a)$.

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RESEARCH OF A SHALLOW DONOR CENTRES IN A STRONG MAGNETIC FIELDS

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In this paper, we present the results for magnetic freezing of the conductivity band electrons on a shallow donor levels in InP. As a magnetic field modifying an electron wave functions strongly influences upon conditions of an electron localization on the impurity centres the study of a carrier behaviour in the strong magnetic field is interesting to receive an information about the impurity levels nature. The experimental data given in this report are the results of Hall measurements in strong pulse magnetic field up to 300 kOe in temperature interval from 1.4 K to 300 K.

The threshold magnetic field values from which the electron freezing process begins and donor concentrations of investigated samples are given in the Table 1.

Tab.1

Tab.2

samp.	H _c , exp., kO		N _d	H, kO	B	x	N, cm ⁻³ ·10 ¹⁵	E _b , eV
	4.2 K	20 K						
1	10	26	5,4·10 ¹⁵	60	9.5	3	7.6	4.8
2	16	30	9·10 ¹⁵	90	12.5	5.	4.9	5.5
3	32	36	1,8·10 ¹⁶	120	15.3	6.6	4	6.1
4	56	58	3,1·10 ¹⁶	150	18.5	8.5	3.2	6.5
5	68	68	3,7·10 ¹⁶	180	21.5	10.8	2.6	6.84
6	87	87	4,7·10 ¹⁶	210	24.2	11.8	2.4	7.3
				240	27.5	13	2.2	7.9
				270	30	14.2	2	7.9
				300	33.2	16.2	1.78	8.15

It is seen, as a temperature rises the magnetic field increases noticeable for investigated samples. For all investigated samples a temperature dependences of Hall constant testify to existence of a two sections corresponding to a continual and activated conductivity, respectively. If the R_e is the Hall constant at the impurity exhaustion temperature then

$$R/R_e = (x+b^2)(x+1)/(x+b)^2$$

where $x=n_1/n_2$ is the electron concentration relation in a conduction and impurity bands, $b=u_1/u_2$ is the mobility relation. The characteristic data for a sample N3 are shown in Table 2.

The data received as a result of evaluation of the donor ionization energy and the possibility to study the conductivity type in the impurity band allow us to hope for the further prospects of this method.

IMPURITY STATES IN NARROW BAND SEMICONDUCTOR IN A HIGH MAGNETIC FIELD

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Studied is the ground state of a shallow impurity in a narrow-band semiconductor in a high magnetic field ($H \cdot 10^5$ Oe) for the value of the parameter $x = \frac{a_B}{a_H} \gg 1$ (a_H is the magnetic length, a_B is the Bohr radius of bound state). To the two-band approximation the total energy E of the impurity state is determined from the Kane's analog of the Klein-Gordon equation in a magnetic field ($\vec{H}$ is directed along the z-axis) with additional potential energy $U(r) = -\frac{Ze^2E}{\mu s^2 r} - \frac{Z^2 e^4}{2\mu s^2 r^2}$ (Z is the impurity center charge, e is the effective charge and μ is the effective mass of electron, s is the nonparabolicity parameter, $s \approx 10^8$ cm/s for InSb).

To the adiabatic approximation $\hbar\omega_H \gg \mu e^4/\hbar^2$ ($\omega_H = eH/\mu c$) the analytic form for the lowest energy E_{z0} , corresponding to the motion along $\vec{H}$, is found from the expression [1]

$$E_{z0} = -\frac{\mu}{2\hbar^2} \left[\int_{-\infty}^{+\infty} \bar{U}(z) dz \right]^2 = \frac{E_0^2 - \mu^2 s^4}{\mu s^2} - \frac{\hbar\omega}{2}, \quad (1)$$

where $\bar{U}(z)$ is the effective potential along the z-axis obtained by the averaging of $U(r)$ over the radial wave functions R_{00} of the ground state for transverse motion in magnetic field. By solving the equation (1) the explicit form for $E_0(H, s)$ and then for $E_z(H, s)$ is obtained; at $s \rightarrow \infty$ the expression for $E_{z0}(H, s)$ transforms in an analogical expression for the standard dispersion law i.e. $E_{z0} = -\frac{2\mu Z e^2}{\hbar^2} \ln^2(x)$ [2]. The graphical dependence of $E_{z0}(x)$ is obtained. It is shown, that the nonparabolicity leads to the increase of bound energy of impurity states.

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ANOMALIES AND ZEEMAN SPECTRA OF THE LYMAN SERIES OF NEUTRAL ZINC IN GERMANIUM

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Neutral zinc in germanium is a double acceptor, binding two holes at low temperatures. The site symmetry of this substitutional impurity is T_d with $\{\Gamma_8 \times \Gamma_8\} = \Gamma_1 + \Gamma_3 + \Gamma_5$ as the symmetries of the "ground state" orbitals. It has been established that the Γ_1 state, a singlet, has the lowest energy of this manifold [1-3]. The earlier Zeeman studies [3] were for the magnetic field $B \parallel \langle 100 \rangle$ and concentrated on the G line to a large extent. We have now extended these measurements to the D line and with $B \parallel \langle 111 \rangle$.

The unperturbed Lyman series for this impurity is typical of all the neutral acceptors except that the lowest energy transition, the G line, is split into two lines with a spacing of 0.22 cm^{-1} , unlike the single G line of the group III acceptors [4]; this splitting is the same for samples cut from several ingots. However, it cannot be due to splitting of the above $\Gamma_1 + \Gamma_3 + \Gamma_5$ manifold, as is the case for Be in Ge [5], since only the G line exhibits it, which also rules against internal strain as the origin of this effect. In addition, the energy spacings between the G line and the other lines of neutral zinc are different to those for all other neutral acceptors. Further, at temperatures where the energies of the lines of group III acceptors stop changing, those of neutral zinc continue to decrease in energy as the temperature is further lowered. Another observation is that all the neutral zinc lines are significantly broader than are those of the other acceptors. A conjecture regarding the origin of the latter has been put forward [6]. These results will be presented and discussed.

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EFFECTS OF IN-PLANE MAGNETIC FIELDS IN THE ACCEPTOR-RELATED PHOTOLUMINESCENCE SPECTRA OF p-DOPED COUPLED-WELL SUPERLATTICES

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A theoretical study of the acceptor-related photoluminescence spectra of p-doped coupled-well GaAs-(Ga,Al)As semiconductor superlattices under in-plane applied magnetic fields is presented. We use an expansion in terms of sine functions¹ to obtain the electron and hole magnetic Landau levels whereas the acceptor states² are described in the effective-mass approximation, with envelope-wave functions taken as products of sine and hydrogenic-like variational functions. The full quantum-mechanical photoluminescence spectra associated with Landau conduction magnetic carriers recombining with acceptor states are calculated for a homogeneous distribution of acceptor impurities throughout the semiconductor superlattice. The theoretical photoluminescence peak positions for GaAs-(Ga,Al)As superlattices with different ratios of well and barrier widths are in excellent agreement (see one particular result in Figure 1) with available experimental data³.

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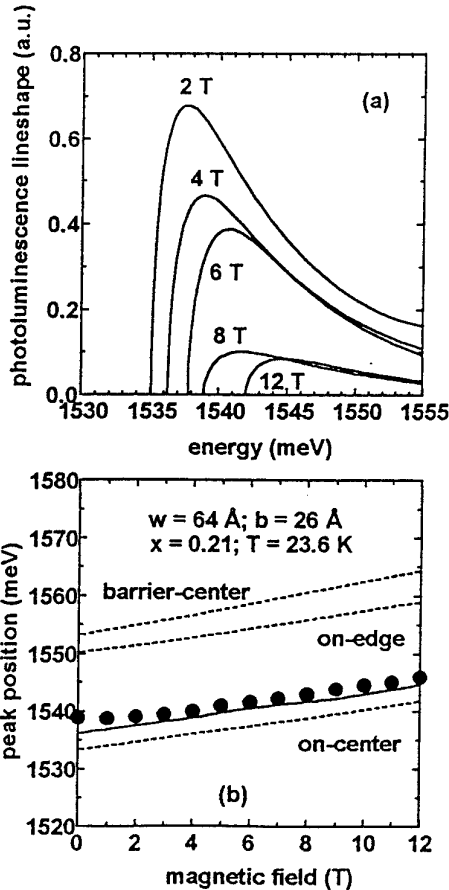


Figure 1. (a) Acceptor-related photoluminescence spectra, for in-plane magnetic fields, for a 64 Å well, 26 Å barrier GaAs-Ga_{0.79}Al_{0.21}As superlattice, and T = 23.6 K. (b) In-plane magnetic-field dependence of the photoluminescence peak position for electron-to-acceptor transitions for the same superlattice as in (a). Dashed lines are associated to theoretical transitions to acceptors at the barrier-center, on-edge (at the interface), and on-center (center of the GaAs well) positions. The full curve corresponds to the peak positions of the theoretical photoluminescence spectra, whereas full dots are the experimental data by Skromme et al³.

RESONANCE EFFECT IN AN IMPURITY QUANTUM WELL SUBJECT TO ELECTRIC AND STRONG MAGNETIC FIELDS

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An analytical approach to the problem of an impurity electron (or hole) in a quantum well (QW) subject to electric and strong magnetic external fields both directed perpendicular to the hetero-planes is developed. The effect of the magnetic field on the electron is much greater than that of the Coulomb field of the impurity centre. It is shown that the combined potential acting on the electron (or hole) resembles that of a double quantum well. One effective well is formed by the Coulomb potential and the QW boundary closest to the impurity. A second triangular effective well is formed by the electric field potential and the other boundary of the QW.

For a weak electric field in the zeroth approximation the system of the energy levels is the sum of two independent series of energies. The first series is the quasi-Coulomb levels slightly changed by the electric field. The electron having these energies is localised within the impurity well. The second series is formed by the "electric" levels and the electron is localised within the triangular effective well. For a sufficiently weak electric field the group of the "electric" levels has a higher energy than the quasi-Coulomb group, so that the relevant states are not in resonance. If the electric field increases in magnitude the shift of the "electric" levels toward lower energies exceeds the shift of the quasi-Coulomb levels. As a result, the relevant quasi-Coulomb and "electric" levels appear to be in resonance.

In the next approximation when these resonance levels associated with the two effective QWs anti-cross, the impurity single QW can be treated as a resonance structure. The explicit dependencies of the resonance splitting upon the width of the QW, the magnitudes of the electric and magnetic fields and the position of the impurity centre are obtained. The resonance splitting of energy levels ΔW having the resonance energy $W = -R/2\lambda^2$ where R is the impurity Rydberg constant and λ is the quantum number, has the form

$$\Delta W = 2R\beta^{1/2}s^{1/3}\lambda^{-3}\exp\{-[2/(3s\lambda^3) + \lambda\ln(s\lambda^3/8)]\}; \quad \beta = \text{const.}$$

where $s = E/E_0$ is the electric field E scaled relative to the impurity electric field

$$E_0 = (1/2)[e/4\pi\epsilon\epsilon_0 a_0^2] \quad (a_0 \text{ is the impurity Bohr radius}).$$

This gap defines the tunnelling time $\pi\hbar/\Delta W$ and in turn the frequency of the emitted radiation $\omega = \Delta W/\hbar$ relevant to the inter-well oscillations of the electron. Estimates of the expected splitting and frequency are made using typical values associated with GaAs QWs. We take $a_0 = 98.7 \text{ \AA}$, and $B = 40 \text{ T}$. For the splitting of the ground quasi-Coulomb and "electric" levels ($\beta = 0.01$) caused by the resonance electric field $E = 710 \text{ kV m}^{-1}$ we obtain $\Delta W = 1.84 \text{ meV}$. This gap corresponds to a frequency of 0.44 THz for the emitted radiation. The considered electric field causes the penetration through the potential barrier separating the effective well to be relatively weak. This in turn leads to the result that a wide GaAs QW width of $d = 600 \text{ \AA}$ is needed to demonstrate this effect. When the QW becomes narrower the penetration increases and the analytical approach becomes inappropriate. However, clearly in the presence of a stronger electric field the effect of the resonance splitting holds for QWs of standard width $d \sim (3-5)a_0$. In this case, a numerical approach should be used.

POSTER SESSION P1

Doping limits and control over impurities

P1-14 ./ P1-20

Shallow doping of wide-band gap II-VI compounds

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For wide-band gap II-VI semiconductors, doping limits and compensation phenomena are typical. Native defects and residual impurities as well as interactions between each other control the doping efficiency in a complex manner. In this paper we present a comprehensive study about the incorporation of p- and n-type dopands in CdTe, ZnTe and ZnSe. Electrical and photoluminescence measurements, being sensitive on shallow levels, were performed on samples doped by ion implantation (ISOLDE, CERN). Proper thermal treatment prior and subsequent to implantation ensures a well-defined deviation of stoichiometry and allows to remove almost completely radiation damage. Transmutation doping turned out to be a powerful tool to clarify defect interactions. Besides stable elements, we have implanted native or isoelectronic isotopes ($^{107}\text{Cd} \rightarrow \text{Ag}$, $^{115}\text{Cd} \rightarrow \text{In}$, $^{85}\text{Sr} \rightarrow \text{Rb}$, $^{75}\text{Se} \rightarrow \text{As}$) transmuting into relevant dopands or instable isotopes of the dopands themselves ($^{111}\text{Ag} \rightarrow \text{Cd}$, $^{73}\text{As} \rightarrow \text{Ge}$). Using half-life as fingerprint, doping features or compensating centres occurring in electrical and optical measurements can be assigned unambiguously to extrinsic dopands. We have found an almost one-to-one doping efficiency, suppressing thermally determined compensation.

Gap states caused by oxygen precipitates in Czochralski silicon wafers

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Many trials have been made to clarify how the variation of heat-treatment condition, i.e., the temperature and the time duration, influences the shape, size and density of oxygen precipitates (OP). However, there are only a few studies about impurity levels throughout the band gap caused by oxygen precipitation and moreover, there have been no common understanding for gap-state energies. We clarify the gap levels caused by the oxygen precipitation.

Samples used for experiments were p- and n- type Czochralski Silicon wafers both having (100) surface orientation, initial oxygen concentration of $1.5 \times 10^{18} \text{ cm}^{-3}$ and a resistivity $10 \text{ } \Omega \text{ cm}$. We used three wafers for both conduction types, which were subjected to the following types of two-step heat treatments : (I) $500 \text{ }^{\circ}\text{C}$, 10 h + $700 \text{ }^{\circ}\text{C}$, 60 h, (II) $500 \text{ }^{\circ}\text{C}$, 10 h + $900 \text{ }^{\circ}\text{C}$, 60 h, (III) $500 \text{ }^{\circ}\text{C}$ 10 h + $1100 \text{ }^{\circ}\text{C}$ 60 h. The first step of these annealings was performed to increase the number of OP. The second step of the annealings was carried out to control the shape and size of OP.

From the observation of chemically etched cross section of the p- and n-type wafers subjected to the above-mentioned heat treatments, we found that a large number of small size OP have been formed during the low-temperature heat treatments (I) and (II). In contrast, in the case of high-temperature heat treatment (III), a small number of large OP have been formed. From the transmission electron microscope (TEM) observation, the typical shapes of the OP formed in heat treatment (I), (II) and (III) are sphere, platelet, octahedral, respectively.

Gap levels caused by oxygen precipitation were determined by deep level transient spectroscopy (DLTS) technique. Results for heat treatment (I) are shown by the solid curve in Fig. 1. The peaks of the density of states caused by oxygen precipitation exist at about $E_v + 0.3 \text{ eV}$ and $E_c - 0.25 \text{ eV}$. This distribution is very similar to that of the Si/SiO₂ interface states in MOS structure. There are some papers reporting that the oxygen precipitates cause the levels at about $E_v + 0.3 \text{ eV}$, but there have been no earlier papers reporting the state at about $E_c - 0.25 \text{ eV}$. We conclude that both these levels are caused by the oxygen precipitation and their energies are very close to those of Si/SiO₂ interface states. In the case of annealing (II) and (III), the peak intensities are less than 1/10 of that for the annealing (I). This phenomenon that the peak intensity decreases with increasing annealing (OP formation) temperature is also similar to the case of Si/SiO₂ interface states. For all cases of the annealings, the position and the over all shape of the peaks are almost same, suggesting that the same defect (impurity) levels are produced independent of the annealing temperature i.e. independent of the shape of OP.

In order to confirm the analogy between the gap-states caused by oxygen precipitation and the Si/SiO₂ interface formation, we examined the hydrogen passivation effect for the gap states. The hydrogen passivation of the Si/SiO₂ interface states is a well known. For this purpose, some p- and n- type wafers subjected to the heat treatment (I) were further annealed at $450 \text{ }^{\circ}\text{C}$ for 30 minutes in pure hydrogen atmosphere. The density of states after annealing in hydrogen atmosphere are described by the dashed curves in Fig. 1. Both peaks of the density of states in the gap (solid curve) have been greatly reduced by hydrogen annealing, showing that the gap states associated to oxygen precipitates have been at least partially passivated. When similar experiments were performed in a pure nitrogen atmosphere, the density of states did not change, confirming that the reduction of the peaks of gap-state density are due to the hydrogen passivation, not to a simple heat treatment effect, such as annihilation of the defect.

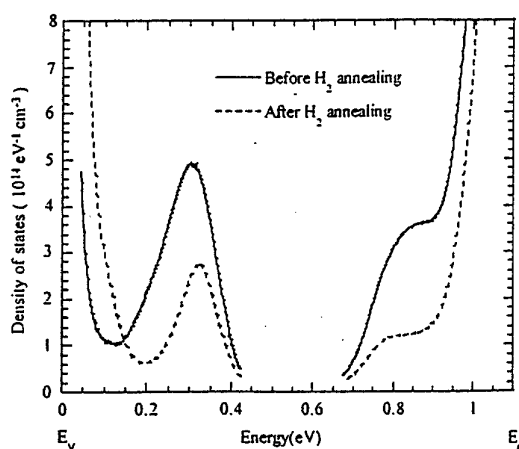


FIG. 1. Distributions of the gap-state density caused by oxygen precipitates in the wafer subjected to the two-step heat treatment (I) $500 \text{ }^{\circ}\text{C}$, 10 h + $700 \text{ }^{\circ}\text{C}$, 60 h in nitrogen atmosphere. Solid and dashed curves are the gap-state densities before and after the annealing in hydrogen atmosphere, respectively.

Shallow donors in silicon crystallized from amorphous phase via a silicide mediated epitaxy

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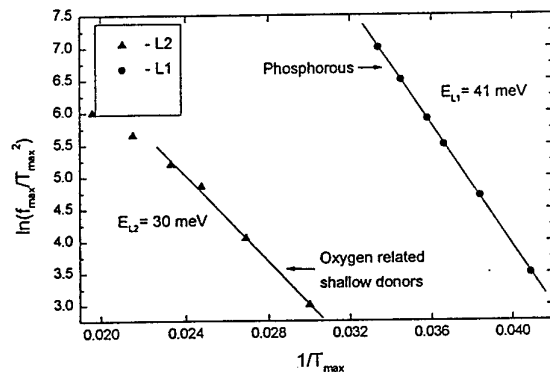
Solid phase epitaxial crystallization of amorphous silicon (a-Si) is, frequently, an inevitable step in the fabrication process of Si-based electronic devices. In particular, the crystallization of a-Si layers, deposited on large-area substrates, is one of the few possibilities to improve the performance of thin film transistors. During the recent decades it was a continuous target (i) to improve the structural quality of the crystallized silicon layers and (ii) to decrease the crystallization temperature. Recently, silicide mediated epitaxy has been suggested to satisfy both challenges. The low-temperature epitaxy of a-Si was demonstrated indeed, e.g., in a-Si/Ni/c-Si structures.¹ However, the degradation of electrical properties in the silicon layers crystallized at low temperatures has not been addressed in detail so far. For instance, the role of the generation of oxygen related shallow thermal donors (STD) was never addressed. In its turn, (i) oxygen incorporation is very probable during the deposition of a-Si layers and (ii) the temperature of the crystallization anneals limits the thermal budget of the further processing.

Extensive electrical characterization of silicon layers crystallized via the low-temperature silicide mediated epitaxy was undertaken in this study. Capacitance and conduction measurements, applying capacitance-voltage (C-V), deep level transient spectroscopy (DLTS), thermally stimulated capacitance (TSCAP) and admittance spectroscopy (ADSPEC), were used to correlate carrier concentration profiles with impurity profiles (measured by secondary ion mass spectrometry) and

elucidate the energy levels of electrically active defects. In addition to the phosphorous related level (L1 in Fig.1) another shallow level (L2 $\cong$ 30 meV below the conduction band) was discovered and attributed to oxygen related donors.

It has been suggested that STD's are singly passivated thermal double donors (TDD)² but we found no such TDD's in our measurements. Furthermore, the concentration of STD was never previously found at such high level ($4 \times 10^{16} \text{ cm}^{-3}$ according to TSCAP), and it is therefore not clear if the shallow level originates from STD's. However, since oxygen

was the only contamination in the film available at the amount comparable with the carrier concentration in our structures, we, therefore, strongly assume that shallow defects (L2 in Fig.1) are oxygen related.



¹ For instance, a-Si layers were successfully crystallized at 400 °C, see A.Yu.Kuznetsov, I.I.Khodos, J.Linnros, B.Mohajeri, E.V.Monakhov and B.G.Svensson, Mat.Res.Soc.Symp.Proc., 355 427(1995).

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MAGNESIUM IMPLANTATION IN SILICON BY MEANS OF
LASER RADIATION

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This is a report on the results of a series of experiments connected with magnesium implantation into silicon by laser beam with the purpose of manufacturing photoresistors working in the infrared range of atmospheric optical windows (3-5 μm and 8-14 μm).

It is known that magnesium impurity doping in silicon at melting temperature during its growing process is difficult because of the low segregation factor and high value of magnesium vapor springiness.

As a primary material plates (p-Si<111>) with the resistivity of $\rho \sim 20\text{-}40\text{k}\Omega\cdot\text{cm}$, on whose surface magnesium was thermally evaporated in vacuum, were used. The conductivity type of the samples was measured by means of termoprobes.

After the laser irradiation of the samples by pulses ($\lambda=1,06\text{ }\mu\text{m}$, $\tau \sim 0,4\text{ }\mu\text{s}$, $W=1,5\text{ J/cm}^2$) melting of the samples' surface and change of the conductivity type from p-type to n-type with $\rho \sim 5\text{ }\Omega\cdot\text{cm}$ resistivity was observed. The current-voltage curves of sandwich structures prepared on the base of irradiated samples showed rectifying behavior, which indicates the formation of n-p junction. The penetration depth of the n-p junction indicates a very high "nonequilibrium" diffusion coefficient of magnesium atoms in silicon in the course of the laser pulse duration. This does not coincide with well-known data about the thermal diffusion coefficient.

The energy parameters of the trap level were determined by the measuring the spectra of thermostimulated currents (TSC) in 77-300 K temperature range.

As distinct from the primary samples where no peaks on the spectra of the thermostimulated currents indicated, the irradiated samples showed a current peak at the $T_{\text{max}} = 105\text{K}$ on the TSC of Si<Mg>.

It is known [1] that under certain conditions TSC intensity on the initial part can be presented as:

$$I_{\text{TSC}} \sim \exp (-E_i / kT),$$

where E_i is the trap level calculated from the nearest permissible band. The energy of the trap level determined in this way was $E_i = E_c - 0.13\text{eV}$, and the depth of the level defining dark conductivity was $E_c - 0.29\text{eV}$. These values coincided with the known data about the energy levels of magnesium in silicon [2].

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LATTICE DEFECTS IN UNDOPPED CdAs₂ MONOCRYSTALS

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Cadmium diarsenide is an anisotropy semiconductor with energy band $\epsilon_s \approx 1$ eV and has a great birefringence value, $\Delta n = 0.32$ [1]. Low-temperature Hall measurements show that the electron concentration in undoped CdAs₂ is determined by the concentration of intrinsic defects responsible for a shallow donor level in the band gap with an activation energy $\epsilon_1 < 0.02$ eV [2]. Information about the other levels created by structural defects is absent.

Recent advances in the directional growth of CdAs₂ crystals by the vertical Bridgeman technique allowed us to prepare large perfect single crystals. For these crystals at 77-293 K we have investigated the spectra of optical absorption $\alpha(h\nu)$ and photoconductivity (PC) at the edge of the fundamental absorption ($h\nu = 1.4$ eV); the PC spectra in the range of impurity absorption ($h\nu = 0.5$ eV); Hall effect and conductivity. The concentration (n) of electrons, their mobility (μ) and the absorption coefficient (α) at 293 K of the investigated samples were about $n = (0.6-5) \times 10^{15} \text{ cm}^{-3}$, $\mu = (1.7-1) \times 10^3 \text{ cm}^2/\text{V.s}$, $\alpha(h\nu = 0.84 \text{ eV}) = (0.4-4) \times 10^{-2} \text{ cm}^{-1}$. We established the existence of two donor levels with energies $\epsilon_2 = 0.25$ eV and $\epsilon_3 = 0.42$ eV. We have evaluated the concentration of the defects responsible for the levels with ϵ_1 , ϵ_2 , ϵ_3 . The scheme (model) of formation of these defects was suggested: the interstitial Cd_i atoms in different charge states created the ϵ_1 and ϵ_3 levels, the As vacancies created the ϵ_2 level.

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Effect of melt stoichiometry on shallow acceptor formation in heavily doped GaAs

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The behaviour of group II, III, IV and VI dopants in vertical Bridgman (VB) grown GaAs was studied in dependence on the stoichiometry of the melt. The melt composition was abruptly changed from stoichiometric to Ga-rich by intentional injection of Gallium during the crystal growth. This results in significantly different concentration of native point defects in the crystal which, in turn, strongly influence the incorporation of dopants and the formation of related complexes.

The samples investigated were vertical ingot sections photoetched using diluted Sirtl-like etchant to reveal the stoichiometric and Ga-rich sample areas. Both areas were investigated by photoluminescence (PL) spectroscopy which gives qualitative information about electrically active defects from the characteristic spectral positions of the related PL modes. Most of the samples show strongly different PL features between stoichiometric and Ga-rich areas. In GaAs co-doped with Si and B, for instance, the dominating PL mode includes (e, h) - and (Si_{Ga}, h) -transitions in the stoichiometric part whereas (e, Si_{As}) - and $(e, B_{As}^{o/-})$ -related modes dominate in the Ga-rich part. Pronounced PL intensities related to As-sublattice acceptors also appear in B, Ge and (Ge+B) doped samples. In some cases, the assignment of the PL modes was possible in comparison with data from literature and with respect to the results of complementary SIMS, Hall and Raman measurements. In GaAs:Sn and in group VI doped samples, however, the Ga-injection causes acceptor-related PL modes not yet reported.

Ag AND CuAs SHALLOW DOPANTS IN TlInSe₂ SINGLE CRYSTALS

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TlInSe₂ is a p-type A³B³C₂⁶ semiconductor with a layer-chain structure. The objective of this work was to study the effect of doping with Ag and Cu on the electric and photoelectric properties of TlInSe₂ single crystals.

TlInSe₂ was synthesized by heating a mixture of high-purity Tl, In and Se for 4-6 h at 1086 K in quartz tubes evacuated to 10⁻²-10⁻³ Pa. Single crystals were grown by the Bridgman method at 0.5-0.8 mm/h and cooled to room temperature at 5-10 K/min. Group I (Cu,Ag) dopants (0.01 at %) were introduced during crystal growth.

Conductivity of doped and undoped TlInSe₂ crystals was measured between 256 and 1100 K. At high temperatures, all of the crystals exhibit intrinsic conduction with a thermal activation energy of 1.2 eV, as assessed from the slope of Arrhenius plots. In the range 256-500 K, the plots have different slopes. The corresponding activation energies E_t are listed in the table together with room-temperature resistivities. These data show that the introduction of 0.01 at % copper and silver results in decrease of resistivity of TlInSe₂ by ~ 6 and ~ 30 times, respectively.

Electric and photoelectric properties of undoped and doped TlInSe₂ single crystals

Composition	ρ_{293} ($\Omega \cdot \text{cm}$)	E _t (eV)	τ_1 (ms)	τ_2 (ms)
TlInSe ₂	2.5×10^4	0.23	0.26	0.26
TlInSe ₂ <Cu>	4.0×10^3	0.09	0.40	0.38
TlInSe ₂ <Ag>	8.7×10^2	0.04	0.58	0.60

The photoconductivity buildup and decay times, τ_1 and τ_2 , in these crystals are evaluated and given in the table.

Thus, doping with group I (Cu,Ag) elements provides a means of controlling the electric and photoelectric properties of TlInSe₂.

POSTER SESSION P1

Defect interactions and metal-insulator transitions

P1-21 ./ P1-31

**ELECTRONIC PROCESSES RELATED TO DONOR-ACCEPTOR PAIR
BLUE ANTI-STOKES LUMINESCENCE IN ZnSe CRYSTALS**

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Low temperature blue “edge” photoluminescence (PL) of ZnSe consists of free and bound excitonic transitions and of free-to-bound and shallow donor - shallow acceptor pair (DAP) processes. Recently we have reported the observation of a strong blue PL of ZnSe bulk crystals excited with the light of the energy smaller than the emission energy [1]. PL excited at these conditions is called anti-Stokes luminescence (ASL). In ZnSe:Cr crystals strong blue ASL, with a zero phonon line (ZPL) at 2.692 eV, is due to shallow donor- shallow acceptor DAP PL and is observed at the excitation energy of 2.41 eV. The appearance of the ASL and its relatively large quantum efficiency (about 10^{-3}) we explain by two complementary ionisation transitions of chromium ions. The ASL emission we also observe in undoped ZnSe samples. There, the ASL excitation is partly explained by ionisation transitions of lattice acceptors of ZnSe. This process of the ASL excitation is less efficient than that observed in chromium doped ZnSe samples. Both for Cr-doped and for undoped samples the ASL emission consists of “shallow” DAP transitions, which are replaced by free-to-bound processes for temperatures above 20 K. However, for the above band gap excitation the “edge” PL is dominated by excitonic processes. The mechanisms of the ASL excitation and of carrier trapping are discussed aiming to explain the ASL and PL emissions and their relative intensities observed under various excitation conditions. In particular, in addition to simple two-step excitation processes, due to complementary ionisation transitions of chromium (acceptor) ions, co-operative Auger-type processes are also suggested. The observed differences of the ASL and PL spectra for below (ASL) and above band gap (PL) excitations are related to competition of recombination and trapping processes of free electrons and holes.

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**MOBILITY EDGE IN NONDEGENERATE SEMICONDUCTOR
WITH RANDOM POTENTIAL OF CHARGED IMPURITIES**

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The low-temperature mobility saturation and the negative magnetoresistance (NMR) in a nondegenerate three-dimensional (3D) electron gas in compensated *Ge* were observed and shown to be due to strong localization and magnetic field suppression of electron-wave interference, respectively. Localization of electrons at the presence of charged impurities is due to mobility edge existence. The latter, in turn, has usually believed as a result of interference of electron waves at multiple coherent backscattering. On the other hand, a disorder in charged-center positions gives rise to a random Coulomb potential and classical percolation threshold. The question is what is the physical cause for the mobility edge in this case. The data presented in this report show that for a system of charged scatterers, the mobility edge arises due to quantum percolation and not due to multiple coherent backscattering.

Ge crystals doped with deep multiply charged impurities (*Cu*) and compensated with shallow donors (*Sb*) were studied. The mobility saturation and NMR were observed at the temperatures of freeze-out of shallow donors being in thermal equilibrium with the conduction band. The quasi-Fermi level position depended on donor population. The latter, in turn, was determined by extra donor concentration, when more than acceptor concentration, and by light excitation from deep acceptors, when partially compensated. The quasi-Fermi level in these crystals lies in the gap and so the electron gas is nondegenerate. The mobility edge for conducting electrons exists due to strong charged impurity scattering. Near the mobility edge, the electron wavelength, λ , should be of order of its mean free path, l . This strong-localization condition can be easily fulfilled in compensated semiconductor. In our crystals, the mobility edge energy can exceed mean thermal energy, kT , at the temperatures up to 60K and moderate impurity concentration. At low T , due to Boltzmannian 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. The electron-electron interaction is negligible because of small electron concentration.

The low-temperature saturation of mobility determined from classical magnetoresistance confirms the mobility edge existence. The electron mobility near the mobility edge is highly non-classical. The saturated mobility value appears to be inversely proportional to the mobility edge energy rather than the impurity concentration and is, in fact, Mott's minimum metallic conductivity for single electron.

The negative magnetoresistance near the mobility edge turns out to be small (several percents) although it is expected to be of order of unity as relative quantum corrections to the conductivity in 3D case should be of order of λ^2/l^2 . Small values of NMR and low magnetic fields for NMR saturation show that the electron-wave interference on closed trajectories of small radii is strongly suppressed at the mobility edge. The reason for vanishing short closed trajectories is the long-scale random potential of charged impurities.

All three effects: shallow donor freezeout, NMR and mobility saturation, were observed below some critical temperature, T_c , obeying the condition $kT_c = \gamma$, γ is the random potential magnitude. The influence of the random potential of charged impurities on transport and recombination phenomena is discussed.

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NITROGEN-OXYGEN COMPLEXES IN SILICON

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Nitrogen is an electrical inactive impurity in silicon. It has been widely studied because of its advantages of the suppression of microdefects and the increase of mechanical strength. Interacting of nitrogen with oxygen impurity in NCZ has been reported. It is well known that nitrogen atoms in Czochralski silicon interact with oxygen impurity to form N-O complexes which can display electrical activity as shallow thermal donors. Furthermore, N-O complexes have been found to suppress the formation of thermal donors. Some researchers have considered that a N-O complex consisted of a bridging oxygen atom adjacent to a nitrogen pair or of one oxygen atom and two or three pairs of nitrogen atoms. It has been reported that the 240, 242, 249 cm^{-1} absorption lines are associated with N-O complexes in the spectra of Fourier Transmission Infrared Spectroscopy (FTIR) in the far infrared range. It was also proven by FTIR experiments at room temperature and at low temperatures ($< 8 \text{ K}$) that the 1026, 996, 801 cm^{-1} absorption lines are the local vibration modes of the N-O complexes in the middle infrared range. It was reported that two other weak absorption lines whose positions are 1018 and 810 cm^{-1} are also associated with the local vibration mode of the N-O complexes and are due to the disturbance of oxygen atoms on nitrogen pairs. However, these two lines were not observed and confirmed by the other experiments.

In this paper, the annealing behavior of the N-O complex in Cz silicon has been investigated. The samples containing N-O complexes were cut from a Cz silicon ingot grown in a nitrogen protective gas. The samples were annealed at the temperature of 450-1150 $^{\circ}\text{C}$ for 10, 20, 30, 60, 90 and 120 min. in a argon atmosphere, and were measured by FTIR at the low temperature (8 K) at the middle and far infrared range. Subsequently, the samples were annealed up to 24 h and were measured by FTIR at room temperature. The relations of N-O complex absorption lines between the middle and far infrared range have been built up. It is found that only during annealing at 550 $^{\circ}\text{C}$, the two weak 1018 and 810 cm^{-1} lines were found in FTIR spectra. It is considered that there are the five types of N-O complex which are represented by the different infrared absorption lines, and have the different thermal stability.

BREAKDOWN OF SHALLOW DONORS LOCALIZED STATES ON
INSULATING SIDE OF STRAIN-INDUCED METAL-INSULATOR TRANSITION
IN SILICON AND GERMANIUM CRYSTALS

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The strain-induced transition from metallic-type conductivity to the activation-type one was investigated in uncompensated Si:Sb, Si:P, Si:As and Ge:Sb crystals at $T=4.2$ K. In order to extend essentially the range of the donors concentration where MI transition takes place we decided to control the critical concentration by extremely high uniaxial strain which remarkably changes the values of the conduction band parameters. Therefore, silicon and germanium specimens were deformed in $[111]$ and $[001]$ directions, respectively. In Si the pressure $X // [111]$ causes the deformation-induced non-parabolicity of $\delta(1)$ -minima. In germanium the uniaxial pressure $X // [001]$ leads to the $L(1)$ - $\delta(1)$ -inversion of the type of the conduction band absolute minima at $X > 2.1$ GPa. Due to these transformations of Si and Ge conduction bands the essential increase of shallow donors ionisation energy takes place. In degenerately doped silicon and germanium crystals these mechanisms lead to the strain-induced transition from metallic-type conductivity to the activation-type one. MI transition observed is accompanied by the decrease of Si and Ge conductivity by (3-6) orders of magnitude and by the transformation of the linear low stress CV-characteristics into the s-shaped ones in the high uniaxial stress range. The dependences of the activation energy value vs. uniaxial pressure ($E(a) = f(X)$) were determined for Si:Sb, Si:P, Ge:Sb crystals. The dependences $E(a) = f(X)$ exhibit two different slopes which correspond to a weak and more strong localization of electrons. The occurrence of the localized states in degenerately doped n-Si and n-Ge has been demonstrated clearly in shallow impurity concentration range $N(c) < N(d) < 5N(c)$ as well. The analysis of the data obtained demonstrates that the effective mass donors conception and scaling theory of localization are the fairly good treatments of the strain-induced MI transition phenomenon.

OPTICAL ABSORPTION LINES DUE TO H₂-RELATED DEFECTS IN Si

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Recently, experimental and theoretical studies have been shown on the vibrational frequency of hydrogen molecule (H₂) in semiconductors. Fukata et al.[1] first reported a Raman line of H₂ at 4158 cm⁻¹ in n-type Si doped with H by remote hydrogen atom treatment. On the other hand, Pritchard et al.[2] reported some optical absorption lines, 3788.9, 3730.8 and 3618.3 cm⁻¹, in hydrogen-doped CZ.Si crystal. The last one was also observed in FZ.Si doped with H. They proposed that the former two and the last one correspond to H₂ molecule bound to oxygen atom and free state, respectively. Theoretical calculation supports the above interpretation.[3] Fukata et al.'s result was interpreted to be due to H₂ in a void, a cluster of vacancy.[3] It is interesting for us that the vibrational frequency strongly depends on impurities near to H₂. The aim of our research is to study optical absorption peaks due to H₂ in electron- and neutron-irradiated Si to investigate vibrational frequency of H bound to irradiation-induced point defects.

Specimens were prepared from FZ.Si and CZ.Si. After hydrogenation by high temperature annealing of specimens in H₂ gas, specimens were irradiated with high energy (3MV) electrons. We measured optical absorption spectra with FT-IR equipment at about 10 K with the resolution of 0.25 cm⁻¹.

In FZ.Si without electron irradiation, we observed a peak at 3618.4 cm⁻¹, in good agreement with Pritchard et al. This was also observed in CZ.Si with much weaker intensity. After electron-irradiation, we observed 3 peaks at above 3000 cm⁻¹ and a lot of peaks around 2000 cm⁻¹. The latter were studied already by other group [4] and will not be shown here. The former 3 peaks are at 3618.4, 3942.0 and 4154.5 cm⁻¹. The first one is at the same position to that before irradiation. Naturally, its intensity was weaker than that before irradiation. The intensity of 3942.0 cm⁻¹ peak is fairly strong. The intensity of 4154.5 cm⁻¹ peak is very weak. However, this peak is interesting since its position is near to that observed by Fukata et al. from Raman spectroscopy. The latter two are probably due to vibration of H₂ bound to vacancy. Thermal stability of those peaks will be shown.

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**METAT-INSULATOR TRANSITION INDUCED BY
SHALLOW DONOR IMPURITY IN n-ZnSe**

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By means of dosed variation from 2×10^{16} to $2 \times 10^{18} \text{ cm}^{-3}$ of the shallow donor Al impurity concentration in n-ZnSe a metal-insulator (MI) transition from activated conductivity to non-activated one is obtained in the low-temperature limit. In the temperature range from 1.6 to 300 K the peculiarities of resistivity ρ , Hall coefficient R and electron mobility $R\sigma$ dependencies on temperature are investigated while transition from a metallic conduction to an activated one. On the dielectric side of the transition as the temperature decreases the conduction with an activation energy ε_1 induced by electron excitation from the impurity states into the conduction band is replaced by the hopping conduction with a constant activation energy ε_3 , which in the lowest temperature region is transferred to a hopping conduction of variable activation energy. It is established that the replacement of the activated conduction by a metallic one occurs at $N_D = 1.3 \times 10^{17} \text{ cm}^{-3}$ and takes place within the impurity band before it attains the bottom of the conduction band. Actually, the weak dependence of $R\sigma$ upon temperature in sample with the concentration $N_D = 1 \times 10^{17} \text{ cm}^{-3}$ (near to critical concentration $N_c = 1.3 \times 10^{17} \text{ cm}^{-3}$) is indicative of the already metallic character of the conduction in the impurity band, while the coupling of the impurity band with the bottom of the conduction band takes place at somewhat higher donor concentration ($N_D > 5 \times 10^{17} \text{ cm}^{-3}$). The MI transition obtained by the dosed change of the shallow donor impurity concentration of aluminum in n-ZnSe crystals in the critical region has properties which are similar to the Anderson transition, i.e. it is caused by localization of electrons in the density-of-states "tails" of the impurity band. The electron concentration at the transition from the metallic state to the dielectric one is continuously varied as a consequence of a chaotic distribution of donors in the crystal.

It is established that at sufficiently low temperatures on the dielectric side of the MI transition $\rho \sim \rho_0 \exp(T_0/T)^{1/2}$ which is indicative of the presence of a parabolic Coulomb gap at the Fermi level. The main parameters of the Coulomb gap: width, depth and density of states are determined and their concentration dependencies also investigated. The critical behavior of the Coulomb gap parameters within the scope of the scaling theory and the dynamics of its collapse at the transition are described. Attention is drawn to the behavior of the concentration dependence of the preexponential factor ρ_0 . Following the decrease in ρ_0 while approaching the transition an abrupt increase is observed and after that the decrease of this parameter in the critical region of the transition is repeated. As the ρ_0 value is determined by the probability of hopping between localized impurity states, the decrease of this parameter left-hand of the minimum reflects the approaching of the impurity atoms as the donor concentration grows. Further increase of N_D leads to a growth of ρ_0 . This experimental fact was not observed previously and is explained as start of electron localization in the Anderson sense, as a result of which the electron localized in the density-of-states tails are found to be separated by hardly permeable barriers, which present difficulties for the tunneling process. Thus the deep minimum in the $\rho_0(N_D)$ dependence is due to replacement of electron localization on separated impurity centers (at low N_D) by Anderson's localization. The decrease of ρ_0 in the critical region of the transition reflects the increase of the tunnel transparency of the fluctuation barriers separating the density-of-states tails in the immediate vicinity of the MI transition.

It is found that the localization radius of the electron wave function, dielectric permittivity, density of states at the Fermi level as well as several other parameters characterizing the conductivity at the dielectric side of the transition are continuously varied over the critical region of the transition according to the scaling theory of localization. It is shown, that the critical concentration and critical indices for the MI transition obtained by doping have somewhat lower values than that for the transition produced by compensation. The symmetry of the MI transition formed by doping is established.

**EXCITED STATES OF A HYDROGEN-INTRINSIC DEFECT-
RELATED DOUBLE DONOR IN SILICON**

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IR absorption appeared due to electronic excitations in the vicinity of a hydrogen-intrinsic defect-related double donor in proton-implanted crystalline silicon (Si:H) was studied. 30 MeV protons were implanted into p-type silicon at temperatures of $< 50^{\circ}\text{C}$ and at doses of 10^{16} - $5 \times 10^{17} \text{ H}^+/\text{cm}^2$ through aluminum screens. After annealing at 400 - 450°C during 15 min, the Si:H samples were kept for sufficient time at 70 - 230°C with following quenching in water.

IR studies of the quenched Si:H samples at 300 K shows that a strong free-carrier IR absorption associated with the conduction band electrons is reversibly changed by quenching at various temperatures. It is found that a decreasing of the measurement temperature up to 80 K causes the considerable decreasing of the free-carrier IR absorption while a broad feature in the range of 500 - 2800 cm^{-1} , with the maximum intensity at $\sim 600 \text{ cm}^{-1}$, and the 375 cm^{-1} band appear in the spectra. The intensities of these absorption bands are also reversibly changed by quenching. It is shown that the broad feature arises due to electronic transitions between the conduction band and the $E_s \sim E_c - 0.1 \text{ eV}$ and $E_t \sim E_c - 0.06 \text{ eV}$ levels while the 375 cm^{-1} band is related to the $E_s \Rightarrow E_t$ excitation. The data obtained allow to conclude that the E_s and E_t levels are connected with a ground spin-singlet and an excited spin-triplet neutral states of the hydrogen-intrinsic defect-related shallow donor, respectively.

It is interesting that the triplet E_t state also shows the properties of the ground state. The broad feature in the range of 500 - 2800 cm^{-1} and the 375 cm^{-1} band strongly correlate with a set of the relatively weak IR absorption bands at 400 , 440 and 465 cm^{-1} . The energy differences between the 400 , 440 and 465 cm^{-1} bands are in a good agreement with those predicted by the EMT theory for the $2p_0$, $2p_{\pm}$ and $3p_{\pm}$ excited states of a hydrogen-like donor. So, it is reasonably to conclude that the 400 , 440 and 465 cm^{-1} bands are related to the electronic excitations from the triplet E_t state to the $2p_0$, $2p_{\pm}$ and $3p_{\pm}$ excited states of the hydrogen-intrinsic defect-related shallow donor.

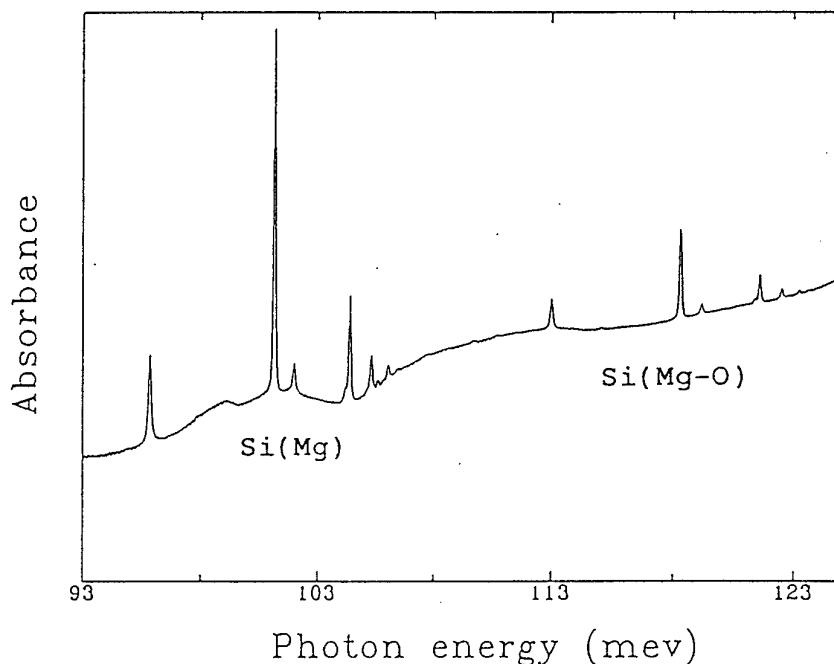
The data obtained and the data of the Si-H bond-stretching and bond-bending local vibrational modes analyses allow us to suggest that the hydrogen-intrinsic defect-related donor is an interstitial-type complex with two possible configurations of C_2/C_s - and C_{2v} -symmetry. The configuration of an another acceptor-type H-related complex which acts as a compensating center is also proposed.

MAGNESIUM-OXYGEN COMPLEX IMPURITIES IN SILICON

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It is well-known that lithium is an interstitial impurities in silicon. Lithium can also complex with dispersed oxygen in silicon to form lithium-oxygen complex impurities. Both Li and Li-O in silicon are shallow donors.

Magnesium is another interstitial donor impurities in silicon. When diffused into silicon containing oxygen, the excitation spectrum observed clearly demonstrates for the first time that magnesium, similar to lithium, can also complex with oxygen to form magnesium-oxygen complex donors.



**NEW COMPLEX DEFECT IN HEAVILY DOPED GaAs:Zn GROWN BY LIQUID PHASE
EPITAXY**

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The electrical and photoluminescence properties of heavily doped GaAs:Zn (100) layers grown by liquid phase epitaxy from gallium and bismuth solutions at various temperatures have been studied. It is shown that a new line at 1.35 eV appears in low-temperature photoluminescence spectra of the layers doped at a level above 10^{19} cm^{-3} . It is found that this line is not associated with Cu but it is connected with the novel defect. The concentration of the defects increases with the doping level proportionally to the concentration of free holes to the power 5.35 ± 0.1 . The power index is independent of the growth solution used (gallium or bismuth) and the growth temperature. In order to identify the nature of this defect data on the changes of defects concentration depending on the growth temperature, doping level, and metal solvent was analysed. The data obtained in electrical measurements was also analysed. It has been found that the defect is a neutral complex consisting of the native point defects of GaAs – an antisite defect of gallium on arsenic site and two arsenic vacancies.

A scheme describing the formation of a complex composed of intrinsic point defects in GaAs:Zn was proposed. This scheme is universal and not bound to any specific impurity or to a method of material preparation. The formation of similar defects can be expected in heavily doped GaAs layers and possibly in other compounds of the type A_3B_5 obtained by different methods and doped with an impurity (for example, beryllium) which gets built into the crystal in two forms, i.e., as a substitution atom and as an interstitial atom.

NITROGEN-HYDROGEN DEFECTS IN GaP

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Nitrogen impurities are important exciton traps in GaP and the observations that hydrogen can complex with N has stimulated wide interest. Recently, three vibrational modes due to a nitrogen-hydrogen defect have been reported and assigned to an NH_2 defect. However, *ab initio* calculations of the vibrational modes of this defect leads to modes which do not exhibit the observed isotope shifts. We thus propose that the defect consists of a single H atom bonded with N. This new model can account for the observed modes and their isotope shifts, as well as the effect of photo-excitation which leads to changes in the frequencies. The model assumes that one of the high frequency modes is an overtone of a H-bend mode and the evidence for this is discussed.

SHALLOW - LEVEL CENTERS OF INTERCALATION IN LAYERED STRUCTURES

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The investigation of energy spectra of the layered crystal with the interstitial impurities has been carried out. As follows from the studies of the intercalation phenomenon the random distributed impurities interact with the atoms of the neighbouring layers and form the "covalent bridges". Naturally, the radical change of the band structure of the layered crystal under the intercalation takes place. Therefore, the problem of localized and delocalized states appears.

Using the Fivas model of the electron dispersion law as the initial one we investigated the energy spectrum of the layered crystal with the "covalent bridges" in the region of the special points (the edges of the main band and the impurity level, real boundaries of the spectrum) in the framework of the method of the group decomposition on the Green's function relative to the concentration of the interacting impurities. It is shown that the presence of the impurity states leads to the complicated rearrangement of electron spectra. It is accompanied by the appearance of the anisotropic impurity band of quasi - Bloch type in the vicinity of the impurity level. It is established that the energy of the local level and the conditions of the formation of the impurity band depend on the ratio between the parameters of the initial dispersion law and the parameter of the hybridization. Other parameters of the crossing rearrangement of the spectrum have been also estimated: the concentration broadening the impurity level, the characteristic concentration at which the formation of the impurity band arises; the concentration dependencies of the boundary wave vectors formed bands in results of the spectrum crossing rearrangement. It is shown that the conductive and the impurity bands reconstruct in dependence on the impurity concentration so as the general anisotropy of the spectrum decreases what promotes the increase of the conductive in the direction perpendicular to layers.

At the same time we carried out the calculation of the percolation threshold taking into consideration the model of a layered crystal with the "covalent bridges", mentioned above. As a result of the computer simulation of the simple anisotropic net the anisotropy of the percolation threshold was found. It is shown that the percolation threshold in the direction perpendicular to layers, decreases by the increase of the "covalent bridges" concentration. It correlates with the obtained decrease of the spectrum anisotropy owing to the crossing rearrangement. This investigation allows us to understand the problem of the activation energy anisotropy in the electro - conductivity phenomenon what does not follow from the classical percolation theory, but it is observed in many chained and layered crystals experimentally.

POSTER SESSION P1

Bound excitons and related topics

P1-32 ./ P1-38

EFFECTS OF CYLINDRICAL BENDING ON BOUND EXCITON LUMINESCENCE IN EPITAXIAL GaAs

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Modern growth techniques such as MBE and MOCVD allow growth of thin high purity semiconductor layers on a much thicker and less pure substrate wafer. Piezo-spectroscopic investigations can provide valuable information on exciton, impurity and defect properties. However, conventional piezo-spectroscopic techniques are not well suited for the thin wafer geometry common for epitaxial samples, and are difficult to implement, while bulk samples are usually of insufficient purity to allow high resolution spectroscopic measurements.

Bending creates a non-uniform strain distribution across a semiconductor wafer. We demonstrate, however, that under certain bending geometries the strain can be highly uniform within thin epitaxial layers. Photoluminescence (PL) of the epilayer can be separated from PL of the substrate under appropriate excitation conditions. This technique allows detailed piezo-spectroscopic investigation of electronic centers in high quality epilayers with very sharp spectroscopic features. In our cylindrical bending geometry, the strain field within the epilayer can be considered as almost uniaxial. This geometry allows measurement of the luminescence polarization in the plains parallel and perpendicular to the strain axis. Polarization measurements provide additional information facilitating tests of theoretical models.

Our piezo-spectroscopic investigations reaffirm that contrary to a wide spread belief the acceptor bound excitons (A^0X) in GaAs should be described by the crystal-field scheme [1, 2] rather than by the original $j-j$ - coupling scheme [3, 4]. This conclusion is reached on the basis of observation that one of the A^0X energy levels which is expected to split in the $j-j$ - coupling scheme under [001] stress, in fact, does not split in agreement with the crystal-field scheme.

We also observe distinct anti-crossing of the two lowest energy levels of donor bound excitons (D^0X) in GaAs under uniaxial stress from the evolution of the polarized PL spectra. This anti-crossing and complex behavior of the D^0X energy levels under uniaxial stress is difficult to explain within the existing models of D^0X [5 - 7]. Further analysis of the piezo-spectroscopic data including polarizations of the spectral components may help to develop a more realistic model of D^0X .

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DYNAMICAL BEHAVIOR OF EXCITONS IN ZnSe STUDIED BY OPTICALLY DETECTED CYCLOTRON RESONANCE

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Optically Detected Cyclotron Resonance (ODCR) is a serviceable technique that combines photoluminescence (PL) with cyclotron resonance (CR) measurements. In ODCR measurements, the change in PL intensity induced by CR are monitored as a function of the applied magnetic field or PL wavelength using highly sensitive optical detection system. Thus, the sensitivity is enhanced and the study of dynamical behavior of free as well as bound excitons becomes possible in ODCR measurements.

ZnSe is one of the most promising materials for fabricating optical devices. We have investigated characteristics of excitonic system in ZnSe single crystals grown via the recrystallization method. The experimental setup for the ODCR was composed of a PL measurement and a 35GHz microwave systems. For PL measurements, He-Cd laser was employed as the excitation source. PL was dispersed by a single monochromator and detected by a photomultiplier. The ODCR signal was caught by a Lock-in amplifier with a microwave modulation technique.

An ordinary electron cyclotron resonance spectrum is shown in Fig.1. A sharp resonance line demonstrates the high quality of the ZnSe sample. Figure 2 shows the spectrum of ODCR at the fixed magnetic field 0.18T, which corresponds to the electron CR condition. The spectrum is dominated by neutral acceptor bound exciton line I_1 , deep acceptor bound exciton line I_1^d , free exciton line FE and their LO-phonon replicas. The ODCR signals of I_1 and I_1^d are negative, which means reduction in PL intensity induced by electron CR. The ODCR signal of FE, on the other hand, is positive. As regards ODCR signals obtained by the microwave modulation technique under CR condition, some peaks among various PL lines increase and surplus peaks decrease. Through ODCR signals gain and loss, we can discuss dynamical behavior of excitons bound by shallow and deep impurities in ZnSe.

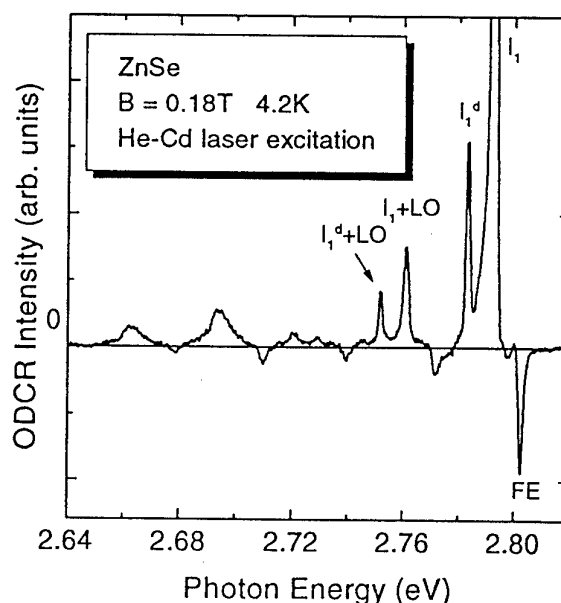
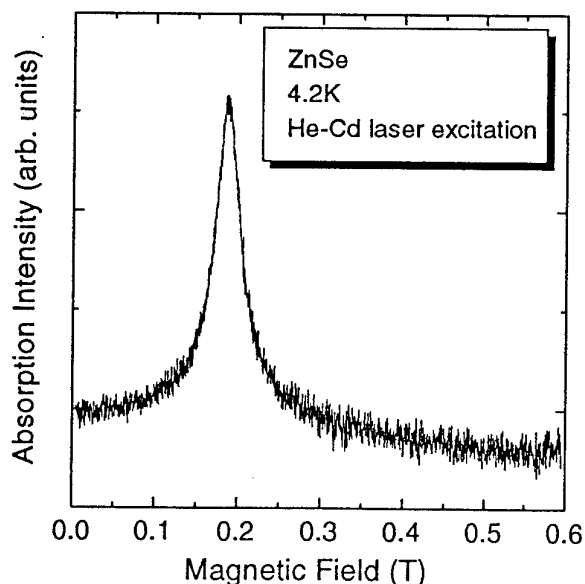


Fig. 1. Cyclotron resonance absorption at 4.2K.

Fig. 2. ODCR signal induced by electron CR.

VISIBLE LUMINESCENCE FROM Si/SiO₂ QUANTUM DOTS AND WELLS: SURFACE LOCALIZATION OF EXCITONS

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Efficient visible photoluminescence (PL) has been observed in low-dimensional Si nanostructures such as porous Si, nanocrystals, and quantum wells. A size reduction to a few nanometers is required for the observation of efficient light emission from Si materials when their band structures are modified from that of bulk Si, which has an indirect gap of 1.1 eV. In low-dimensional nanostructures, quantum confinement effects play essential roles in controlling the optical responses. However, experimental observation of the PL wavelength from Si nanostructures do not show the dependence on size which is expected from simple quantum confinement. In this work, we discuss luminescence mechanisms and electronic structure of shallow surface states in Si/SiO₂ nanostructures.

Zero-dimensional (0D) Si nanocrystals were fabricated by laser breakdown of SiH₄ and microwave plasma decomposition of SiH₄ [1]. Two-dimensional (2D) Si single quantum wells were formed on SIMOX wafers [2]. The surface of 0D nanocrystals was covered by thin SiO₂ layer, and 2D quantum wells were sandwiched by SiO₂ layers. Luminescence properties of 0D nanocrystals are very similar to those of 2D quantum wells. These quantum dots and wells show broad PL in the red spectral region at room temperature. These broad PL spectra suggest that Si/SiO₂ quantum structures are inhomogeneous systems and the inhomogeneously broaden PL spectrum will be due to the fluctuation of the well size, strains and structural variations between c-Si well and SiO₂ barrier layers. In the study of inhomogeneous materials, selective excitation spectroscopy is a powerful method to extract intrinsic properties from inhomogeneously broadened spectra.

For selective excitation at energies within broad PL band, TO-phonon related structures are observed in Si nanocrystals, like bulk c-Si. Since c-Si is an indirect gap semiconductor, the absorption and emission of momentum-conserving phonons are needed for the light absorption and emission processes. However, there is a small energy difference in the TO-phonon assisted luminescence between Si nanocrystals and bulk c-Si (the luminescence Stokes shift). With a decrease of the nanocrystal size, the luminescence Stokes shift increases. Moreover, the phonon-related structures are sensitive to the surface structure of Si nanocrystals. In oxidized Si nanocrystals, the luminescence Stokes shift is large and TO-phonon structures are unclear, compared with the case of H-terminated Si nanocrystals. The Stokes shift of H-terminated Si nanocrystals can be explained by the exciton exchange splitting. The shallow band-edge surface states are formed in surface-oxidized Si nanocrystals.

The asymmetric PL spectra in 2D wells are observed in the red spectral region at low temperatures and can be divided into two PL bands. The peak energy of the strong PL band is almost independent of the well thickness and appears near ~ 1.65 eV. The shallow localized states at the interface between the c-Si interior and the outer SiO₂ layer affects the luminescence properties. Under selective excitation at energies within the weak PL band, TO-phonon structures are observed in both PL and PL polarization spectra. TO-phonon structure in the PL spectrum of 2D Si quantum wells is similar to that of 0D Si nanocrystals. Both the surface and interior c-Si states contribute to efficient PL in c-Si/SiO₂ nanostructures.

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PHOTOLUMINESCENCE OF NITROGEN DOPED ZnSe LAYERS.

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Photoluminescence spectra are widely used to assess the incorporation of nitrogen in the ZnSe and related compounds epitaxial layers. ZnSe layers have been epitaxially grown by MOVPE on GaAs substrates, using dimethylzinc-triethylamine (DMZnTEN) and ditertiarybutylselenide (DTBSe) as precursors and were doped with nitrogen plasma. Photoluminescence measurements at different excitation intensities in the temperature range of 4.2 K to 80 K have been performed on ZnSe layers. It is shown that the presence of nitrogen leads to a photoluminescence spectra revealing acceptor and donor-bound exciton lines, together with a donor-acceptor pair (DAP) band at 2.69 eV and a free-to-bound transition accompanied by their longitudinal optical - phonon side bands. A detailed and coherent analysis of the position, shape and relative intensities of the spectral lines has been carried out by means of an analytical model correlating the position of the zero-phonon lines to the relative intensities of the phonon side bands. The model includes central-cell correction and describes the effect of the charge carrier LO - phonon interaction in the framework of the adiabatic approximation within the envelope function approach. The same model is successfully used to analyse the excitation intensity and temperature dependence of the zero-phonon lines associated to the DAP and free to bound transitions. From the comparison between experiment and theory we obtain the following coherent physical parameters: $E_A = 112 \pm 2$ meV and $r_h = 7.8 \pm 0.5$ Å respectively for the acceptor ionisation energy and radius, $E_D = 25 \pm 2$ meV and $r_e = 24 \pm 0.5$ Å and $S = 0.5 \pm 0.1$ for the Huang-Rhys factor.

SURFACE CENTERS IN PHOTOLUMINESCENCE AND ELECTROLUMINESCENCE OF SILICON MOS STRUCTURES

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A recombination radiation line (D-line) of surface two-dimensional electrons and nonequilibrium holes, bound to surface centers, is observed in photoluminescence spectra of [100] silicon MOS structures [1]. A decrease of a charge of the surface centers with increasing density of bound holes results in a shift of the D-line into the high energy side of the spectrum. The surface centers are identified as surface acceptors with the binding energy of holes about 40 meV and the average distance from the surface about $2 \cdot 10^{-6}$ cm. The states of heavy and light holes of these centers are splitted by the surface potential. Measurements of the circular polarization degree of the D-line in a transverse magnetic field gives the value of the heavy hole g-factor equal to $g_h \approx 0.6$. An origination of the surface centers is discussed.

A recombination radiation line (S-line) of surface 2D holes and 2D nonequilibrium electrons, bound to the [100] hole layer by the hole polarization attraction, is observed in electroluminescence spectra of tunneling silicon MOS diodes under tunneling injection of electrons into the selforganized electron quantum well at $T=1.5$ K. The injection efficiency is close to unit. Besides the S-line, a new recombination line (S_B -line) is observed in the low energy side of electroluminescence spectra. The intensity of the S_B -line goes to a saturation with increasing diode current. The S_B -line can be attributed to radiative recombination of 2D holes and electrons, bound to shallow states of surface centers, or to radiative recombination of surface centers. The nature of these centers is still unknown, but the role of surface chromium and nickel atoms, originating from the metal gate, is discussed. For some structures the S_B -line dominates in the electroluminescence spectrum indicating, that the 2D holes and 2D injected electrons serve as a very effective pumping source for the surface centers. 2D electrons and 2D injected holes have been observed recently in electroluminescence of tunneling silicon MOS structures [2,3] under tunneling injection of holes into the selforganized hole quantum well, but in this case the S_B -line is absent in electroluminescence spectra. The luminescence of surface 2D electrons and holes and surface centers can be used in semiconductor optoelectronic devices.

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CARRIER LIFETIME RELATED WITH IMPURITY-BOUND EXCITONS

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The ultimate performance of many semiconductor devices is limited by the recombination lifetime of the charge carriers. Very recently recombination processes have attracted much interest for two reasons: (i) A.Hangleiter and R.Hacker [1] have developed a new theory about excitonic Auger recombination that has been supported experimentally by many authors (see e.g. [2] and ref.s) in silicon without deep centers; (ii) V.A.Kholodnov [3,4] has shown that the dependence of carrier lifetime on concentration of deep impurities may be non-monoton and its maximal value may be increased by several orders of magnitude. However, Kholodnov [3] did not take into account intrinsic processes such as excitonic-Auger recombination [1,2] that will limit the maximal value of τ . Moreover, Kholodnov studied mainly abstract models of Shockley-Read-Hall [3] and donor-acceptor pair [4] type centers.

The aim of the paper is the investigation of carrier lifetime τ related with impurity-bound excitons. The theory of Kholodnov [3,4] about carrier recombination and lifetime will be modified and extended to describe recombination through excitons bound to impurities. The dependence of τ on concentration of traps N_t and shallow impurities N_d will be presented. Single crystalline silicon samples with radiation defect isoelectronic hydrogen-containing centers [5] and bistable defect interstitial-carbon-substitutional-carbon [6] will be considered. It is well known that non-equilibrium charge carriers recombine through excitons bound to the impurity complexes [5,6]. Total value of carrier lifetime will be evaluated within the theory of [1] and our theory. Experimental results of [2] will be used.

Our calculations showed that the dependence of carrier lifetime τ on doping level N_d in the range $10^{14} \div 10^{17} \text{ cm}^{-3}$ for temperature interval $260 \div 500 \text{ K}$ is non-monoton and has its maximal value when $N_t \approx N_d$. The maximal value of τ is not giant as it was shown in [3] and may be increased only up to excitonic Auger-recombination lifetime.

Temperature dependence of τ when $N_t \approx N_d$ is also non-monoton while when $N_t \neq N_d$ τ monotonically increases with increasing T . For $N_d \leq 10^{12}$ and $N_t \approx 1.4 \times 10^{17} \text{ cm}^{-3}$ temperature dependence of τ fits well with experimental data.

The reason of the unusual dependence of carrier lifetime on trap concentration is discussed in detail in [3] and is related with inertiality of occupancy of deep impurity. For this case the investigation of semiconductor device performance is of great interest.

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IMPURITY-BOUND EXCITONS IN ORDERED GaP:N SYSTEM

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For years, properties of bound excitons were not so attractive and understandable as properties of free excitons. It seems, however, bound excitons (singles, pairs, excitonic molecules) after their proper investigations will be interesting objects for solid state physics and its applications in the nearest future. Especially it concerns to collective properties of high density bound excitons, excitonic molecules as well as phase excitonic transitions in ordered GaP:N system. Except initial theoretical generalization and a set of experimental data in this field to the recent moment there is not any complete picture of the observed phenomena. The main goals of this paper are (i) to discuss the results of investigations of long-term ordering of nitrogen atoms along P sites in 30 years ago grown GaP single crystals and related phenomena in N impurity-bound excitons, (ii) to propose a combine molecular beam and laser assisted method of growth of GaP thin epitaxial films periodically doped with N atoms and (iii) to discuss possible properties of bound excitons in these epitaxial films.

It was early shown by us the system of high density bound excitons can be considered as a solid excitonic phase like to an inverted alkali metal and consisting of a net of negatively charged heavy nuclei (N atom + captured electron) which interacts with a free hole gas. Since electrons are being captured by a short-range potential of impurity states while holes are being bound by a long-range Coulomb interaction, N isoelectronic impurities localize electrons much stronger than holes. Creation of this phase was revealed by p-type photoconductivity of highly optically excited GaP:N in photo-Hall measurements compared to always n-type dark conductivity of these crystals as well as by a specific deformation of luminescent spectrum at high density of bound excitons. It is also shown by luminescence investigations that in spite of nearly random distribution of N impurities along P sites just after growth of bulk GaP:N crystals occupation by the impurities only the anion sites of the crystal lattice, as well as intense Auger recombination between closely located bound excitons (with a distance less than their Bohr radius) give some initial ordering to the solid excitonic phase.

A new stage of Raman scattering and luminescence experiments with the aged (grown in the middle of 60-th) GaP:N crystals started in the end of 80th revealed the following dramatic evolution of their properties.

1. Luminescence of excitons bound to NN pairs which is very intense in heavily doped fresh crystals (average spacing is equal to 3 -5 nm) is completely absent in the same crystals investigated 25 years after their growth. This experimental finding means that the degree of impurity ordering in the aged crystals is rather high compared to the fresh ones. Instead of the pair exciton lines the luminescence spectra of the ordered crystals develop a broad uniform band which maximum shifts to low energies with nitrogen concentration.

2. Zero phonon line A and its phonon replica of single N impurity-bound excitons in the aged crystals shift their positions with concentration of N impurities according to known relation between its position and spacing between nitrogen atoms in GaP anion sites, meanwhile the fresh crystals demonstrate only broadening of the lines when the nitrogen concentration increases. It means that N impurities create in the aged GaP crystals a superlattice with equal to each other spacing. Energies of lattice phonons depend on N impurity concentration reflecting some changes in lattice dynamics.

3. All the details of luminescence and Raman spectra of N impurity-bound single excitons can be observed in aged crystals more clearly than in the fresh ones. It concerns to a very low background of the exciton lines as well as to their small halfwidth and distinct position in the spectrum. In general, GaP:N crystals are considerably more perfect after 25 years than just after their preparation.

New growth technique, such as combine molecular beam and laser vacuum epitaxies discussed in the paper can be applied for preparation of ordered GaP:N epitaxial films, taking into account that the ordered N impurity-bound exciton phase of high density gives new opportunities for appearance of various non-linear optic phenomena, accumulation, conversion and transport of light energy. Thus, the important properties of high density bound excitons observed in long-term ordered bulk GaP:N crystals can be used for application in an artificially created solid bound exciton phase.

POSTER SESSION P1

Wide-gap materials

P1-39 ./ P1-51

Photoluminescence Studies of Mg-doped and Si-doped Gallium-Nitride Epilayers

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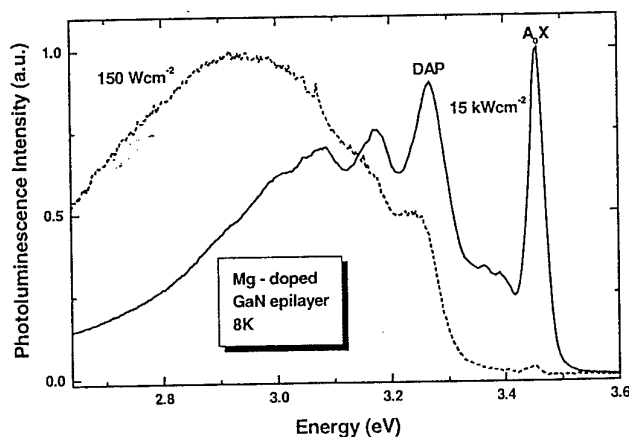
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We present temperature and intensity dependent photoluminescence (PL) measurements of the near band-edge luminescence of Mg-doped (p-type) and Si-doped (n-type) Gallium-Nitride (GaN) epilayers. These were grown by MOCVD on an AlN buffer layer on a sapphire substrate. The p-type layer was post-growth annealed and had an ionized impurity concentration of $3 \times 10^{18} \text{ cm}^{-3}$, and the n-type layer had a carrier concentration of $1 \times 10^{19} \text{ cm}^{-3}$.

The samples were photoexcited using a frequency doubled copper vapour laser producing up to 130 mW of ultraviolet light at 255 nm (4.85 eV) with a pulse duration of 12 ns. The PL was collected using a 0.25 m spectrometer and a nitrogen cooled CCD. The temperature could be varied from 8K to 300K and the intensity of the pump laser beam could be varied from 150 Wcm^{-2} to 15 kWcm^{-2} using neutral density filters.

The low temperature spectrum of the Mg-doped samples shows three different emission bands (see figure). The line at the highest energy (3.455 eV) is attributed to excitons bound to the neutral acceptor Mg. The strong emission line at $\sim 3.2 \text{ eV}$ with several LO-phonon replicas is assigned to a shallow donor to shallow acceptor (DAP) transition. The shallow acceptor is assigned to Mg with an acceptor energy of $\sim 200 \text{ meV}$. The transition shows a blue shift with increasing excitation density, which is typical for distant shallow DAP transitions. The third luminescence band in the low temperature spectrum of Mg-doped GaN is a strong Mg induced blue PL band centred at 2.9 eV. It shows a strong blueshift of $\sim 250 \text{ meV}$ with increasing excitation. This luminescence band has been observed previously in strongly doped GaN films, but its nature is still under discussion. At temperatures under 200 K the overall intensity of the DAP transition and the blue PL show identical linear intensity dependence and identical temperature dependence, which is strong evidence that the blue PL band has donor-acceptor pair character. With increasing temperature, the excitation intensity dependent blueshift of both the DAP transition and the blue PL band gets smaller. This suggests that the DAP transitions are gradually replaced by a free carrier to acceptor (e,Mg) recombination. At room temperature, the PL spectrum is dominated by a deep blue luminescence band centred at 2.7 eV, which doesn't show any blueshift with increasing excitation density. The high efficiency at higher temperatures is probably due to a radiative recombination of free carriers at a deeper Mg related acceptor complex. Further increase in the excitation density leads to the observation of free exciton recombination at an energy of 3.42 eV.

The low temperature PL spectrum of Si-doped GaN layers is dominated by neutral donor bound excitons at an energy of 3.462 eV. At 3.26 eV a weak shallow donor to shallow acceptor transition is observed, together with its phonon replica. The shallow donor is assigned to silicon and the shallow acceptor is probably due to residual magnesium in the growth system. As the temperature is increased, the DAP emission is rapidly quenched and is hardly observable at temperatures above 150K. The energy of the excitonic emission line follows closely the temperature dependence expected for the band gap, confirming that recombination processes in our samples are excitonic in nature.



SELECTION RULES FOR OPTICAL TRANSITIONS
INVOLVING IMPURITIES OR DEFECTS IN HEXAGONAL GaN

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In hexagonal GaN, substitutional impurities and single vacancies occupy sites with C_{3v} symmetry. Interstitial impurities and molecular point defects (paired impurities, double vacancies and vacancy-impurity complexes) occupy sites with C_{3v} , C_s or C_1 symmetry.

We have performed a complete group-theory analysis of state symmetry for bound carriers and bound excitons in hexagonal GaN. At sites with C_{3v} symmetry, bound excitons offer a wider panel of possible state symmetries than single carriers do. In our calculations, we induced representations of full groups from the irreducible representations of subgroups. The main concepts of this method are given elsewhere¹. The spin-orbit interaction has been taken into account. We considered not only s and p states of impurities but also d ones since the latter orbitals correspond to the upper occupied states in, for example, transition metals.

The selection rules for the optical transitions involving bound states as initial and/or final states have been established, including the photon-assisted processes. The results are valid for any crystal with the wurtzite structure.

Polarizations of light respectively along and perpendicular to the symmetry axis are shown to induce very different selection rules. The transitions between bound states and Γ extended ones are of particular importance since GaN is a direct-gap semiconductor : we discuss various situations, such as, for example, the case of some acceptors.

Polarized light experiments are suggested to help in determining the site symmetry of impurities and point defects as well as the symmetry of bound carrier and bound exciton states.

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AB INITIO ACCEPTORS AND DONORS IN GaN AND AlN

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In recent times we have addressed in detail several nitride related doping problems using ab initio LDA calculations. First, we dealt with the issue of identifying theoretically acceptor dopants other than Mg for wurtzite GaN, studying Be, Zn, C, Ca, Cd, and Li (double acceptor), and finding Be and Li to be shallow (albeit difficult to incorporate), with first-ionizations at 0.06 eV and 0.1 eV, respectively, above the valence edge. An analysis of Be-O codoping and of H-acceptor complex incorporation was also performed. We also demonstrated that implanted Li can be thermally activated into substitutional sites, as suggested by channeling experiments.

Secondly, we studied potential dopants for AlN (along with some basic native defects). We found Be and Mg to be deeper than in GaN but still presumably useful (0.24 and 0.44 eV above the valence band respectively). Donors, however, are deep (1.4 eV and 2.1 eV below the conduction band for Si_{Ga} and C_{Ga} respectively); along with the midgap N vacancy levels and with the acceptor character of the Al vacancy, this suggests that n-doping of AlN will be difficult. To properly analyze donors, the AlN theoretical gap was calculated, as all other extrinsic levels, from total energy differences with varying electron number, and found to be about 6 eV.

PHOTOLUMINESCENCE AND ABSORPTION EDGE OF UNDOPED AND DOPED GaN FILMS

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Despite of great achievements in research of III-nitride materials in the last few years, some fundamental problems still remain unsolved, preventing the full realisation of their potential applications. These are, in particular, identification of defects responsible for n-type conductivity and origin of emission bands in nominally undoped films. Our work studies native and impurity related centers in GaN films deposited on sapphire.

The samples were grown by MOCVD technique. Undoped films used were generally n-type with the carrier concentration of $(1-3) \cdot 10^{17} \text{ cm}^{-3}$. The Si doped samples were obtained by doping during growth procedure and showed the carrier concentration of about $3 \cdot 10^{18} - 3 \cdot 10^{19} \text{ cm}^{-3}$. In photoluminescence spectra of the undoped samples, a bound exciton line usually dominates at 3.479 eV and the free exciton A is manifested at 3.498 eV. As a rule, the bound excitons are prescribed to unidentified shallow neutral donors. Some authors suppose these donors to be O, N or Si.

Increasing in Si doping level brings about the following variations in the photoluminescence spectra: the bound exciton line 3.479 eV shifts to the long-wave side so that its position is equal to 3.474 eV at the concentration of $3 \cdot 10^{19} \text{ cm}^{-3}$ and the line intensity grows. We have studied the temperature dependence of photoluminescence spectra and have shown that the bound exciton line has a complicated structure. The half-width of the bound exciton line in undoped samples was found to be $\sim 15 \text{ meV}$, which is probably due to its strong inhomogeneous broadening. The broadening increases with Si doping. As the temperature increases the bound exciton line in the undoped samples shifts to the short-wave side by approximately 2 meV. Such a shift can be considered as due to thermoactivated population of upper energy states in the inhomogeneously broaden line.

It should be noted that although the bound exciton line quenches rapidly with temperature, the intensity of free exciton line does not change in the studied temperature range. This fact means that free excitons decay is mainly nonradiative (for example, through Auger processes).

Comparison of photoluminescence spectra of undoped samples with that of Si doped ones shows the unidentified donor in our undoped GaN cannot be Si. More probably this donor could be associated with O.

Absorption edge tail in Si doped GaN was also studied in the work. It was found that the steepness of the exponential absorption edge changes with doping. Incorporation of Si into GaN lattice gives rise to the long-wave shift of the absorption edge, which can be described in terms of the Urbach rule.

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POLARIZED PHOTOLUMINESCENCE WITH LONG LIFE TIME IN AgGaS₂

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Semiconducting compound AgGaS₂ with chalcopyrite type structure has been extensively investigated as nonlinear optical material. A distortion free and large single crystal is required for the device fabrication. High quality single crystals were successfully grown by a self-seeding vertical gradient freezing method.¹⁾ The large anisotropy of the crystal structure makes difficult both observations of absorbance and reflectance for different polarizations. For the polarization of incident lights that is parallel to c-axis of crystal ($E_{ex} // c$), the 1s and 2s states of allowed A (band gap) exciton are observed at 2.694eV and 2.721eV by reflection measurements.^{2,3)} For $E_{ex} \perp c$, 1s of B (band gap) exciton is observed at 2.98eV.³⁾ Using good single crystals we determine precisely the absorption coefficient near the fundamental absorption edge on thin samples of 100 μ m and observe the polarization effect of photoluminescence (PL) near A exciton.

The absorption coefficient shows the behavior of Urbach tail from 2.60eV to 2.67eV, increases up to 2.685eV and saturates above 2.687eV. It is considered that this saturation above 2.685eV originates in mixing of $E_{ex} \perp c$ -axis component. For $E_{ex} \perp c$ -axis there are sharp peaks of weak absorption at the same energies, 2.694eV and 2.721eV as $n=1$ and 2 excitons in the case of $E_{ex} // c$ -axis. But this absorption coefficient near an $n=2$ exciton state is too large comparing with one for $n=1$. It is considered that this large absorption coefficient at 2.721eV originates in the mixing of 2p states and the absorption is followed by Elliott step. A bump is observed at 2.74eV. As this bump is higher than an $n=1$ exciton state by 50meV, it is considered that this structure comes from the phonon side band of $n=1$ exciton states.

We observe PL peaks near the absorption edge in detail. In the excitations of the high density and the high energy by a cw Ar⁺ laser, PL peaks are observed at 2.695eV of a 1s bound state of free excitons and in its low energy side. But in the low-density excitation by a Xe lamp through a monochrometer, there is no PL originated in free excitons. The observed features are complex and PL peaks depend on measuring methods. Using photon counting measurements of the former case, a sharp distinctive PL peak is observed at 2.610eV near the threshold of absorption coefficient and the broad PL follows it. In the latter case PL peak is at 2.603eV for photon counting measurement. Also this sharp PL shows short decay time, very long decay time as 6.5ms, and longer decay time than 100ms. The PL peak for short decay time is observed at 2.61eV, that is the same energy as the high density case. For the components of long and very long decay time, the peak is observed at 2.603eV. Also the peak energy shifts linearly to higher energy with increasing excitation power density. These imply PL to be donor acceptor pair emission. This sharp PL shows also the following peculiar features. In the case of the polarization $E_{ex} // c$, its excitation spectrum increases from the low energy threshold of absorption in experiments, shows a peak at 2.69eV and decreases up to 2.705eV. It shows a peak at 2.720eV again and decreases to almost zero. In the case of $E_{ex} \perp c$, PLE shows a small peak, a step like increase at 2.715eV and a gradual decrease with increasing excitation energy. For both polarizations of excitation lights, PL with the polarization $E_{PL} // c$ is stronger than PL with the polarization $E_{PL} \perp c$. And there is almost no peak at 2.603eV for excitation by both polarized lights of higher energy than the main absorption peak (2.98eV) for $E_{ex} \perp c$. From the polarization behavior both the centers of donor and acceptor are shallow and they have the characters of the conduction band and the valence band in the band gap A. The main relaxation process from photo-excited states to a donor and an acceptor of the band gap A is the path through the tail states of the gap.

In conclusion PL spectra assigned as DA pair emission with long decay time of PL intensity is observed in AgGaAs single crystal, and their relaxation process is discussed in connection with its absorption spectra.

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Vibrational properties of perfect and imperfect β -SiC

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The electrical and optical properties of silicon carbide have made it attractive for high temperature, high power, high frequency and radiation applications where as the chemical, thermal and mechanical stability of the material has favored it in the utilization of microelectronics devices for blue-green emission, thermistors, and switching devices. This resurgence of interest is caused primarily by the progress in the growth of quality thin films and single crystals. Although the cubic form of SiC (known as β -SiC or 3C-SiC) is the most promising polytype for device applications, the more stable structures are the many hexagonal forms labeled as α -SiC or 6H-SiC. More recently, some useful information about the electronic, vibrational and structural properties of SiC has been obtained both at ambient and high pressures. Several thermodynamic quantities (*viz.*, the mode Grüneisen parameter γ , specific heat, and thermal expansion coefficient $\alpha(T)$) along with lattice, phonon and elastic properties have also been measured experimentally in an extended pressure range. The role of electrically active *shallow*- and *deep*- point defects in β -SiC is, in many aspects, still poorly known. However, studying the vibrational spectrum through infrared (IR) absorption and Raman scattering spectroscopy is an alternative way of investigating the behavior of impurity centers in semiconductors. Earlier, we used the electrical data in conjunction with the expected defect symmetries and calculated the absorption features to assign the site selectivity of defects in semiconductors responsible for the observed bands in optical experiments. The purpose of the present work is to study the vibrational properties of perfect and imperfect β -SiC using realistic lattice dynamical theory. Here, we report our theoretical results for the temperature dependence of thermal expansion coefficient $\alpha(T)$ using a rigid-ion-model in the quasiharmonic approximation. Unlike most other tetrahedrally coordinated materials, we find that the $\alpha(T)$ in β -SiC exhibits a variation with temperature much like that of the specific heat, and it does not attain a negative value at lower temperatures. We also used a Green's function theory to treat the structural and dynamical properties of isolated donors (d^+) [*e.g.*, N-, P-], acceptors (a^-) [*e.g.*, Al-, and B-] and donor acceptor-pairs [N(P)(d^+)-Al(B)(a^-)]. The advantage of our approach over an *ab initio* calculation is that it allows the coupling of the vibrations of the defect to the bulk crystal, and provides a clear visualization of vibrational modes that remain localized around the defect. Theoretical results of the dynamical behavior of N-donors is discussed in relation to the existing IR data. We also predict the possibility of observing 'donor-acceptor' pair vibrations by optical experiments in β -SiC.

STRUCTURAL DISORDERING AND RECOMBINATION PROCESSES IN Co-DOPED ZnSe-BASED ALLOYS

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Transition metal impurities are common inadvertent dopants in wide-gap II-VI semiconductors and can act both as activators and deactivators of visible photoluminescence (PL). Cobalt in binary ZnSe and ZnS was the subject of numerous experimental and theoretical studies (see, e.g. [1, 2]). But to date there is only little information about it in ternary compounds, where one can expect interesting phenomena because of variation of conduction and valence band edges and modified overlap of d-orbitals of Co ions with the p- and s-orbitals of the anions and cations of the host crystal. Besides, unlike other 3d impurities Co is a perfect "probe" for investigation structural and compositional disordering of ZnSe-based alloys, because the covalent radius of Co is similar to that of Zn and, thus, it should not introduce additional distortions into the crystals.

It is accepted [1] that Co²⁺ ions in ZnSe form two levels for d⁷/d⁶ and d⁷/d⁸ charge-transfer transitions. The ground states of these levels are either close to the valence band (d⁷/d⁶) or overlap with the conduction band (d⁷/d⁸). Recently, we reported [3] about drastic change of recombination channels in ZnCdSe:Co and ZnSSe:Co alloys in comparison with the host binary compounds ZnSe and ZnS. Both bound excitons, DAP PL, phonons and internal d-d Co²⁺ transition bands are strongly modified. Two additional bands appear in emission, arising from the excited internal d-d Co²⁺ states, located very close to the conduction band edges.

To understand reasons for the new emission bands observed, ESR and photo-ESR investigations have been done for the same sets of ZnCdSe:Co and ZnSSe:Co alloys for the wide range of Cd (0.0 - 0.5) and S (0 - 1.0) compositions and temperatures (2 - 300 K). The Co concentration of all samples was equal to 1.10¹⁸ cm⁻³, approximately. Essential change of low temperature ESR spectra is observed in the alloys in comparison to those in the host binary compounds ZnSe and ZnS, beginning from Cd or S content x=0.001. A character of the change is different for the alloys with anion and cation substitutions, and for the last ones it is more pronounced. Several new bands with a fine structure appear which predominate over Co-induced ESR signal (on a site with tetrahedral symmetry) with an increase of Cd or S content. An analysis of trigonal Co centres and complexes of Co ions with donors and acceptors is presented. The observed signals are photo-sensitive and their nature is under consideration.

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PIEZOSPECTROSCOPY OF SHALLOW LYING EXCITED STATES OF ACCEPTOR EXCITONS ON (TiN)⁺-PAIRS IN 6H-SiC CRYSTALS

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The excitation spectrums of photoluminescence (PL) of separate lines of a known ABC-spectrum due to three inequivalent sites of atoms in the lattice 6H-SiC [1] have shown that ABC-spectrum and observable near the long-wavelength edge of a fundamental band the $\alpha\beta$ -absorption lines [2, 3] are caused by impurity centers of same chemical nature [4]. At that turned out that $\alpha\beta$ -absorption is caused by transitions in shallow-lying excited singlet states and PL – by transitions from more deep-lying triplet states of the bound excitons [4]. This assumption was confirmed by investigations of Zeeman effect of zerophonon lines of PL A_0 , B_0 and C_0 , at that the interaction of moments of an electron and hole has the $L-S$ -type coupling. Moreover, the conclusion is made that the B-center is a pair defect [5].

Further was found out that the ABC-spectrum is caused by the isovalence impurity atoms of Ti [6], which in configuration $3d^3 4s$ isoelectronically substitute atoms of Si and return four valence electrons for formation of hybrid bonds with $2s2p^3$ orbitals of the carbon neighbours [7]. Ti is the getter for nitrogen, therefore meets in a lattice SiC only in pair with N. In n-type nitrogen-doped crystals the weakly bound electron of neutral N which substitutes the carbon in one of three equivalent sites (in plane (0001)) is being captured in a $3d$ -shell of Ti. In an outcome the low-symmetric (C_s) neutral center (TiN)⁰ with a spin $S = 1/2$ is forming [8]. On such isoelectronic $3d$ -center in crystals of a p-type or in strongly compensated – of n-type ones, when the center (TiN)⁺ is ionized, the only acceptor exciton (AE) [$d^{n+1}h$] can be formed what corresponds to experiment [3, 5]. At the photoexcitation the electron from valence band is being captured by a short-range potential on a $3d$ -shell of Ti, and the weakly bound by Coulomb interaction hole from valence band remains on a hydrogen-like orbit. Hence, the $\alpha\beta$ -absorption spectrum should reflect not only the complicated energetical structure of AE caused by combination of wave functions of a d -electron and p -hole with antisymmetric spin function, but also the structure and parameters of valence band similarly to RS-absorption spectrum of excitons bound to neutral nitrogen donors [9].

We have carried out an investigation of $\alpha\beta$ -absorption spectrum at $T = 4.5 K$ and strain of uniaxial compression along crystallophysical axes $Z\langle 0001 \rangle$, $X\langle 2\bar{1}\bar{1}0 \rangle$ and $Y\langle 01\bar{1}0 \rangle$ for various directions of a wave vector and polarization of the radiation. As well as it was expected, the group of α -lines caused by A-centers [3, 4] with cubic coordination of the nearest environment, which can be described by symmetry C_{3v} parentaging from T_d , except splitting of some of them, are shifting with growth of stress similarly to RS-absorption lines, and with close displacement velocities. The spectrum of β -lines due to B-centers with hexagonal coordination of the nearest environment [3, 4] is a little bit more complicated than the α -spectrum. It is caused by a lower symmetry of the B-center C_s parentaging from a symmetry C_{3v} . Proposed genesis of energetical states of AE and the group theoretical selection rules qualitatively describe the complicated $\alpha\beta$ -absorption spectrum and its behaviour in a field of uniaxial stresses.

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NATIVE-DEFECTED NATURE OF ELECTRICAL ACTIVE CENTRES IN LOW-RESISTIVITY ZINC SELENIDE

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ZnSe single crystals grown by various methods have a high resistivity ($\rho \sim 10^8 \dots 10^{10} \Omega \text{ cm}$). High-temperature annealing in liquid Zn sharply reduces their resistivity. It has been supposed previously that the increase of conductivity in process of such thermal treatment is stipulated by a decrease of compensation degree of unknown nature shallow donors, concentration of which is changed slightly. On the other hand, the results of excitonic spectroscopy of n-ZnSe crystals annealed in Zn melt have shown cogently that occupation of acceptor defects V_{Zn} leads to generation of the shallow donors V_{Se} . The question arises, what of two factors is responsible for decrease of n-ZnSe crystal resistivity in the process of annealing in liquid Zn: either the increase of electrical activity of the shallow non-controlling donor impurity because of their compensation decrease or the increase of concentration of the donor type native defects V_{Se} . A single meaning answer on this question is not exist at present.

In this work it has been shown for the first time that the native defects of donor type – selenium vacancies, compensation of which increases sharply at such annealing, are the shallow donors determining the high conductivity of n-ZnSe crystals annealed in Zn melt. Hall effect, electrical conductivity and charge carrier mobility in n-ZnSe crystals annealed in liquid Zn during the 100 h are studied in the temperature range from 55 K up to 500 K. The annealing temperature has been varied in the range from 500 °C up to 950 °C.

It has been established that the donor concentration increases on the order and it reaches the value of $N_D = 1.6 \times 10^{17} \text{ cm}^{-3}$ as the annealing temperature increases from 600 °C to 800 °C. The acceptor concentration increases more weakly to the value of $N_A = 5.5 \times 10^{16} \text{ cm}^{-3}$. Thus, the sharp increase of the shallow donor concentration is accompanied by the decrease of their compensation from $K = N_A/N_D = 0.91$ to $K = 0.35$ as the annealing temperature increases. Then the activation energy of the shallow donors E_D is decreased from 28 meV to 9 meV. The annealing temperature increase above 800 °C leads to saturation of N_D , N_A , K and E_D parameters on the value levels indicated above. Then the equilibrium in composition of the native defects V_{Zn} and V_{Se} in the investigated crystals is reached. It has been affirmed that at low annealing temperatures of n-ZnSe crystals the conductivity is determined by electrons activated from the shallow non-controlling donors as Al_{Zn} (20 meV), Ga_{Zn} (22 meV), In_{Zn} (24 meV). The concentration of V_{Zn} compensating the shallow donors is sharply decreased with increase of the annealing temperature in liquid Zn. In one's turn, it leads to increase of V_{Se} concentration, which are shallow donors with ionization energy of ~ 10 meV. Thus, the observing increase of the shallow donor concentration and the decrease of their ionization energy to 9 meV, as the annealing temperature increases, are the consequence of sharp increase of V_{Se} native defects concentration. The results of the exciton spectroscopy indicate also the increase of V_{Se} concentration with increase of annealing temperature of n-ZnSe in Zn melt. It has been established that the charge carrier scattering on the impurity ions is weakened with the increase of n-ZnSe crystals annealing temperature in liquid Zn and the role of phonon scattering increases in the investigated temperature range. Electron mobility increases with the annealing temperature increase and it is saturated at the temperatures above 700 °C. It has been shown that the decrease of the charge carrier scattering on the impurity ions and the increase of mobility with the increase of the crystal annealing temperature are stipulated by the decrease of the shallow donor compensation degree and by the increase of the impurity ions screening by free electrons.

Anomaly low values of charge carrier mobility ($\sim 8 \dots 10 \text{ cm}^2/\text{Vs}$ at 77 K) and extremely high photosensitivity of n-ZnSe samples annealed in Zn melt at 600 °C can't be explained within the limit of homogeneous isotropic semiconductor model. High concentration of acceptor type V_{Zn} native defects, that compensate non-controlling shallow donor impurity, promotes the forming of random impurity potential, modulating band edges. Arising drift and recombination barriers in this case impede the transfer of charge carriers and their recombination. The increasing of crystal annealing temperature promotes the effective occupation of V_{Zn} and the disappearance of anomalous phenomena connected with high level of major impurity compensation.

TWO-ELECTRON RECOMBINATION PROCESSES IN THE WIDE-BANDGAP SEMICONDUCTORS WITH SHALLOW IMPURITIES.
THE BLUE SHIFT OF THE RADIATION BAND.

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Two-electron recombination processes in the impurity centers of the wide-bandgap semiconductors for the case of low temperature are considered. The energy of the emitted photon is $\hbar\omega = \varepsilon_1 + \varepsilon_2$, where $\varepsilon_1, \varepsilon_2$ - are the energies of the bond electrons of the local centers 1 and 2, respectively.

In the case of optical recombination through the elastic scattering mechanism the exact two-electron Coulomb wave function in the conduction band is taken into account. The case of the nonelastic scattering mechanism which is accompanied by the generation of photon and phonons is considered as well. It is shown that the shape of the optical radiation band is narrow enough if the elastic scattering mechanism of recombination processes is realized under the low temperature. For the nonelastic scattering mechanism of recombination processes the width of the optical radiation band is larger due to the phonon emission. The intensity of the recombination processes depends on the square of the impurity concentration (for the impurity of the same type) and linearly depends on the carrier concentration. In the case of the optical recombination on the levels of shallow acceptors the luminescence band shift in the blue side is expected to be observed. In this case the energy of the luminescence maximum is nearly two time larger in comparison with the energy of the intrinsic luminescence maximum. The role of the virtual states in the position of the band maximum and the band shape of the two-electron optical recombination is discussed using the Feynman diagram method.

SHALLOW-LEVEL STATES IN AMORPHOUS SILICON CARBIDE

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The physical properties of shallow electrically active centers in SiC and in the SiC/Si interface are of interest because the presence of such centers, associated with the structural defects, dramatically affects the parameters responsible for the operation efficiency of optoelectronic and microelectronic devices, such as, for example, the efficiency of radiative recombination and the minority carrier lifetime.

Low-temperature thermally stimulated charge release (TSCR) technique was used for investigations of shallow traps in the amorphous SiC. TSCR measurements have been carried out in the structure Al-SiC-pSi at temperatures from 6 to 160 K. The TSCR currents were found to consist of two parts manifested in different temperature ranges. The lower-temperature peak, with the maximum at about 15 K, was attributed to the shallow traps situated in the thin transition layer near the SiC/Si interface. Activation energies of the charge release process are 28, 36 and 45 meV for electron traps possessing levels near the bottom of the conduction band, and those for hole traps near the top of the valence band equal to 20, 26, 36, 45 and 55 meV.

The levels $E_C-0.036$, $E_C-0.045$, $E_V+0.036$, $E_V+0.045$ and $E_V+0.055$ eV were observed in the Al-SiO₂-pSi structures and were attributed to the presence of local defect centers in the transition SiO_x layer in the silicon-oxide interface. The similar behaviour of the TSCR currents in SiO₂-Si and SiC-Si structures enables one to draw the conclusion that near the SiC/Si interface the transition non-stoichiometric layer exists containing shallow traps with the same properties as those in the transition SiO_x layer. Such traps are commonly related to the presence of dangling silicon bonds, strained Si-Si bonds, other structural defects. The levels $E_C-0.028$, $E_V+0.020$, $E_V+0.026$ are specific for the SiC/Si interface.

The broad higher-temperature TSCR peak was observed in the temperature range from 40 to 160 K. This peak was associated with the deeper electron traps located in the SiC layer. Mathematical processing of the experimental spectra has shown that the SiC/Si heterojunction contains, in addition to the system of shallow centers, the system of deeper electron traps possessing levels situated at 0.016, 0.08, 0.16 and 0.22 eV below the conduction band. Investigations of deeper traps in the lower half of the bandgap using the TSCR technique are not possible, since an attempt of filling the hole traps by the forward bias did not result in any measurable charge release current in this temperature range. In this case the negative voltage at the metal electrode (forward biased heterojunction) does not lead to an increase of band bending near the interface but results in the higher forward currents.

Investigations of the traps in the lower half of the bandgap were carried out by measuring the forward current-voltage (I-V) characteristics in the temperature range from 40 to 80 K. In this case the current is controlled by the well-known Poole-Frenkel thermally activated emission of holes via the system of centers near the top of the valence band. From these measurements the well-depths of the hole traps in the SiC layer were found to be 0.15 and 0.23 eV. The above results indicate that activation energies of hole traps have the same values as that of the electron traps. This means that the structure of localized shallow-level states in the bandgap of amorphous silicon carbide is symmetrical.

PHOTOCONDUCTIVITY OF ZnSe CRYSTALS UNDER HIGH EXCITATION RATES

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The physical nature of defects of crystal lattice and electronic levels in wide-bandgap semiconductors can be investigated effectively using pulsed laser irradiation. The generation-recombination processes in zinc selenide have been studied on the basis of investigations of pulsed and steady-state photoconductivity of different crystals before and after irradiation with ruby or neodymium laser pulses of 20 ns duration of subthreshold intensity. Also the role of laser-induced point defects and related levels in the revealed phenomenon of the laser photosensitization of ZnSe single crystals has been analyzed.

Depending on the method used to prepare ZnSe the samples distinguished both by the defect structure and by the concentration of accidental impurities. Undoped, cubic, high-resistivity n-type ZnSe single crystals with different degrees of purity as well as Mg- and Cu-doped ZnSe were the subjects of investigations. The energy of laser quanta was less than the band gap of ZnSe thus uniform generation of carriers took place in the bulk of samples. This allowed the parameters of impurity centers with short relaxation time to be estimated from results of measurements of lux-ampere characteristics and the photoconductivity kinetics.

Lux-ampere characteristics of ZnSe crystals consisted of the linear, quadratic and again linear ranges. These three ranges corresponded respectively to impurity generation of carriers with linear their recombination, band-band generation resulting from the two-photon absorption and putting the quadratic recombination channel. At low excitation rates the slow component in the photocurrent relaxation curves was observed and an amplitude of this component was saturated with increasing the intensity of laser radiation pulses. The fast component of the photoconductivity relaxation appeared with putting the two-photon absorption at the intensity of laser pulse $\sim 10^{24}$ quant $\times$ cm $^{-2}$ $\times$ c $^{-1}$. The peculiarities of lux-ampere characteristics and photocurrent kinetics signified that recombination of the nonequilibrium carriers occurred on two channels S_1 and S_2 . The concentration of the recombination centers S_1 and S_2 , their recombination coefficients and trapping sections were calculated.

It was established that multiple irradiation of ZnSe crystals with laser pulses of the intensity close to breakdown threshold increased the steady-state photoconductivity and altered the profile of the photoconductivity spectra. The integral photosensitivity increased by a factor of ~ 20 -100, depending on the sample. The photosensitization was observed only for samples with low accidental impurity concentration ($\leq 10^{16}$ cm $^{-3}$); in this case the dark conductivity was not affected.

The reasons for the photosensitization of ZnSe crystals were determined and the mechanisms of laser irradiation were identified using the results of investigations of the photoluminescence and Raman scattering spectra. A reduction in the intensity of the exciton photoluminescence, and the appearance of two additional peaks in the Raman scattering spectra, and also a rise of the optical absorption were evidence of an increase in the total number of point defects in ZnSe crystals after laser irradiation.

An increase in the photoconductivity was due to an increase in the nonequilibrium carrier lifetime that was manifested in a rise of the slow component of the photocurrent relaxation. This was explained by the formation of the slow recombination centers, which could be Zn vacancies counter-balanced by shallow donor centers (possibly of interstitial Zn). The change in the occupancy of the recombination centers (or an increase in the number of these centers) occurred in such a way that the contribution of the recombination flux via the fast recombination centers decreased. Lux-ampere characteristic of the photosensitizative sample was similar to one of unirradiated samples at higher amplitudes of photocurrent pulses.

Doping of ZnSe crystals led to formation of deep levels in band gap of ZnSe and the changed the recombination fluxes via S_1 and S_2 centers. The certain features of lux-ampere characteristics of ZnSe:Cu and ZnSe:Mg crystals before and after irradiation were studied and nature of the electronic levels was analysed. Based on study of the photoconductivity spectra the depths of impurity levels in the doped ZnSe crystals were determined.

It was shown that an increase in the steady-state photosensitivity which took place in ZnSe crystals with low concentration of accidental impurities after irradiation with laser pulses of wavelengths corresponding to the transparency range, could influence the operation of optical components based on ZnSe and used in the of power infrared optics.

NONRADIATIVE CARRIER RECOMBINATION IN P-TYPE ZnSe THIN FILMS GROWN BY MOLECULAR BEAM EPITAXY

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Zinc selenide (ZnSe) is one of the promising materials for blue light-emitting devices. Recently, the study on nonradiative recombination processes due to crystal defects in ZnSe are great paid attentions since these crystal defects may prevent the CW laser oscillation at room temperature.

Piezoelectric photoacoustic (PPA) measurements have recently been carried out as one of the new methods to know the physical properties of semiconductors. The great advantage of using the PPA measurements is that the nonradiative recombination processes are able to be measured directly. Therefore, the PPA technique may complement a photoluminescence (PL) technique.

In the previous paper [1], piezoelectric photoacoustic (PPA) measurements of high quality nondoped ZnSe thin films grown by molecular beam epitaxy (MBE) were carried out at liquid nitrogen and room temperatures. Three types of the intrinsic defects on nonradiative recombination processes in the nondoped ZnSe epitaxial layers were obtained for the first time. In this work, we can observe the nonradiative recombination processes in the p-type ZnSe epitaxial layers for the first time.

Figure 1 shows the PPA spectra of p- and n-type ZnSe at 77K with the modulation frequency of 200 Hz. In the n-type sample, we can observe two peaks which may be due to bandgap of GaAs and ZnSe. However, the bandgap peak of ZnSe is not clearly observed because it is overlapped by a peak of an intrinsic defects which forms a shallow level. The 3 peaks (labelled B, C and D) are observed in both n- and p-type samples. Additionally, a distinct peak (labelled A) is observed in the p-type sample. The activation energy of the peak is about 180 meV. This value corresponds to that reported by Yao *et al* [2]. Therefore, the origin is due to the nonradiative recombination center, attributed to N_{∞} -Zn- N_{∞} complex defect.

Figure 2 shows the PPA spectral changes of p-type ZnSe with varying the temperatures from 77 to 300 K. We found that the intensities of A, B, C and D increase with increasing temperatures. On the other hand, the intensities of PL spectra decrease with increasing temperatures. This indicates that the quantum efficiency (η) consists by the equation of $\eta = P_r / (P_r + P_{nr})$, where P_r and P_{nr} are probability of radiative and nonradiative recombination, respectively. We can obtain the nonradiative recombination centers in the p-type ZnSe thin films grown by MBE for the first time.

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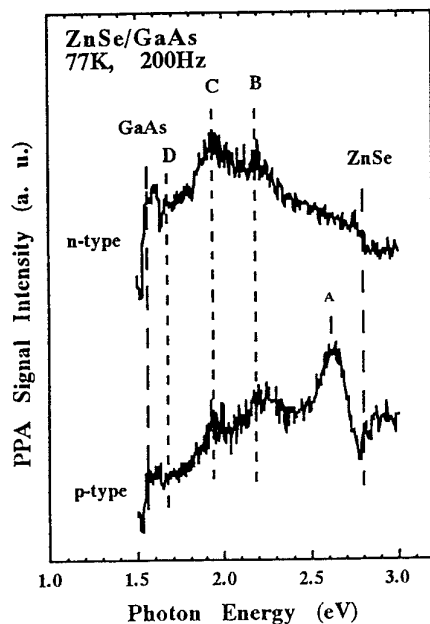


Figure 1

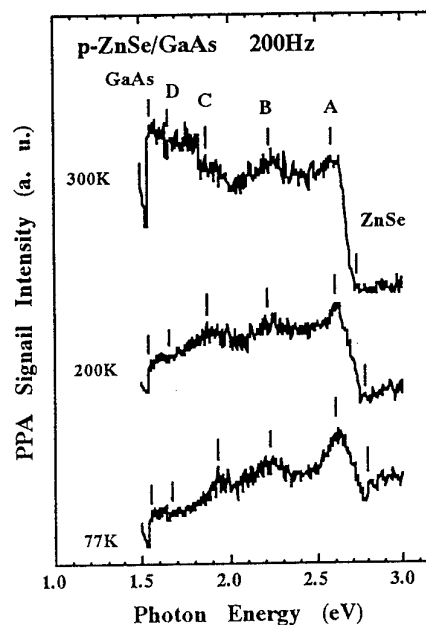


Figure 2

POSTER SESSION P2

WEDNESDAY JULY 29th

16.00-17.00

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POSTER SESSION P2

Low D Systems

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DIPOLE SHALLOW-LEVEL CENTRES IN SELF-ASSEMBLY SILICON QUANTUM WELLS

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We present the first findings of the quantized conductance (QC), local tunneling spectroscopy (LTS) and EPR-EDEPR techniques which reveal the spin-dependent confinement and quantization phenomena in the silicon nanostructures created electrostatically by the dipole shallow-level centre's ordering. These C_{3v} symmetry dipole boron ($B^+ - B^-$) and phosphorus ($P^+ - P^-$) centres are regularly arranged along the edges of self-assembly longitudinal and lateral quantum wells (SLQW and SLaQW) 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. The working and back sides of the wafers were previously oxidized. Impurity doping was done on the working side of the wafers after covering the oxide overlayer with a mask and performing the subsequent photolithography. By varying the parameters of the surface oxide overlayer and diffusion temperature (800°C-1100°C) it was possible to define the criteria leading to the ultra-shallow p-n junction (5nm-30nm), which were controlled using the 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 obtained by the kick-out (1100°C, thin oxide overlayer thickness) and vacancy - related (800°C, thick oxide overlayer thickness) diffusion mechanism consist of SLaQW, whereas the SLQW dominate inside ultra-shallow diffusion profiles realized under parity between different diffusion mechanisms (900°C, medium oxide overlayer thickness). The logarithmic temperature dependence of resistivity and the quantized conductance findings obtained at 77K and 300K have revealed the regime of a weak localization inside SLQW. The thermo-emf, EPR and tunneling CV measurements demonstrate that the reconstructed centres of dopants at the edges of self-assembly silicon quantum wells represent the C_{3v} symmetry dipole defects of the $B^+ - B^-$ -type, which are ordered in the external electric field and cause a correlation gap in the DOS of the hole gas in the SQW. The dynamic quantum wire system has been found to be created by the electrostatic confinement potential of the self-assembly dipole $B^+ - B^-$ centres under the voltage applied along both the SLQW and SLaQW. The crystallographically dependent QC and LTS measurements carried out at 77 K and 4.2 K, respectively, have revealed the dynamic quantum wires in the Coulomb blockade regime with semi-transparent redouts that contribute to the process of hole's elastic backscattering. The relation $\Delta E \cdot \Delta \tau \sim \hbar$ is found to be carried out, thereby confirming the number of redouts that take part in the elastic backscattering of holes: where $\Delta E = e\Delta U$, ΔU is the period of the current step; $\Delta \tau = 2l/v$, l is the distance between two semitransparent redouts, which is equal the width of the quantum wire and corresponds to the distance between two neighbour impurity dipoles. The valley's effect on the quantized conductance is also exhibited. The nanotechnology suggested enables to obtain ultra-shallow field-effect transistor structures with capacitances up to 10^{-19} F, which are enough to observe the charging effects of discrete holes at high temperatures.

The quantized conductance technique has identified new near-edge resonances as well as Kondo resonances that appear in the $I(V)$ dependence and are due to hole scattering on single transition metal 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 the spin-dependent scattering and spin-dependent recombination. Besides signals from phosphorus, oxygen thermal donors and iron-related centres, 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 inside the quantum wires created electrostatically by the dipole shallow-level centre's ordering.

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SHALLOW ACCEPTOR STATES IN SiGe QUANTUM WELLS

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The selectively doped *SiGe* quantum well (QW) structures are of great interest for study of acceptor states which are degenerate in bulk material and should be split in two-dimensional 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. So-called A^+ states (acceptors binding an additional hole) are of specific interest as they should exist in *SiGe* QW structures in thermal equilibrium in contrast to the bulk material where they can appear only due to excitation, e.g., by light. The experimental data presented in this report give evidence for existence of A^+ centers in boron doped *SiGe* QW structures. The thermal emission of holes from these centers determines the conductivity along the QW at low temperatures. At higher temperatures, the conductivity is shown to be due to thermal activation of holes from the ground to strain-split B states following by hole tunneling into the QW valence band. The tunneling is possible due to a potential drop across the QW which arises due to hole capture at surface states of the *Si* cap layer making the surface charged. The external potential applied across the QW is shown to change essentially the lateral conductivity as well as the activation energy. Note that in structures with doping profile and level investigated, it is possible to find the A^+ center binding energy and the energy splitting of acceptor levels induced by internal strain from temperature dependence of conductivity.

The *p*-type *Si/SiGe/Si* QW structures 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 20 nm. The B concentration inside the QW was of $6 \cdot 10^{11} \text{ cm}^{-2}$. Two boron δ -layers outside the QW with concentration of $2 \cdot 10^{11}$ to $2 \cdot 10^{12} \text{ cm}^{-2}$ were used to obtain A^+ centers. The lateral conductivity and magnetoconductivity of the structures were studied to obtain hole concentration and mobility. Two activation-law regions were observed in the temperature dependence of conductivity. The low-temperature region was shown to be due to thermal activation of holes from A^+ centers. The binding energy of A^+ centers was found to be of about 2 meV and practically independent of *Ge* content, x . The activation energy at higher temperatures was of 12 and 18 meV for $x = 0.1$ and 0.15, respectively. It is shown to be due to thermally activated tunneling holes from the strain-induced split-off state of neutral boron atoms. The model of two-stage excitation of free holes including the thermal activation of holes from the ground to split-off neutral boron state and then tunneling into the valence band is proposed. The tunneling is explained by charging *Si* cup-layer surface inclining the valence bands. The model is confirmed by the transverse field-effect measurements.

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INTERACTION OF A LASER FIELD WITH A SEMICONDUCTOR SYSTEM: APPLICATION TO SHALLOW-IMPURITY LEVELS OF QUANTUM WELLS

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We present a simple theoretical approach to treat the interaction of a laser field¹ with a semiconductor system, in which the effect of the laser field is incorporated within a renormalized - semiconductor effective - mass concept [see Figure 1(a)]. We use a simple two-band isotropic scheme that incorporates all the essential physical features of a more complex scheme. As an application, we present a theoretical study of the effects of laser dressing on the transition energies between the $1s$ - and $2p_z$ - like states of hydrogenic donors in GaAs-Ga_{1-x}Al_xAs QWs, in the presence of an external homogeneous magnetic field^{2,3}. It is shown that the modifications on the intradonor transitions due to weak intensity-laser dressing may be as important as the effects of a strong applied magnetic field. These changes [see Figure 1(b)] due to the laser interaction are clearly measurable, and indicate that laser effects may play a fundamental role in other effective-mass-related phenomena in semiconductor heterostructures in general.

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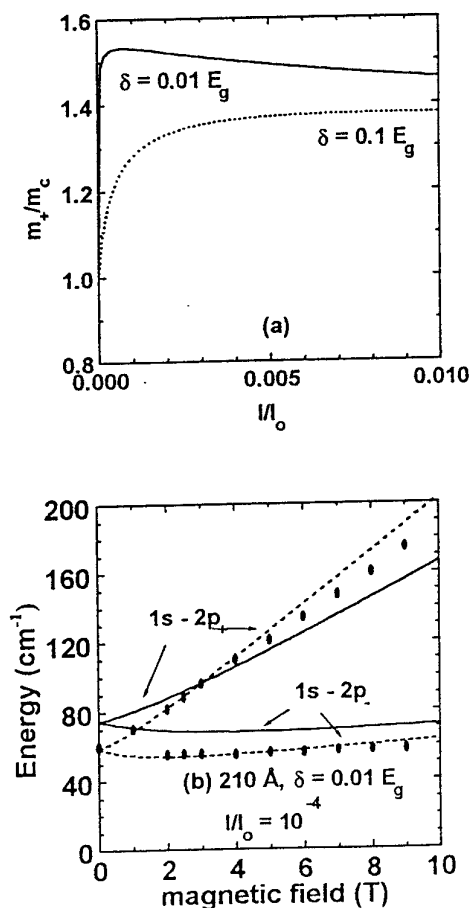


Figure 1. (a) Laser-dressed conduction-band effective mass (in units of the bulk GaAs effective mass, $m_c = 0.0665 m_0$, where m_0 is the free electron mass), as function of the normalized laser intensity I/I_0 , with $I_0 \approx 5 \times 10^{13} \text{ W/cm}^2$, for two values of the detuning parameter $\delta = E_g - \hbar\omega$, where E_g is the bulk GaAs gap energy, and $\hbar\omega$ is the laser energy. (b) $1s$ - $2p_z$ intradonor-transition energies, as functions of the applied magnetic field, for a 210 Å GaAs-Ga_{0.7}Al_{0.3}As quantum well. Dashed curves are theoretical transition energies for on-center donors in the absence³ of the applied laser, whereas the full curves represent the corresponding theoretical laser-dressed transitions for a normalized laser intensity $I/I_0 = 10^{-4}$, and a detuning parameter $\delta = 0.01 E_g$. Full dots are the experimental data² in the absence of the laser field.

INFLUENCE OF DONOR IMPURITY ON OPTICAL TRANSITIONS
IN QUANTUM DOTS

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Neutral and negatively charged donor centers were studied in semiconductor quantum wells, for which the joint action of the one-dimensional confinement and external magnetic field allows one to observe optical transitions to excited states of a D^- center. The present paper consists of a theoretical study of the effect of the three-dimensional confinement potential on the properties of one-electron (D^0), two-electron (D^-), and three-electron (D^{2-}) donor centers in semiconductor quantum dots. We consider a single quantum-dot nanocrystal embedded in an insulating material and describe the electron and donor states in the frame of the effective mass approximation with the confinement potential taken on as a spherical potential well of a finite depth. We study the properties of the few-electron systems in the quantum dot, which can contain the donor center. For the two- and three-electron systems in the quantum dot, i.e., electron pair, electron triple, D^- and D^{2-} donor centers, we have performed the variational calculations for the ground state and excited states with the total angular momentum $L = 0, 1, 2$ and with the singlet and triplet total-spin configurations. The application of the many-element variational basis (number of elements ~ 150) allows us to obtain accurate results for all the considered states. It is well known that – in a bulk crystal without external fields – the hydrogen-like D^- center possesses only one bound state, i.e., only the ground state is bound. We have shown that several excited states of both the D^- and D^{2-} donor impurities located at the center of the spherical quantum dot are bound if the confinement potential is sufficiently strong. The values of the depth and range of the confinement potential, for which the excited states of the negatively charged donors are bound, correspond to the parameters of the recently fabricated quantum dots. We have calculated the energies of dipole-allowed optical transitions between the few-electron states in the quantum dot for the cases of the presence and absence of the donor center and discussed their dependence on the depth and range of the confinement potential and on the number of electrons. We have found that – in both the cases – the transition energies weakly depend on the number of electrons confined in the quantum dot. In particular, the calculated transition energies for the neutral (D^0) and negatively charged (D^- and D^{2-}) centers are close to each other. Until now, this property was known for the quantum dots with the parabolic confinement potential and without the donor center and interpreted with the help of the generalized Kohn theorem. The results of the present work suggest that this property is more general and holds true for the spherical quantum dots with as well as without the donor impurity provided that the confinement potential is strong enough. Moreover, we show that the presence of the donor impurity center leads to a considerable increase of the dipole-transition energy. In summary, the present paper shows that the optical spectroscopy on quantum dots should be sensitive to the presence of the donor center, but not to the number of electrons confined in the quantum dot.

RESONANCES IN GaAs/Al_xGa_{1-x}As HETEROJUNCTIONS
DUE TO PROTUSIONS RELATED TO Si SHALLOW DONORS

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Recently, scanning tunneling microscopy was used to study dopants in GaAs. [1,2] Johnson *et al.* [1] reported the observation of individual doping sites in GaAs. They were detected as hillocks with a diameter of about 2 nm. Zheng *et al.* [2] have identified and characterized substitutional donor Si in GaAs sites, showing that its delocalized electronic structures give rise to protusions with typical spatial diameters of about 25 Å in the scanning tunneling microscopy image. With the shrinkage of semiconductor devices, the probability of the occurrence of carrier scattering events with these individual dopants increases considerably. We address in this work how the transmission properties of electrons in GaAs/Al_xGa_{1-x}As heterojunctions change due to their scattering with protusions related to Si shallow donors. As in the work of Bastard *et al.* [3], the individual Si dopants are described through a Gaussian potential profile whose mean width is of the order of a typical spatial diameter of a Si related protusion, and whose potential depth is such that its first bound state has the same energy as that calculated when the Si shallow donor is described by a Coulomb potential. The electron transmission properties are obtained by solving Schrödinger-like equations with a position dependent kinetic energy operator, and by imposing continuity of $\Psi(z)$ and $[m(z)]^{-1} d\Psi(z)/dz$ in all the structure. The numerical solutions are calculated using the multistep scheme as proposed by Ando and Itoh [4]. We show that protusions due to individual dopants can change remarkably the transmission properties of electrons through GaAs/Al_xGa_{1-x}As heterojunctions, being even capable to produce transmission resonances. The modifications on the electron transmission are stronger when the dopant is localized in the Al_xGa_{1-x}As alloy, but depends also in the distance of the individual dopant to the heterojunction interface. When the existence of two simultaneous dopants is considered in the heterojunction, the electron transmission coefficient can present several resonance peaks. They are stronger when both dopants are localized in the Al_xGa_{1-x}As alloy.

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BINDING ENERGY AND STRUCTURE OF LOCALIZED BIEXCITON IN QUANTUM WELLS.

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The binding energy of biexcitons in GaAs/AlGaAs quantum well has been the object of great attention in the last few years, both experimentally and theoretically. At present there is still a big discrepancy between the measured binding energy of the biexciton and the theoretical calculated values which can be as much as a factor of two smaller. Here we investigated theoretically the effect of localization of the biexciton in the plane of the quantum well on its binding energy. It is generally believed that quantum well width fluctuations of one to two monolayers will localize the biexciton. Such fluctuations are modeled using a parabolic confining potential in the plane orthogonal to well growth axis.

Our approach is based on the stochastic variational technique from which we obtain the biexciton and exciton energy for given quantum well width and in-plane confinement of the biexciton. We evaluate the energy levels and the properties of the biexciton molecule (i.e. the electron-electron, electron-hole and hole-hole correlation function), for different quantum well width and for different strength of the confining potential. The dependency of the frequency of the confining potential on the quantum well width is obtained. The theoretical results are compared with the experimental data from different groups both for the biexciton binding energy and of the Haynes factor which is the ratio between the biexciton binding energy and the exciton binding energy. The Haynes factor is only very weakly dependent on the quantum well width, good agreement is obtained between experiment and theory. The analysis of the theoretical results for the different correlation functions suggests that the structure of the biexciton is similar to the structure of the H_2 molecule. This is clear from Fig. 1, where the probability of finding an electron in the position with coordinate (x,y) is plotted for a fixed distance d between the holes.

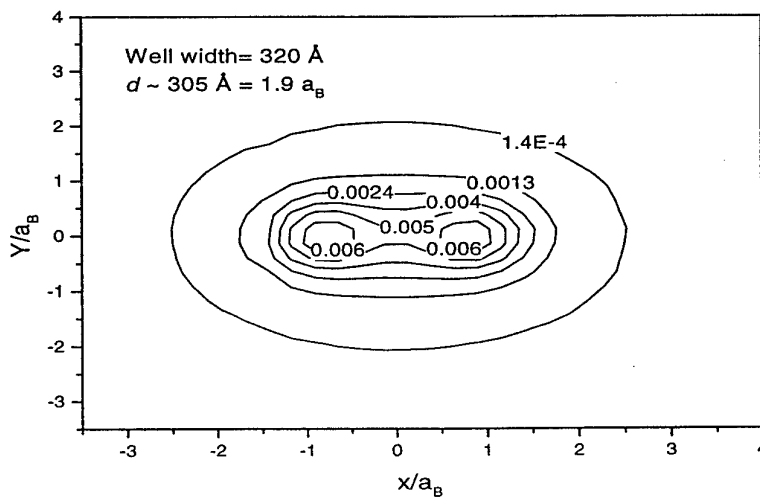


Figure 1: Conditional probability. The length are measured in effect Bohr radius for the exciton in GaAs/GaAlAs, i.e. $a_B = 160\text{\AA}$

Theoretical study of shallow acceptor states in strained quantum well structures

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A comprehensive understanding of the acceptors confined in lattice matched quantum well (QW) structures during last decade, has been achieved through extensive experimental [1-6] and theoretical [7-11] investigations. Corresponding studies of impurities confined in strained systems, such as InGaAs and nitride based structures (both with great application potential), are very limited. The purpose of this theoretical study is to gain a more detailed understanding of the acceptor electronic structures under the influence of both the QW confinement and the deformation potential.

Because of the complexity of such calculations, the number of reports in the literature which deal with the presence of a deformation potential, is very limited. Schmidt [12] has analytically discussed the splitting of acceptor ground states and their shift under the influence of axial stress or noncubic crystal field on the basis of a spherical or cubic valence band structure with large spin-orbit splitting in bulk material. Recently the N-acceptors confined in strained CdZnTe QW structures were reported experimentally [13]. To the best of our knowledge, the only theoretical and experimental work, which considers the strain dependence of the acceptors in QW structures, was reported by Loehr *et al.* [14]. However, the excited states of acceptors have not been studied up to date. In our recent investigation [15], we employ a well established theoretical model to calculate the ground states and the excited states of acceptors, which are subjected to an influence from both a confinement potential and a deformation potential.

In this work, we have studied acceptors confined in strained $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ system in more detail. In order to study the competition between the confinement and strain effects, the electronic structures of acceptors are examined with varying well widths and indium concentrations. If we assume a simple proportional relationship between the acceptor ground state splitting and the first heavy-light hole (hh-lh) subband splitting, the calculated results suggest that the deformation potential has a stronger influence than the confinement potential, on the acceptor ground state splitting relative to the first hh-lh subband splitting.

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LOW DIMENSIONAL SYSTEMS OF INTRINSIC DEFECTS IN InP: STRUCTURAL AND ELECTRONIC PROPERTIES

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Recent experimental results indicated the possibility of epitaxial growth of n-type doping in InP based heterostructures, where intrinsic defects (P_{In} antisites) can provide high concentration of carrier density [1]. The P_{In} antisite is obtained by off stoichiometric deposition of InP at low temperature. Similar structure, with intrinsic defects, has been obtained in the InAs/AlSb heterostructure, where the formation of As_{Al} antisite between InAs and AlSb interface is responsible for the two-dimensional (2D) electron gas formation [2]. The configuration and electronic structure in high concentration of antisite defects (P_{In}) are not well understood.

We performed a systematic first-principle calculation to investigate the electronic and structural properties of P_{In} antisite defects in InP. We verified that the antisite- δ system can be a stable configuration with a 2D electron gas. In a 128 atoms supercell we increased the number of antisites in a plane perpendicular to the growth direction ($<001>$). The nearest neighbors of a single defect relax 0.11 Å tetrahedrally towards the antisite position. As the number of neighbor antisite defects are increased, these relaxations still almost the same around the defect, but there is a collective rearrangement so that the formation energy decrease about 0.1 eV per additional defect. The impurity level in the gap region started to become a delocalized band. Each antisite defect contributes with two electrons in that band, screening the ionic coulomb repulsion between the defects. We infer that the δ -like structure of P_{In} is a stable configuration.

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**DONOR-ACCEPTOR RECOMBINATION IN TYPE-II GaAs/AlAs
SUPERLATTICES GROWN ON (100) AND (311)A GaAs SUBSTRATES**

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Photoluminescence (PL) of the type-II GaAs/AlAs superlattices (SL's) grown on (100) and (311)A GaAs substrates by molecular beam epitaxy (MBE) have been studied. The SL's was either intentionally undoped or homogeneously doped with silicon to a concentration of up to $3 \cdot 10^{16} \text{ cm}^{-3}$.

The exciton line and its phonon replicas dominated the continuous-wave (cw) PL spectra at temperatures $T < 30 \text{ K}$. The PL spectra of the SL's grown on (311)A substrates was shifted to lower energies as compared with the spectra of their (100)-counterparts. The exciton line exhibited a temperature quenching, and an unidentified broad low-energy band appeared in the spectra at $T > 30 \text{ K}$. In order to identify the nature of the band, the temperature and excitation intensity dependencies of time-resolved and cw PL were studied. The band displayed a red shift with temperature, with the slope of the temperature dependence of the band position being greater than the temperature coefficient of the bandgap of GaAs. With the cw excitation power increased, the band shifted to shorter wavelengths. After transient excitation the band first drops rapidly in several tens of nanoseconds, and then slowly decays on the time scale of tens of microseconds following an approximately power law $I(t) \sim 1/t$, broadening and red-shifting with time.

The experimental results allow us to connect the novel band with the recombination of donor-acceptor pairs between donors (S or Si) located in the AlAs layers and acceptors (C or Si) in the GaAs layers of the SL's. The sum of the carrier binding energies of pair constituents was determined to be $198 \pm 10 \text{ meV}$ for undoped SL's, while for doped SL's grown on (311)A substrates it equals to $174 \pm 10 \text{ meV}$. Assuming that the acceptors in the center of the wells play a major role in the corresponding transitions, we deduce the electron binding energy on donors in AlAs layers as $140 \pm 10 \text{ meV}$ in undoped and $115 \pm 10 \text{ meV}$ in Si-doped SL's.

Electronic and structural properties of as grown and α -particle irradiated GaAs doping superlattices

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Abstract :

Using shallow impurities Zn and Te with concentration $n_D = n_A = 1 \times 10^{18} \text{ cm}^{-3}$, three different series of GaAs doping superlattices (SLs) have been grown by MOCVD. They have layer thickness $d_N = d_P = 20, 40$ and 60 nm , respectively.

First, by collecting low temperature photoluminescence (LTPL) spectra, we have investigated the electronic properties. The variation of the effective optical bandgap versus thickness and excitation intensity has been checked. It demonstrates clearly the SLs structure. The energy position of the main PL band (electron to Zn-acceptor transitions) has been investigated. In the temperature range 11K-50K we find a shift toward low energy, while the half width at half maximum (HWHM) increases.

In the high excitation intensity regime, we have performed time-resolved experiments. We find a complex time dependence response with a non-exponential decay. Within the main PL band, the decay time varies in the nanosecond range and increases when moving from the high to low energy side.

Next the samples were subjected to α -particle irradiation up to a dose of about 10^{12} cm^{-2} . This resulted in structural damage and, at high dose, the PL answer disappeared. At lower intensity, the PL signal still remained but was shifted toward high energy. After annealing, partial recovery has been found.

The degree of structural damage was investigated by AFM (Atomic Force Microscopy) but no sizable effect could be found. This remains true even if we use Ar⁺-ion irradiation, instead of the much lighter He atoms. Finally, investigations have been conducted using spin-density excitation experiments. Three single particle excitation bands have been found in all luminescent samples, of which frequency shifts directly correspond to the energy separation of the sub-bands. They differ for different layer thickness and, after irradiation, exhibit changes in the position, shape and intensity.

**"Quantum yield of the Auger-type nonradiative transitions in
low-dimensional systems"**

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Transition metal impurities, such as iron, nickel or chromium are known to be efficient centers of nonradiative recombination in wide gap II-VI bulk materials. The overall picture of the carrier generation-recombination processes in these materials is now well established. It was recently shown (M. Godlewski et al. Mat. Sci. Forum 258-263, 1677(1997)) that chromium impurity effectively deactivates excitonic emission coming from (CdTe,CdMgTe) quantum wells. The question is, whether the same mechanisms, which are responsible for the photoluminescence quenching in bulk samples, are also active in low-dimensional systems. Results of our previous studies indicate, that contrary to the bulk materials, in the case of (CdTe,CdMgTe) quantum wells doped with chromium, Auger-type transitions are the most important among various nonradiative processes.

In this communication we present a semiempirical analysis of such excitonic Auger process, responsible for deactivation of photoluminescence intensity in CdTe-based heterostructures. During this process an immobilized exciton recombines nonradiatively, and the energy is transferred to a nearby chromium center. Assuming that the transition probability is proportional to the spatial extent of the excitonic envelope function, the decay kinetics of the luminescence is calculated. A good agreement of experimental and theoretical results indicates that the proposed model can be successfully used for semiquantitative estimation of the quantum yield of the excitonic Auger-type nonradiative recombination processes in low-dimensional systems.

CONFINED AND INTERFACE PHONON-INDUCED SHIFT IN SHALLOW DONOR BINDING ENERGY OF QUANTUM WIRES

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The effect of the interaction of electrons with polar optical phonons on the binding energy of shallow donors is investigated with taking into account the phonon confinement in a cylindrical quantum wires.

By analogy to the work on bound polarons in bulk semiconductor [1] using the Lee-Low-Pines unitary transformations the following expression for the additional effective potential induced by the coupling of the electrons with the polar confined LO and interface phonons is obtained:

$$V(r) = - \sum_{j=1,2} \sum_{q,n,l} |\Gamma_{nl}^{(j)}(r,q)|^2 \left[\omega_{nl}^{(j)}(q) + \frac{q^2}{2m_e} \right]^{-1},$$

where $\Gamma_{nl}^{(j)}$ is the Fourier coefficient of the electron-phonon interaction, $\omega_{nl}^{(j)}(q)$ the confined or interface phonon frequency [2], q the phonon wave vector along the wire axes. The labels n, l characterize the phonon modes, $j=1$ corresponds to the confined phonons and $j=2$ to the interface ones.

Minimizing the effective Hamiltonian with respect to the variational parameter, one can get the donor binding energy shift $\Delta E_n^{(j)}$ as a function of the impurity position R_0 and wire radius R . As an example the numerical calculation of $\Delta E_n^{(j)}$ is carried out for the GaAs cylindrical quantum wire embedded in AlAs. By representing $\Delta E_n^{(j)}$ in the form $\Delta E_n^{(j)}(R_0, R) = A_n^{(j)}(R_0) R^{-\alpha_n^{(j)}(R_0)}$ (R_0 and R are given in the effective Bohr radius units) the following results are obtained: $A_0^{(1)}(0) = 1.38 \text{ meV}$, $\alpha_0^{(1)}(0) = 0.28$; $A_1^{(1)}(0) = 0.57 \text{ meV}$, $\alpha_1^{(1)}(0) = 0.25$; $A_2^{(1)}(0) = 0.32 \text{ meV}$, $\alpha_2^{(1)}(0) = 0.3$. Other confined phonon modes ($n=3, 4, \dots$) make negligible shifts in the binding energy.

Note, that the total contribution in polaronic shift from all confined phonon modes $\sum_n \Delta E_n^{(1)}$ in the donor binding energy increases from 4% to 7.5% when wire radius increases from 3 to 20nm.

When the donor position moves from the center to the edge of the wire, $\Delta E_n^{(1)}(R_0, R)$ increases for the given R . Thus, for a donor at the edge of the wire $A_0^{(1)}(R_0) = 1.6 \text{ meV}$, $\alpha_0^{(1)}(R_0) = 0.234$. For the wire with $R = 3 \text{ nm}$ the relative change of the binding energy counts 8% and tends to increase when R increases.

For the electron interacting with higher energy interface phonon mode $m=0$ a strong coupling limit of the energy there takes place, since in long-wave-limit $\Gamma_{0n}^{(2)} \sim q^{-1}$. For the interaction with higher energy interface phonon mode $m=1$ one obtains $A_1^{(2)}(0) = 0.023 \text{ meV}$, $\alpha_1^{(2)}(0) = 2.33$, i.e. these phonon interactions show stronger R -dependence of the binding energy polaronic shift. Therefore, their contribution is considerable for $R < 10 \text{ nm}$.

Note, that phonon interaction effects on the binding energy in these quasi-one-dimensional structures more significantly than it does in the case of quasi-two-dimensional systems.

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PHOTOLUMINESCENCE FROM SHALLOW AND DEEP TRAPS IN SEMICONDUCTING NANOPARTICLES EMBEDDED IN GLASS

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The confinement of charge carriers into a small volume of semiconductor material, such as into $\text{CdS}_x\text{Se}_{1-x}$ nanoparticles embedded in a glass matrix, leads to a strong modification of the electronic and optical properties of the semiconductor nanoparticles compared to those of the corresponding bulk material. The spectrum of such a material consists of a series of discrete lines which correspond to electron-hole transitions and changes its spectral position with the particle size. Due to the small size, surface effects become prominent and provide shallow traps to the photoexcited carriers, which can also relax into deep traps located in the neighbouring glass matrix before making a radiative transition. We have studied photoluminescence (PL) from several glass samples containing $\text{CdS}_x\text{Se}_{1-x}$ nanoparticles of various sizes and various compositions obtained from Schott Glass Inc., with a special emphasis on the sample OG550, which has an absorption edge at 550 nm and contains nanoparticles of radius 3.6 nm with $x = 0.67$, as measured by low-frequency Raman spectroscopy in a separate study. The PL spectra of the $\text{CdS}_x\text{Se}_{1-x}$ nanoparticles are governed by a band-to-band recombination appearing at the absorption edge of the sample, by transitions involving shallow traps within nanoparticles including surface states which appear between 680 and 760 nm in dependence on particle size, and by recombinations from deep traps, located most probably in the glass matrix, which appear at about 860 nm for all samples. The radiation at the absorption edge is blue shifted with respect to the corresponding bulk material due to the confinement effects and shows a pronounced asymmetry at the low energy side, probably due to the mixing of bulk conduction band and shallow trap wave functions when the particle size becomes of the order of the shallow trap Bohr radius. The shallow trap luminescence comes from all kinds of defects present in nanoparticles as well as from the surface states and is weaker for large particles, where the relative number of surface states is smaller. In order to get more insight in the spatial location of the traps, we measured PL spectra from the base material used for the sample OG550. This material contains Cd, S and Se in the batch glass background and is the same as the sample OG550 in all respects, apart from the fact that it does not contain any nanoparticle. The spectrum from this material consists of two luminescence bands, one around 610 nm, which appears due to normal glass luminescence and probably also has contributions from the radiative recombinations of the Cd, S and Se material present in glass, and another at about 860 nm, which is comparatively weaker. The latter structure is most probably due to states present in the glass matrix which provide deep traps to the photoexcited carriers of Cd, S and Se materials. Since a structure similar to this, but with greater intensity, is also present in samples containing nanoparticles, we propose that the origin of deep traps in samples containing nanoparticles lies within the glass matrix. The photoexcited carriers are exchanged between nanoparticles and the neighbouring glass matrix, first from an excited state in the nanoparticle to the traps in the glass matrix via fast non-radiative processes and then from these traps to the ground states in nanoparticles via radiative processes. Both the shallow and the deep trap luminescence show an effect of photodarkening, which is manifested in a decrease of luminescence after a strong illumination of the sample. The luminescence decreases as much as by a factor of 5 when measured after a laser illumination of 200 kW/cm^2 for 40 minutes. The photodarkening effect is found to depend both on the illumination time and illumination intensity and is almost absent for very low laser intensities. Apart from this, the darkening effect also depends upon the sample temperature during illumination. When illuminated at liquid nitrogen temperature, the darkening effect was lower compared to the case when samples are illuminated at room temperature. This indicates that the photodarkening effect, which results in a loss of radiative traps, is not only an optical process, but also includes thermal processes. The most probable mechanism includes permanent trapping of photoexcited carriers in traps located in the glass matrix and a process similar to thermal annealing which removes the radiative traps within the nanoparticles. Thermal processes can remove defect related traps whereas optical process under strong illumination can affect both defect related and surface related traps. This can explain the increase of photodarkening when the sample is illuminated at room temperature.

OPTICAL SPECTRA OF SHALLOW ACCEPTORS IN QUANTUM DOTS

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The energy levels and wave functions of a shallow acceptor placed in the center of a spherical quantum dot are calculated within the effective mass approximation (EMA). Using previously developed numerical-analytical method for solving coupled Schroedinger equations [1], like EMA equations describing acceptor states, we obtain exact expressions for the wave functions of the discrete bound states and continuum states. These wave functions are used to calculate oscillator strengths for the dipole optical transitions from the ground state to the odd excited states and the photoionization cross-section spectrum as a function of dot radius and material parameters. In the spherical approximation the dependencies of the energy levels and oscillator strengths are found as a function of a dimensionless parameter μ , $\mu=(4\gamma_2+6\gamma_3)/5\gamma_1$, where γ_i are Luttinger parameters of the valence band, which makes it possible to estimate these quantities for acceptors in quantum dots made of various materials and to study the change to the case of shallow donor, as $\mu \rightarrow 0$. We show that acceptor optical spectra (energy levels, oscillator strengths) depend drastically on both, dot radius and μ (i.e on the heavy- to light-hole mass ratio, which equals $(1+\mu)/(1-\mu)$). When, at given values of the potential barrier and μ , we decrease the dot radius, we proceed from the bulk case to the case when almost all acceptor absorption correspond to transitions to the continuum, where resonant states appear. The shapes of the photoionization cross-section spectrum are completely different for small and large values of μ ($1 > \mu \geq 0$).

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IMPURITY-RELATED ENERGIES OF SEMICONDUCTOR SUPERLATTICES: PERIODICITY AND MAGNETIC FIELD EFFECTS

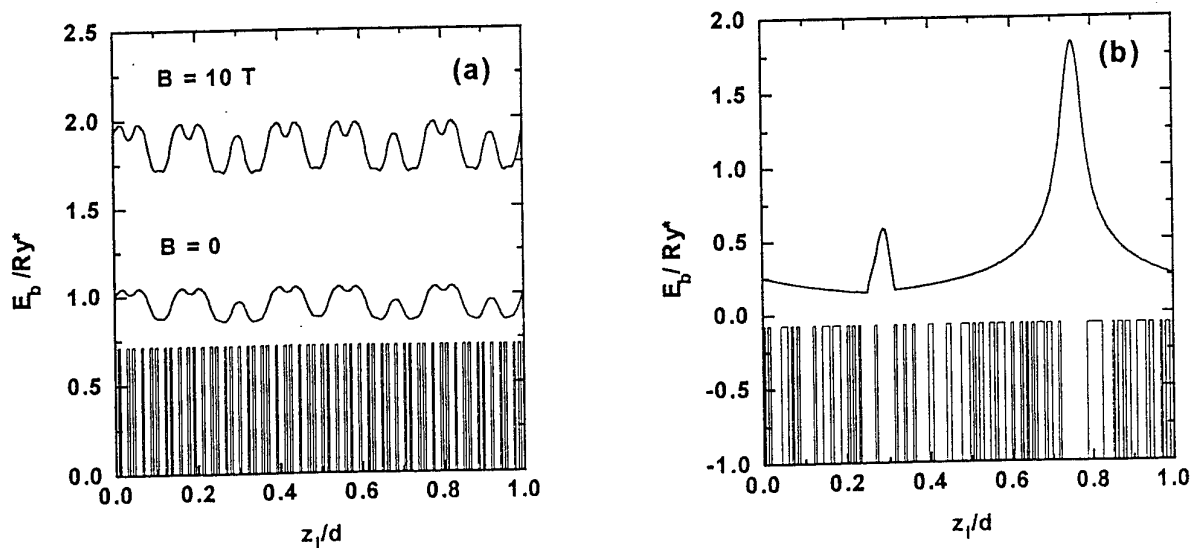
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The nature of impurity states in semiconductor nanostructures has been largely studied in the last years, since the presence of impurities can modify the physical properties of quantum devices. Moreover, many of these physical properties, such as impurity binding energies and impurity-related photoluminescence spectra, can be directly controlled by choosing appropriate geometries and external conditions (magnetic and electric fields).

In the present work we are concerned with the calculation of the donor ground-state binding energy in GaAs-GaAlAs SLs as a function of the impurity position along the structures. We take into account several layer sequences, namely, periodic, quasiperiodic and disordered arrangements, and consider the effects of an external uniform magnetic field applied perpendicularly to the SL interfaces. The calculations are performed within the context of the effective-mass approximation and follow variational schemes.

The results, discussed on the basis of the effects of the periodicity of the system on the binding energies, show that for the case of periodic and quasiperiodic SLs the ordering is reflected in the impurity binding energies. However, for the disordered systems considered, the electronic states without impurities are localized by the disordered potential and this is the main feature apparent in the binding energy curves.

Also, we consider the effects of magnetic fields on the energies associated to transitions from electron-conduction subband to acceptor states. The results are analysed and compared to available experimental data obtained via magnetoluminescence measurements. In all cases, the magnetic field increases the lateral confinement of the electron wave function increasing the binding energy and its sensibility to the impurity position along the structure. For transitions involving those impurity states the associated, spectra should exhibit a peak whose width clearly depends on the value of the applied magnetic field.



Binding energy of a donor impurity in (a) Fibonacci and (b) random $GaAs-Ga_{0.79}Al_{0.21}As$ SLs with well and barrier widths of 16.9 Å and 11.2 Å, respectively, as a function of the impurity position z_l . Notice that d stands for the length of the whole unit cell taken as a Fibonacci (a) and random (b) sequences, both with 144 layers. Results for different values of the magnetic field B are shown for Fibonacci SLs, and schematic representations of the potential profiles are displayed.

ACCEPTOR SPECTRA IN QUANTUM DOTS: EFFECT OF A MAGNETIC FIELD

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We investigate theoretically the influence of an external magnetic field on the energy levels of ground and excited shallow-acceptor states in GaAs-Ga_{1-x}Al_xAs quantum dots. We calculate the impurity states in the multiband effective-mass approximation using a formalism based on a four band model that includes the coupling of spin to the magnetic field as well as the valence band mixing. The potential of the acceptor is taken to be the screened Coulomb potential of a point charge taking into account the mismatch of the dielectric constant through the method of image charges. We assume the quantum dot have the form of a disk obtained from a laterally confined quantum well structure and a magnetic field is applied parallel to the disk axis. The confinement along this axis is modeled by a square potential and the lateral confinement is modeled by a parabolic potential. We present a complete analysis of the acceptor binding energies as a function of the lateral confinement of the quantum dot and as a function of the magnetic field strengths. Our results illustrate the competing action between the magnetic field confinement and the quantum-size confinement. Also we discuss the role of the mixing of heavy holes and light holes on the acceptor spectrum in the different regimes of confinement.

THE BINDING ENERGY AND THE DENSITY OF SHALLOW IMPURITY STATES IN GaAs-(Ga,Al)As QUANTUM BOXES UNDER APPLIED ELECTRIC FIELDS

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ABSTRACT

The binding energy and the density of states of a shallow donor impurity in a rectangular-cross-section GaAs-(Ga,Al)As quantum-well wire are calculated under the action of an applied electric field applied perpendicular to the axes of the wire, using the effective-mass approximation and within a variational scheme^{1,2}. Calculations were performed as a function of the impurity position in a quantum-well wire of infinite depth and for various sizes of the wire cross-section. We compare our results of the binding energy and of the density of impurity states with available results in GaAs-(Ga,Al)As quantum wells and quantum dots³⁻⁵. Our results suggest that the density of impurity states and its modifications due to applied electric fields must be taken into consideration in the understanding of future experimental data on optical phenomena in which the geometrical confinement competes with applied electric fields.

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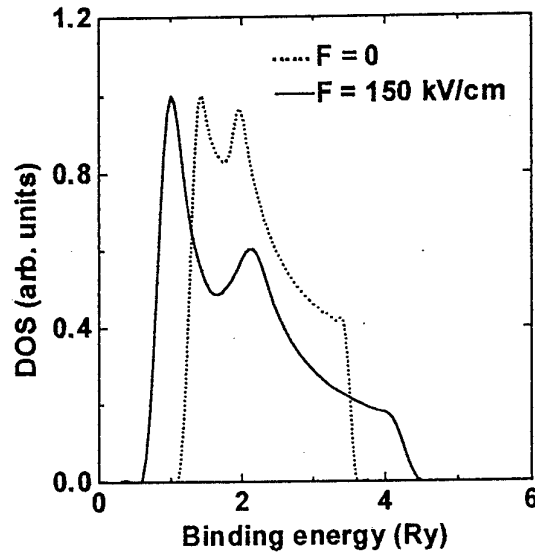


Figure 1. Densities of donor impurity states as a function of the impurity binding energy for a QWW with $L_x=200\text{\AA}$ and $L_y=100\text{\AA}$, under the action of an applied electric field (solid line) and without the electric field (dashed line).

BINDING ENERGIES OF DONORS IN QUANTUM DOTS IN THE PRESENCE OF A
MAGNETIC FIELD

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We report calculations for the binding energies of the ground and the excited shallow-donors states in GaAs-Ga_{1-x}Al_xAs quantum dots subject to an external magnetic field. We work in the effective mass approximation and we adopt a variational approach to compute the donors states. We assume the quantum dot has the shape of a disk obtained from a laterally confined quantum well structure and we model the confinement along the disk axis by a square well potential and the lateral confinement by a parabolic potential. We consider the impurity located anywhere in the quantum dot and the potential to be the screened Coulomb potential of the point charge. We present a complete analysis of the binding energies as a function of the lateral confinement of the quantum dot and as a function of the magnetic field strengths. The results illustrate the competing action between the magnetic field confinement and the quantum-size confinement. Also we discuss the role of the position of the impurity on the energy spectrum in the different regimes of confinement.

PHOTOLUMINESCENCE STUDIES IN CYLINDRICAL QUANTUM WELL WIRES IN THE PRESENCE OF SHALLOW IMPURITIES AND MAGNETIC FIELD

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We present a systematic study of photoluminescence spectra in cylindrical quantum well wires in the ground state for shallow acceptor impurities in the presence of a uniform magnetic field applied parallel to the wire axis, which conserves the rotational symmetry of the problem. In this work, in first instance, we calculated the binding energy for an impurity localized in the axis of the wire. The calculation uses the parabolic effective-mass approximation and a variational method in which the trial wave function contains a hydrogenic part and takes into account the electron confinement and the appropriate confluent hypergeometric functions ${}_1F_1(a, b; x)$ and $U(a, b; x)$. Here, ${}_1F_1(a, b; x)$ is the radial solution of an electron in an infinite potential cylindrical wire while ${}_1F_1(a, b; x)$ and $U(a, b; x)$ are the corresponding solutions for the finite potential. In the case of the photoluminescence, we report the calculated carrier densities, electron and hole quasi-Fermi-levels and various radiative times under steady-state excitation conditions, as functions of the *cw* laser intensity, room temperature, radii of wire, acceptor distribution profiles and different magnetic field intensities. In the photoluminescence, the final steady-state situation for the conduction-band electron density occurs when the rate of creation of photoexcited electron-hole pairs are equal to the radiative and non-radiative electron-holes recombination rates. We have observed changes in the photoluminescence lineshape as compared to those obtained when magnetic field is zero. Our calculations are in good agreement with theoretical and experimental data.

ELECTRON STRUCTURE OF QUANTUM DOT WITH CHARGED IMPURITY UNDER MAGNETIC FIELD

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The electron structure of two-dimensional circular symmetric dot with positive charged impurity and N spinless electrons in a confining parabolic potential $V(r)$ and a perpendicular magnetic field is studied. The ground state electron structure is obtained by solving the Kohn-Sham equations

$$\left\{ -\frac{\partial^2}{\partial \rho^2} - \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{\rho^2}{4L^4} + \frac{m^2}{\rho^2} - \frac{m}{L^2} + V_{\text{eff}}(\rho) \right\} \psi_m = E_m \psi_m$$

Here energies are in units of $E_B = e^2/2ka$, and lengths are in units of $a = \hbar^2/m_e e^2$.

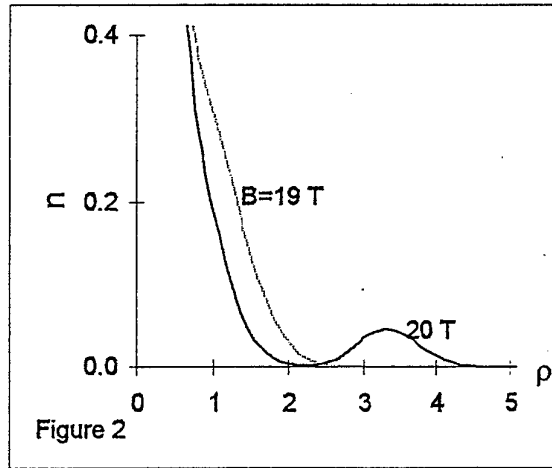
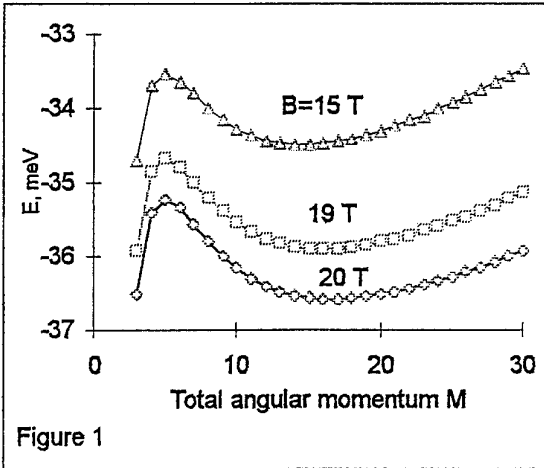
The effective potential is given by

$$V_{\text{eff}}(\rho) = V_H(\rho) - V_{H,m}(\rho) + 2\alpha(n - n_m) - \frac{2}{\rho} + V(\rho),$$

$$\text{where } V_H(\rho) = 2 \int \frac{n(\rho') d\rho'}{|\rho - \rho'|}, \quad V_{H,m}(\rho) = 2 \int \frac{n_m(\rho') d\rho'}{|\rho - \rho'|}, \quad V(\rho) = \frac{\omega_0^2}{4} \rho^2.$$

The exchange energy per electron is $\varepsilon_x(n) = -\sqrt{\frac{\pi}{2}} 2\pi L n(\rho) = \alpha n(\rho)$, where L is magnetic length,

$$n_m(\rho) = \psi_m^2(\rho), \quad n(\rho) = \sum_{\text{occ } m} n_m(\rho).$$



The results of self-consistent calculations for GaAs quantum dot are shown in figures ($N=3$, $\hbar\omega_0 = 2$ meV). The ground-state energies are shown in Fig. 1. The energies are given relative to the vacuum energy that is $(1/4\hbar\omega_c^2 + \hbar\omega_0^2)^{1/2}$ per electron. It is found that the ground state configuration is (0,1,2) for $B < 19.2$ T and (0,1,16) for $B = 20$ T. Fig. 2 demonstrates density profile for $B = 19$ T and $B = 20$ T.

It should be noted that for $N=4,5,6$ and 7 electrons the new series of magic numbers with interval of $\Delta M = N-2$ was found.

The Giant Lifetimes of Impurity Atoms Excitons Rydberg States in Zero- and One-dimensional Conditions .

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The possibility of lifetime increase for shallow impurity atoms and Mott excitons Rydberg states in semiconductor medium of limited dimensions is theoretical investigated. Three types of conditions with different dimensions are considered: 2D-thin semiconductor layer limited by conducting walls; 1D-cylindrical semiconductor thread, situated in conducting medium; 0D-spherical semiconductor ball surrounded by conducting medium. In any of considered cases it is supposed that limited dimensions of semiconductor medium are less excited states of impurity electrons and excitons. The main reason of spontaneous radiation characteristics change and the increase of excited states lifetime in the investigated systems is the interaction with the mirror image of these systems in conducting mediums. It was theoretically shown that for a certain semiconductor dimensions the role of specified interaction is considerably increasing with the limitation of semiconductor medium dimension. In zero-dimensional medium the excited states are characterized by macroscopical lifetime. The phenomena which are considerably limiting the excited states lifetime are investigated: <1> the cascade recombination of charge carriers and excitons at the interaction with acoustical and optical lattice oscillations; <2> the interaction with electromagnetic radiation of charge carriers thermal motion; <3> the deviation of semiconductor – surrounding medium boundary from a right geometrical form. It is shown that the considered deviation from ideal situation are considerably limiting lifetimes.

At the consideration of enumerated spectral lines broadening mechanisms the excited states lifetime for the investigated systems remains considerable. The increasing factor exceeds the value 10^3 comparable with ordinary situations.

THE BINDING ENERGY OF A HYDROGENIC IMPURITY IN A QUANTUM WIRE WITH COATING

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We consider the binding energy of an electron moving in the field of a hydrogenic impurity located at the axis of the wire. The $GaAs$ wire of radius R_1 is embedded in a $Ga_{1-x}Al_xAs$ cylinder of radius R_2 coaxial with the wire so that the wire has a coating of thickness $R_2 - R_1$. The confining potential at the boundary of the wire R_1 is $V_0 = Q_e 1.247x$ eV, where Q_e is the fraction of potential discontinuity of conduction band, x is the alloy concentration, and at the R_2 the confining potential is taken infinite.

The electron wave function in the wire ($0 \leq r < R_1$) and in the coating ($R_1 \leq r \leq R_2$) is found and the standard boundary conditions on wave function is used to find the energy spectrum when the Coulomb potential in Hamiltonian is taken being zero.

The inclusion of the impurity Coulomb potential in the Hamiltonian of a free electron in the well forces to use the variational approach[1,2]. Thus, the ground-state wave function we take as

$$\Psi_0 = \exp(ikz)\exp(-\lambda\sqrt{z^2 + r^2}) \begin{cases} C_1 J_0(\eta_1 r), & \text{when } r \leq R_1 \\ C_2 K_0(\eta_2 r) + C_3 I_0(\eta_2 r), & \text{when } R_1 \leq r \leq R_2 \\ 0, & \text{when } r > R_2 \end{cases}$$

where $\eta_1 = \sqrt{2m_1 E_{10}/\hbar^2 - k^2}$, $\eta_2 = \sqrt{2m_2(V_0 - E_{10})/\hbar^2 + k^2}$, E_{10} is the ground-state energy without impurity, m_1 and m_2 are the effective masses in the wire and in the coating, respectively, C_i ($i = 1, 2, 3$) are the normalization constants, J_0, K_0 and I_0 are the zero-order Bessel's function of ordinary, first and second kind, respectively, k is the wave vector, and λ is the variation parameter.

When $R_2 \rightarrow \infty$, the binding energy $E_b(R_1)$ has the same behavior as in [2] but has the value $(m_2/m_1)E_R$ at $R_1 = 0$ ($E_R = m_1 e^4 / 2\hbar^2 \epsilon^2$ is the Rydberg energy, ϵ the dielectric constant of the system).

When R_2 is finite, $E_b(R_1)$ -dependence begins from the value $E_b(0)$ corresponding to the case of a wire with the parameters of $Ga_{1-x}Al_xAs$. In the range $0 < R_1 < R_2$ $E_b(R_1)$ has a maximum for the value $R_1 \simeq 0.2R_2$, then with the increasing of R_1 it decreases till $R_1 \simeq 0.8R_2$ and afterwards increases reaching the value $E_b(R_1 = R_2)$ corresponding to the case of the wire with the parameters of $GaAs$ with infinite potential at $R_1 = R_2$. Such a behavior of the binding energy caused by the presence of the wall when electron „feels“ the wall because of tunneling.

For fixed R_1 the $E_b(R_2)$ -dependence has a maximal value $E_b(R_1 = R_2)$ and falls abruptly tending to the value given according to[2] by the $E_b(d = R_1, \rho_0 = 0)$.

In examining the results, one sees that the binding energy for any given x and R_1, R_2 is always greater for $Q_e = 0.85$, than it is for $Q_e = 0.6$ (except for $R_1 = R_2$ and $R_1 = 0$), because the well depth in the former case is greater.

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EFFECTS OF AN ELECTRIC FIELD ON THE BINDING ENERGY OF SHALLOW HYDROGENIC IMPURITIES IN GaAs-(Ga,Al)As QUANTUM BOXES

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ABSTRACT

The binding energies of shallow hydrogenic donor impurities in GaAs-(Ga,Al)As Quantum Boxes (Q.B) are calculated as a function of the structure size and as a function of the intensity of an applied electric field. The calculations are performed within the effective-mass approximation and using a variational method. The electronic confinement is modeled by an infinite potential well. We have found that when the size of the quantum box is reduced, both the energy of the ground state and the binding energy increase. Likewise we found that when the electric field intensity is increased, both the energy of the ground state and the binding energy decrease. In comparing our results with reports based on other geometries, we found that the binding energy essentially depends on the volumen of the zero-dimensional structure^[1]. Also, we have compared our results with theoretical reports on GaAs-(Ga,Al)As semiconductor quantum wells^[2,3], quantum well-wires^[4] and quantum dots^[5,6,7] when we reach the corresponding limits.

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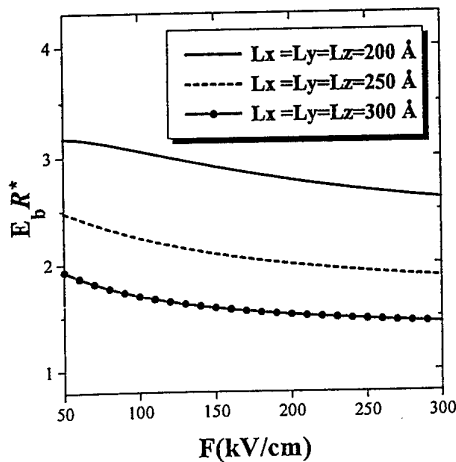


Figure 1. Binding energies for a donor impurity for three GaAs-(Ga,Al)As quantum boxes as a function of an applied electric field in the z direction.

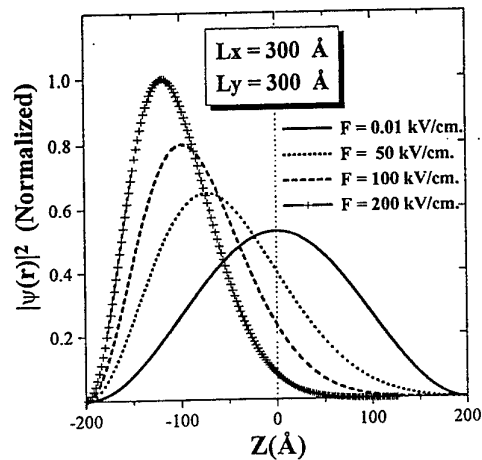


Figure 2. Probability density for a donor impurity in the center of a GaAs-(Ga,Al)As quantum box under the presence of different electric fields.

THE EFFECTS THE QUANTUM CONFINEMENT AND MAGNETIC FIELD ON THE BINDING ENERGY OF HYDROGNIC IMPURITIES IN LOW DIMENSIONAL SYSTEMS

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ABSTRACT

Using a variational procedure within the effective-mass approximation we calculated the binding energy of a shallow hydrogenic impurity on-center located in cylindrical shaped GaAs-(Ga,Al)As low dimensional systems (LDS), such as : quantum-well (QWs), quantum-well wires (QWWs), and quantum dots (QDs), considering an infinite confining potential in all surfaces of the structures. The binding energy of the ground-state is calculated as a function of the length and of the radius of the structure. We show that the geometric confinement increases the binding energy of a shallow impurity in GaAs-(Ga,Al)As structures when the dimensionality is reduced. Also, we found that the binding energy augments with a constant magnetic field applied parallel to the axis of the cylindrical structures. Finally we show that ours results are in good agreement with those obtained in previous calculations in GaAs-(Ga,Al)As QWs, QWWs^[7] and QDs^[11,13,14] of comparable dimensions.

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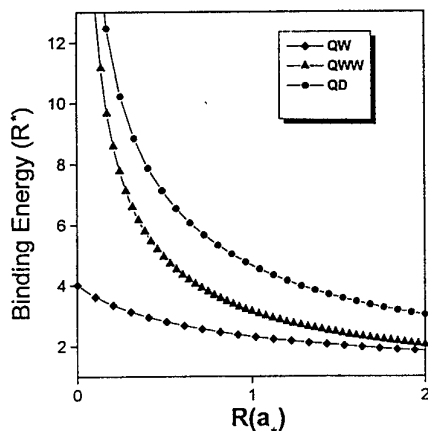


Fig. 1. We display the variation of the binding energy of a hydrogenic impurity located at center in three structures like a: QW, QWW and QD. As a function of the radius for QWW and QD, and as a function of the length for QW.

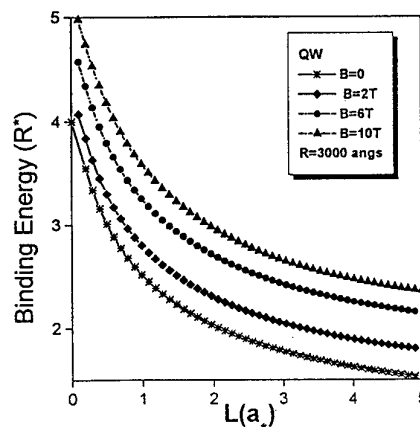


Fig.2 Variation of the binding energy as a function of the length of a hydrogenic impurity located at the center of cylindrical QW of GaAs-(Ga,Al)As.

Binding energy of the ground and first few excited states of a shallow-donor impurity in rectangular-cross-sectional area GaAs quantum-well wires under applied electric field

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Abstract

We present a study of the role of the electric field on the binding energy of the ground and first few excited states of a shallow impurity in rectangular cross-sectional area GaAs quantum-well wires, where the electric field is applied perpendicular to the symmetry axis of the wire. Using the effective-mass approximation within a variational scheme we calculate the binding energy of the 1s-like ground state as well as of some excited states (2s, 2p_x, and 2p_z-like) as a function of the geometry, applied electric field, and donor-impurity position. We found that the presence of the electric field breaks down the degeneracy of states for impurities symmetrically positioned within the structure, and that the geometric confinement and the electric field are determinant for the existence of bound excited states in these structures. Future interpretations of optical phenomena related with shallow donor impurities in GaAs QWWs, in which the effects of an applied electric field competes with the quantum confinement, must take into consideration these results.

POSTER SESSION P2

**Hydrogen in semiconductors, vibrational
properties, electron-phonon interactions**

P2-27 ./ P2-35

EPR STUDY OF HYDROGEN-RELATED RADIATION-INDUCED SHALLOW DONORS IN SILICON

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Hydrogen behavior in semiconductors has been studied extensively since hydrogen significantly influences the properties of semiconductor materials and devices. The most common effects of hydrogen are known to be the termination of electrical activity of dangling bonds and the passivation of shallow-dopant impurities. But hydrogen also activates electrically inactive impurities, passivates some deep-level defects, and creates its own electrically and optically active centers.

Recently, by means of electrical (Hall effect, DLTS) and optical (FT-IR) measurements we have found three new hydrogen-related shallow donor centers, labeled D1-D3, in n-type Czochralski-grown (Cz) Si crystals doped with hydrogen [1-3]. These defects were observed in Si:O,H crystals after irradiation with fast electrons and subsequent annealing at 300-500 °C. It was found that one of the defects, D1, has properties of a negative-U system, i.e., a system with inverted order of location of energy levels in the band gap. The levels of the D1 defect were determined as $E(-/0) = E_c - 0.11$ eV and $E(0/+) = E_c - 0.043$ eV. The atomic structure of the centers, however, is not determined with certainty, and the role of hydrogen in appearance of these defects is not clear.

To obtain further information about the structure of the D1-D3 centers, electron paramagnetic resonance (EPR) study of the defects has been performed. An X-band EPR spectrometer ($\nu_{\text{EPR}} \approx 9$ MHz), equipped with a continuous flow type liquid helium cryostat, was used. Hydrogen (deuterium) was introduced into the samples by annealing in H_2 (D_2) gas ambient at 1200 °C.

A new EPR signal, labeled TU1, has been found in hydrogenated Cz-Si crystals which were irradiated with fast electrons and annealed at 300-400 °C. Isotropic g factor of 1.9987 indicates the shallow donor nature of the defect given rise to the signal. From the comparison of the EPR data with the results of optical and electrical measurements on identical crystals it has been established that the TU1 signal is related to the shallow donor state of the D1 center.

Following annealing at temperatures higher than 400 °C resulted in transformation of the D1 to the D2 center. This leads to the transformation of the TU1 spectrum to another one with $S = 1/2$ and anisotropic g tensor characteristic for shallow donor centers with C_{2v} symmetry. The principal values of g tensor after annealing at 450 °C were found to be $g_{11} = 1.9997$ (axis || [001]), $g_{22} = 1.9993$ (axis || $[1\bar{1}0]$), and $g_{33} = 1.9975$ (axis || $[110]$). These values are close to those of Si-NL10 centers in silicon.

Incorporation of hydrogen (deuterium) atoms into the D1-D3 defects were suggested since the formation of the centers were observed only in hydrogenated Cz-Si samples. Our attempts to confirm hydrogen incorporation into the centers by means of the EPR measurements were unsuccessful. We have not found any changes in the spectra of deuterated samples compared with those of hydrogenated ones. However, this result can indicate only that the hyperfine interactions of unpaired electron with hydrogen (deuterium) atoms are rather small and not resolved in EPR spectra. A similar situation has been shown to take place for H-related NL10 EPR spectra in Si.

The observed EPR spectra are compared with those of Si-NL10 and possible atomic structures and formation mechanisms of the defects which give rise to these spectra are discussed.

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ELECTRON PARAMAGNETIC RESONANCE STUDIES OF HYDROGEN-ASSOCIATED SHALLOW DONOR IN SILICON

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Heat treatment of silicon crystals grown by the Chochralski (CZ) method at around 350°-450°C has long been known result to formation of thermal shallow donors which give rise to dominant ($S=1/2$) EPR spectra with g-tensors of C_{2v} symmetry, labeled NL8 and NL10 [1]. It should be emphasized here, that oxygen is a necessary impurity for thermal donor formation as well as for related with them the NL8 and NL10 EPR spectra and no other impurities were detected into structure of the NL8 [2]. On the other hand an analogous donors are created in H-implanted float-zone-refined (FZ) silicon after short duration (~20 min) heat treatment at 300-450°C. Two dominant EPR spectra: a C_{2v} symmetry AA1 and the NL10-like spectrum (which is almost isotropic line for X-band EPR) were detected [3]. The AA1 spectrum is observed on the early stages of annealing at ~260-350°C and was supposed to originate from positive charge state of hydrogen-related double donor (HDD⁺). The g-tensor parameters and linewidth of individual lines of the AA1 spectrum are very close to those of the NL8 one. No hyperfine interactions are detected in the AA1 spectrum (as well as in NL8). The NL10-like defect grows in at a more high temperature annealing than the AA1 and its intensity correlates strongly with the H-related shallow donor concentration, which can amount to $\sim 1 \times 10^{17} \text{ cm}^{-3}$ [3].

In this paper the comparative studies for H-implanted oxygen-poor (FZ) and oxygen-reached (CZ) silicon were performed and it is shown unambiguously that hydrogen and intrinsic defects only can be involved into structure of both the (HDD) AA1 and (HSD) NL10-like defects. Oxygen presence suppresses the formation rate of these donors.

In order to detect a distinction between molecular structures of the (TDD⁺) NL8 and its H-related analogy, the (HDD⁺) AA1, an uniaxial stress-induced alignment and recovery kinetics of the AA1 center were studied and the data were compared to those of the (TDD⁺) NL8, which have recently been obtained [4]. In these experiments the FZ Si with low ($\leq 10^{16} \text{ cm}^{-3}$) content of oxygen were used. The recovery kinetics reveal that reorientation rate of the (HDD⁺) AA1 defect is on four order larger than of the (TDD⁺) NL8 one. Activation energy for the AA1 atomic reorientation was determined to be $E_R = 2.3 \pm 0.1 \text{ eV}$. Analysis of the effective C_{2v} piezo-spectroscopic tensor **B** indicates that AA1 defect, as well as NL8 one, produces strong compressional strain field along its C_2 [001] 3-axis. However, in contrast to the NL8, there is also large compressional strain along its [110] 1-axis (i.e., both B_3 and B_1 components of the AA1 defect have a negative sign). These findings unambiguously indicate that AA1 (HDD⁺) EPR spectrum, arising from defect of C_{2v} symmetry with principal g-tensor parameters very close to those of the NL8 (TDD⁺), really is defect with another molecular structure. On the other hand the strong resemblance between the AA1 and NL8 spectra and also fact that both derive from shallow double donors, it seems, can not be accidental, and we can propose that their cores are very similar (or even the same) while shells are different. We suggest that core of the HDD consists of the <001> self-interstitial aggregation (<110> chain at least of the two <001> Si di- or split-interstitials), while hydrogen atoms (or oxygen atoms in the case of TDD) are located mainly in shell and influence strongly on atomic reorientation and formation kinetics. Presented results also demonstrate that the NL8 EPR spectrum have not a unique nature (as well as the NL10), that is, the defects with different microscopic structures give rise to the very similar NL8-like EPR signal. Tentative model of the (HDD) AA1 are presented and discussed.

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EFFECT OF LOCALIZED VIBRATIONS ON THE SILICON SURFACE CONCENTRATIONS OF HYDROGEN OR DEUTERIUM

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This paper deals with the calculations of the concentrations of adatoms H (or D) on the surface of the silicon crystal which is in the thermodynamic equilibrium with hydrogen or deuterium gas. Being isotopes, deuterium and hydrogen have identical electronic properties. Therefore the difference in adatom behavior can be related to their vibrational properties only. The description of the equilibrium between the Si surface and the gas of molecules requires the knowledge of both the chemical potential of H (D) on the surface and the chemical potential of H (D) in the gas. Along with the electronic contribution, the chemical potential of the adatom has the vibration contribution. It is found from the lattice dynamics of the impurity atoms on the surface. The chemical potential of H (D) atoms in the gas is known from the thermodynamics of two atomic gases. The equality of the chemical potentials of H (D) atoms on the surface and in the gas in the thermodynamic equilibrium enable us to find the surface equilibrium concentrations of the adatoms. It is shown that at the same thermodynamic conditions (the equal pressures and the equal temperatures), the D surface concentrations is significantly higher than the H surface concentrations due to the difference of H and D surface localized vibrations. The major contribution to the value of the ratio of the D and H surface concentrations is given by the exponent

$$e^{\frac{3\hbar(\omega_{loc}^{(H)} - \omega_{loc}^{(D)})}{2T}},$$

where $\omega_{loc}^{(H)}$ and $\omega_{loc}^{(D)}$ are the localized vibration frequencies of the H- and D-adatoms, respectively, and $\omega_{loc}^{(H)} > \omega_{loc}^{(D)}$. At the passivation temperature of 700K this ratio is about 10.

It is quite probably that this effect is an important factor for the observation of the large isotope effect of a factor of 10 (and at instances 50) increase of MOS-transistor lifetime when hydrogen is replaced with deuterium during the process of the silicon wafer passivation [1, 2]. The larger equilibrium populations of surface dangling bonds by deuterium as compared to hydrogen becomes significant for the passivation process described in these works.

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LOCAL-VIBRATIONAL-MODE ABSORPTION OF TWO O-H CENTRES IN GaP

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In GaAs a local-vibrational-mode (LVM) absorption line at 3300.0 cm^{-1} has been assigned to the stretching mode of an O-H centre [1]. This line shows unusual behaviour under uniaxial stress, and the microscopic structure of this O-H defect has not been clarified so far.

We have investigated a large number of LEC-grown GaP samples by FT-IR spectroscopy and measured at $T = 7\text{ K}$ two LVM lines at 3250.9 cm^{-1} (half-width $\Gamma = 0.32\text{ cm}^{-1}$) and at 3106.0 cm^{-1} ($\Gamma = 0.08\text{ cm}^{-1}$). The high frequency of these vibrational lines suggests that they are due to O-H stretching modes. To verify that hydrogen is indeed part of the vibrating defects, we prepared a LEC-grown GaP crystal containing also deuterium. For such GaP:D samples, the above mentioned lines are again measured, and in addition, new lines are found at 2415.0 cm^{-1} ($\Gamma = 0.8\text{ cm}^{-1}$) and 2306.9 cm^{-1} ($\Gamma = 0.06\text{ cm}^{-1}$). The frequency ratio of both groups of lines amounts to $r = 1.346$. This result evidences that centre I (lines at 3250.9 cm^{-1} and 2415.0 cm^{-1}) as well as centre II (lines at 3106.0 cm^{-1} and 2306.9 cm^{-1}) contain one hydrogen or one deuterium atom, where the low value of $r = \omega(\text{X-H}) / \omega(\text{X-D})$ indicates that this H(D) is bonded to a light atom. The possible candidates for the light atom X available in the investigated samples are carbon, nitrogen, and oxygen. C and N can be excluded as the C-H and N-H centres in GaP and GaAs are well known and their LVM lines are identified. Therefore, we assign the new lines to two different O-H centres in GaP.

The LVM lines of both centres are measurable up to $T = 300\text{ K}$. This indicates that they are weakly coupled to the GaP lattice. The shift and broadening of the lines with temperature are measured and discussed. Both O-H centres have been found to be photosensitive at $T < 100\text{ K}$.

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NEW HYDROGEN RELATED LVMS IN INP

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Hydrogen acts as a passivator neutralizing electric-active imperfections in InP, it also can acts as an actuator for generation of antistructure defect. That is to say it plays an important role in defects reaction process. Local vibrational modes in tenths of InP samples reveal clearly existence of complexes related to hydrogen. Complexes of vacancy at indium site (V_{In}) with one to four hydrogen atoms and isolated hydrogen or hydrogen dimers and other optical absorption lines which tentatively be assigned to hydrogen related defects were investigated by FTIR. However, not enough is known about the nature and role of hydrogen in InP. This paper presents a detailed FTIR study of novel hydrogen related LVMS in InP single crystal. We have found a series group of LVMS related to hydrogen in InP include complexes involving iron precipitate and hydrogen, complexes involving iron at indium site and hydrogen as well as complexes involving hydrogen with some other transition metals other than Be Zn Fe Mg Cd V Ti. Sharp LVMS related to complexes involving iron at indium site and hydrogen can be seen in room temperature. Microscopic model of hydrogen related defects was given. Structural, electronical and vibrational properties of LVMS related to hydrogen as well as their temperature effects are discussed.

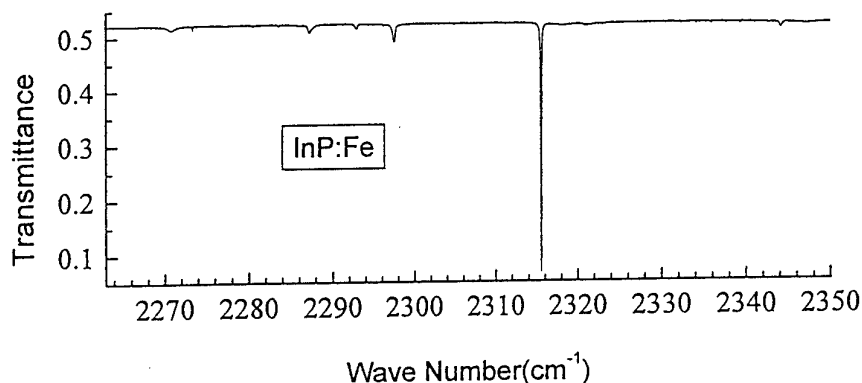


Fig.1 Transmission of hydrogen related LVMS from 2263 to 2350 cm^{-1} in semi-insulating InP:Fe at 12K. The resolution is 0.05 cm^{-1} .

HYDROGENATION OF B IN Si BY PRESSURIZED WATER BOILING: COMPARISON BETWEEN H₂O AND D₂O BOILING

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It is well known that hydrogen incorporated in p-type semiconductors neutralizes the acceptor and passivates its electrical activity. It has been shown that a pressurized water boiling at 2 atmospheric pressures(atms) and 120 °C accelerates significantly hydrogenation and passivation of B in Si compared with boiling at atmospheric pressure.¹⁾ In this work, the boiling has been extended to the higher-temperature, higher-pressure one, by using a specially designed stainless-steel autoclave, which can operates at 200 °C and 100 atms. The heavy water (D₂O) boiling has also been performed for comparison. Passivated B-doped Si has been annealed to study the passivation mechanism.

It has been found, by C-V carrier profiling for p-type wafers and sheet-resistivity or IR-absorption measurements on B-doped layers, that passivation of B in Si by high-pressure light water boiling for 6 hrs is enhanced up to 8 atms, but, beyond 8 atms, it decreases. However, in the heavy water boiling, the passivation increases still beyond 8 atms, although the degree of passivation is lower than that of light-water boiling below 8 atms. Annealing experiment shows that the light-water passivated B-doped layer is annealed out around 175 °C, which is near the temperature required for boiling beyond 8 atms, while the heavy-water passivated B-doped layer is annealed out at much higher temperatures of e.g. 225 °C, which corresponds to a boiling pressure higher than 10 atms. The activation energies for the annealing rates obtained for light-water and heavy-water passivated B-doped layers were 0.7 and 0.9 eV, respectively. These activation energies may be associated with dissociation of H and D, respectively, from passivated B atoms. The above-mentioned passivation behavior for light-water boiling, therefore, is understood in terms of a competing, high-temperature annealing effect.²⁾ On the other hand, passivation by heavy water still increases beyond 8 atms because of less annealing effect. The lower passivation effect of heavy-water boiling below 8 atms may be due to the one-tenth smaller ion product of heavy water than that of light water.

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HYDROGEN ENHANCED SHALLOW THERMAL DONOR FORMATION IN P AND N TYPE CZOCHRALSKI GROWN SILICON

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The results of the hydrogen enhanced thermal donor (TD) formation in both n- and p-type Czochralski grown silicon are presented. The hydrogenation of the samples were performed in a DC hydrogen plasma reactor normally used for reactive ion etching or in standard PECVD setup. The CV measurements were used for the determination of the carrier concentration of the samples. In some cases the spreading resistance measurements were used for the depth resolved measurements. A conversion of p-type into n-type Cz silicon by hydrogen enhanced TD formation occurs. One can distinguish one step process (p-n junction formation appears just after the hydrogen plasma exposure of p-type CZ Si at 400 C) and two step process (p-n junction formation requires subsequent post hydrogenation annealing at 400 - 450 C of p-type Cz Si). For n-type Cz Si an increase of carrier concentration at these processes was observed. Detailed studies show that the maximum TD concentration depends on the oxygen concentration, the temperature and the duration of hydrogen plasma treatment as well as the post-hydrogenation annealings. A kinetic model for hydrogen enhanced TD formation in both n and p-type Cz Si is presented.

CATALYTIC ROLE OF HYDROGEN IN ENHANCEMENT OF IMPLANTED DOPANT ACTIVATION IN SI: QUANTUM CHEMICAL RESEARCH AND EXPERIMENT

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Nowadays it is common knowledge that atomic hydrogen can passivate the electrical activity of shallow donor and acceptor dopant in crystalline silicon. However, there is another class of the phenomena related to hydrogen where hydrogen plays a role as catalyst for defect reactions with the impurities localized in interstitials of the semiconductor crystalline lattice. Enhanced activation of electrical activity of implanted dopant by atomic hydrogen is the process linked to such a kind of the reactions.

In the paper the quantum chemical investigations of incorporation of the different dopants (B, P and As) in the silicon lattice vacancy site bonded with atomic hydrogen have been performed. The SCF MO LCAO technique in the NDDO valence approach that takes into account the relaxations of all atoms in the cluster shows the considerable decrease of the potential barrier for incorporation of the interstitial dopants into hydrogenated vacancy in comparison with the unhydrogenated one. The calculations have been performed for different localization of hydrogen in the vicinity of the vacancy (inside or outside the vacancy), for differently charged hydrogen localized outside the vacancy (H^+ , H^0 and H^-) and for different transport directions of the doping atoms to the vacancy ($\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$). The results are presented in Table.

Table. The potential barrier heights (eV) for incorporation of different dopants into vacancy site for hydrogen localized outside and inside (in perentheses) the vacancy

State of vacancy	B			P			As		
	$\langle 111 \rangle$	$\langle 110 \rangle$	$\langle 100 \rangle$	$\langle 111 \rangle$	$\langle 110 \rangle$	$\langle 100 \rangle$	$\langle 111 \rangle$	$\langle 110 \rangle$	$\langle 100 \rangle$
V	6.3	8.5	7.6	7.2	9.5	8.6	8.8	12.1	11.1
VH_4^0	3.7 (4.4)	5.8 (6.4)	5.0 (5.6)	4.5 (5.1)	6.9 (7.4)	6.2 (6.9)	5.4 (5.9)	8.1 (8.6)	7.3 (8.0)
VH_4^+	3.3	5.1	4.4	4.1	5.9	5.6	4.8	7.7	7.3
VH_4^-	4.7	6.7	6.0	5.7	7.6	7.1	6.5	9.0	8.0

Hydrogen localization outside the vacancy was shown to lead to the greater decrease of the potential barrier height than hydrogen localization inside the vacancy due to additional energy needed for moving aside the hydrogen atoms. For both type of hydrogen localization for the case of the VH^+ structure the decrease of the potential barrier height is maximal and equals to 1.8 in comparison to unhydrogenated vacancy. For the case of the VH^- structure the decrease of the potential barrier is minimal and equals to 1.3. The decrease of the potential barrier height was shown to result in the decrease of the implanted dopant activation temperature more than 300°C.

The calculations demonstrate that hydrogen has to leave his position in the bond near the vacancy when the dopant is incorporated into the hydrogenated vacancy and to capture preferably by neighbouring dangling bonds. So, the hydrogen is catalyst for this sort of the reactions.

The theory was compared with the experimental data on enhanced activation of implanted arsenic in the hydrogen implanted silicon and have shown the good agreement.

**EFFECT OF ELECTRON-PHONON INTERACTION IN COPPER DOPED II-VI AND
IRON DOPED III-V CUBIC SEMICONDUCTORS**

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Optical absorption and emission measurements of Cu^{2+} as a substitutional impurity in ZnS and of Fe^{2+} in InP are analyzed by means of an electron-phonon coupling model. The model is based on crystal-field theory and includes hybridization with the orbitals of the ligands of the host crystal, spin-orbit interaction and a dynamic Jahn-Teller coupling of the orbital doublet and triplet states of the magnetic ion with phonons of Γ_3 and Γ_5 symmetries, respectively. While in Cu^{2+} the orbital triplet of Γ_5 symmetry has lower energy than the doublet of Γ_3 symmetry, the opposite is the case in Fe^{2+} . The measured positions and relative intensities of the spectral lines are described with good accuracy by the theoretical model. It is shown that, in the case of Cu^{2+} , a strong Jahn-Teller interaction between the Γ_5 orbital ground state and transverse acoustic phonons of Γ_5 symmetry is the predominant interaction. By contrast, the iron-based III-V compounds exhibit a weak electron-phonon coupling in the electronic ground state with overtones of transverse acoustic phonons ($\text{TA}(L)$) of Γ_3 symmetry. It is also necessary to introduce a weak interaction between the electronic excited state and a local vibrational mode of Γ_5 symmetry to explain the observed resonant absorption lines. Finally, the larger covalent character of the bonds in III-V semiconductors compared to II-VI compounds is reflected in a larger reduction from the free ion value of the magnitudes of the spin-orbit coupling parameters.

POSTER SESSION P2

Impurity states in semiconductors: general

P2-36 ./ P2-51

EXCHANGE-CORRELATION EFFECTS ON A MULTICOMPONENT HOLE GAS IN SEMICONDUCTORS

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The description within density functional theory of an interacting multicomponent hole gas of a semiconductor in an external potential has been for decades a long standing problem of solid state physics. The importance to find its rigorous solution increased recently due to the fact that the p-type delta-doping quantum wells and superlattices had received a great attention as suitable systems for device applications. Self-consistent band structure calculations for holes in such systems have been performed by various authors using the Luttinger-Kohn multi-band effective mass equation. The exchange-correlation (XC) effects were either neglected or accounted for in ad-hoc manner. When XC effects are neglected, remarkable differences between experimental and theoretical results are observed.

In this work we describe the rigorous derivation of a set of self-consistent one-particle equations for holes in semiconductors which solves the problem mentioned above [1]. Using the effective mass theory for the non-interacting hole gas we obtain a plane-wave expansion of the multi-band effective mass equation in hole representation. Combining effective mass theory with density functional theory for the interacting hole gas we generalize the Hohenberg-Kohn theorem and obtain a set of generalized Kohn-Sham equations for the multicomponent gas. It is demonstrated how the XC potential matrix may be calculated by the local density approximation (LDA). As it is the spirit of LDA to take locally the same XC energy expression for the inhomogeneous gas as for the homogeneous gas, local partial hole densities occur in the LDA expression of the XC energy. We neglect heavy-light hole cross terms in the density operator, as these terms are small if the inhomogeneity is small. It is fully justified as the small inhomogeneity is just the condition for the applicability of LDA. On the other hand, in the XC energy functional heavy-light cross terms are present even in the homogeneous case, and there we do take these terms fully into account in both, homogeneous and inhomogeneous case.

Due to the spin mixed character of hole states the exchange interaction also takes place between holes of different types, while that between holes of the same type is reduced. The exchange potentials depend on the mixture ratio between heavy and light holes, and tend to a finite value if the density of the hole type under consideration approaches zero while that of the other type differs from zero. Expressions are provided to calculate the XC potential for the various hole components in LDA without employing results derived for the electrons. XC effects are found to increase the splitting between the heavy and light holes ground state levels. Hole valence band structure calculations including the rigorous treatment for the XC effects were carried out for p-type δ -doped isolated quantum wells and superlattices in Si and GaAs. The luminescence spectra of such structures were also calculated by using a 8-bands Kane model.

We calculated the exact functions determining the exchange energy potentials for the anisotropic and isotropic cases and found the fitting functions to provide a simple and accurate way to account for many body effects in an interacting multicomponent hole gas. Explicit results are given for the exchange energy and potentials for valence band holes in zincblende and diamond type semiconductors.

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SHALLOW DEFECTS IN SiGe BULK CRYSTALS

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We have investigated boron doped Si-rich and phosphorus doped Ge-rich $\text{Si}_{1-x}\text{Ge}_x$ bulk crystals by photoconductivity, photoluminescence, and temperature-dependent Hall effect measurements. We have determined the shift of the impurity levels with alloy composition and have studied the influence of alloy fluctuations on the impurity levels.

Up to now, only little is known about the properties of shallow impurities in $\text{Si}_{1-x}\text{Ge}_x$ and the influence of alloy composition on the impurity levels. In strained $\text{Si}_{1-x}\text{Ge}_x$ epitaxial layers grown on Si substrate, both alloy effects and strain due to the lattice mismatch between Si and $\text{Si}_{1-x}\text{Ge}_x$ influence the properties of dopants. In bulk crystals, alloy effects alone can be studied.

For the boron doped Si-rich samples, Hall effect measurements yield the relation $E_i = (44.4 - 108 \cdot x)$ meV for the change of the boron ionization energy E_i with alloy composition over the composition range $0 \leq x \leq 0.13$. The far-infrared photoconductivity onset caused by the shallow acceptor boron does not shift as much to lower energies with increasing Ge content as previously reported [1]. This experimental result is in good agreement with theoretical calculations in the literature [2]. Comparison of the Hall effect data with the shift of the photoconductivity spectra, and the evaluation of photoluminescence linewidths give experimental evidence for inhomogeneous distribution of Ge atoms in the alloy.

Photoconductivity measurements of Ge-rich $\text{Si}_{1-x}\text{Ge}_x$ doped with the shallow donor phosphorus for $0.9 < x < 1$ indicate a stronger shift of the impurity ground state for the Ge-rich side than previously reported for the Si-rich side of the alloy composition. This strong influence on the Ge-rich side can be caused by the rapid increase of the indirect band gap due to the increase of the conduction band minimum at the L-point of the Brillouin zone from $x=1$ to $x=0.85$. Transitions that involve excited levels of the shallow acceptor boron and the shallow donor phosphorus are recognizable as a red shift of the photoconductivity onset with increasing temperature.

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RADIATION-INDUCED SHALLOW-LEVEL COORDINATION CENTERS IN AMORPHOUS CHALCOGENIDE SEMICONDUCTORS

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Amorphous chalcogenide semiconductors (AChS) based on quasi-layer As_2S_3 pyramidal units and three-dimensional GeS_2 tetrahedral ones are typical wide-bandgap materials characterized by a variety of specific structural defects with shallow-level electronic states. Such defects represent themselves as anomalously coordinated atoms of the AChS structural network in respect to the normally coordinated ones. They appear in the result of high-energetic irradiation by ^{60}Co gamma-quanta, accelerated electrons, neutrons, protons.

The above mentioned processes have coordinating character in contrary to the crystalline semiconductors. It means that defect centers appear in the AChS structure due to chemical bonds switchings: one covalent bond is destroyed and another one is formed instead. Consequently, created defects are characterized by electron charge excess and anomalous coordination relatively to normal atoms involved in the structural network.

The differential Fourier spectrometry technique in $400-100\text{ cm}^{-1}$ region have been used for the first time for coordination defects investigation in the binary and ternary AChS systems, such as As-S, As-Se, As-S-Sb, As-S-Ge, As-Se-Sb, As-Se-Ge, Sb-S-Ge, As-S-Ta and others [1-3]. All topological variants of the coordination defects formation processes statistically possible in these AChS systems have been taken into account for physical consideration of the real microstructural transformations.

It is shown that coordination defects formation processes in AChS associated with certain schemes of bond destructions and polymerizations are the results of the following stages:

1. Initial microscopic process - excitation of electron and (or) hole pairs localized at soft atomic configurations [4] or excitation of electron-hole pairs (excitons) [5];
2. Intermediate process - weakening of intermolecular interactions that causes the possibilities to displacements of atoms and atomic blocks;
3. Formation of new metastable state (exciton self-trapping) at the level of short-range ordering due to observed chemical bonds transformations [1,2] as well as at the level of intermediate-range ordering in accordance with EXAFS data obtained earlier [6].

These stages are interconnected and depend on not only the chemical-technological peculiarities of the AChS samples, but also temperature in source cavity, as well as power and absorbed doses of high-energetic ionizing irradiation.

It is shown that an alternative way to explain the obtained experimental data is the model of random covalent network transformations considering the process of photoinduced two-bonds switchings in AChS [7].

It is established at the first time that coordination defects can be characterized by two principally different levels of time stability. The first ones (coordination defects with high level of time stability) have a deep-level electronic states in the forbidden band-gap, and the second ones (coordination defects with low level of time stability) have a shallow-level electronic states.

The new experimental results on shallow-level coordination defects investigation in AChS using photoconductivity and ESR spectroscopy methods are discussed.

The topological mathematical approach to the modelling of coordinating defects formations processes in the investigated AChS of above mentioned chemical compositions is discussed.

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SHALLOW DONOR MAGNETOSPECTROSCOPY IN MBE- GROWN CdTe
LAYERS DOPED WITH INDIUM AND IODINE

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The progress of obtaining controlled structures in semiconductor technology as well as an increasing understanding of phenomena influencing the intra-shallow-donor transitions make possible a deeper analysis of processes occurring on a microscopic scale of a crystal. In this paper we present results and analysis of magnetooptical measurements (up to 9 Tesla) done at LHe temperatures on thin n-CdTe layers doped with In or I grown on undoped CdTe buffer (thickness of the order of 4-7 μm) and the semiinsulating GaAs substrate by means of MBE technique. The photoconductivity spectra were measured during simultaneous illumination with an infrared light (causing intra-shallow-donor transitions) and a visible light. A comparison with the spectra obtained with no visible light illumination shows that it is possible to populate shallow donor states in the undoped CdTe layer in a metastable way by illumination with visible light. This comparison allowed to estimate an order of magnitude of the lifetime of electrons populating metastably shallow donor states in undoped CdTe. Under visible light illumination there is also clearly visible a pronounced signal from residual shallow donors in GaAs substrate. A small differences in chemical shifts between In and I in CdTe were observed. A dependence of the shape of obtained spectra with respect to the location of donor centers relative to the interface is discussed. A detailed analysis of the temperature and voltage dependence of the shape of spectra show that the a different (from the Gaussian one) shape of the peaks should be considered. We show that there is no influence of possible contribution of electron gas of reduced dimensionality on the shape of discussed spectra.

METASTABLE ELECTRONIC STATES AND THERMOELECTRICAL INSTABILITIES IN THE PbTe(In) BASED FILMS.

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The impurity centres of indium in PbTe based alloys are characterised by DX-like behaviour [1,2] (see fig.1). The ground state E_2 with two electrons localised at the impurity centre is responsible for the effect of Fermi level (FL) pinning. The position of pinned FL depends on the alloy composition and temperature T . The metastable electronic state E_1 with one electron localised at the impurity centre appears to have a higher energy position and may exist closely to conduction band edge E_C . These states are separated from each other and the conduction band edge by energy barriers. That leads to a long term character of kinetics processes, the persistent photoconductivity at low temperatures $T < T_C$ and thermoelectrical instabilities caused by the redistribution of charge carriers.

The $Pb_{1-X-Y}Sn_XGe_YTe(In)$ ($0.06 < X < 0.2$; $0.08 < Y < 0.12$, $0.5\% < C_{In} < 1\%$) films on the BaF_2 substrates have been prepared by hot wall epitaxy method. All the samples are photosensitive at temperatures lower than $T_C \sim 35$ K. The standard method of the thermally activated current spectroscopy after IR-illumination has been applied to study the peaks of the thermally induced currents (TIC) in the temperature range 4.2-30 K. The temperature corresponding to the maximum of single TIC peaks T_M appears to be extremely low being varied from 6 K up to 14 K for the films with different composition (fig.2). It should be mentioned that T_C is found to be close to constant value for all the samples. It is established that the influence of the magnetic field up to 5 T on the shape and T_M values of TIC peaks is negligible. The experimental results are interpreted in terms of thermal excitation of charge carriers from metastable impurity level E_1 to conduction band E_C . The estimations show that the energy $(E_C - E_1)$ lies within the interval (5-15) meV and depends on the composition of the films.

At low excitation levels under the IR-illumination the instabilities of the photoresponse have been observed at temperatures close to 4.2 K. The combined effect of lighting and slight heating of the sample up to ~ 6 K results in reducing or increasing of the photoresponse depending on the experimental regime. This process may be controlled.

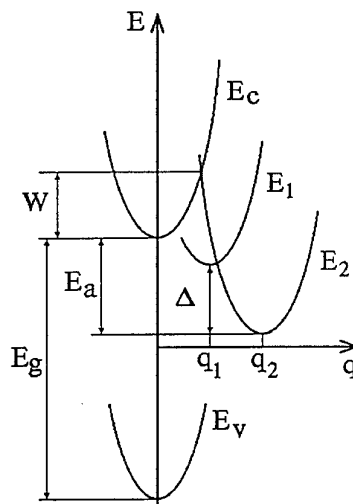


Fig.1 The energy diagram for impurity states in $Pb_{1-X-Y}Sn_XGe_YTe(In)$ films.

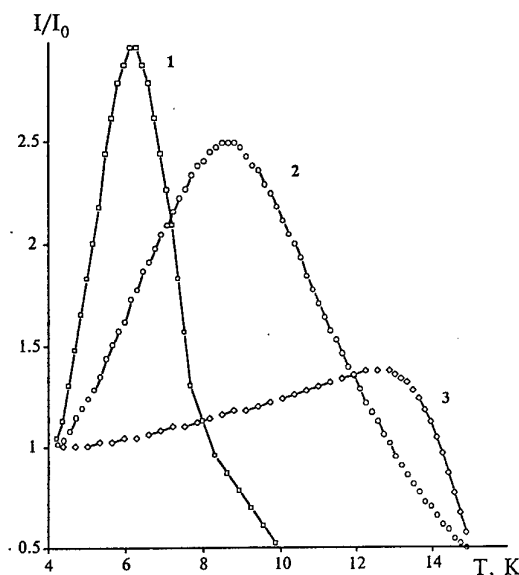


Fig.2 The thermally induced currents in $Pb_{1-X-Y}Sn_XGe_YTe(In)$ films.

curve 1 : $X=0.20$, $Y=0.12$, $C_{In}=1.0\%$

curve 2 : $X=0.06$, $Y=0.08$, $C_{In}=1.0\%$

curve 3 : $X=0.10$, $Y=0.10$, $C_{In}=0.5\%$

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**STUDY OF THE DEPOSITION MECHANISM IN THE GROWTH OF HYDROGENATED
AMORPHOUS SILICON LAYERS BY TOPOGRAPHICAL APPROACH**

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The hydrogenated amorphous silicon (a-Si:H) films investigated are deposited by plasma enhanced CVD under various sets of conditions. As expected various film surface morphologies are obtained which reflects some differences in the growth process occurred. By means of an atomic force microscopy (AFM) study, the topography of the films obtained is considered here in specific cases using two quantitative statistical parameters namely, the root-mean-square surface roughness (σ) and the lateral correlation length (L_c). Together, the two parameters give a local picture of the surface irregularities formed. The evolution of each of them with the image scan length (L) provides a relevant indication on the particular role of the conditions applied on the film surface morphology.

First, we examine by this way, the effect of the temperature of the film deposition substrate. It is shown that high temperatures (i.e. $T_s = 350^\circ\text{C}$) give rise to only one growth mechanism which leads to small grains originated by the polymerization of SiH_x radicals. Secondly, we study the role of the opto-electronic optimization of the samples obtained by the dilution of silane in hydrogen prior to the film deposition. It is shown that this fact restricts the last mechanism to the lowest L values. This behavior implies the occurrence of a second mechanism justified by the formation of the large-sized grains obtained. These grains are mainly originated by silicon clusters or nano-particles. Thirdly, we study the role of doping on the film surface morphology. It is observed here that n or p -type doping leads to a tremendous smoothening of the film surface which concurs with the brightening phenomenon observed with pure metal samples as a result of a little amount of a foreign element.

It is established now that the surface morphology greatly contributes in the specific behavior of material surface properties. The present work shows that the technology of local probe microscopy supplies a modern and interesting tool of research in this direction.

BOUND ELECTRON AND HOLE STATES DUE TO LONG RANGE DEFORMATION POTENTIAL OF DISLOCATION AND RELATED OPTICAL PROPERTIES OF DIRECT-GAP SEMICONDUCTORS

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Experimental observations of new components of luminescence and the additional absorption within the gap depending on the dislocation density in direct-gap semiconductors with dislocations were reported in a series of publications. Theoretical results presented deal with spectrum of bound electron and hole states, and corresponding optical transitions as well as spectral dependences and polarization of the interband dislocation absorption and luminescence in direct-gap semiconductors with edge and screw dislocations. A possible explanation of the experimentally observed predominant polarization of the interband dislocation absorption and luminescence along the Burgers vector is proposed.

In cubic crystal the spectra of electron and hole states bound to a single straight edge dislocation and screw one due to its long range deformation potential are calculated. The one-band approximation is used, *i.e.* the spectrum of the electron dislocation states close to the conduction band (Dc states) and the spectrum of the hole dislocation close to the valence band (Dv states) are treated separately. The threefold degeneracy of the valence band maximum in a perfect crystal, an effective mass anisotropy and a real structure of deformation potential tensor are taken into account. The anisotropic field of dislocation removes this degeneracy originating the series of one-dimensional bands of Dv states.

In the dislocation absorption spectrum each Dv band gives its own absorption edge located according to the band depth. The contributions to absorption from different Dv bands are added. Due to a definite symmetry of Dv states some selection rules arise.

The predominant polarization of interband dislocation absorption and luminescence is determined by the transition with the lowest energy between the deepest dislocation hole band and the conduction band (c-band). The calculations under the real values of parameters show that the dipole momentum of this transition for an edge dislocation is perpendicular to the dislocation line and parallel to the Burgers vector. For a screw dislocation the dipole momentum of the lowest energy transition is shown to be parallel to the dislocation line and to the Burgers vector.

For a screw dislocation, each dislocation hole band is characterized by an azimuthal quantum number $m = 0, \pm 1, \dots$. The lowest Dv band ($m = 0$) is slightly affected by the anisotropy of the effective mass. Only the change of the effective mass is observed. The states with azimuthal number $m \neq 0$ are considerably more affected by the anisotropy of the effective mass. A mixing of longitudinal and transverse motions with respect to the dislocation line direction takes place and terms linear in $k_{\parallel}$ appear in the dispersion law. Thus, an optical circular dichroism (*i.e.* a different absorption of light with right and left polarizations) is evident to be observed.

For an edge dislocation a contribution of the transitions from the dislocation hole band to the c-band to the dislocation absorption coefficient has the form $(\hbar\omega - E_0)^{1/2}$, where E_0 is the lowest energy of transition from the band. For a screw dislocation, contributions of such bands to the dislocation absorption coefficient are of the form $(\hbar\omega - E_0)^{|m-s|+1/2}$, where $s = 0$ for the polarization of light along the dislocation line and $s = \pm 1$ for the two orthogonal circular polarizations. The general view of the dislocation absorption spectrum for a screw dislocation in different polarizations of light is analyzed.

MECHANISM OF DEFECT FORMATION PROCESS IN ELECTRON-IRRADIATED
Pb_{1-x}Sn_xSe ALLOYS WITH INVERSE BAND STRUCTURE

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In the present work the kinetics of the electron concentration variation in n -Pb_{1-x}Sn_xSe ($x=0.20, 0.25$) alloys irradiated with electrons ($T \approx 300$ K, $E=6$ MeV, $\Phi \leq 7.1 \cdot 10^{17}$ cm⁻²) was investigated. A decrease of the free electron concentration n with increasing the radiation flux Φ was observed (Fig.1). In the alloys with low initial electron concentration the electron concentration decreased up to zero and the metal-insulator

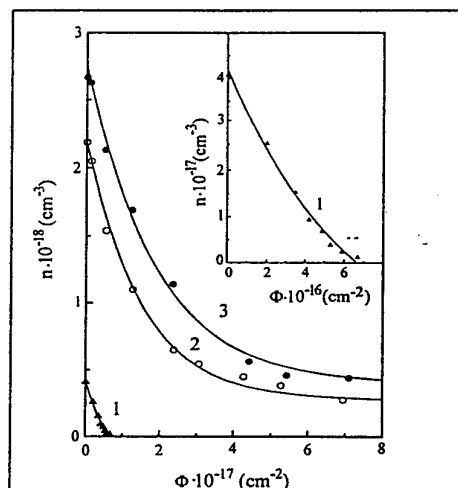


Fig.1 Dependence of the electron concentration in n -Pb_{1-x}Sn_xSe on the radiation flux at $T=4.2$ K.
Samples: 1 - $x=0.25$; 2,3 - $x=0.20$.

transition induced by electron irradiation was revealed. But in the alloys with high initial electron concentration the decrease of the variation rate of electron concentration upon an increase in the radiation flux occurs and $n(\Phi)$ dependences tend to saturation.

According to the existing conception the electron irradiation of Pb_{1-x}Sn_xSe ($0.19 < x < 0.35$) alloys with inverse band structure leads to appearance of the radiation defect states E_i of acceptor type located within the forbidden band. Under the irradiation the electron concentration decreases as a result of electron flowing from the conduction band to the empty radiation defect states E_i . In this case the dependence of electron concentration on radiation flux is determined by the introduction rate of defect generation. So one can suppose that the effect of the decrease in the variation rate of electron concentration under irradiation can be explained by decreasing the radiation defect generation rate with increasing the radiation flux. Besides, it can be connected with the considerable width of the defect level E_i and its overlapping with the conduction band edge in the investigated alloys.

To explain the effect of the decrease of radiation defect generation rate under irradiation the model of the defect formation process was put forward. According to this model the major mechanism of defect formation process is the generation under irradiation the complexes including the primary radiation defects (vacancies) and intrinsic point structure defects typical of the initial crystals. We suppose that the electron concentration decreases exponentially under irradiation due to the decrease in the concentration of free intrinsic structure defects N_d resulting in the exponential decrease in the rate of the defect generation:

$$n(\Phi) = n_0 \cdot \exp\left(-K \cdot \frac{\Phi}{n_0}\right), \quad \frac{dn}{d\Phi} = -K \cdot \exp\left(-K \cdot \frac{\Phi}{n_0}\right), \quad N_i(\Phi) = N_d \cdot \left[1 - \exp\left(-K \cdot \frac{\Phi}{N_d}\right)\right], \quad \frac{dN_i}{d\Phi} = K \cdot \exp\left(-K \cdot \frac{\Phi}{N_d}\right)$$

where N_i is the density of defect states, K is the initial rate of the defect generation.

In order to determine the energy position of defect states E_i relative to allowed band edges and to estimate the main parameters of defect formation process model the comparison of theoretical and experimental dependences $n(\Phi)$ was carried out. Theoretical dependences were obtained assuming that the sum of electron concentrations in the conduction band $n(\Phi)$ and in the radiation-induced defect states $n_i(\Phi)$ is equal to the initial electron concentration n_0 in the sample and the density of states function in the E_i level $g_i(E)$ may be described by the Gaussian-type curve:

$$n_0 = n(\Phi) + n_i(\Phi), \quad n_i(\Phi) = \int_{-\infty}^{E_F} g_i(E) dE, \quad g_i(E) = \left(\frac{N_i}{\sigma \sqrt{2\pi}}\right) \cdot \exp\left[-\frac{(E - E_i)^2}{2\sigma^2}\right]$$

where E_F is the Fermi energy and σ is the width of the radiation defect level E_i .

It was found that theoretical dependences obtained in such a way are in a good agreement with experimental data over the entire range of irradiation fluxes (solid curves in Fig.1). In the alloys with $x=0.2$ the irradiation-induced defect level E_i lies close to the conduction band edge ($E_c - E_i \approx 6$ meV) and in the alloys with $x=0.25$ - close to the valence band top ($E_v - E_i \approx 25$ meV). For all investigated samples defect level have an appreciable width ≈ 18 meV and partially overlaps with the allowed band. Initial concentration of intrinsic point defects $N_d = (0.7 \div 2.5) \cdot 10^{17}$ cm⁻³ and the initial rate of the defect generation $K \approx 10$ cm⁻¹.

**THE SHALLOW ACCEPTOR EIGENSTATES AND SPIN-HAMILTONIAN
IN GaAs-TYPE SEMICONDUCTORS.**

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In cubic semiconductors the light and heavy hole masses ratio is small and it is maximum for Si (0.4). This mass inequality makes possible the simplification of the some problems. Last years there were some attempts to describe these crystals by the model supposing the light hole mass to be zero. But in all papers investigations were limited by the ground state. We take a more general approach which yields an exact analytical solution of the acceptor problem for that model. This approach gave us the possibility to determine both the whole acceptor energy spectrum and eigenfunctions within the arbitrary accuracy, especially, at great radius that is important in some other problems, for instance, for impurity-impurity interaction. Moreover, the acceptor wave function has a some feature at the large radius. For example, the ground state wave function behaves predominantly as a d-like hydrogen function. This method is also suitable for theory of the more actual case of the arbitrary mass relation.

This model may be useful for wide range of the investigations with acceptors and we have adopted it to describe the effect of the electric-dipole spin resonance in GaAs with Mn ions being acceptors. The impurity center can be simulated by the 4-dimensional matrix - spin-hamiltonian with electric field depended terms. A good model for the deep acceptor potential is the Coulomb interaction with dielectric constant decreasing at the small radius. This model describes experimental values both the ionization potential and behaviour of the spectrum levels in electric field.

A NEW METHOD OF THE DETERMINATION OF SHALLOW TRAPS PARAMETERS

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Presence of impurity forming shallow traps in a forbidden gap of the semiconductor can leads to different useful effects in semiconductors and semiconductor devices. The study of such effects caused by impurity and defects in semiconductors with well controllable properties enables more full to understand physics of the appropriate processes. However, experimental research and the measurement of parameters of impurity and various defects levels is a rather laborious work as values of the appropriate parameters differ often after measurements by different methods.

In the present work a new technique of the determination of parameters of shallow traps in semiconductor materials is proposed. The method is based on the found out by us earlier effect of an increase at a low level of injection on the absolute value of the dynamic negative resistance (DNR) in injection- transit-time diodes (ITTDS) doped with traps [1,2]. It is received that in a silicon p^+-n-p^+ (n^+-p-n^+) ITTD, at the presence in transit $n(p)$ region of an impurity creating traps for injected minority charge carriers, with an increase of the traps concentration N_t , DNR is increased on absolute value. Thus, a frequency range where DNR takes place narrows and displaces in a region of lower frequencies. This effect is explained first of all by an increase of a delay of the phase between an alternating current and electric field because of the capture of injected charge carriers by traps and an increase of their "effective" flight time. It is obvious that the effect of a change in the DNR absolute value with an increase in the traps concentration can be used for the determination of parameters of traps (N_t , p_t , E_t , the capture cross-sections etc.).

In Refs. [1,2] it is established that the maximum value of DNR (R^-) for the $Si p^+ n p^+$ ITTD with hole traps is observed at the flight angles $\theta \approx 1.5\pi/\beta$ (at the current density $\mathcal{J}_0 \leq 100 \text{ A/cm}^2$). Parameter β is equal $1+N_t/p_t$, where p_t is the Shockley-Read statistical factor for holes and equal $N_v \exp(-E_t/kT_0)$, where N_v is the effective density of states in the valence band, E_t is the energy difference between the shallow traps position and valence band, k is the Boltzmann constant, T_0 is the absolute temperature. Hence, measuring of R^- at fixed frequency (θ) and carrying out the converse transformation in the expression $R^- = f(\theta, \mathcal{J}_0, \beta)$, it is possible to determine N_t , p_t , E_t and other parameters of traps. For example, if $R^-_{\max} = 3.3 \text{ Ohm}$ at $\theta = 0.942$ (that corresponds to the value $\beta = 5$), we obtained $N_t = 4p_t$. Further, from the diagram of the dependence of the velocity of injected holes on the density of d. c. current $\mathcal{J}_0$ and the traps concentration [1,2], we determined the value of N_t (in this case $N_t = 0.25 \cdot 10^{15} \text{ cm}^{-3}$). From the expression for p_t we can determine also E_t which is equal 0.31 eV. Or, on the contrary, creating a certain impurity, the energy spectrum of levels of which is known or measured or determined by other method, it is possible to find the traps concentration from the expression $N_t = (\beta - 1)N_v \exp(-E_t/kT_0)$. It is possible to determine also, for example, an average time τ_g on expiration of which the captured charge carrier is again released ($\tau_g = \frac{1}{N_v \cdot S_p \cdot V_{tp}} \exp(-E_t/kT_0)$,

where V_{tp} is the hole thermal velocity). It is possible to calculate also the time constant describing the hole capture by traps as well as the concentration of captured holes at equilibrium according to expressions $1/\tau_t = 1/\tau_g + S_p V_{tp} p_0$, $N_{to} = p_0 N_t / p_{o+} p_t$. Here p_0 is the concentration of holes injected in the transit region of ITTD.

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ANISOTROPIC INTRINSIC DEFECTS IN PHOTOREFRACTIVE $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ CRYSTALS

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During the last few years the study of CdTe crystals doped with 3d-elements, first of all V, Ti and Fe, to a great extent have been stimulated by increasing interest to these crystal as a new most perspective photorefractive material in the near-infrared spectrum range. However the status of controlling and understanding intrinsic defects in these crystals, their influence on the photorefractive properties of such materials are at a first stage.

In this work were carried out the complex low-temperature measurements of optical and photogalvanic current spectra (PGC) for $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ ($x=0.0038$). In last case it was possible to determine both the energy and a type of photoionization transition as well as to study the anisotropic centers which are excited unequally for the different directions of light relatively of the crystal orientation.

In figure the PGC spectra of $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ at $T=78$ K is represented where the positive sign band correspond to the photoionization transitions of electrons from the defect levels to the conduction band and the negative sign band - excitation of valence band electrons to the discrete levels arranging in energy

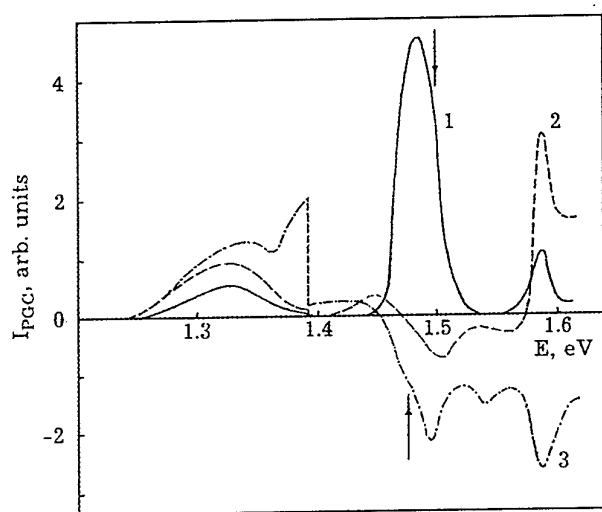


Fig.1. PGC spectra of $\text{Cd}_{1-x}\text{Fe}_x\text{Te}$ ($x=0.0038$) at $T=78$ K for the different directions of light (curves 1-3 correspond to $\langle 110 \rangle$ -, $\langle 100 \rangle$ - and $\langle 111 \rangle$ -directions).

gap. For the light directed along $\langle 110 \rangle$ -direction a PGC spectrum involve two bands of positive sign at 1.485 eV and 1.585 eV. A short-wavelength band is due to the dissociation of excitons. Since an intensive band at 1.485 eV presence only for $\langle 110 \rangle$ -direction therefore such acceptor level correspond to the anisotropic center and probably is due to by a singly charged center including a double charged cadmium vacancy ($\text{V}_{\text{Cd}}^{2-}$) and once ionized donor (D^+), i.e. ($\text{V}_{\text{Cd}}^{2-}\text{D}^+$)-center. In this case the ionized donors probably are noncontrolled impurities of III group elements which substitute of vacancy cadmium arranging along $\langle 110 \rangle$ -direction.

The results shown in figure illustrate that a negative sign band at 1.495 eV for the $\langle 111 \rangle$ -direction of light are a complex. This band has a singularity (indicated by pointer on the curve 3). The energy position it coincide with the position of positive sign band at 1.485 eV, which has also singularity (indicated by a pointer on the curve 1). It indicates that the PGC band in the region 1.48-1.50 eV are a complex and is due to the manifestation of the different photoionization transitions. In particular, the band at 1.495 eV may be due to the transitions from the vacancy band to the level $E_c - 0.10$ eV which correspond to a complex acceptor centre including Cl atoms substituted of anion site. Such anisotropic centers oriented along $\langle 111 \rangle$ -direction. In the case $\langle 100 \rangle$ -direction the negative sign band arranged at 1.505 eV which is due to the photoionization complex including III group atoms substituted of cation site along $\langle 100 \rangle$ -direction. For this direction the positive sign band are observed at 1.45 eV, which correspond to the transition from the acceptor level $E_v + 0.14$ eV to the conduction band. Such level correspond to a $(\text{In}_{\text{Cd}}\text{V}_{\text{Cd}})$ -complex.

In summary it should be noted that carried out in this work investigations of PGC spectra for the different crystal directions indicates that such measurements are enough effective method of the founding of anisotropic centers in the cubic photorefractive semiconductor, the determination of their photoionization energy as well as the orientation in crystal.

MANY - VALLEY SPLITTING OF SHALLOW DONOR BINDING ENERGY IN SEMICONDUCTORS

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A successive application of the perturbation theory to solving the Schredinger's equation that describes the shallow - donor state in many - valley semiconductors has allowed us to obtain a secular equation its order being equal a valleys' number. That equation enables us to get both a character and values of the donor centre ground state splitting. Intervalley interaction matrix elements entering a secular determinant have been constructed in the Bloch pseudo - function representation. The pseudo - wave functions have been computed from the local empirical form - factors and a basis set of 65 plane waves. These matrix elements differ considerably from those constructed in plane wave approximation.

The impurity centre perturbing potential was approximated by the point screened Coulomb potential.

The numerical calculations have been illustrated by examples of the shallow isochoric donors of 5 groups in Ge and Si. Our results are in excellent agreement with the experimental data for the lowest level $A_1(1x)$ and differ by 14 -15% for the levels $T_1(3x)$ and $E(2x)$.

**THE ELECTRIC BREAKDOWN OF SHALLOW-LEVEL CENTERS AS A BASE OF
RANDOM OSCILLATIONS IN COMPENSATED SEMICONDUCTORS**

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The compensated semiconductor with shallow, hydrogen-like donor centers at the temperature of liquid helium is considered. At such low temperatures almost all electrons are "frozen" on impurity centers and the conductivity of semiconductor is extremely low. At sufficiently high electric fields, because of free carriers heating, the avalanche process of impact ionization becomes possible. It leads to the rapid multiplication of free electrons in the conductive band, i.e. to the transition of semiconductor from low to high-conductivity state. This is a general principle of low-temperature electric breakdown in semiconductors, under of which the complex, nonlinear behaviour of semiconductor can be observed.

We have investigated such nonlinear behaviour of compensated n-Ge connected in series with load resistor and d.c. battery in high magnetic field in regime of current's given direction. A new mathematical model, describing system's dynamics, is introduced. It contains the differential equations, characterising the recombination-ionization processes of free carriers from shallow-level impurity centers and the dielectric relaxation of applied and hall fields (these two last fields determine the total heating electric field in semiconductor). On the basis of this model, by means of bifurcation theory, a simple analytical criterion of continuous (and chaotic among them) auto-oscillations arising is established.

By means of computer modeling the nonlinear oscillations of free carriers concentration, applied and hall fields, magnetoresistance and Hall constant is investigated. While in pre-breakdown range of electric field the regular auto-oscillations have been observed only, in post-breakdown range - beside of regular oscillations the complex, random behaviour of above mentioned quantities have been also obtained. The transition from regular into chaotic regime occurs according to well known Feigenbaum scenario.

Obtained results are in good agreement with experimental datas, according of which the continuous auto-oscillations can be observed in post-breakdown range of electric field in a case of high compensation degree.

THE GROUND-STATE ENERGIES OF SHALLOW ACCEPTORS IN
Ge_{1-x}Si_x CRYSTALS

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On the basis of the hall measurement of Ge_{1-x}Si_x solid solution in the range 6-300 K the ground-state energies of the shallow acceptors in different crystal compositions ($0 < x < 0,3$) are determined.

The investigations are carried out on crystals grown without special doping. It is shown that the activation energy of the shallow acceptors increases linearly with silicon concentration in investigated crystal compositions and is described by the relation:
($E = (10,2 + 28,4x)$ meV).

It is shown that the effective mass theory gives only qualitative agreement with the experimental values. It is also shown that the central core effect part of the impurity potential rises with increasing of silicon concentration in the crystals.

On the basis of obtained data it is assumed that uncontrolled shallow acceptor centres in Ge_{1-x}Si_x are boron atoms.

LONGLIVING EXCITED STATE OF Te DONOR IN GaP

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It was shown [1], that in diamond, silicon and germanium some simple donors and acceptors have longlived excited states, splitted from ground states by valley-orbital or spin-orbital interactions. It should be expected that longlived excited states of impurities can exist not only in diamond-like semiconductors, but in other semiconductors with similar band structure. Really, in GaP doped with Te a slow relaxation of extrinsic photoconductivity (PC) was observed in DC electric field after impurity ionization by short powerful pulses of far infrared radiation [2]. Results were explained by existence of longlived excited state $1S(T_3)$ of Te donor. The investigation was possible only at relatively high temperatures $T > 30K$, because free electrons in the experiment were created by thermal ionization of excited states. So, the value of lifetime of the excited state (7 ms) was obtained as adjusting parameter in the temperature dependence of PC relaxation time. It was also possible an influence of contacts on the obtained results.

To clarify the situation we studied the kinetics and temperature dependence (5 - 35 K) of extrinsic PC of similar GaP samples doped with Te ($\sim 3 \cdot 10^{17} \text{ cm}^{-3}$) in microwave (MCW) and DC electric field. The samples, placed in 8-mm waveguide, were excited by periodically modulated laser radiation (3.39 or 10.6 mcm). A modulated component of rectifier response proportional to the PC was registered as MCW PC. We observed slow and fast components of MCW photoresponse. The relaxation time of slow component was close to 8 ms at 5 K, in agreement with [2]. At low temperatures the slow component exceeded the fast component by 2 - 3 orders of magnitude. It decreased with increase of the temperature and disappeared at $T > 30 \text{ K}$. The dependence of fast component on the temperature was insignificant. DC PC had no slow component and its temperature dependence was similar to that of MCW PC fast component.

We also studied the kinetics of room temperature background radiation absorption by excited GaP samples at 4.2 K. The sample was placed before Si photoresistor and excited by 3.39 mcm modulated laser radiation. Between the sample and photoresistor was settled a polyethylene film to protect the photoresistor from exciting radiation. Background radiation, going through the excited sample from the cryostat window, also became partially modulated because of absorption due to modulation of Te excited states population. A photoresistor's response was proportional to a magnitude of that modulated background radiation component. The dependence of the response on excitation frequency points that the induced absorption was also slow process (approximately 5 ms). Si photoresistor has a high sensitivity in a range till 45 meV, so the absorption can be due to photoionization of $1S(T_3)$ state of Te donor with energy 49.8 meV [2]. The phase of response really corresponded to predominance of absorption, but not radiation excited GaP sample, in contrast with [2]. It should be mentioned that in [2] infrared radiation was observed only during intensive excitation and had a very short relaxation time.

So, the important dependencies of MCW and DC photoconductivity and induced absorption established for GaP doped with Te are very similar to that for diamond-like semiconductors [1]. It points to the existence of longlived ($\sim 10 \text{ ms}$) excited state $1S(T_3)$ of Te donor. The result was expected because band structure of GaP and diamond-like semiconductors are similar.

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COMPETITION BETWEEN LONGLIVING AND $D^- (A^+)$ STATES
OF DONORS AND ACCEPTORS IN SILICON

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There are, at least, two slow processes of relaxation of extrinsic excitation in Si. The first one is due to accumulation of electrons or holes in longliving excited states of donors or acceptors. It leads at low temperature and impurity concentration $N > 10^{16} \text{ cm}^{-3}$ to predominance of polarization hopping photoconductivity in microwave (MCW) electric field and appearing of absorption bands in a far infrared, due to ionization of longliving states. It was shown [1], that lifetime of excited states depend on chemical nature of impurities and changes in the range 0.5 - 8 ms. The second slow process is due to existence of $D^- (A^+)$ states created by capture of carriers to neutral impurity atoms. The aggregates of neutral, negative and positive charged majority impurities create at $N > 10^{16} \text{ cm}^{-3}$ $D^- (A^+)$ bands. We also observed a slow relaxation of far infrared photoconductivity (PC) in DC electric field, due to ionization of the $D^- (A^+)$ bands. So, both slow relaxation phenomena exist in the same concentration and temperature range.

To separate the phenomena we investigated PC and absorption spectra and kinetics by Fourier spectrometer in a range 10 - 70 meV. Intensive ($\sim 10^{17} \text{ cm}^{-2} \cdot \text{s}^{-1}$) background radiation exceeded a few order of spectrometer beam intensity, so it determined steady-state population of longliving impurity states and concentrations in $D^- (A^+)$ bands. In low compensated Si doped with B, Ga and As in various concentrations at 4.2 K spectral response of PC corresponded to photoionization of $D^- (A^+)$ bands. It was established, that in the regions, corresponding to ionization of populated excited states of B and As impurities, wide dips were observed similar to induced absorption spectra of the impurities. It points to a quenching of PC by longliving impurity excited states and to predominance of the absorption connected with longliving states ionization. In Si doped with Ga longliving excited state was not observed [1], so for this impurity we have not observed a quenching phenomenon. We have not observed any remarkable absorption due to $D^- (A^+)$ bands in the same conditions.

The longwave PC can be determined by slow recombination and hopping processes in $D^- (A^+)$ bands. Really, the dependence of PC on modulation frequency of spectrometer beam in 10 - 30 meV region points, that relaxation time in Si doped with B, As and Ga was of the order of 10^{-4} s. At higher photon energies corresponding to ionization of ground states of impurities no frequency dependence was observed. It points, that PC frequency dependence at low photon energies is due to processes in $D^- (A^+)$ bands themselves, but not of free carriers.

The competition between both slow processes was observed also in absorption of background radiation induced by population of longliving excited states and $D^- (A^+)$ bands under extrinsic 3.39 mcm modulated laser excitation. However, under low excitation the most important contribution in induced absorption was determined by longliving excited states of impurities. The conclusion is confirmed by comparison of dependencies on electric field strength E of longwave PC and induced absorption. It was established that PC decreased approximately 10 times at $E = 200 \text{ V/cm}$. Practically no dependence on E was observed for induced background absorption and MCW hopping PC for the same Si samples at similar conditions.

The presented results show that in heavily doped low compensated Si, both $D^- (A^+)$ and longliving excited states of donors and acceptors appear simultaneously, and their competition must be taken into account. It is possible that the longliving excited states play an important role in relaxation processes in $D^- (A^+)$ bands.

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