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**WORKSHOP ON
HYDROGEN EFFECTS IN InP
AND RELATED COMPOUNDS**

Tuesday 24 and Wednesday 25 October 1989

**Centre National d'Etudes des Télécommunications (CNET)
LANNION, FRANCE**

and

**Ecole Nationale Supérieure
des Sciences Appliquées et Technologie (ENSSAT)
LANNION, FRANCE**

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PREFACE

This booklet contains the extended abstracts presented at the Workshop on Hydrogen Effects in InP and Related Compounds, held in Lannion, France, in October 24 and 25, 1989.

The general objectives of this workshop are to make people active in the field of hydrogen in InP and related compounds to present recent results and analyses and to discuss together in order to try to achieve a better understanding of the different ways hydrogen can be introduced in InP-based semiconductors and of the phenomena and properties related to its presence.

This Workshop is intended as a small meeting and 19 contributions are presented.

The sponsors, who have supported the Workshop are gratefully acknowledged.

J. CHEVALLIER, B. CLERJAUD, J.M. DUMAS and J.M. ZAVADA.



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LANNION, FRANCE**

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- Direction des Recherches et Etudes Techniques (D.R.E.T.)
- Association Pour l'Animation Scientifique du Trégor (A.P.A.S.T.).

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SCIENTIFIC PROGRAM

TUESDAY 24th OCTOBER

- 8 : 30 Registration
- 9 : 00 Opening Session : J. Zavada

SESSION A : DEVICE-RELATED APPLICATIONS

Moderator : E. Davis, USEORD London

- 9 : 15 A1 Plasma hydrogenated low threshold wide band
1.3 μ m buried ridged stripe MOCVD lasers
C. Kazmierski^{*}, B. Theys^{**}, B. Rose^{*}, A. Jalil^{**}
M. Mircea^{*}, J. Chevallier^{**}
^{*} CNET, Bagneux, France
^{**} CNRS, Meudon, France
- 9 : 50 A2 Hydrogenated amorphous silicon gates in InP
field effect transistors : drift measurement at
elevated temperatures
N. Roditi^{*}, A.A. Iliadis^{**} and A.Christou^{***},
^{*} FORTH, Heraklion Greece
^{**} U. of Maryland, USA
^{***} NRL, Washington, USA
- 10 : 25 Coffee break
- 10 : 45 A3 Dopant desactivation due to process-induced
hydrogen incorporation in InP, InGaAs and GaAs
D. Rondi, N. Behar, P. Collot
TH-CSF/LCR, Paris, France

11 : 20 A4 Thermal and photo-assisted interaction of ammonia,
silane and oxygen with InP substrates
J.M. Moison, F. Houzay, C. Licoppe and J.Y. Nissim
CNET, Bagneux FRANCE

12 : 00 Lunch

SESSION B : HYDROGEN-SURFACE INTERACTION

Moderator : P. Viktorovitch, ECL, Lyon, France

14 : 00 B1 Interaction of hydrogen with clean and
intentionally modified InP surfaces
J.A. Schaefer
U. Kassel, Kassel, FRG

14 : 35 B2 Interaction of atomic hydrogen with InP (110) and
InP (100) surfaces
F. Proix, C.A. Sebenne and O. M'Hamedi,
U. P. et M. Curie, Paris, France

15 : 10 B3 Electrochemical study of interaction between
hydrogen and InP surface
A. Etcheberry, J. Gauton and J.L. Salfat
CNRS, Meudon, France

15 : 45 Coffee break

SESSION C : ACCEPTORS AND DONORS PASSIVATION

Moderator : R.C. Newman, U. of London , UK

16 : 15 C1 An overview of work carried-out at Bell Labs
will be reported by M. Stavola, Lehigh U., USA

VI

- 16 : 50 C2 Hydrogen-dopant interaction study in zinc doped InP and GaInAs
A. Jalil^{*}, B. Theys^{*}, J. Chevallier^{*}, N. Behar^{**},
D. Rondi^{**} and P. Hirtz^{**}
^{*} CNRS, Meudon, France
^{**} TH-CSF/LCR, Paris, France
- 17 : 25 C3 Hydrogen interaction with defects in InP and related ternary and quaternary solid solutions
E.M. Omeljanovsky, A.V. Pakhomov and A.Y. Polyakov
IRM, Moscou, USSR

WEDNESDAY 25th OCTOBER

SESSION D : UNINTENTIONAL HYDROGENATION

Moderator : M. Stavola, Lehigh U., USA

- 9 : 00 D1 Hydrogen in LEC grown InP
B. Clerjaud, F. Gendron, M.K. Krause and C. Porte
U. P. et M. Curie, Paris, France
- 9 : 35 D2 Dopant passivation phenomena in MOVPE of InP
S. Cole, W.J. Duncan, M.J. Harlow and N.M. Stewart
BTRL, Ipswich, UK
- 10 : 10 Coffe break
- 10 : 40 D3 Characterization methods for hydrogen induced effects in III-V compounds
A. M. Huber and C. Grattepain
TH-CSF/LCR, Paris, France

VII

- 11 : 15 D4 Unintentional neutralization of InP : Zn by hydrogen
B. Pajot^{*}, B. Theys^{**} and B. Rose^{***}
^{*} U. Paris 7, Paris, France
^{**} CNRS, Meudon, France
^{***} CNET, Bagneux, France
- 12 H Lunch
- 14 : 00 D5 Post-epitaxial activation of unintentionally hydrogenated p-type InP and InGaAs P grown by MOCVD
M. Glade, D. Grützmacher and P. Bolk
RWTH, Aachen, FRG
- 14 : 35 D6 SIMS hydrogen analysis in III-V compounds
M. Gauneau, R. Chaplain and M. Salvi
CNET, Lannion, France

SESSION E : PROTON IMPLANTATION AND RELATED PROBLEMS

Moderator : J. Zavada, ERO, London, UK

- 15 : 10 E1 As implanted and annealing behavior 0.3 and 1 meV ¹H and ²H implants into InP, and comparison with GaAs
R.G. Wilson^{*}, J.M. Zavada^{**} and S.W. Novak^{***}
^{*} HRL, Malibu, USA
^{**} ERO, London, UK
^{***} Ch. Evans and Associates, San Francisco, USA
- 15 : 45 Coffee break
- 16 : 15 E2 Infrared and near-edge optical properties of proton implanted InP, GaP and GaAs
H. Neumann
Karl-Marx U., Leipzig, GDR

VIII

- | | | |
|---------|----|--|
| 16 : 50 | E3 | Hydrogen vibrations in proton-implanted semi-conductors
J. Tatarkiewicz
Inst. of Physics, Warsaw, Poland |
| 17 : 25 | | Coffee break |
| 18 : 00 | | Final talk
N. Johnson
Xerox, Palo Alto, USA. |

SESSION A : DEVICE-RELATED APPLICATIONS

Moderator : E. Davis, USEORD London

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J.M. Moison, F. Houzay, C. Licoppe and J.Y. Nissim
CNET, Bagneux FRANCE
- 12 : 00 Lunch

High Performance 1.3 μ m Buried Ridge Structure Laser with Plasma-Hydrogenated Current Confinement Insulation

C.KAZMIERSKI, B.THEYS*, B.ROSE, A.MIRCEA, A. JALIL*, J.CHEVALLIER*

CNET - 196, avenue Henri Ravera, 92220 - BAGNEUX, FRANCE

*CNRS Laboratoire de Physique des Solides de Bellevue - 1, place Aristide Briand, 92190 - MEUDON, FRANCE

Abstract : The plasma hydrogenation of p-type InP has been applied to the fabrication of Buried Ridge Structure (BRS) lasers. The threshold current, output power and modulation bandwidth of the obtained devices compare favourably to those of the more conventional ones fabricated by proton implantation on the same wafer.

The use of plasma hydrogenation for decreasing the conductivity of p-type InP by several orders of magnitude has been the object of recent reports^{1,2}. The physical phenomenon involved is the neutralization of electrically active acceptors by the in-diffused hydrogen species, with the formation of hydrogen acceptor pairs as detected by infrared vibrational spectroscopy³. An obvious application of this effect is the realization of electrical isolation in various electronic and optoelectronic InP-based devices. The BRS laser^{4,5} technology makes use of proton-implantation in order to enhance the output efficiency by reducing the current leaks across the InP/InP homojunction.

While proton implantation provides adequate electrical insulation, it is also likely to introduce defects which can act as nonradiative centers. In the present paper we report for the first time the realisation and preliminary characterization of high performance lasers by plasma hydrogenation instead of proton implantation.

Fig.1 shows the main fabrication steps and the structure cross section of the plasma hydrogenated 1300 nm wavelength BRS laser. This structure was realized by a two-step Atmospheric Pressure Metalorganic Vapor Phase Epitaxy (APMOVPE) and by a hydrogenation process. The hydrogenation conditions were defined with reference to preliminary experiments carried out on InGaAs/InP structures^{1,2}. In the active region TiPt contact metalisation has been used as a mask against hydrogen diffusion during the plasma hydrogenation.

In order to check the neutralization effect of hydrogen, we measured the spreading capacitance (C_s) of the laser structure. The main contribution to this capacitance comes from the forward polarized InP/InP p-n homojunction parallel to the active stripe -fig.1. Before any current confinement treatment the BRS structures had an excess spreading capacitance at 1 MHz of 100 pF at 0 V bias. The same structure had C_s of only 9 pF after deuteration. This value still comes mainly from the residual InP/InP junction capacitance and some other parasitics. In the case of proton implantation applied to the same structure with a 6 μ m wide photoresist mask, we measured a C_s of 15 pF under the same conditions. The lower C_s obtained by deuteration is thought to be a result of two factors : 1) the lateral diffusion of deuterium and thus reduced InP/InP junction surface, 2) a thicker neutralized p-layer corresponding to the hydrogen diffusion depth in contrast to a relatively narrow implantation profile.

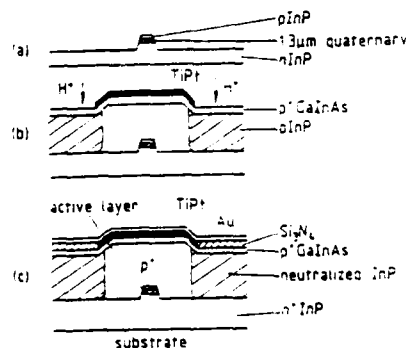


Fig.1. Fabrication steps of the hydrogenated BRS. a) first epitaxy step and ridge etch, b) epitaxial regrowth and hydrogenation, c) final structure.

The average threshold current of the hydrogenated BRS lasers was about 11 mA with the best value as low as 8.2 mA CW. This value compares favourably to the thresholds around 10 mA we obtained for the proton implantation insulated structures. Fig.2 shows an optical output power versus current characteristic of hydrogenated laser. High maximum output power above 15 mW CW per facet and good maximum external quantum efficiency of 0.25 were found.

The small signal modulation bandwidth at -3dB was about 4 GHz at 3 mW output power and above 7.5 GHz at 10 mW output power - fig3. The bandwidth would seem to be limited by the intrinsic resonance frequency rather than the RC parasitics showing clearly an important effect of the neutralization by deuterium.

In conclusion, plasma hydrogenation can be successfully used to fabricate insulating zones in optoelectronic InP-based device technology. Applying plasma hydrogenation to the BRS process we obtained high-performance lasers. The threshold current and frequency response of the hydrogenated lasers compare favourably to those of other carrier confinement methods. However, even if good thermal stability of the hydrogen-acceptor complex has been already observed^{1,2}, more studies are needed on current flow and optical power effects on the reliability of such devices.

Acknowledgments : We wish to thank C. Grattepain for the SIMS profiles, Annick Godin and Didier Robein for technical assistance .

References :

- 1 CHEVALLIER, J., JALIL, A., THEYS, B., PESANT, J.-C., AUCCOUTURIER, M., ROSE, B., KAZMIERSKI, C., and MIRCEA, A. "Hydrogen diffusion and shallow acceptor passivation in p-type InP", 15th Int'l Conf. Defects in Semiconductors, Budapest, Aug. 1988.
- 2 CHEVALLIER, J., JALIL, A., THEYS, B., PESANT, J.-C., AUCCOUTURIER, M., ROSE, B., and MIRCEA, A. "Hydrogen passivation of shallow acceptors in p-type InP", *Semicond. Sci. Technol.*, 1989, **4**, p. 87
- 3 PAJOT, B., CHEVALLIER, J., JALIL, A. and ROSE, B. "Spectroscopic evidence for hydrogen-phosphorous pairing in zinc-doped InP containing hydrogen", *Semicond. Sci. Technol.*, 1989, **4**, p.91
- 4 BOU, Y., J. C. CHARIL, J., CHAMENANT, G., "1.55µm strip buried schottky laser", Abstracts of 9th IEEE international semiconductor conference, 1984, Papier D.4
- 5 KRAKOWSKI, M., BLONDEAU, R., KAZMIERSKI, C., RAZEGHI, M., RICCIARDI, J., HIRTZ, P., and DE CREMOLUX, B. "High yield manufacture of very low threshold high reliability 1.3µm buried heterostructure laser diodes grown by metalorganic chemical vapor deposition", *J. Lightwave Technol.*, 1986, **LT-6**, p.1470
- 6 ROSE, B., MIRCEA, A., CHEVALLIER, J., and PESANT, J.-C. : French Patent No :8810983

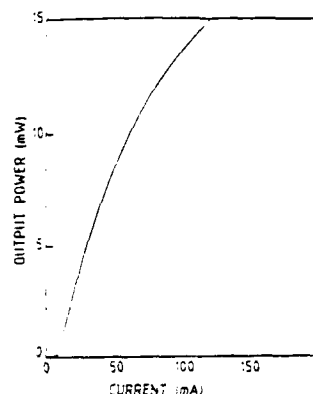


Fig.2-P-I characteristics of a hydrogenated laser : $I_0=8.2$ mA, $\eta=0.22$, and P_{out} per facet >15 mW.

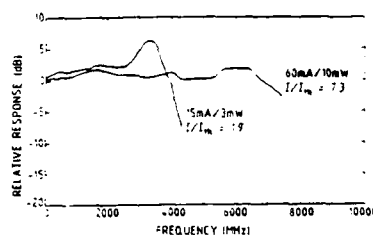


Fig.3. Frequency response of a hydrogenated laser : a) $f_{3dB}=4$ GHz at 3mW optical power, b) $f_{3dB}=7.5$ GHz at 10 mW optical power

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"A Stable n-Channel InP Metal-Insulator Field Effect Transistor with an Amorphous Si:H Gate"

E. Roditi, A.A. Iliadis^(a) and A. Christou^(b)

Foundation for Research and Technology-HELLAS,
Heraklio Crete, Greece

^(a) Electrical Engineering Department,
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Summary

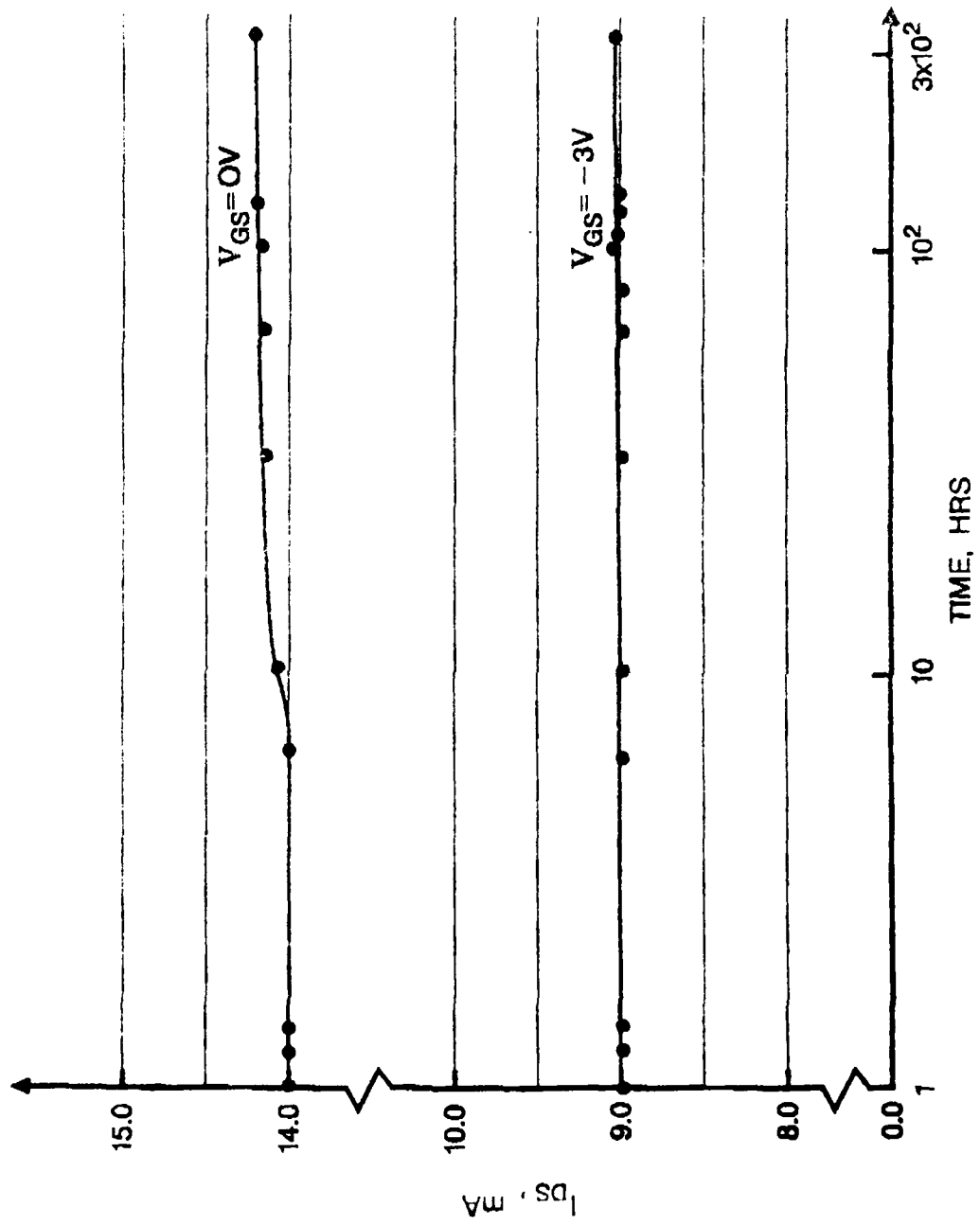
Indium Phosphide and its ternary and quaternary lattice matched systems have wide potential applications in optoelectronic, high speed digital and microwave technologies. Conventional n-channel MESFET's have not been fully developed due to a low Schottky barrier ($\phi_b < 0.5\text{eV}$) resulting in an excessively high reverse bias leakage current. In order to correct the leakage problem, insulated gate systems have been developed based on deposited insulators⁽¹⁾ or epitaxially grown wide band gap semiconductors. The deposited insulators continue to exhibit a high interface state density and drift in the gate. The epitaxially grown semiconductors are usually lattice mismatched to InP which results in strain induced interface states and thermal instabilities. Amorphous semiconductors have distinct advantages over the epitaxially grown semiconductors because of lower deposition temperatures, easier passivation and lower stress induced interface states.

In this work, we report for the first time the fabrication and dc characteristics of a highly stable n-channel InP FET using a hydrogenated amorphous silicon gate (a-Si:H).

The devices were made on Si implanted ($N_D - N_A = 5 \times 10^{16}\text{cm}^{-3}$) semi-insulating (100) InP substrates after nitride encapsulation and annealing. The a-Si:H was deposited by dc magnetron sputtering in H_2 ambient at 200°C, followed by the deposition of the Pt/Au gate metals. The $1\mu\text{m}$ gates were defined by standard photolithography and lift-off techniques. The I-V characteristics of the devices showed channel pinch-off at $V_{GS} = -7\text{V}$ and a maximum transconductance (g_m) between 30 and 38 mS/mm. The transfer characteristics showed a flat g_m region for V_{GS} between -2 and -4V. The I_{DS} drift of the FET's was tested at $V_{GS} = 0$ and -3V. No observable change in I_{DS} was measured in the first 300 hours. After the first 300 hours of testing a 3% increase was indicated for $V_{GS} = -3\text{V}$. The high stability of this gate system is attributed to the low temperature of deposition and the particular passivation of the InP surface followed here, as shown by Auger and Low-Energy Electron Probe analysis.

The combination of stable characteristics and good pinch-off voltages make this device the best reported to date with a-Si:H gates⁽²⁾.

1. K. Oigawa, S. Uekusa, Y. Sugiyama and M. Tacano, Jap. J. Appl. Phys., 26, 1719 (1987).
2. S. Loualiche, C. Vaudry, L. Henry and A. LeCorre, Electronics Lett., 22, 896 (1986).



**DOPANT DESACTIVATION DUE TO PROCESS-INDUCED
HYDROGEN INCORPORATION IN InP, GaInAs and GaAs**

**D. ROND, N. BEHAR, P. COLLOT, C. GAONACH
THOMSON-CSF/LCR, Domaine de Corbeville, 91404 ORSAY Cedex (France)**

The electrical desactivation of dopant in silicon due to hydrogen incorporation has been reported many years ago. More recently dopant desactivation in III-V compounds of which InP has also been observed. Such desactivation can occur unexpectedly during different steps of a device process : the growth of the layers when using MOVPE or their etching when using RIE.

We report here various experiments performed with both techniques in order to check the influence of different parameters.

I. DESACTIVATION INDUCED BY THE USE OF MOVPE

1. GaInAs/InP heterostructures

Using this classical heterojunction, we investigate the influence of diverse parameters on the desactivation of Zn, on its reactivation through thermal annealing and on hydrogen incorporation. These parameters were the doping levels of the ternary and the binary layers, the growth temperature and the annealing temperature. The following observations have been performed. Though the desactivation of Zn in InP can be obtained for a wide range of doping level, no desactivation in GaInAs has been observed when highly doped and only a weak one when lowly doped. The desactivation of the binary layer seems not to be depending on the doping level of the ternary layer. On the contrary the restoration through thermal annealing under inert atmosphere is more efficient when the ternary is highly doped. The activation energy of the restoration has been estimated to be between 2.1 and 2.5 eV. Finally the desactivation of Zn in InP depends on the growth temperature of the ternary layer.

SIMS measurements of hydrogen content in the layer fit well with the desactivations observed.

2. InP substrats

In order to study by it self the phenomenon of the desactivation of P type dopant in InP under pyrolysed hydride exposure, we perform diverse annealing experiments directly on p type InP substrates. Various parameters have been scanned : Nature of the dopant species, doping level, nature of hydride, annealing duration and temperature. It has been observed that the desactivation rate varies with the dopant concentration. Desactivation is not the same for different dopant : Cd is more weakly desactivated than Zn. Whereas Zn desactivation seems not to depend on annealing temperature, Cd is more desactivated when annealing temperature is lower (between 650 and 450°C). On the other hand for both Zn and Cd the duration of annealing (at 650°C) doesn't change the desactivation. Finally whereas annealing under AsH₃ is much more efficient than under PH₃ to desactivate Zn the same is not true for Cd.

II. DESACTIVATION INDUCED BY THE USE OF RIE

1. InP

As RIE provides an other way to desactivate dopants, it was interesting to compare the characteristics of the desactivation induced by the two techniques. More specially we were interested in comparing the influence of dopant species and exposure time. And it has been observed that as with hydride exposure, Cd is more weakly desactivated than Zn, but here it is also more deeply. Furthermore the desactivation increases with the exposure duration.

2. GaAs

In order to investigate the electrical damage induced in Si-doped GaAs by CH₄-H₂ RIE, capacitance-voltage characterizations of Schottky diodes fabricated on the dry-etched surface were performed : the specific consequence of CH₄-H₂ RIE of N-GaAs is a marked reduction in carrier concentration in the surface region. This carrier loss is attributed to the passivation of donors (Si) by atomic hydrogen. The extent of the neutralized surface region is inversely dependent on the initial doping level, typically : 0.1 µm for 8.10¹⁷cm⁻³, 0.5 µm for 2.10¹⁶cm⁻³ and 2 µm for 2.10¹⁵cm⁻³. Thermal reactivation of the doping level is possible by thermal annealing at moderate temperature : after a 360°C-5 min anneal, a full recovery of the carriers is observed. According to a first order reactivation kinetic, the reactivation energy is around 1.8 eV.

Workshop "Hydrogen Effects in InP and Related Compounds"
Lannion, October 24-25, 1989

**PHOTON AND THERMALLY-ASSISTED INTERACTION OF
InP SUBSTRATES WITH NH_3 , SiH_4 AND O_2**

J.M.Moison, F.Houzey, C.Licoppe and Y.I.Nissim

Centre National d'Etudes des Télécommunications

Laboratoire de Bagneux

196 Avenue Henri Ravera, F-92220 Bagneux, FRANCE

Abstract: The first stages of the interaction between InP substrates and gases used in chemical vapor deposition processes (NH_3 , SiH_4 and O_2) with and without the assistance of UV illumination have been studied for the first time in an ultra-high-vacuum environment by surface techniques. Photo-assisted NH_3 exposures lead to a nitrogen uptake in opposition to thermally-assisted exposures. Photo- and thermally-assisted SiH_4 exposures partly remove the native oxide and drive silicon atoms to form covalent bonds to InP. Successive exposures to SiH_4 and O_2 build the first silica layers.

Dielectric deposition for the fabrication of metal/insulator/semiconductor (MIS) devices is mostly achieved by chemical vapor deposition (CVD) or derivate techniques such as plasma-assisted CVD or UV-assisted CVD (UVCVD). For InP-based devices, the commonly used dielectrics SiO_2 and Si_3N_4 are obtained from precursor gas combinations ($\text{SiH}_4 + \text{O}_2$ or N_2O) and ($\text{SiH}_4 + \text{NH}_3$) respectively. In spite of the importance of the electrical quality of the dielectric/InP interface in the final MIS performance, in situ studies of the reactions which built the interface are very scarce. We have previously reported on studies by surface techniques of the reactions occurring at the surface of heated (300°C) InP substrates, exposed to SiH_4 ⁽¹⁾ and NH_3 ⁽²⁾ gases, and of the build-up of the insulator/InP interface ("hot CVD process"). We report here for the first time on similar studies of processes which occur during room temperature (RT) exposures under UV illumination ("cold UVCVD process").

The experimental setup and procedure have been described previously ^(1,2). The ultra-high-vacuum chamber is equipped with standard surface analysis techniques such as Auger electron and X-ray photoemission spectroscopies (AES, XPS) and in addition with a low pressure mercury lamp with suprasil envelope providing 185nm UV irradiation. The (100)InP substrates are slightly chemo-mechanically polished. The exposure unit is the Langmuir ($1\text{L}=10^{-6}\text{Torr}\cdot\text{sec}$). The coverage unit or monolayer (ML) is defined as the atom density in the (100)InP plane.

The interaction of InP substrates with NH_3 is first described. The surface of chemically-polished InP substrates is usually covered by $\approx 2\text{ML}$ of native oxide ^[2]. During hot CVD, a two-step deoxidizing process takes place, that is, (i) $\approx 10^6\text{L}$ exposure to unexcited NH_3 removes the weakly-bonded oxygen atoms and stabilize the one-monolayer oxide and (ii) excitation of NH_3 by the ion gauge removes completely the oxygen atoms strongly bonded to InP. The final surface free of contaminants and of oxygen is mostly InP covered by adsorbed hydrogen with a small coverage of indium atoms liberated by the native oxide reduction and grouped as metallic clusters. The cold UVCVD process is quite different (figure 1). After the same 10^6L exposure, no modification in the oxygen coverage or bonding is observed but a strong nitrogen (AES)XPS signal corresponding to $\approx 1\text{ML}$ is observed. This is associated to the first stages of RT nitride formation. However, this nitride grows on the native oxide layer, which may lower the interface electrical characteristics. This suggests that the optimum process would consist of a rapid reduction of the oxide film by heating under unexcited NH_3 exposure, followed by the RT growth of the nitride under UV.

The InP substrates have been exposed at RT to SiH_4 , O_2 or mixture of these gases without and under UV illumination (figure 2). Without UV, no appreciable change in the surface properties are obtained with exposures to either gas or mixture up to 10^6L . On the other hand, strong modifications in the AES/XPS spectra and then in the surface composition and/or bonding are observed with UV. Exposure to $\approx 10^6\text{L}$ of SiH_4 leads to the same effects already observed for hot CVD exposures: silicon is adsorbed under SiO_2 form, InP oxides are reduced and the oxygen present in the native oxide changes its bonding from InP-O to Si-O (figure 2). For both cold UVCVD and hot CVD processes, pre-silanisation results in the ideal InP-Si-O-Si interface. Further SiH_4 exposures with UV deposit more silicon, but under a less oxidized form, which is not observed in hot CVD where silicon deposition stops when the oxygen present in the native oxide is used. A next exposure to O_2 with UV induces the build-up of the first silica layers ($\approx 2\text{ML}$).

In conclusion, hot sample exposures to unexcited ammonia stabilize the ultra-thin oxide left by the chemical cleaning/polishing process, and that hot sample exposures to excited ammonia (by means of a hot filament) reduce it fully, leaving the surface with only hydrogen but no nitrogen adsorbed. With cold sample exposures to unexcited ammonia under 185 nm illumination, a nitrogen uptake without oxide reduction is observed. Photo- or thermally-assisted silane exposures partly remove the native oxide and restore the covalent bonding of surface InP atoms because silicon inserts between them and oxygen; successive exposures to silane and oxygen build the first silica layers.

[1] C.Licoppe, J.M.Moison, Y.I.Nissim, J.L.Regolini and D.Bensahel, *Applied Physics Letters* 53(1988)1291; C.Licoppe and J.M.Moison, *Surface Science* 211/212(1989)979

[2] J.M.Moison, Y.I.Nissim and C.Licoppe, to be published in *J. of Appl. Phys.*

SESSION B : HYDROGEN-SURFACE INTERACTION

Moderator : P. Viktorovitch, ECL, Lyon, France

- | | | |
|---------|----|---|
| 14 : 00 | B1 | Interaction of hydrogen with clean and intentionally modified InP surfaces
J.A. Schaefer
U. Kassel, Kassel, FRG |
| 14 : 35 | B2 | Interaction of atomic hydrogen with InP (110) and InP (100) surfaces
<u>F. Proix</u> , C.A. Sebenne and O. M'Hamedi,
U. P. et M. Curie, Paris, France |
| 15 : 10 | B3 | Electrochemical study of interaction between hydrogen and InP surface
<u>A. Etcheberry</u> , J. Gauton and J.L. Salfat
CNRS, Meudon, France |
| 15 : 45 | | Coffee break |

"Interaction of Hydrogen with Clean and Intentionally Modified InP Surfaces,"

J.A. Schaefer, Fachbereich Physik, Universität Kassel,
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InP is an important material in the technology for fabricating microwave and high frequency devices. Surprisingly, only a few studies with surface sensitive techniques have been reported in order to determine the geometric and chemical bonding configuration of clean surfaces.

The most common cleaning technique is sputtering and annealing, which provides a clean surface, as detected by x-ray photoelectron spectroscopy (XPS), AUGER-spectroscopy, low-energy electron diffraction (LEED) or high resolution electron energy loss spectroscopy (HREELS). But problems arise with respect to the determination of the stoichiometry and the chemical bonding situation at the very surface. The latter may be studied very effectively through HREELS measurements by using hydrogen as a probe for the determination of unsaturated dangling bonds at differently prepared InP surfaces, as demonstrated recently also for other semiconductor surfaces¹. Also, the interaction of hydrogen with the surface atoms may be studied in detail. Simultaneously, HREELS provides information of possible contaminants via the measurement of characteristic vibrational frequencies. As the preparation of a clean surface greatly influences the uptake of hydrogen, it is reasonable to study first the cleavage surface² which does not need any surface treatment before deposition of atomic hydrogen and then, after that, to study the InP (100) surfaces, in the form of wafers.

Some of the experiments (HREELS) were carried out at Montana State University (U.S.A.), in a Leybold UHV system (base pressure 10^{-10} torr) which contained HREELS, XPS and LEED for the characterization of the investigated surfaces as well as heating and cooling facilities for the samples and an ion gun for sputtering. The hydrogen dosing was done at 10^{-4} torr with a heated W-filament (2000 K) in line (distance 4 cm) or not in line (sample in HREELS chamber) of sight of the sample surface, depending whether initial or advanced stages of hydrogen interaction were investigated. The InP(110) bars were cleaved in situ, while the (100) wafers were etched ex situ in HF (48%) and rinsed in deionized water. Cleaning of the InP(100) wafers in UHV was done with successive cycles of Ar⁺ - or Ne⁺ - sputtering at 500 eV and 2.5×10^{-7} A and heating up to 300°C.

Shortly summarizing our results, the HREELS measurements taken at well ordered (100) and (110) surfaces of indiumphosphide show that the initial uptake of atomic

hydrogen in both cases is essentially by the In surface atoms, although the origin for this behaviour might be different. For the ion bombarded surfaces the P-H stretching mode is *very strong* as compared to the corresponding In-H mode. The results for the cleavage surface and the sputtered-annealed wafers are interpreted in the framework of existing models in terms of the geometric and chemical bonding configuration. The sputtered surfaces are assumed to be composed of metallic indium islands and predominately broken phosphorous bonds. After very high hydrogen exposures, a strong decrease of the phosphorous hydride lines may be interpreted as phosphine desorption. Modification of the InP surface by deposition of cesium in the submonolayer range shifts the In-H stretching frequency to lower energy values as a function of the Cs exposure. This indicates charge transfer from the alkali atoms to the substrate surface atoms.

Fruitful discussions with G.J. Lapeyre, J. Anderson, Th. Allinger and F. Lodders and support by A. Goldmann is greatly appreciated. Also, I would like to acknowledge the financial support by the Deutsche Forschungsgemeinschaft.

¹J.A. Schaefer, Surface Science, 189/190 (1987) 127.

²J.A. Schaefer, D.J. Frankel, G.J. Lapeyre, Z. Phys. B., submitted.

Extended abstract : workshop on hydrogen effects in InP and related compounds, Lannion (France), 24-25 Oct. 1989.

INTERACTION OF ATOMIC HYDROGEN WITH InP(110) AND InP(100) SURFACES

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The interaction of atomic H with InP has been studied under ultrahigh vacuum as a function of exposure using low energy electron diffraction (LEED), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS) and photoemission yield spectroscopy (PYS). Atomic H was produced by thermal dissociation of H₂. A clean and ordered surface was prepared in the vacuum chamber either by cleavage for InP(110), or by repeated cycles of ion erosion and annealing for InP(100).

The initial clean surfaces are different : the (110) face is (1 x 1) reconstructed, has neither intrinsic surface states in the gap nor band bending, whereas the (100) face is (4 x 2) reconstructed, has both empty and filled surface states in the gap and a Fermi level surface pinning position at about 0.45 eV below the conduction band edge.

Atomic H interaction with both faces is analyzed in terms of a two-stage process. The first is an adsorption stage, the second is a dissociation stage, the main features of which are the following.

The adsorption stage saturates at half a monolayer ($0.5 \text{ ml} = 4.1 \times 10^{14} \text{ atoms/cm}^2$) along the (110) face and one monolayer ($5.8 \times 10^{14} \text{ atoms/cm}^2$) along (100). Along (110), in the few 10^{-2} monolayer coverage range, LEED shows some signs of disorder, a band bending develops with the Fermi level reaching its usual surface pinning position and a band of surface states shows up 0.06 eV below the valence band edge E_{VS} . This is a general observation typical of many 3-5 compounds which we explain by a reconstruction change in the vicinity of any surface defect or impurity ; it is not specific of hydrogen. Upon increasing H coverage, the surface reorders into a new (1 x 1) reconstruction involving one H atom per surface unit cell which contains two atoms. The surface peak at 0.06 eV below E_{VS} saturates and the ionization energy is decreased by about 0.4 eV. This surface is thermally more stable than the clean one. Along (100), as expected from the character of the clean surface, no remarkable effect occurs at low coverage. As the coverage gets towards one monolayer only the surface state peak 0.1 eV below E_{VS} increases while both the band bending and the ionization energy remain unchanged.

The dissociation stage occurs at a much slower rate : while the sticking coefficient of H is close to one on a clean surface, after completion of the first layer it becomes orders of magnitude smaller. This stage is characterized by the breaking of In-P bonds leading to the formation of indium metal and adsorbed hydrogenated phosphorous species. The formation of In metal is shown by the rise, in EELS, of the corresponding bulk and surface plasmons and, in PYS, by the stabilization of the work function at $\Phi_{In} = 4.17$ eV. The formation of phosphorous hydrogenated species is proved by the appearance of a dip in the photoemission yield, then a total quenching of the photoemission signal at photon energies which coincide with electronic transitions of molecules of the form R-PH₂ (R being something between the crystal itself and a third H atom). These species desorb at room temperature from (100) and up to 550°C from (110), bringing the surface back to the end of the first stage with some In metal in excess.

This interaction scheme is confirmed by ultraviolet photoemission spectroscopic studies performed on InP(110) at the Orsay synchrotron radiation laboratory. The kinetic energy distribution curves of normally emitted electrons from the valence band and In 4d core levels have been observed after characteristic H exposures with photons in the 30-65 eV energy range. It appears that H penetrates somewhat in the bulk of InP at the dissociation stage.

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ELECTROCHEMICAL STUDY OF INTERACTION BETWEEN HYDROGEN AND INP SURFACE

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Hydrogen interaction with surfaces of semiconductors may be obtained under electrochemical conditions. Under adapted electrode polarization, semiconductor surfaces give electrons necessary to realize the reduction of solvated protons (or water molecules) in molecular hydrogen.

This electrochemical process generates at the semiconductor surface on specific partial "hydride" which has different properties depending on the semiconductor and on the intensity of hydrogen evolution. The mechanism of reduction is a two electrons one with an intermediate step which gives a specific adsorption of hydrogen [1] on the surface. According to the material the resulting interaction may be strong or weak and can break in some cases the superficial structure of the electrode. For III-V compounds the behaviour are very different particularly for GaAs and InP [2] which are totally reverse in their apparent reactivity with respect to hydrogen evolution. A typical mechanism of cathodic decomposition which appears on InP electrodes [3] is not observed on GaAs samples. This process, on InP electrodes, may be separated in several steps.

To observe the beginning of the surface modification, in-situ photoluminescence seems to be the more sensitive probe. The strong enhancement of the PL during hydrogen evolution may be interpreted as a large decrease of the surface recombination velocity. To associate this phenomenon only to the hydrogen adsorption, we have also studied the process (pH, solvent...) under different chemical conditions.

After this well defined "passivation step", the follow up of the reaction makes damages on the surface and involves characteristic falls of the PL intensity. For studying the interaction mechanism and to detect surfaces damages, coupled electrochemical and ellipsometric experiments have been also used [5]. They demonstrate that the interface becomes rich in cations. Then the association between all these experimental results gives an overview of the process at each step of the reaction and brings some additional information to those obtained for other hydrogen interacting systems.

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SESSION C : ACCEPTORS AND DONORS PASSIVATION

Moderator : R.C. Newman, U. of London , UK

- | | | |
|---------|----|--|
| 16 : 15 | C1 | An overview of work carried-out at Bell Labs
will be reported by M. Stavola, Lehigh U., USA |
| 16 : 50 | C2 | Hydrogen-dopant interaction study in zinc doped
InP and GaInAs
A. Jalil [*] , <u>B. Theys</u> [*] , J. Chevallier [*] , N. Behar ^{**} ,
D. Rondi ^{**} and P. Hirtz ^{**}
[*] CNRS, Meudon, France
^{**} TH-CSF/LCR, Paris, France |
| 17 : 25 | C3 | Hydrogen interaction with defects in InP and
related ternary and quaternary solid solutions
E.M. Omeljanovsky, <u>A.V. Pakhomov</u> and A.Y. Polyakov
IRM, Moscou, USSR |

PASSIVATION OF ACCEPTORS IN InP BY HYDROGEN

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Sherman Fairchild Center for Solid State Studies, Lehigh University,
Bethlehem, PA 18015

W. C. Dautremont-Smith, J. Lopata, S. J. Pearton, T. R. Hayes, and V.
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Recent work performed at AT&T Bell Laboratories on the passivation of acceptors in InP by exposure to atomic hydrogen is surveyed below.

I. Surface Protection

Direct exposure of InP to a hydrogen plasma causes preferential loss of P as PH_3 . In droplets are observed on the InP surface even for low power density plasmas and low exposure temperatures ($<150^\circ\text{C}$). Experiments to protect the InP surface at AT&T Bell Laboratories were performed initially with thin (80-200 Å) SiN_x capping layers [1]. Other groups have reported schemes for protecting the surface with thin overlayers [2,3]. Such layers permit diffusion of hydrogen into the InP but prevent PH_3 loss thereby minimizing surface damage. Following plasma exposure the SiN_x layer can be stripped with HF.

SIMS measurements show that the deuterium (which is used instead of hydrogen because of its lower background concentration) incorporation depth, following exposure to a D_2 plasma, is a strong function of dopant type and concentration [1]. For n-type material, D is incorporated to depths greater than $20\text{ }\mu\text{m}$ with a concentration of $\sim 10^{16}\text{ cm}^{-3}$ following an 0.5 h exposure at 250°C . For p⁺ material (Zn, $3 \times 10^{18}\text{ cm}^{-3}$) and a similar plasma exposure, D is incorporated to a depth of $\sim 1.5\text{ }\mu\text{m}$ with a concentration of $7 \times 10^{16}\text{ cm}^{-3}$.

Other capping materials have been examined recently [4]. Thin layers of SiO_2 , W, a-Si, and Ti have been tried. Hydrogen permeation through all of these capping materials except Ti leads to efficient acceptor passivation in the underlying InP.

II. Dopant Passivation and Photoluminescence Yield Increases

CV measurements show that the Zn acceptors in the hydrogen plasma treated p-InP are passivated to a depth of 1 to $2\text{ }\mu\text{m}$ in good agreement with the SIMS determination of the D diffusion depth [1]. Annealing at 325°C for 60 s causes the acceptor activity to recover. Sulphur donors are not passivated in n-type InP. The hydrogen concentration was found to be only a few times 10^{16} cm^{-3} whereas the donor concentration was $5 \times 10^{17}\text{ cm}^{-3}$. Even if donor-H complexes were formed, they would be of insufficient concentration to passivate the S donors.

The effect of hydrogenation on the low temperature (5.5 K) photoluminescence of Cd or Zn doped p-type InP was examined [5]. For samples with either dopant, deep level luminescence features were eliminated and there was a strong increase in the yield of near band edge photoluminescence.

following H_2 plasma exposure. The Zn doped sample had a lower luminescence yield than the Cd diffused sample before hydrogenation and showed a greater increase in luminescence efficiency ($\times 2000$) as compared to the Cd diffused layer ($\times 30$). The increase in luminescence efficiency was removed by annealing for 30 s at 325°C and 425°C for the Zn and Cd dopants, respectively.

III. Unintentional Passivation from CH_4/H_2 Reactive Ion Etching

CH_4/H_2 reactive ion etching (RIE) of InP gives room temperature etch rates of $700 \text{ \AA}/\text{min.}$ and verticle/horizontal etch rate anisotropies of 8:1 or better. Macroscopic In droplets are not formed on the wafer surface in contrast to direct H_2 plasma exposure. Zn acceptors are found to be passivated in the etched InP [6], similar to the donor passivation reported for GaAs following CH_4/H_2 RIE.

SIMS profiles of p-type InP (Zn, $1.5 \times 10^{14} \text{ cm}^{-3}$) etched in CH_4/D_2 showed that the D_2 diffuses to a depth of $2000 \text{ \AA}$. The total etch depth was $1.2 \text{ \mu m}$ and the unintentional plasma induced heating during RIE gives wafer temperatures of 70 to 80°C . SIMS profiles following similar RIE treatment of n-InP (S or Sn, $7 \times 10^{17} \text{ cm}^{-3}$) showed D incorporation to depths of $7000 \text{ \AA}$. Capacitance-voltage measurements of the carrier concentration showed that in the p-InP, the depth of Zn acceptor passivation is in good agreement with the D incorporation depth determined by SIMS. The S and Sn donors in the n-InP were not passivated by RIE just as they are not passivated by H_2 plasma exposure through capping layers.

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HYDROGEN-DOPANT INTERACTION STUDY IN ZINC-DOPED GaInAs

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We have investigated the behaviour of atomic hydrogen (or deuterium) introduced by plasma in Zn doped GaInAs epitaxial layers. For this study, different experimental techniques have been used: SIMS profiling, electronic transport measurements and IR absorption spectroscopy.

1 - MATERIALS.

We have worked on a series of $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ layers grown by liquid phase epitaxy on SI Fe-doped InP substrates. Those epilayers were Zn-doped with the hole concentration in the range $1\text{ to }2 \cdot 10^{19}/\text{cm}^3$.

The samples have been exposed to a deuterium plasma under different conditions of duration, temperature and R.F. power.

2 - SIMS PROFILING.

The diffusion profiles of deuterium into GaInAs, as obtained by SIMS, are shown on figure 1 for different temperatures of diffusion.

These profiles can be correctly fitted with an erfc function. The effective diffusion coefficient D_{eff} increases from $1 \cdot 10^{-12} \text{ cm}^2/\text{s}$ to $2 \cdot 10^{-12} \text{ cm}^2/\text{s}$ when the temperature of diffusion is raised from 110 to 160°C. The temperature dependence of D_{eff} is given by :

$$D_{\text{eff}} (\text{cm}^2/\text{s}) = 4 \cdot 10^{-10} \exp(-0.2 \text{ eV}/kT)$$

3 - ELECTRONIC TRANSPORT MEASUREMENTS.

The density of carriers and their mobility have been determined by resistivity and Hall effect measurements by using the Van der Pauw method. After deuteration, the concentration of free holes is drastically reduced. Simultaneously, the mobility undergoes an important increase. Moreover the shape of the mobility vs temperature curves are strongly influenced by the deuteration of the layers (Fig. 2).

These effects are reversible. A 10 min. annealing at 375°C under an Argon ambient totally restores the original electri-

and properties of the samples.

4 - DISCUSSION AND CONCLUSION

From the above experimental results, it seems clear that the diffusion of hydrogen into Zn doped GaInAs leads to an efficient neutralization of Zn acceptors. Similar electrical effects have been recently reported after hydrogenation of highly Zn doped InP (1). However, unlike the case of InP:Zn, no plateau is observable in the hydrogen diffusion profiles after plasma exposure of GaInAs. This consideration might be indicative of a relatively weaker pairing tendency in GaInAs:Zn as compared to InP:Zn. In the ternary compound, the situation is probably closer to the one which has been reported for GaAs:Zn (2) where a plateau exists only for low temperatures of diffusion (equal or less than 200°C). These results are consistent with a scheme where hydrogen is bonded to the column V element (As-H in GaAs:Zn and GaInAs:Zn, P-H in InP:Zn).

Infrared absorption measurements are now in progress for a direct observation of these As-H bonds in GaInAs:Zn. However, for this ternary compound, observation of hydrogen vibrational modes might be more difficult to detect because of the alloy broadening of the corresponding absorption bands.

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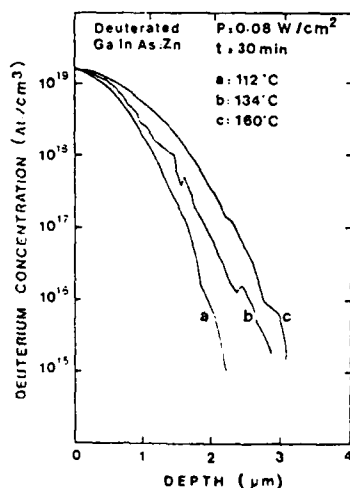


Fig. 1: Deuterium concentration profiles in GaInAs:Zn layers exposed to an R.F. plasma.

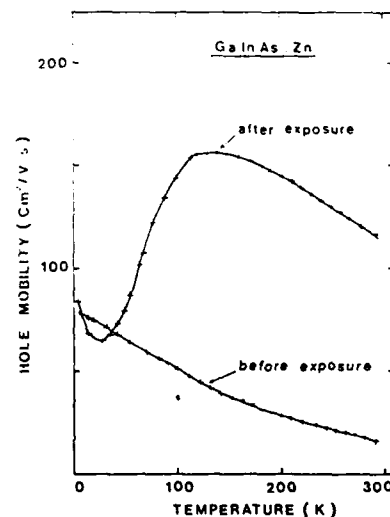


Fig. 2: Hole mobility vs temperature of a GaInAs:Zn layer before and after plasma deuteration (2h., 200°C, 0.08W/cm²).

Hydrogen Interaction with Defects in InP and Related Ternary and Quaternary Solid Solutions.

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Hydrogen passivation experiments on InP and InGaAsP are reported. It is shown that in InP passivation efficiency for acceptors is much higher than for donors. SIMS profiling experiments reveal that hydrogen diffusivity is also higher in p-InP. The above results clearly indicate that hydrogen in InP is a deep donor.

In addition we have shown that in InP hydrogen passivation can proceed through thin metallic and anodic oxide layers. Direct SIMS measurements confirm that hydrogen (or in that case, rather, deuterium) is present in passivated Schottky diodes and MIS-capacitors whereas C-V measurements show substantial passivation of donors and acceptors in both cases. This passivation in Au/n-InP Schottky diodes is accompanied by drastic improvement in reverse current due to passivation of the surface states.

The stability of hydrogen-impurity complexes was studied under different conditions. These complexes begin to disintegrate thermally at temperatures above 350°C with activation energy 1.6 eV. Besides, hydrogen-donor complexes can be destroyed by intense light, presumably due to capture of electron-hole pairs.

In $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ solid solutions as a result of passivation p-n conversion occurred in p-type material whereas in n-type layers the concentration of donors was reduced but only

to a certain extent. The donor concentration in converted samples is close to the concentration of compensating donors in initial state. SIMS profiling shows that hydrogen diffusivity is again higher in p-type material. The analysis of experimental data led us to conclusion that hydrogen has a donor level near $E_c - 0.1$ eV in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$.

We use this established donor level position to construct the level scheme of hydrogen in different III-V materials assuming that these levels are pinned to the level of vacuum. These calculations are shown to be consistent with the known experimental results. As a example of practical application of the model we calculate hydrogen level position in $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ system and show that in these solid solutions formation of semi-insulating layers is expected for y-values less than 0.3 whereas for larger y p-n conversion must take place instead. The validity of these calculations is confirmed by the results for solid solution with $y = 0.63$.

All passivation experiments were performed in a specially designed so-called crossed-beams apparatus which is shown to be essential in observing the above described effects.

Finally, we discuss some possible applications including production of current confining regions in DH stripped lasers. Some detrimental effects of hydrogen are also discussed including parasitic passivation of dopants by H injection from the metal gate of Schottky diodes or MIS capacitors or in the process of growth. The employment of n^+ -caps is expected to be useful to avoid such phenomena.

SESSION D : UNINTENTIONAL HYDROGENATION

Moderator : M. Stavola, Lehigh U., USA

- | | | |
|---------|----|---|
| 9 : 00 | D1 | Hydrogen in LEC grown InP
<u>B. Clerjaud</u> , F. Gendron, M.K. Krause and C. Porte
U. P. et M. Curie, Paris, France |
| 9 : 35 | D2 | Dopant passivation phenomena in MOVPE of InP
<u>S. Cole</u> , W.J. Duncan, M.J. Harlow and N.M. Stewart
BTRL, Ipswich, UK |
| 10 : 10 | | Coffe break |
| 10 : 40 | D3 | Post-epitaxial activation of unintentionally
hydrogenated p-type InP and InGaAs P grown by
MOCVD
<u>M. Glade</u> , D. Grützmacher and P. Bolk
RWTH, Aachen, FRG |
| 11 : 15 | D4 | Unintentional neutralization of InP : Zn by
hydrogen
<u>B. Pajot</u> [*] , B. Theys ^{**} and B. Rose ^{***}
[*] U. Paris 7, Paris, France
^{**} CNRS, Meudon, France
^{***} CNET, Bagneux, France |
| 12 H | | Lunch |
| 14 : 00 | D5 | Characterization methods for hydrogen induced
effects in III-V compounds
<u>A. M. Huber</u> and C. Grattepain
TH-CSF/LCR, Paris, France |
| 14 : 35 | D6 | SIMS hydrogen analysis in III-V compounds
<u>M. Gauneau</u> , R. Chaplain and M. Salvi
CNET, Lannion, France |

HYDROGEN IN LEC GROWN InP

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Optical absorption spectroscopy evidences hydrogen related local modes of vibration in all the LEC grown materials.

It is shown that hydrogen forms complexes either with impurities (such as shallow acceptors or transition metal impurities) or lattice point defects.

Complexes with impurities are of the bond center type, the hydrogen being bound to a phosphorus atom which is nearest neighbour to the impurity.

The complexes involving lattice defects are the same as those observed in proton implanted materials. It is shown that the complex having the lowest frequency of vibration (2202.4 cm^{-1}) has a trigonal symmetry. The microscopic nature of this complex is discussed ; it is proposed that it consists of an indium vacancy having one of its dangling bonds saturated by an hydrogen atom. Contrarily to what has been observed in the case of the equivalent defect in GaAs, the hydrogen does not move among the four possible configurations of the defect up to 160 K. The second complex involving a lattice defect has a lower symmetry and its microscopic nature is not clear at present.

The sources of hydrogen contamination of the material are discussed. It is shown that hydrogen is already present in the polycrystalline material obtained after the InP synthesis. Traces of water in the phosphorus are probably responsible of the hydrogen contamination at this stage of the process. After the LEC growth, the hydrogen concentration increases. The wet boric oxide used as the encapsulant is very likely responsible of this second contamination. The unintentional hydrogen concentration in LEC grown InP can be in the 10^{16} cm^{-3} range.

Anomalous behaviour of dopants in MOVPE growth of InP and related compounds

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In MOVPE of III-V compounds the most commonly used precursors for the group V elements are the hydrides AsH_3 and PH_3 . In common with other workers, we have previously reported how the use of these precursors can result in passivation of p dopants in InP ([1], [2], [3], [4]). This appears to be caused by the formation of inactive complexes between the dopant and H, which in turn is formed during the surface catalysed pyrolysis of the hydrides. In this paper we will describe our more recent results on these effects, and in particular we will discuss some related phenomena resulting from exposure to dopant precursor ambients in MOVPE.

In our earlier work ([1], [2]) we showed how exposure to AsH_3 or PH_3 during cooling of a p InP layer from a typical growth temperature of 650°C can result in a lowering of the electrical doping level accompanied by incorporation of a significant quantity of H as evidenced by SIMS profiling, see figure 1. In the present study [5] we have cooled both bulk (Czochralski grown) and MOVPE p InP crystals doped with Zn, Cd or Be at various levels in the range 10^{17} cm^{-3} to 10^{18} cm^{-3} from 650°C under ambients containing PH_3 and a dopant precursor such as $DMZn$, $DMCd$ or Cp_2Zn . As can be seen from the example in figure 2(a), the doping level is lowered significantly with respect to that obtained when PH_3 alone is present; indeed the resulting electrical doping profile is remarkably similar to that obtained on cooling in AsH_3 (cf figure 1). It was considered possible that this was the result of enhancement of the pyrolysis of PH_3 by the $DMZn$, resulting in a higher level of H in the crystal. However, SIMS can detect no H in the samples above the detection limit of $3 \times 10^{17} \text{ cm}^{-3}$. Indeed, SIMS shows that the original dopant has in fact begun to diffuse out of the material, and is being replaced by the new dopant in-diffusing from the surface (figure 2(b)). The rate of interdiffusion of the dopants is very large, since the observed penetration of 10-15 μm occurs in only a few minutes during cool down from 650°C. The active doping profile roughly follows the new chemical distribution of the original dopant, that is, the in-diffusing dopant is not electrically active. The lack of H in the material, however, rules out any obvious passivation mechanism. Other workers have shown that in pInP H is bound to the P atom adjacent to the substitutional dopant atom [6]. Since it appears that the interdiffusion process results in a loss of suitable stable binding sites for the H in the crystal, it seems reasonable to suggest that a significant proportion of the dopant atoms, specifically the in-diffusing species, are in interstitial rather than substitutional sites. The existence of such a high concentration of interstitials has recently independently been demonstrated in Zn doped InP [7].

The authors are indebted to the Directors of Research and Technology, British Telecom and of BT&D Technologies for permission to publish this work.

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Figure 1 (a) Carrier concentration and (b) SIMS profiles for Cd doped InP substrate heated to 650C under PH_3 and cooled under PH_3 and AsH_3 containing ambients

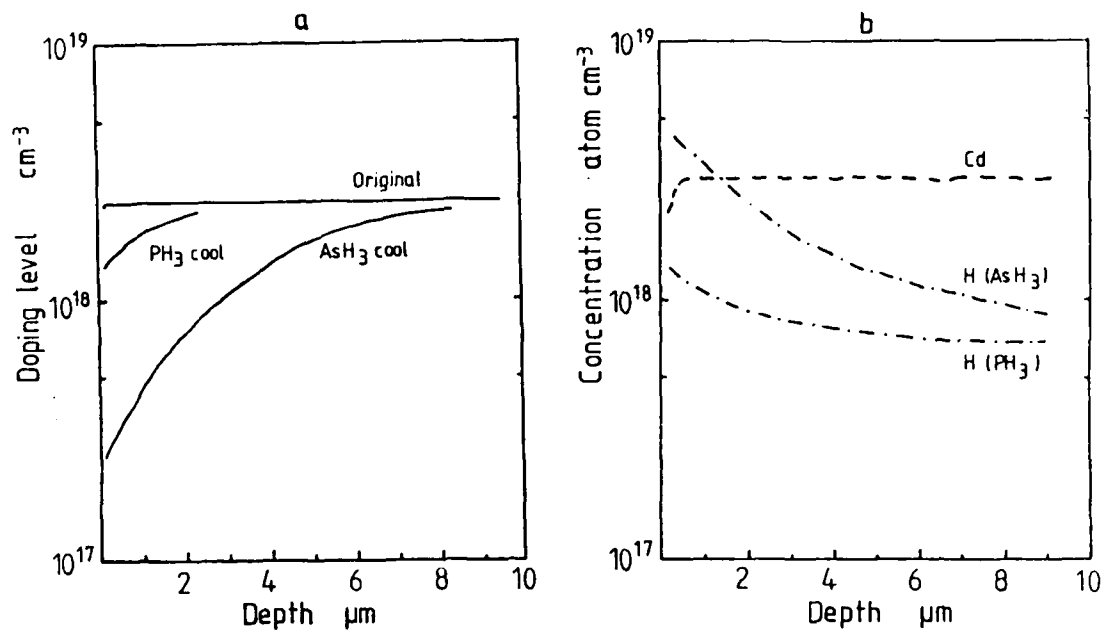
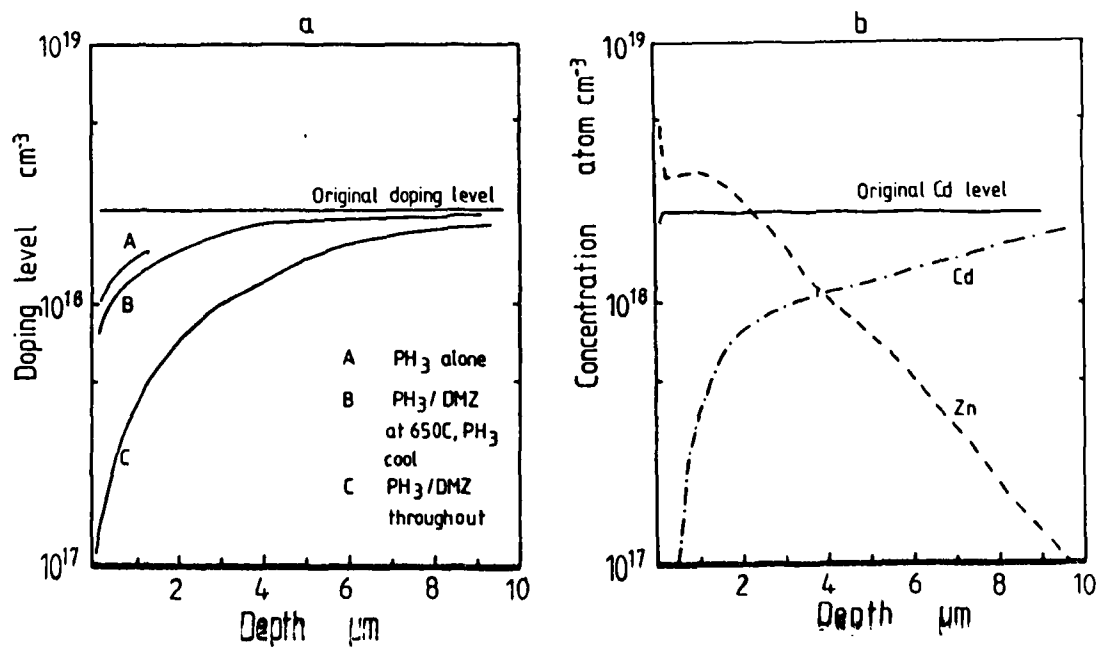


Figure 2 (a) Carrier concentration profiles for Cd doped InP substrate heated to 650C under ambients shown and (b) SIMS profile corresponding to curve C



Post-epitaxial Activation of Unintentionally Hydrogenated p-type InP and InGaAsP Grown by MOVPE

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Incorporation of acceptors during MOVPE growth of InP was recently reported to exhibit anomalous behaviour¹⁾. Also in our laboratory it was observed that a large fraction of acceptor dopants in the InP film becomes deactivated when cooling the samples in some group V hydride (not necessarily PH_3) after growth²⁾. The magnitude of the effect is dependent on the particular hydride used; it is rather large for AsH_3 . The deactivation is commonly attributed to interaction with atomic hydrogen which originates from the hydride pyrolysis. By driving out the hydrogen by annealing those samples at 470°C for 2 min in a N_2 atmosphere full activation can be obtained. A smaller, but identical effect has been observed in the quaternary material InGaAsP grown lattice matched to InP. In this paper we present results of a detailed study on this activation phenomenon for both materials.

InP and quaternary layers were grown by MOVPE at 20 mbar (Zn-doped samples) and at atmospheric pressure (Cd-doped samples) using TmIn , TMGa , PH_3 , AsH_3 , DEZn and DMCd as sources. After growth the samples were cooled in an atmosphere containing AsH_3 to ensure a maximum deactivation effect. To protect the binary material against surface deterioration during the subsequent cooling step it was covered by a thin InGaAs over-layer. Post-epitaxial annealing was carried out at temperatures between 320°C and 470°C for various lengths of time consecutively in an N_2 atmosphere. By comparing the doping levels of the as grown and fully activated samples we attained levels of deactivation as high as 80-90% in InP and 10-15% in InGaAsP.

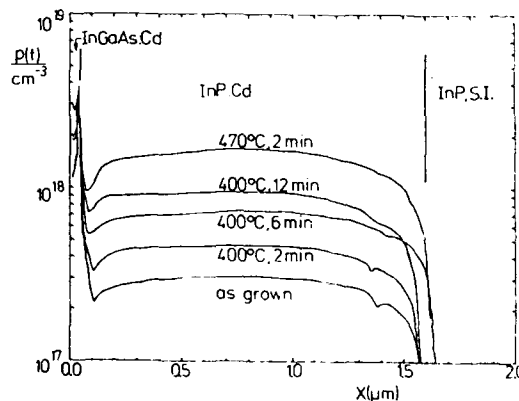


fig. 1: Carrier profiles in Cd doped InP-films after different annealing steps in N_2 .

The carrier concentration was determined using a polaron etch profiler and the standard van-der-Pauw-method. We observed a uniform increase in the concentration throughout the entire layer as shown in fig. 1. Thus, it is unlikely that a

macroscopic diffusion of hydrogen, which element is believed to cause the de-activation limits the activation process. However, effusion measurements confirm that hydrogen is driven out in the same temperature range.

For very short annealing times (less than one minute) the carrier concentration first shows a slight decrease. In contrast to the activation process, the initial deactivation entails a change in the carrier concentration profile. The activation process was found to develop with the square root of the annealing time, which is typical for a diffusion process. We assigned a time constant to this behaviour; this constant τ is displayed in an Arrhenius plot in fig. 2. The plot reveals an activation energy of 3.1 ± 0.3 eV for both Zn and Cd acceptors in InP. In the quaternary material only Zn-doped samples were investigated. Due to the small magnitude of the effect the scatter in the τ values is considerable for InGaAsP:Zn. Nevertheless we can observe that the process takes place at lower temperatures than in InP whereas its activation energy appears to be the same in both materials. Moreover we observed a distinct acceleration of the process when annealing with the InGaAs over-layer in all cases. material.

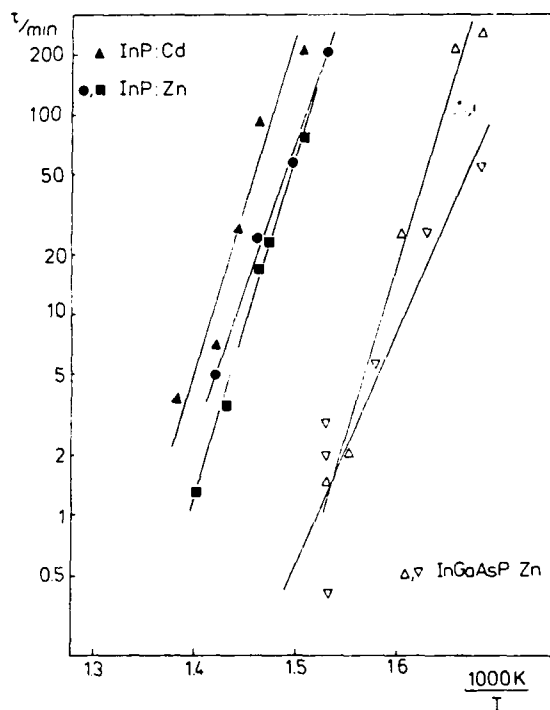


fig. 2: Temperature dependence of time constant τ activation process of acceptors in InP and InGaAsP.

On the basis of these data we will argue that an electrically neutral defect causes the rate limiting step in the activation process of InP and InGaAsP. We will discuss vacancy diffusion and diffusion of H_2 as possible rate limiting steps to explain the observed behaviour.

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UNINTENTIONAL NEUTRALIZATION OF InP:Zn BY HYDROGEN

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Unintentional neutralization of InP:Zn in GaInAs:Zn/InP:Zn structures during their elaboration has been simultaneously reported in 1988 by two groups (1, 2).

We have reported previously the electrical and optical effects of the exposure of GaInAs/InP:Zn structures to H and D plasmas (3, 4). From SIMS profiles, it was confirmed that hydrogen could diffuse into InP:Zn through undoped GaInAs capping epilayers. From correlation between IR and electrical measurements, it was firmly established that the production of neutral (P-D, Zn) or (P-H, Zn) complexes was responsible for the electrical desactivation of the Zn acceptors since the complexes are formed by the nesting of a proton or of a deuteron on a P-Zn bond. We have used the results obtained on the intentional neutralization by hydrogen to study unintentional neutralization using again IR absorption coupled with electrical and SIMS measurements. This study includes a calibration of the IR absorption of the (P-H, Zn) and (P-D, Zn) complexes and an investigation of their dissociation kinetics as a function of the annealing conditions.

The samples investigated were MOVPE-grown GaInAs/InP:Zn structures. For one sample, the GaInAs layer was Zn-doped, but for the other ones, it was undoped. After removing of the capping, the transmission of the samples was measured near liquid helium temperature to detect the presence of the (P-H, Zn) or (P-D, Zn) complexes which give rise to sharp P-H and P-D vibrational lines at 2288 and 1666 cm^{-1} respectively.

We have correlated the difference between the Zn and free hole concentrations with partial neutralization of the InP:Zn epilayer from H diffusion through the undoped GaInAs layer during the cooling down of the structure. It was also established that during the deuteration of the as-grown structure, about 40% of the native (P-H, Zn) complexes was destroyed. The integrated absorption of the P-H line at 2288 cm^{-1} could be related quantitatively to the concentration of the corresponding complexes, i.e. to the concentration of zinc neutralized by hydrogen. From this, it was also possible to obtain a calibration factor for the 1666 cm^{-1} line allowing to determine the concentration of zinc neutralized by deuterium.

The results on the as-grown undoped GaInAs/InP:Zn structures seem to indicate that a) the maximum concentration of zinc neutralized cannot be larger than $\sim 1.5 \times 10^{18}/\text{cm}^3$ and b) the neutralization efficiency in this case is not greater than 0.5 while it can reach to 0.8 in GaInAs:Zn/InP:Zn structures.

The dissociation of the complexes was found to be complete in deuterated InP:Zn with no capping after 10 minutes annealing at 375°C in an argon atmosphere. This is at a difference with the situation with a hydrogen atmosphere where only 30% of the zinc activity was restored in the same samples; in this ambient, 100% restoration of the zinc activity was obtained only after annealing at 450°C. Electrical reactivation annealing of zinc in InP have also been performed on as-grown GaInAs:Zn/InP:Zn structures in a nitrogen atmosphere (5) and it seems to show an influence of the presence of the GaInAs:Zn cap on the overall reactivation process. A determination of the dissociation energy of the (P-D, Zn) complexes using isochronal annealing in an argon atmosphere yields a value of about 2 eV, to be compared with ~ 1.6 eV for the (As-D, Zn) complexes in GaAs:Zn (6, 7).

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CHARACTERIZATION METHODS FOR HYDROGEN
INDUCED EFFECTS IN III-V COMPOUNDS.

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ABSTRACT.

In this paper we present some new results of the III-V compound crystal quality assessment. They concern the study of defects created during hydrogen or deuterium plasma exposure. One of the most suitable methods used for this purpose is the etching technique on chemically angle polished samples ETOCAPS (1). ETOCAPS, associated with optical microscopy observation, is a fast and easy-to-use characterization method. With its high depth resolution (less than one nm) and sensitivity, it is one of the most suitable methods for near surface, bulk and interface analysis.

ETOCAPS is based on the achievement of an angle of $\sim 0.01 - 0.1$ degrees to the III-V compound surface by progressive dissolution with 15% Br methanol which gives $\sim 6 \times 10^3 - 6 \times 10^2$ magnification of layer and interface thickness. Observing this sample with the X 1000 magnification of the optical microscope, the result is a $6 \times 10^6 \times 6 \times 10^5$ magnification in the direction parallel to the bevel, hence the possibility of studying the crystal perfection of even a 1-5 nm thick quantum well or superlattice. ETOCAPS provides this new possibility of examining simultaneously the general picture and localised crystal quality problems in three-dimensional distribution. For the chemical etching, baths appropriate to III-V compounds are used²⁻⁴. These specific baths dissolve preferentially precipitates, inhomogeneous and dislocated materials. The etch figures are also "indirect magnifications" of the defects.

The origin of crystal defects can often be correlated to unwanted impurities⁵ (in our case H or D). So, to complete the assessment of these materials, secondary ion mass spectrometry SIMS analyses are carried out

on the same (though unetched) sample. SIMS mass spectra and depth profiles are obtained with a CAMECA IMS 4F ion microanalyzer.

Presentation of some results :

- 1) donor concentration dependence of subsurface damage due to hydrogen plasma effect in (n)GaAs. ($n = 2 \times 10^{15} \text{ cm}^{-3}$ and $n = 1 \times 10^{17} \text{ cm}^{-3}$).
- 2) RF power dependence subsurface damage due to deuterium plasma effect in (n) GaAs sample ($n = 1 \times 10^{18} \text{ atcm}^{-3}$).
- 3) RIE (CH_4/H_2) damage in p (Zn) doped epitaxial InP layer.

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SIMS HYDROGEN ANALYSIS IN III V COMPOUNDS
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As evidenced by the organisation of this workshop the determination of chemical concentrations of hydrogen in semiconducting materials, in particular in III-V compounds, is of primary importance. Among the analytical methods which have been developed to address this problem the secondary ion mass spectrometry (SIMS) is certainly one of the most powerful. Nevertheless, due to gaseous residual contaminants present in sample chambers, the technique meets some difficulties to reach very low detection limits. The aim of this paper is to present recent results and capabilities which have been attained so far. We performed analyses for H in InP, GaAs, and GaInAs.

1 - Problems encountered when analysing gaseous species (H, C, N, O) by SIMS

C.W. Magee¹, a few years ago, showed that the detection limit, when analysing H in Si, was really dependent on the residual partial pressure of H₂O. The lowest detection limits were obtained for the lowest partial pressure. More recently, Kobayashi et al.² investigated the variation of the detection limit of carbon in GaAs by varying the primary ion density: decreasing the primary current for a fixed raster-scanned area, or decreasing the rastered area for a fixed primary current. They demonstrated there was a different etching rate dependence of the detection limit for the two measurement conditions. There was two contributions of the gaseous species: 1) a deposition of carbon-containing molecules onto the sample surface, 2) a memory effect, i.e. redeposition of C, CO or C_xH_y from the metallic parts surrounding the sample, or from the crater edges. Finally, it turns out that the lowest detection limits were obtained with the required experimental conditions: 1) Crater area as small as possible, 2) Primary ion current as high as possible, 3) Residual partial pressure as low as possible. They obtained $(1-2) \times 10^{15} \text{ cm}^{-3}$ for a beam density of 40 mA/cm^2 and a residual vacuum of about 1×10^{-9} torr. Meuris et al.³, after Homma et al.⁴, undertook similar experiments for oxygen in (AlGa)As multilayers and they confirmed the previous results. They obtained $5 \times 10^{15} \text{ O.cm}^{-3}$ in GaAs, and $1 \times 10^{17} \text{ O.cm}^{-3}$ in AlAs, for a beam density of 5 mA/cm^2 and a residual vacuum of about 1×10^{-9} torr. The limiting factors, governing the choice of the primary ion density are: 1) the required sensitivity, 2) the dynamic range, 3) the depth resolution. For hydrogen, we know results in silicon and referring to J.B. Clegg⁵ the limit would be $4 \times 10^{16} \text{ H.cm}^{-3}$.

2 - Experiments for hydrogen in InP, GaAs, and GaInAs

We performed experiments for H-implants in InP, GaAs, and GaInAs with experimental conditions very similar to those defined by M. Meuris et al., i.e. a 100 nA cesium primary beam over a raster-scanned area of 75, 50, or 25 μm^2 (density of

1.8, 4, or 16 mA/cm², respectively). The standard samples were implanted at 70 keV to 1×10^{15} cm⁻². The observed features were similar to those obtained for C in GaAs, or O in (AlGa)As, i.e. the hydrogen detection limit is differently dependent on the primary current intensity and the raster-scanned area, indicating at least two contributions to the residual contamination. This result confirms the major role played by the residual partial pressure of H₂O.

Together with the primary ion bombardment conditions, the useful yields of cluster secondary ions, possibly monitored for the analysis of hydrogen (³²PH⁻, ³³PH₂⁻, ⁶³P₂H⁻, ⁶⁴P₂H₂⁻, ¹¹⁶InH⁻, ¹¹⁷InH⁻, ¹¹⁷InH₂⁻, ²³¹In₂H⁻), were measured. The useful yield of a monitored ion defines the dynamic range and the sensitivity of the analysis provided that other ion species does not interfere with this ion under investigation. Depending on the matrix, the highest useful yields were obtained for P₂H⁻ negative ions, or As₂H⁻ in GaAs. Nevertheless, monitoring these particular species did not involve lower detection limits.

Finally, the lowest detection limit obtained for H in InP was $1-2 \times 10^{16}$ cm⁻³. Similar results were recorded in GaAs and GaInAs. Referring to previous works^{5,6} such a low limit is probably among the lowest obtained so far.

3 - Application to the determination of hydrogen in Fe-doped InP crystals

With the best experimental conditions defined herein we performed hydrogen analyses in different Fe-doped crystals, within the head and the tail, respectively. The results showed that the H concentrations were in the range of $1-2 \times 10^{16}$ cm⁻³ increasing just a bit from the heads to the tails of the crystals. Correspondingly, the residual concentration of zinc, as an example, were constants at $1-3 \times 10^{15}$ cm⁻³, or slightly decreasing from the heads to the tails.

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SESSION E : PROTON IMPLANTATION AND RELATED PROBLEMS

Moderator : J. Zavada, ERO, London, UK

- 15 : 10 E1 As implanted and annealing behavior 0.3 and 1 meV
 ^1H and ^2H implants into InP, and comparison with
 GaAs
 R.G. Wilson *, J.M. Zavada ** and S.W. Novak ***
 * HRL, Malibu, USA
 ** ERO, London, UK
 *** Ch. Evans and Associates, San Francisco, USA
- 15 : 45 Coffee break
- 16 : 15 E2 *Infrared and near-edge optical properties of*
 proton implanted InP, GaP and GaAs
 H. Neumann
 Karl-Marx U., Leipzig, GDR
- 16 : 50 E3 Hydrogen vibrations in proton-implanted semi-
 conductors
 J. Tatarkiewicz
 Inst. of Physics, Warsaw, Poland
- 17 : 25 Coffee break
- 18 : 00 Final talk
 N. Johnson
 Xerox, Palo Alto, USA.

As-implanted and annealing behavior of 0.20, 0.35, and 1.0 MeV
 ^1H and ^2H implants into InP, and comparison with GaAs

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Indium phosphide (InP) and its related alloys have gained increasing importance in recent years because of their widespread use in optoelectronics. InP materials have been used for sources and detectors in fiber optics communications systems. In addition, there are prototype applications for millimeter wave components and ultra-fast microelectronics, based on the higher electron mobility and greater radiation hardness of these materials.

Ion implantation is one of the primary techniques used to provide the required isolation of these devices. Results of several studies have shown that implantation of various ions, including H, B, and O, can effectively cause electrical passivation of doped InP crystals. These studies have been primarily centered on implantation parameters and on the degree of electrical isolation. Because a major concern of these experiments has been the temperature stability of the isolation, many annealing studies have been carried out. The basic interpretation of the resulting data is that the electrical isolation is the result of charge carriers being trapped by defects created by the implantation. As the defects are annealed at various thermal stages, carriers are released and the electrical conductivity returns.

One of the questions that remains in the study of implantation-induced isolation concerns the location and chemical activity of the implanted atoms. Hydrogen is known to be mobile in the InP crystal at low temperatures and there is evidence that hydrogen can also cause compensation of various dopant atoms. Consequently, studies of InP isolation using hydrogen implantation need to consider the distribution of hydrogen and its behavior with annealing.

In this talk, we present detailed results concerning the distribution of hydrogen implanted into single crystal InP and the redistribution caused by annealing. Using secondary ion mass spectrometry (SIMS), depth profiles of ^1H and ^2H atoms were measured for implantation energies from 0.2 to 1.0 MeV and fluences up to $1 \times 10^{16} \text{ cm}^{-2}$. Implanted samples were annealed and reprofiled to determine the redistribution of the H atoms in the InP crystal. The resulting profiles are compared with those of corresponding implants and anneals in single crystal GaAs.

Figure 1 shows a typical SIMS depth profile of ^2H implanted into an InP (100) crystal. The implant parameters were 200 keV, $2 \times 10^{15} \text{ cm}^{-2}$, room temperature, and random crystal orientation. The SIMS measurements were performed using a CAMECA 4f instrument and 14.5 keV Cs^+ primary ions. The detection limit for ^2H in InP is about 10^{15} cm^{-3} . The range measured here in InP is slightly greater than for a corresponding implant into a GaAs crystal. While InP and GaAs have equivalent numbers of electrons in a unit cell and the average atomic number is the same,

the lattice constant of InP is slightly larger than that of GaAs, possibly accounting for the greater range (R_p) in InP. Another possible influence is the greater difference between the atomic numbers of the two scattering atoms in InP compared with GaAs.

Redistribution of H with thermal processing was observed in both the InP and GaAs samples. In general, the redistribution proceeds in three distinct regions: the lightly damaged region from the surface to the peak, the heavily damaged peak region, and the undamaged bulk. There are different temperature thresholds for the redistribution of H in each of these regions. The details of the H depth distributions and their temperature dependences vary between InP and GaAs crystals; however, the qualitative behavior is similar.

An example of H redistribution in InP is shown in Fig. 2, which is a profile of ^2H implanted in a random direction into a S-doped (100) InP crystal at 350 keV and $5 \times 10^{15} \text{ cm}^{-2}$. The sample was annealed using a proximity cap in flowing dry nitrogen for 20 min, and the implanted ^2H and S dopant atoms were profiled using SIMS. A constant depletion of S of about 11% was measured from the surface through the implant/damage peak region following a 550°C anneal. Hydrogen has redistributed through this region to the surface, as shown by a series of profiles for lower annealing temperatures. The density of H in the peak region has decreased by two orders of magnitude and the redistribution into the bulk has proceeded to the degree that the ^2H is below the detection limit of about 10^{15} cm^{-3} . Hydrogen implants into GaAs show similar characteristics, but details within each of the three regions differ slightly. Post-implantation depletion of bulk dopant atoms was also observed in H-implanted, Zn-doped GaAs.

Additional SIMS profiles that have been obtained for ^1H implanted at 1 MeV into InP and GaAs crystals will be presented. The general features of the profiles described for 200 keV H implants also appear in the profiles for the high energy case, but displaced deeper into the material. However, details concerning the redistribution of H in the two materials are different and will be addressed.

Infrared and near-edge optical properties of proton implanted InP, GaP and GaAs

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By infrared spectroscopy we have studied the localized vibrational modes in proton and deuteron implanted InP, GaP and GaAs single crystals. Comparing the mode frequencies observed in these compounds we were able to unambiguously identify modes due to vibrations of hydrogen (deuterium) - cation and hydrogen (deuterium) - anion bonds, respectively. In GaAs, InP and proton implanted GaP our results are in good agreement with previous measurements. In deuteron implanted GaP we found three vibrational modes at 1260, 1298 and 1332 cm^{-1} due to Ga-D bond vibrations and three modes at 1600, 1635 and 1670 cm^{-1} due to P-D bond vibrations. The localized modes observed in proton and deuteron implanted crystalline GaAs and GaP seem to correlate with experimental and theoretical data for the localized modes in hydrogenated amorphous GaAs and GaP which may be helpful in identifying the nature of the vibrating species.

In studying the depth profile of the localized mode absorptions in proton implanted InP and GaP it was established that all the vibrating species are spatially located in the range of the damage density peak and not in the range of the hydrogen concentration peak. This result explains the sublinear dependence of the integrated absorption A of the modes on the fluence D , since the damage density can be influenced by in-situ annealing effects. In all compounds we found $A = A_0 D^n$ with $n = 0.4 - 0.8$ in dependence on the implanted species and the implantation conditions.

Extending the optical absorption measurements to higher photon energies up to the fundamental edge of the compounds we found that proton implantation results in the formation

of long exponential absorption tails below the gap energy. In the photon energy ranges $h\nu = 0.5 - 1.3$ eV in GaAs and InP and $h\nu = 0.8 - 2.2$ eV in GaP the absorbance of the proton implanted layers can always be well described by $A = A_0 \exp(h\nu/E_0)$. Both A_0 and E_0 increase continuously with the fluence D . For the tailing energy E_0 maximum values of $0.3 - 0.35$ eV were found in proton implanted GaAs and InP and of about 0.5 eV in GaP. The factor A_0 increases by more than five orders of magnitude. It can be estimated that in the photon energy range just below the fundamental edge the absorption coefficient can increase from $1 - 3 \text{ cm}^{-1}$ in the unimplanted material up to values of the order 10^4 cm^{-1} in the implanted compound. Comparative optical absorption studies on helium implanted single crystals of the compounds reveal an analogous increase of the absorption coefficients below the fundamental edge. On the basis of this result it is concluded that this change in the near-edge optical absorption behaviour is essentially due to native defects produced during implantation, probably antisite defects and vacancies. Theoretical model calculations of the tailing energy E_0 confirm this supposition. Consequently, it can be supposed that the large number of bonds between hydrogen and host lattice atoms formed in proton implanted material seems to be of negligible influence on the near-edge optical absorption spectra.

Hydrogen Vibrations in Proton-Implanted Semiconductors

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The technique of double implantation of different isotopes works especially well in the case of hydrogen/deuterium irradiations. The mass difference for these isotopes is as large as possible. This advantage was used intensively in the optical studies of local vibrational modes (LVMs) in implanted semiconductors. Proton irradiation enables the determination of the optical cross section (or the oscillator strength) of the observed LVMs, typical values being between 0.1 and 0.2. The isotopic ratio for hydrogen and deuterium LVM frequencies in all semiconductors varies between 1.37 and 1.39, slightly less than $\sqrt{2}$. This has been explained as being due to small anharmonicity of hydrogen oscillator. For rough estimates (see [1] and [2]), the harmonic oscillator model predicts the observed hydrogen LVM energies quite well - Fig. 1. It was assumed that the force constant k is proportional to the dissociation energy D [3] and is inversely proportional to the square of the bond length a^2 [3] and to the reduced mass μ of the corresponding free molecules to those created by hydrogen bonded in a semiconductor. The experimental, average correction of about 25 cm^{-1} due to the depolarizing field produced by the vibrating dipole in a cavity inside the solid has been obtained by fitting the average energy ω_0 of hydrogen LVMs in covalent semiconductors. Very weakly bonded molecules of group IIA metals (cadmium and zinc) as well as strong bonded of group VII ions (chlorine) deviate from this simple model, probably due to the more ionic character of the bonds. For InP [13] only P-H and for CuCl [7] only H-Cl LVMs are

Table I

Crystal	Bond	D kcal/mol	a Å	$\sqrt{D/a}/\mu$ eV/Å	ω_0 cm^{-1}	ω_0 cm^{-1}	$\Delta\omega$ cm^{-1}	f	Ref.
Si	Si-H	71.4	1.520	1.138	2042	1996	200	0	[4]
SiC	Si-H	71.4	1.520	1.138	2042	2090	150	0.394	[5]
	C-H	80.0	1.120	1.598	2861	2920	25		
Ge	Ge-H	66.8	1.588	1.064	1834	1886	125	0	[6]
GaAs	Ga-H	68.0	1.663	1.025	1604	1711	100	0.310	[6]
	As-H	65.0	1.534	1.087	2130	1998	100		
ZnS	Zn-H	19.5	1.595	0.574	1608	1325	100	0.764	[7]
	S-H	81.4	1.346	1.375	2200	2415	50		
ZnSe	Zn-H	19.5	1.595	0.577	1608	1315	150	0.740	[8]
	Se-H	73.0	1.470	1.210	2400	2150	50		
ZnTe	Zn-H	19.5	1.595	0.574	1608	1215	100	0.560	[9]
	Te-H	48.2	1.520	0.947	2250	1655	25		
CdS	Cd-H	16.5	1.780	0.466	1337	1285	150	0.794	[10]
	S-H	81.4	1.346	1.375	2200	2450	100		
CdTe	Cd-H	16.5	1.780	0.475	1337	1205	100	0.739	[11]
	Te-H	48.2	1.520	0.951	2250	1730	25		
GaP	Ga-H	68.0	1.663	1.025	1604	1849	25	0.361	[12]
	P-H	82.0	1.422	1.305	2365	2204	25		[13]
InP	P-H	82.0	1.422	1.305	2365	2204	25	0.534	[14]
CdF ₂	Cd-H	15.7	1.760	0.466	1337	775	25	0.950	[15]
CuCl	Cl-H	103.	1.275	1.637	2990	2580	100	0.911	[7]

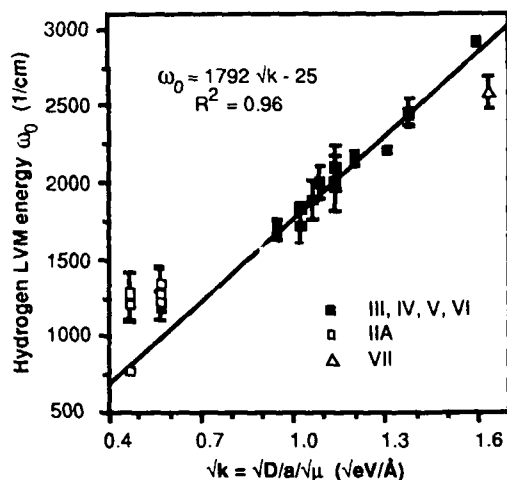


Fig. 1

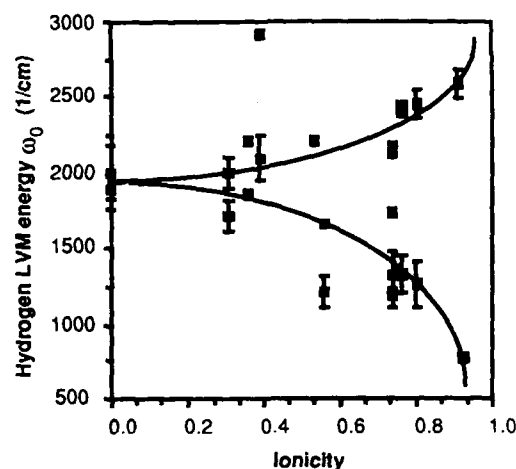


Fig. 2

seen whereas for AlSb [7] no hydrogen-related LVMs were recorded. Table I presents data obtained in a series of papers [4-15]. To explain differences mentioned above for group IIA and VII hydrides let us consider the ionicity f of crystal bonds [16]. As have been already shown [17], electron densities between lattice sites follow two different curves as a function of ionicity. Similar, phenomenological behavior is also observed for hydrogen LVMs (Fig. 2), strongly suggesting that the charge transfer is responsible for the observed differences in LVM energies. However, further theoretical studies are needed to explain this phenomenon - no general theoretical approach to hydrogen bonding has been developed so far.

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