INTERNATIONAL WORKSHOP ON HYDROGEN PASSIVATION OF DOPANTS AND DEFECTS IN III-V COMPOUNDS AND THEIR ALLOYS

PARIS, 3 - 4 NOVEMBER 1988

Campus Jussieu

UNIVERSITÉ PIERRE ET MARIE CURIE

ET

UNIVERSITÉ PARIS 7

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$\mathcal{I}$

INTERNATIONAL WORKSHOP ON
HYDROGEN PASSIVATION OF DOPANTS AND DEFECTS IN
III-V COMPOUNDS AND THEIR ALLOYS

Held in Campus Jussieu, Université Pierre et Marie Curie

and

Université Paris 7

2-4 place Jussieu, Paris 5ème, France

PARIS, 3 - 4 NOVEMBER 1988

Organizers:

Jacques Chevallier, C.N.R.S. Bellevue

Bernard Clerjaud, Université Pierre et Marie Curie

Bernard Pajot, Université Paris 7

Secretary:

Solange Duquesne, Université Pierre et Marie Curie

This Workshop was sponsored by:

SCIENTIFIC PROGRAM

Thursday 3ʳᵈ November

8.00   Registration

8.35   Opening

Morning Session. Chairman: J.Schneider (Fraunhofer IAF, Freiburg)

9.00-9.20   N. Caglio, E. Constant (Université de Lille), J. Chevallier and J. C. Pesant (C.N.R.S. Bellevue): *"New process for the fabrication of GaAs FET using neutralization of shallow donors by atomic hydrogen".*

9.40-10.00   N. Duhamel (C.N.E.T. Bagneux): *"Electrical insulation by proton implantation in III-V materials: Application to micro- and opto-electronics".*

10.20   **Coffee break**

10.50-11.20   W. C. Dautremont-Smith, S. J. Pearton and M. Stavola (A. T. & T. Bell Labs Murray Hill): *"Recent activities in hydrogenation of semiconductors"*

11.40-12.05   J. Chevallier, B. Theys, A. Jalil, R. Rahbi and J. C. Pesant (C.N.R.S. Bellevue): *"Hydrogen disffusion and dopant neutralization in III-V compounds".*

12.25-12.45   J. Neethling and H. C. Snyman (University of Port Elizabeth): *"TEM study of the extended crystal defects in hydrogen-implanted GaAs".*

13.15   **Lunch**

Afternoon Session. Chairman: E. E. Haller (Lawrence Berkeley Lab).

15.00-15.25   R. C. Newman (University of Reading) and B. Pajot (Université Paris 7): *"Localised modes of impurities and of their complexes with hydrogen in gallium arsenide"*

15.45-16.05   J. Weber (MPI-FKF Stuttgart): *"Photoluminescence studies on hydrogen-passivated GaAs".*

16.25   **Coffee break**

1645-17.15   P. Hautojärvi (Helsinki Institute of Technology) and C. Corbel (CEN Saclay): *"Positron annihilation spectroscopy of defects in as-grown and irradiated GaAs"*.

17.35-18.00   J. J. Zavada (ERO London), H. A. Jenkinson (US Army ARDEC Dover). R. G. Wilson (Hughes Malibu) and S. J. Pearton (A. T. & T. Bell Labs Murray Hill): *"Dopant neutralization and defect decoration in proton-implanted gallium arsenide"*.

20.00   **Dinner**

Friday 4th November

Morning session. Chairman: M. Stavola (A.T.&T. Bell Labs Murray Hill).

8.30-8.55   N. M. Johnson (Xerox Palo Alto and Universität Erlangen): *"Charge state of migrating hydrogen in semiconductors"*.

9.15-9.40   Th. Wichert (Universität Konstanz): *"Detection of hydrogen in semiconductors by nuclear methods"*.

10.00-10.25   B. Clerjaud, D. Côte, M. Krause, C. Porte (Université Pierre et Marie Curie Paris) and W. Ulrici (Zentralinstitut für Elektronenphysik Berlin): *"Spectroscopic studies of H-related complexes in bulk III-V compounds"*.

10.45   **Coffee break**

11.10-11.35   G. DeLeo (Lehigh University): *"Theory of interstitial hydrogen and hydrogen-containing aggregates in silicon: Recent semiempirical calculations.*

11.55-12.40   T. L. Estle (Rice University) and R. F. Kiefl (TRIUMF Vancouver): *"Isolated hydrogen and anomalous muonium in semiconductors"*.

13.15   **Lunch**

Afternoon Session. Chairman: J. W. Corbett (SUNY at Albany).

15.00-15.25   C. G. Van de Walle (Philips Briarcliff Manor): *" Theory of hydrogen diffusion and reactions in crystalline semiconductors"*.

15.45-16.05 P. Briddon, R. Jones and G. M. S. Lister (University of Exeter): *"The structure and properties of H complexes in GaAs, a-Si and Diamond"*.

16.25 **Coffee break**

16.45-17.10 J. I. Pankove (University of Colorado at Boulder): *"Pending problems with hydrogen in semiconductors"*.

17.30 **Concluding remarks by J. J. Zavada (ERO, London).**

INTRODUCTION

This Workshop is intended as a small meeting of people active in the field of the interaction of hydrogen with dopants and defects in III-V compounds and their alloys. New results and analyses will be presented and discussed and it is hoped this workshop will provide a better understanding of the different ways hydrogen can be introduced in III-V semiconductors, of the phenomena related to its presence and of its possible use to improve the quality of devices.

The main subjects debated in this workshop will be:

- The practical use of hydrogenation, either by plasma introduction or by proton implantation in the fabrication of III-V devices.

- The study by electrical and optical methods of the neutralization by hydrogen of dopants in III-V compounds.

- The correlation between the distribution of hydrogen, its charge state and the dopant neutralization.

- The nature and properties of point defects and extended defects related to proton implantation.

- The consequences of the presence of hydrogen in bulk , MOVPE and MBE materials non intentionally hydrogenated.

The presentation of channeling measurements which give a good insight of the atomic location of hydrogen in the crystal lattice is a natural transition to the calculation of microscopic models of the hydrogen complexes, first performed for hydrogen in pure and doped silicon and more recently in doped gallium arsenide.

We wanted finally this workshop to include a presentation of the new important results on muonium level crossing spectroscopy in silicon, gallium arsenide and gallium phosphide. They provide information on the configuration of anomalous muonium in these materials and the link with the recent EPR results on isolated hydrogen in silicon could be considered as a serious experimental indication of the bond-centred nature of hydrogen in the pure materials.

This booklet contains the abstracts or extended abstracts of the talks by the invited speakers and the reports we received from the other participants. We have tried to classify them as follows:

1) Applications and technology.
2) General studies and electrical measurements.
3) Extended and point defects.
4) Vibrational spectroscopy.
5) Advanced nuclear methods.
6) Theory.

HYDROGEN PASSIVATION OF DOPANTS AND DEFECTS IN III-V COMPOUNDS AND THEIR ALLOYS

Applications and Technology

N. Caglio, E. Constant (Université de Lille), J. Chevallier and J. C. Pesant: (C.N.R.S. Bellevue) "A new process for the fabrication of field effect transistors using the neutralization of shallow donors by atomic hydrogen".

N. Duhamel (C.N.E.T. Bagneux): "Electrical insulation by proton bombardment in III-V materials: Application to micro- and opto-electronics".

S. Cole, L. Davis, W. J. Duncan, W. J. M. Rothwell, P. J. Skevington and G. T. D. Spiller (British Telecom Ipswich): "The effect of cooling ambient on the electrical activation of dopants in MOVPE of InP".

G. R. Antell, A. T. R. Briggs, B. R. Butler, S. A. Kitching, J. P. Stagg (STC Technology Harlow), A. Chew and D. E. Sykes (University of Technology Loughborough): "The passivation of Zn acceptors by hydrogen during MOVPE growth".

Ph. Collot and Ch. Gaonach (Thomson CSF - LCR Orsay): "Non-intentional neutralization of dopant in GaAs by CH_4/H_2 reactive ion etching".

A NEW PROCESS FOR THE FABRICATION OF FIELD EFFECT TRANSISTORS USING
THE NEUTRALIZATION OF SHALLOW DONORS BY ATOMIC HYDROGEN

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INTRODUCTION

When atomic hydrogen is diffused into n-type silicon doped GaAs,
formation of silicon related hydrogen complexes occurs (Jalil & al, 1987).
As a result, the concentration of active silicon donors drops down, as seen
through the decrease of the free carier concentration which is accompanied
by a simultaneous increase of the electron mobility. It is the goal of this
paper to describe how to realize field effect transistor by using such
phenomena. In a first part, the fabrication process first used to realize
GaAs MESFET is presented, then, we describe the method of modeling which
has been used to optimize this technological process. Lastly, we shortly
describe the first realization of AlGaAs/GaAs MISFET based upon the
neutralisation of donors by atomic hydrogen.

M SFET

The process can be described as follows. We start from a single
highly doped GaAs epilayer. After the mesa and the source and drain ohmic
contacts fabrication, a protecting dielectric layer is deposited and we
proceed to the gate lithography. The processed sample is then exposed to a
hydrogen plasma for hydrogen diffusion in the non-protected regions. The
hydrogen diffusion results in the neutralisation of a more or less large
fraction of the silicon donors depending on the plasma exposure parameters.
As the neutralisation becomes more effective, the electron mobility
increases. After the gate deposition, the devices are expected to have low

access resistances, because these resistances will occur in highly doped regions. Other potential advantages are worthy to be mentioned :

- the possibility of having a completely planar process. Recess is not necessary to achieve low access resistances,

- the concentration of active donors below the gate is expected to be lower than deeper from the surface because of the hydrogen diffusion profile. Then we expect this active donor gradient to improve the transistor linearity and to increase the breakdown voltage.

Practically, we have used MBE grown silicon doped GaAs epilayers. Their characteristics are presented on Fig.1. The gate length was determined by the opening width made in the polyimide protection layer. It was 1.2 μm after exposure. The processed sample was then left in a R.F capacitively coupled hydrogen plasma for 10 minutes at 220°C : In such conditions, only a few per cent of the total donor concentration remains active after exposure. We then proceeded to a small recess of 0.1 μm in the gate region before the gate deposition. Three different geometries have been used with gate width of 75, 150 and 300 μm. We finally annealed the transistor at 300°C for 15 minutes in order to adjust the active donor concentration in the active region to the desired value. Actually, it has been shown that the neutralisation effect is stable for several years or more at 120°C and below, and that, above 280°C annealing leads to a deneutralisation of the donors. A very simular process has been used to relize 0.4 μm gate HFET but electronic lithography has been employed.

Figure 2 shows the static I-V characteristics of the HFET with a 300 μm gate. The corresponding gm value measured for a constant source-drain voltage of 2 volts is as high as 290 mS/mm. A more complete characterization of these devices has been performed by magnetoresistance experiments [Sites & al, 1980]. Applying this technic to our HFET, we find an electron mobility of 3500 cm^2/v.s. in the active layer. Taking into account a doping level of $6.10^{17} cm^{-3}$ deduced from gate-source capacitance, the electron mobility value is satisfactorily good. The equivalent circuit of these transistors in the high frequency regime has been deduced [Dambrine & al, 1987]. The cut-off frequency is higher than 15 GHz and 35 GHz for a gate length of 1.2 μm and 0.4 μm respectively. The high frequency transconductance in both cases is higher than 300 mS/mm. The frequency dependences of the Current Gain, Maximum Available Gain, and unilateral Gain are given on figure 3. For a 1.2μm gate length transistor, the performances appear somewhat remarkable.

MODELISATION

In order to optimize the performances of a transistor processed on an hydrogenated layer, we have conceived a MonteCarlo simulation of 2D hydrogen diffusion to get an idea of the donor profile after plasma exposure. We first consider an isotropic diffusion of hydrogen depending on donors concentration and plasma parameters, and only (H-Si) interactions depending on H density, Si density and plasma parameters. After successif comparisons with experiments we obtain approximatively donor concentration (Fig.4) and mobility profiles, and then, using classical method (Goots & al. 1989) transistors performances.

MISFET

As neutralisation in Si doped AlGaAs is effective, we realize a metal-insulator-semiconductor field effect transistor (MISFET). This FET is usually fabricated on an undoped (AlGaAs/GaAs) heterostructure, where a two-dimensionnal gas (2DEG) is induced in a potential well at the interface by the application of the positive gate voltage. We start with a highly doped AlGaAs epilayer (for good ohmic contacts and low access resistances) as describe Fig.5. Before gate deposition, we expose, with Si_3N_4 as dielectric layer, the active region to an hydrogen plasma, in order to strongly decrease the donor density (with a rate>100). In this first realization, we succeed to observe a negative resistance (Fig.6), which is an important phenomenon of this component. But, we must say, that static and hyperfrequency performances are disapointing. We hope, in a next realization, improve these results with making a change in the layer structure.

CONCLUSION

We have presented new types of field effect transistor based on the neutralisation of shallow donors by atomic hydrogen in the active region, the static and the high frequency characteristics can be considered as very encouraging. A more extended study is necessary to optimize the process and to evaluate its potential use in microelectronics.
We expect give you more details on the different points of this paper, particulary on the last work (MISFET and modeling method), in the oral account.

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FIGURE CAPTIONS

Figure 1 : Shematic device structure of the HFET

Figure 2 : DC voltage characteristics of 300 μm gate HFET. The gate voltage varies from (+ 200 mV) to (- 600 mV)

Figure 3 : Variation of the Current gain, Maximum Available Gain and Unilateral gain versus the frequency for 1.2 μm gate length HFET

Figure 4 : Comparison between static characteristics obtained with the modelisation and experiments

Figure 5 : Shematic cross-section of MISFET structure

Figure 6 : DC voltage characteristics of 100 μm gate H-MISFET

Figure 1

SUBSTRATE   NID

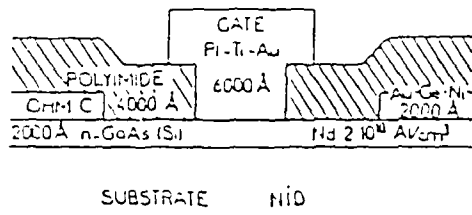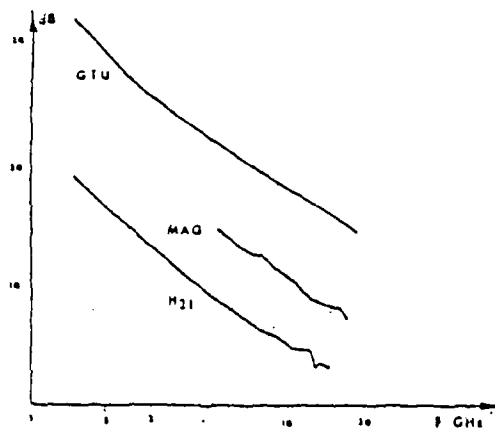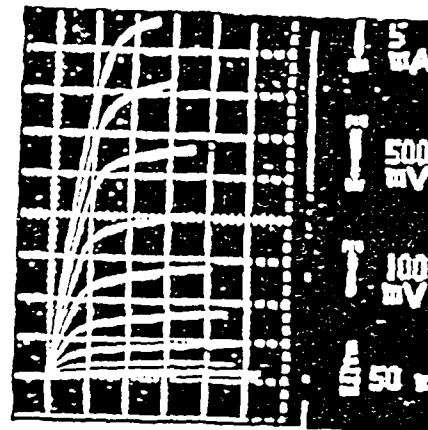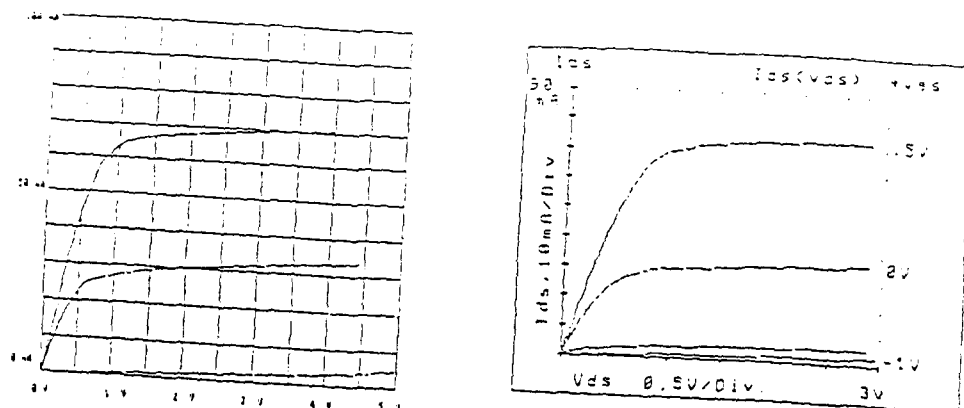- -

Figure 2

Figure 3

Figure_4

200 Å	GaAs	$2.10^{18} cm^{-3}$
500 Å	AlGaAs	$1.10^{18} cm^{-3}$
5000 Å	GaAs	NID

S.I.

Figure_5
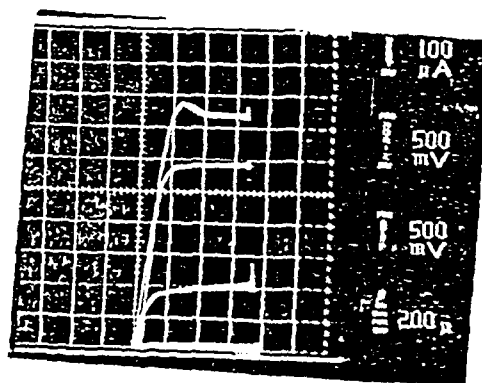
Figure_6

ELECTRICAL INSULATION BY PROTON BOMBARDMENT IN III-V MATERIALS :

APPLICATION TO MICRO AND OPTO-ELECTRONICS

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The successful design and fabrication of III-V integrated circuits requires a high degree of electrical insulation between closely spaced active devices. This can be done by :

. selective implantation of the desired dopant ions through a suitable mask

. mesa etching of the active layer

. ion implantation induced damage

However, the two first techniques produce an insufficient insulation which, for example in GaAs MESFET technology, leads to variation in insulation voltage, or to the well known detrimental backgating effect. This relatively low degree of electrical insulation can result in significant circuit design contraints including an increase in the minimum spacing rules.

In the third case, which we will detail, non-dopant ions are implanted into the active layer, the crystal lattice is damaged, trap centers are created which compensate the shallow dopants. The quality of insulation depend on several parameters : the material of the active layer (GaAs, InP, InGaAs...), its doping level, the implanted species (H, D, B, O) and the implantation and annealing conditions.

Two test structures can be used to measure the resistance of implantation induced damage layers : a vertical geometry test structure employed by several workers /1,2/ and a lateral geometry which reflects the structures of technological interest /3,4/. In the first geometry, since the bulk of doped III-V material has a much lower resistance than the damage layer, values of resistivity can easily be deduced from the measure of the current flow from the front to the back contact of the sample as a function of applied voltage. In the second configuration only insulation resistance can be deduced without any hypothesis on layer thickness and current path but this resistance is the most important parameter to characterize an insulation for microelectronic components.

GaAs : In GaAs, the insulation resistance is higher than 10^{9} Ω after proton bombardment /5/ or Boron implantation /4/. Thus protons or Boron ions have been successfully employed for device insulation in GaAs

MESFET circuits /4,5/. However, protons have the disadvantage of producing an insulation stable in a small temperature range only. Boron ions show temperature stability up to 500°C /1,6/, while protons reach only 400°C, except for multi-energies bombardments /7/. Another point to be underlined is the considerable decrease in insulation for doses higher than an optimum dose due to an enhanced hopping conduction. In the case of active layer MESFET ($n=1\times10^{17}e^-cm^{-3}$), the optimum dose is around $5\times10^{14}cm^{-2}$ for protons /5/ and about $4\times10^{11}cm^{-2}$ for Boron ions /4/. This means that, when using Boron, the implantation time is reduced by three orders of magnitude for the same implantation current.

However, due to their advantage of being the lightest ions, protons are used where thick damaged layers are required. For example, at CNET Laboratories, proton bombardment is routinely performed in the heterojunction bipolar transistors (HBT) technology for device insulation and also for delimiting the resistive paths into the n^+ collector layer /8/. It has also been utilized in HBTs process to reduce extrinsic base-collector capacitance and thus to improve their high speed performance /9, 10/.

Finally, we discuss one of the first use of proton bombardment in devices i.e. the formation of stripe-geometry GaAs/GaAlAs heterostructure lasers /11/ in a simple technological process.

InP and alloys : Coming now to other III-V compounds, especially InP and InGaAs, for the purpose of interdevice insulation, implantation induced damage is comparable in GaAs and p type InP : resistivities of $10^7\Omega.cm$ can be obtained by proton bombardment /12/. However, in n-type InP, the maximum resistivity which has been reported for proton bombardment is about $2\times10^3 \Omega.cm$ /11/ while in In-GaInAs the increase of sheet resistance after hydrogen or Boron implantations, is too small to produce effective insulation in most optical or electronic InGaAs devices /13/. Thus, the insulation is one of the major problems to be solved before a viable technology of medium complexity circuits will be established in these materials. Thereby, in InP technology, proton bombardment has only been used in photodetection /1- or in lasers /15/, i.e. in p-type InP material.

- 12 -

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The Effect of Cooling Ambient on the Electrical Activation of Dopants in MOVPE of InP

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The effect of cooling ambient on the doping level of p-type InP doped with Zn or Cd has been investigated. In MOVPE growth of III-V materials, the group V precursor generally used is the hydride (AsH_3 or PH_3). During cool down from MOVPE growth temperatures, the incongruent loss of P from the InP sample surface is prevented by maintaining an overpressure of PH_3. InP can also be protected by a mixture of AsH_3 and PH_3 for short time periods with no deleterious effect on surface morphology.

Samples were characterised using the electrochemical profiler [1] and secondary ion mass spectrometry (SIMS). Both MOVPE grown layers and Czochralski bulk crystals were studied and found to behave similarly. It was found that if AsH_3 was present in the cooling ambient, the doping level was lower by up to an order of magnitude than if PH_3 was used, which in turn gave a doping level lower by up to a factor of 2 than obtained with H_2 alone. n-type InP and n- or p-type GaAs did not appear to be affected.

SIMS analysis showed that this effect was caused by electrical deactivation rather than loss of the dopant species. Significant quantities of atomic H were found in samples exposed to the hydrides during cooling (figure 1), consistent with their pyrolysis being catalysed by the semiconductor surface. We suspect these phenomena to be caused by deactivation of the dopant by complex formation with H, as observed by Johnson et al. [2] in GaAs exposed to a hydrogen plasma.

On introducing p-dopant precursors into the cooling ambient a similar lowering of doping level was observed. However, SIMS analysis could detect no atomic H in such a sample. A summary of some of our findings is listed below:

1. Doping level of p-Inp depends on cooling ambient such that: $p(AsH_3) < p(PH_3) < p(H_2)$
2. Doping level can be restored by heat-treating in PH_3 or H_2
3. Effects common to MOVPE epilayers and bulk crystals
4. The drop is not due to loss of dopant
5. Magnitude of drop is proportional to original doping level
6. No effect seen in n-InP or n- or p-GaAs
7. Atomic H is found in samples cooled in hydride ambients, such that: $H(AsH_3) > H(PH_3)$
8. Similar effects seen in samples cooled in dopant precursor ambients
9. In these samples the original dopant diffuses out and is replaced by dopant from the ambient-NO H IS FOUND

To conclude, we have seen that the electrical activity of p-dopants in InP is strongly influenced by the cooling ambient and that the relative concentrations of atomic H found in crystals cooled in

hybrides is consistent with the doping level drop, assuming that H
forms inactive complexes with the p- dopant. We believe that the H
originates from the pyrolysis of the hydrides, and so the
concentration of H is dependent on their thermal stability.
However, our results indicate that the doping level drop observed
in crystals cooled in dopant precursor ambients is not caused by
the presence of atomic H and must be attributable to some other
electrical deactivation mechanism.

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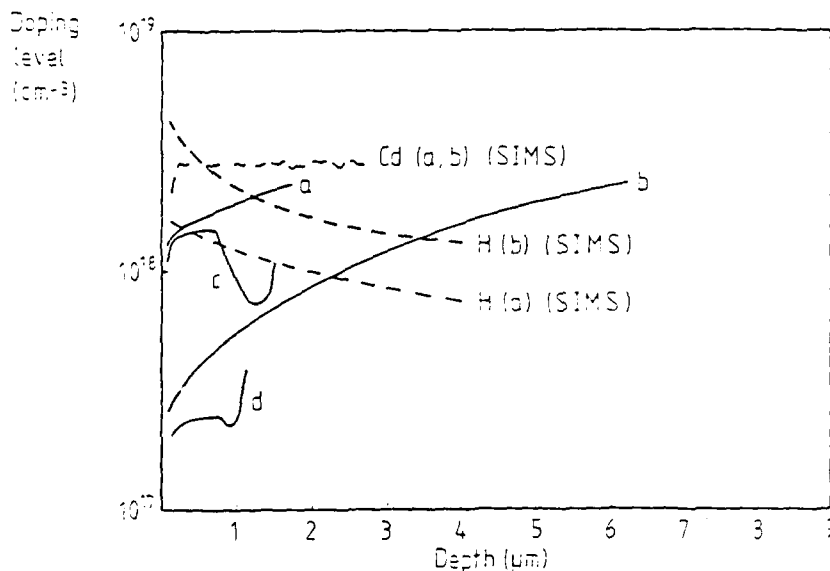(1) M.M.Faktor and J.L.Stevenson, J. Electrochem. Soc. 125 (1978)
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Figure 1
Electrochemical and SIMS profiles for (a) p-InP(Cd) bulk crystal
and (c)P-InP(Cd) MOVPE epilayer cooled in PH_3 in H_2, (b) p-InP(Cd)
bulk crystal and (d) p-InP(Cd) MOVPE epilayer cooled in $AsH_3:PH_3$
1:1 in H_2.

The Passivation of Zn Acceptors in InP
by Hydrogen During MOVPE Growth

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The hole concentrations in zinc doped InP single layers grown
by MOVPE are reasonably stable when annealed at about 400°C.
When a similar type of layer is grown and then capped by a layer
of lattice matched p type InGaAs during the same run it is found
that the hole concentration has been reduced by about a factor
of 3 or more and that this can be restored to the higher value
by annealing.

At first it was thought that this phenomenon might be due to the
rapid diffusion of interstitial zinc between the InP and InGaAs
layers. SIMS analysis of a specially grown structure showed
unequivocally that there was no movement of zinc.

Atomic hydrogen was the next most obvious candidate as a cause
for the reduction in the acceptor concentration but was
considered to be unlikely for the following reasons:

1) There was no obvious source of atomic hydrogen in the
   MOVPE growth.

2) The InP was grown in a predominantly hydrogen ambient and
   yet InP layers could be grown with carrier concentrations
   less than $10^{14} cm^{-3}$ and mobilities in excess of
   200,000 volt sec cm^2 at 77°K and thus were almost
   uncompensated. To produce the reduction of the acceptor
   concentration in p type InP would require more than
   $10^{18} cm^{-3}$ of hydrogen.

Despite these arguments the above test sample was re-examined by
SIMS and hydrogen was detected in the p type InP layers.
Further studies soon established that the arsine which was
present during the growth of the InGaAs capping layer was the
source of the atomic hydrogen and that this hydrogen was trapped
in the InP mainly during the cooling down stage after the
completion of growth.

It is postulated that the H-P bond in InP is stronger than that
of the As-H bond in AsH$_3$ when in contact with the
semiconductor surface and thus hydrogen can be trapped in InP at
temperatures where AsH$_3$ is still cracking.

The passivation of zinc acceptors in InP which has been
overgrown by a layer of p type InGaAs can be avoided by the
following methods:

1) After growth is complete the sample can be cooled as normal in an AsH_3-H_2 ambient to about 500°C at which point the AsH_3 is switched off and cooling continues in H_2.

2) Grow an additional layer of InP on top of the InGaAs and cool in the normal PH_3-H_2 ambient. The additional InP layer can be removed by a selective etch.

3) Grow an addtional layer of n type InGaAs on top of the p type InGaAs and cool as normal in an AsH_3-H ambient. In this case the diffusion rate of hydrogen in n type InGaAs is much slower than in p type InGaAs and thus prevents the hydrogen at the surface from reaching the underlying InP layer.

NON-INTENTIONAL NEUTRALIZATION OF DOPANT IN GAAS
INDUCED BY CH4/H2 REACTIVE ION ETCHING

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In the interaction of hydrogen plasmas and semiconductors, modifications of the electrical properties of the near-surface region are expected: in particular, a reduction of the carrier concentration near the surface is currently observed after H_2-plasma exposure. This effect has been attributed to a chemical neutralization of the shallow-level dopants by atomic hydrogen [1]. So, during the reactive ion etching (RIE) of III-V compound semiconductors in methane-hydrogen plasmas [2], similar effects are more than likely.

In the present work, an investigation of the electrical properties of N-type GaAs (Si-doped) subjected to CH4-H2 RIE is proposed:

-Carrier concentration profiles derived from C-V measurements at 1MHz on Schottky diodes elaborated on the dry-etched surface are shown in figure 1: the expected carrier depletion is displayed and as already observed [3], the extent of the depleted region is inversely dependant on the initial bulk dopant concentration, after the same RIE treatment.

-Electronic mobility as a function of temperature, before and after RIE, is shown in figure 2. The increase of the mobility after RIE is particularly important in the temperature range where the carrier scattering is dominated by interactions with ionized impurities (T<100K).

These results corroborates the hypothesis of a chemical neutralization of the doping centers (Si), induced by hydrogenation of GaAs. Moreover, because of the increase of the mobility, the carrier depletion cannot be attributed to an electrical compensation related to acceptor-like trap centers induced by the RIE treatment.

Fortunatly, this dopant neutralization is not thermally stable and annealing temperatures in the range 350-400°C are sufficient to restore the majority of the dopant activity (see table 1).
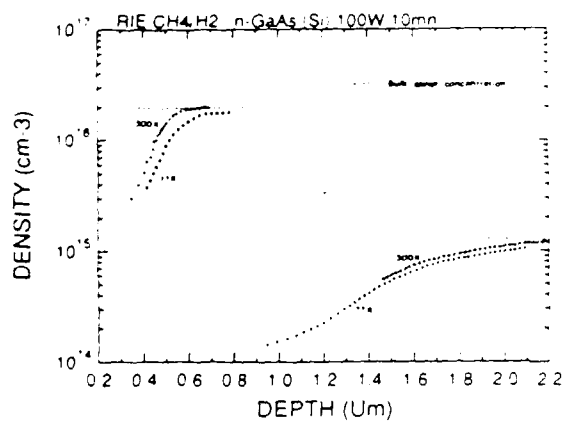
FIGURE 1: Carrier concentration profiles, derived from C-V measurements (1MHz) at 300 and 77K, after RIE in CH4 H2. Influence of the doping level.
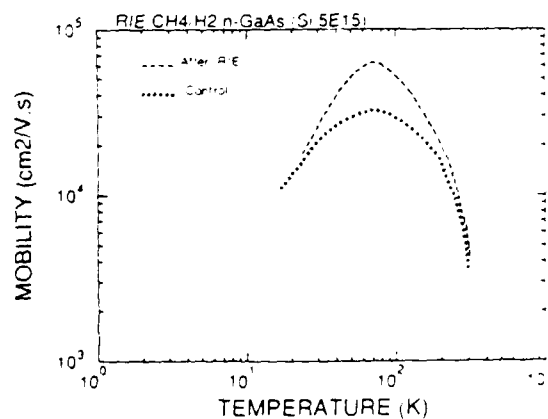
FIGURE 2: Electronic mobility as a function of temperature, before and after CH4 H2 RIE.

	Mobility (cm2/V.s)		Density (cm-3)	
	300K	77K	300K	77K
*Control	3700	28000	8.1E15	0.6E15
*After RIE	4700	61000	1.0E14	1.0E14
*360°C 15mn anneal	4000	32000	3.5E15	2.0E15

TABLE 1 : Carrier mobility and density at 300 and 77K.

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HYDROGEN PASSIVATION OF DOPANTS AND
DEFECTS IN III-V COMPOUNDS AND THEIR ALLOYS

General studies and electrical measurements

W. C. Dautremont-Smith, S. J. Pearton and M. Stavola (A.T.&T. Bell Labs Murray Hill): "Recent activities in hydrogenation of semiconductors". Invited talk.

J. Chevallier, B. Theys, A. Jalil, R. Rahbi and J. C. Pesant (C.N.R.S. Bellevue): "Hydrogen diffusion and dopant neutralization in III-V compounds". Invited talk.

N. M. Johnson (Xerox Palo Alto and Universität Erlangen-Nürnberg): "Charge states of migrating hydrogen in semiconductors". Invited talk.

N. Pan, M. S. Feng, K. C. Hsieh, S. S. Bose, G. S. Jackson, G. E. Stillman and N. Holonyak, Jr. (University of Illinois at Urbana): " Impurity and structural studies of hydrogenated GaAs and GaAs/Si".

G. Pensl (Universität Erlangen-Nürnberg): "Activities on hydrogen passivation of defects in silicon".

RECENT ACTIVITIES IN HYDROGENATION OF SEMICONDUCTORS

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III-V SEMICONDUCTORS

GaAs

Passivation of donors:

— magnitude and depth dependence of passivation, dependence on donor concentration

— thermal stability/reactivation kinetics, dependence on donor species, proposal of donor - H direct bonding passivation model

— H/D in-diffusion SIMS depth profiles, dependence on donor concentration, effects of various doped epi-overlayers

— variation in correlation between elemental and electrically active depth profiles with type of plasma exposure (low frequency vs. high frequency vs. microwave)

— defect generation

— depth dependence of electron mobility changes

— depth dependence of donor reactivation

Passivation of acceptors:

— magnitude and depth dependence of passivation, efficiency relative to donor passivation

— thermal stability/reactivation kinetics

— H/D in-diffusion SIMS elemental depth profiles, effects of variously doped epi-over layers

— correlation of elemental and electrically active depth profiles, influence of type of plasma exposure

Passivation of deep levels:

— passivation of electron trap deep levels in MBE GaAs, shown by DLTS

— thermal stability exceeding that of shallow level passivation

— associated photoluminescence efficiency increase, particularly in AlGaAs capped layers

AlGaAs

Passivation of donors:

— passivation of Si and Te donors

— thermal stability/reactivation kinetics of Si donors

Passivation of deep levels:

— passivation of the DX center

— thermal stability/reactivation kinetics of DX, shown to be basically the same as for Si donors except for exhibiting a distribution of dissociation energies

— supported model of an isolated donor in a non-unique site, in a region of inhomogeneous alloy composition

GaAs-on-Si

Passivation of defects:

— increase in the reverse breakdown voltage of Schottky diodes

— only partial passivation of interface-originating dislocations

— comparison of the effectiveness of H diffusion and H implantation + anneal

InP

Passivation of acceptors:

— evaluation of various H permeable surface protection layers

— strong passivation of acceptors

— thermal stability/reactivation kinetics

— SIMS depth profiling of H/D diffusion into p-InP and correlation with passivation depth

— photoluminescence study of passivated p-InP

ELEMENTAL SEMICONDUCTORS

Si

Shallow level passivation:

— passivation of thermal donors

— vibrational spectroscopy of acceptor-H and donor-H complexes in Si

— thermal stability of donor-H complexes

— uniaxial stress determination of the symmetry of donor-H and acceptor-H complexes in Si.

— determination of the kinetics of the motion of H between bond - centered sites around the B atom in the B-H complex in Si

HYDROGEN DIFFUSION AND DOPANT NEUTRALIZATION IN III-V COMPOUNDS.

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TOPICS OF INTEREST:

. We are currently studying the hydrogen diffusion process and the neutralization of shallow dopants by hydrogen in various III-V crystalline compounds and alloys (GaAs, InP, GaAlAs).
. These studies are very usefully completed by high resolution infrared optical spectroscopy to get information on the microscopic description of the H-dopant complexes (Coll. with B.PAJOT, GPS-ENS Paris).
. Applications of the dopant neutralization by hydrogen are investigated in collaboration with other laboratories (for the HFET see the work presented by E. CONSTANT and N. CAGLIO from the University of Villeneuve d'Ascq).

MATERIALS:

- LPE grown GaAs:Si(p+) (M.C.BOISSY, RTC Compelec, CAEN)
- MOCVD and MBE grown GaAs:Si (n+) and GaAlAs:Si (n) (R. AZOULAY, CNET BAGNEUX; C.W.TU, ATT Bell Laboratories, MURRAY HILL)
- MOCVD grown GaInAs/InP: Zn structures (B. ROSE, CNET BAGNEUX)

HYDROGEN DIFFUSION IN GaAs AND InP:

. Hydrogen is introduced from a R.F. hydrogen plasma:
T_{sample} = 100°C - 300°C, R.F. power = 0.01-0.04 W/cm^2
. Hydrogen detection is performed by SIMS analysis (CAMECA IMS 3f system).

Results: The close correspondence between the net acceptor concentration and the hydrogen concentration in the plateau region for diffusion temperatures up to 300°C [1,2] is a signature of a H-acceptor pair formation (Fig. 1 and 2). Its existence up to 300°C supports the idea of a relative thermal stability of these complexes and then suggests that H-acceptor interactions have to be taken into account in the hydrogen diffusion modelling:
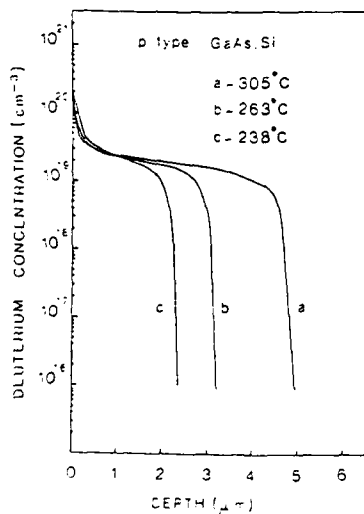

Fig. 1 - D concentration profiles in p+ type GaAs: Si (p=10^{19}cm^{-3}) exposed to R.F. D plasma for 90 min.
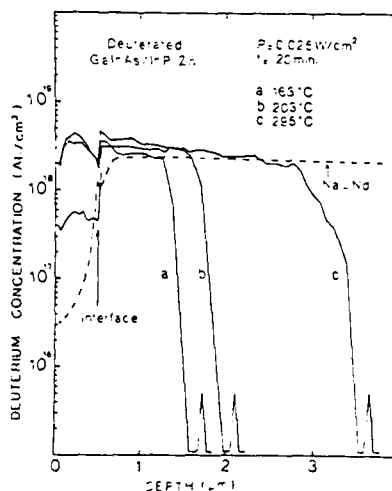
Fig. 2 - D concentration profiles in a GaInAs/p-InP: Zn structure exposed to R.F. D plasma for 20 min.

In n-type GaAs:Si, the hydrogen diffusion study has been performed between 200 and 300°C. These profiles are close to an erfc function. The diffusion coefficient has an activation energy of 1.38eV.

DOPANT NEUTRALIZATION:

. Results: In p-type GaAs:Si and p-type InP:Zn, the electrical activity of the acceptors is significantly reduced after hydrogen diffusion. This is accompanied by an increase of the free hole mobility (fig.3) [2].
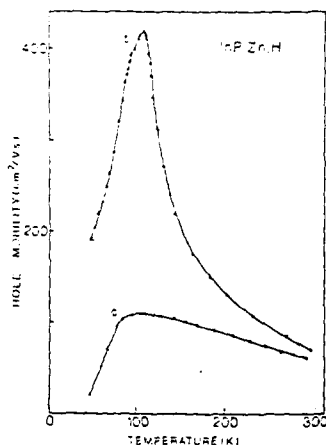
Fig. 3 - Hole mobility vs T curves for an InP:Zn epilayer before (a) and after (b) hydrogen plasma (6h,200°C)followed by an annealing (5min.,275°C)
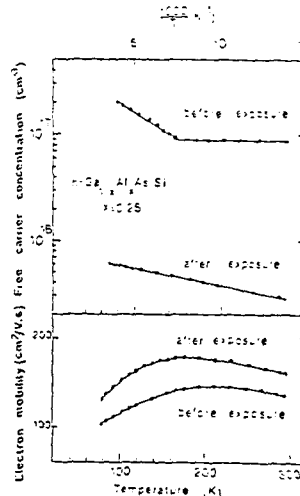
Fig. 4 - Temperature dependence of n and μ_n in a Ga$_{0.75}$Al$_{0.25}$As:Si alloy before and after hydrogen plasma exposure.

The transport properties of GaAs:Si (n) and GaAlAs:Si (n) after hydrogenation show a drastic reduction of the shallow donor concentration. Moreover, in the GaAlAs:Si alloys, D-X centers are also neutralized (fig.4) in agreement with previous DLTS experiments [3,4]. These D-X centers are more efficiently neutralized than the shallow donors for x≈ 0.25 so that, in such a passivated alloy, the transport properties are mainly governed by residual shallow donors [4]. An increase of the electron mobility is observed after hydrogenation as in GaAs:Si(n).

The increase of the free carrier mobility in p-type and n-type materials is due to a reduction of the ionized impurity concentration due to the transformation of dopants into neutral H-impurity complexes. In hydrogenated InP:Zn, the hole mobility is somewhat smaller than the hole mobility in hydrogen free material with similar net acceptor concentrations. The hole mobility limiting factor in InP:Zn,H is partly attributed to the concentration of ionized donors present in the starting material. This assumption is supported by the absence of hydrogen passivation of ionized silicon donors in p-type GaAs:Si [1].

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CHARGE STATES OF MIGRATING HYDROGEN IN SEMICONDUCTORS[a]

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A fundamental issue that continues to challenge our understanding of hydrogen in crystalline semiconductors is the question of whether migrating hydrogen can exist in different charge states. Given below is a summary of the experimental evidence that bears on this issue, with emphasis on the most recent studies; calculations of the electronic states of H in semiconductors are presented elsewhere in this workshop. (Here, the symbols H^+, H^0, and H^- designate charge states of possible complexes involving interstial H and host atoms.) To date, the subject has been addressed almost exclusively in Si. However, the techniques and issues identified in Si should be applicable to compound semiconductors.

Depth profiles of diffused H or D in Si display several distinctive features. In p-type Si the D profile typically displays a plateau at the uniform B concentration with the depth of D penetration equaling the depth of B neutralization [1]. No such plateau accompanies shallow-donor neutralization in n-type Si [2]. The D closely tracks a nonuniform B profile in p-type Si but not in counter-doped n-type Si [1]. Such features have been interpreted with the hypothesis that H possesses a deep-donor level within the bandgap so that H migration in p-type Si includes electric-field-assisted diffusion of H^+ and neutralization of boron proceeds by the reaction $H^+ + B^- \rightarrow (HB)^0$ [3,4].

The dramatic effect of a space-charge layer on B neutralization in Si has also been interpreted in terms of the deep-donor model [3-6]. Both in Schottky diodes that were bias-temperature stressed after hydrogenation [5] and in n^+-p junction diodes that were reverse-biased during hydrogenation [6] it was shown that B neutralization occurs preferentially in the p-region at the edge of the bias-dependent depletion layer. While this can be ascribed to the drift of H^+ in the depletion layer, it does not by itself establish the existence of mobile H^+ since B neutralization could, in principle, involve H^0 and free holes [6].

Studies of hydrogen immobilization in Si p-n junctions have provided further evidence for the deep-donor model [7-9]. The space-charge layer was used to reveal charge-state or Fermi-level effects during hydrogen migration by variations in the depth profile of the total H concentration. In n^+-p junctions, the distribution is highly structured with features that depend on a reverse bias applied during H migration. The features represent accumulations of H in excess of the B concentration and must involve the migration of an H^+ species. Most of the accumulation is in the form of highly immobile neutral entities, which are proposed to be hydrogen pairs, H_2. Formation of H_2 by the conventional reaction $2H^0 \rightarrow H_2$ is, by itself, incapable of accounting for the structure in the depth profiles. However, the results can be

explained by postulating that the competing reaction $H^- - H^0 \rightarrow$ $H_2 - h^-$, where h^- denotes a free hole, becomes dominant in p-type Si.

Depth profiles of D in uniformly-doped n-type Si and in epitaxial n-n layers suggest that H may also possess a deep-acceptor level within the Si bandgap [9].

In a new approach to the study of hydrogen migration, electrical measurements are now being conducted during hydrogenation [8]. The principal value of such "real-time" measurements is the ability to study the charged species as it migrates through the material rather than attempting to infer the charge state of the migrating species from the properties or formation kinetics of the various stable H-related complexes. To illustrate, the resistivity of p-type Si (SOS) was observed to increase with time after exposure to monatomic hydrogen at 300°C. If the $(HB)^0$ complexes are completely dissociated at 300°C, the increase in resistivity should reflect compensation due to in-diffusion of H^-. Similar results have been obtained on n-type Si (SOS) at 300°C [10], which suggests compensation by migrating H^- if H-donor complexing can be neglected. Clearly, in-situ measurements can provide direct access to the properties of migrating hydrogen.

In compound semiconductors the plateau in the depth profile of diffused D at the uniform acceptor concentration, which has been observed in p-type GaAs:Zn [11], p-type GaAs:Si [12], and p-type InP:Zn [13], provides the only available evidence to suggest a bandgap donor level for H in these materials. It is anticipated that this situation will soon change.

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IMPURITY AND STRUCTURAL STUDIES OF HYDROGENATED GaAs AND GaAs:Si

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Hydrogenation of GaAs and AlGaAs is found to result in a significant change of the electrical and optical properties. Much work has been focused on the hydrogenation of various dopants in GaAs and AlGaAs. However, there have been few reports on the structural and optical properties of these materials after hydrogenation.

In this work, the effects of hydrogenation on the residual impurities in high purity n and p-type GaAs will be reviewed. The samples were characterized before and after hydrogenation using complementary characterization techniques; photothermal ionization spectroscopy (PTIS), low temperature photoluminescence (PL), capacitance-voltage (C-V), and Hall-effect measurements. The effects of hydrogenation and subsequent annealing on GaAs grown on Si have been characterized by C-V, Hall-effect measurements, and transmission electron microscopy (TEM). Previous results in which hydrogenation was used to realize isolation regions in single and multiple stripe geometry lasers will also be described.

After hydrogenation, the concentration of Si donors and Si acceptors that are present in GaAs show a decrease. Carbon acceptors in both GaAs and AlGaAs show a large decrease. TEM reveals that the hydrogen plasma slightly etches the surface of GaAs and energy dispersive spectroscopy shows an arsenic deficient surface. The effects of hydrogenation is observed to be more dramatic on GaAs grown on Si. It is speculated that twins and dislocations are responsible for providing a path for significant hydrogen accumulation. The lasers produced using the hydrogenation process are uniform with low threshold currents and cw room temperature operation.

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ACTIVITIES ON HYDROGEN PASSIVATION OF DEFECTS IN SILICON

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Chalcogen double donors in Si

Tellerium, selenium, and sulfur form isolated defects and
pure impurity pairs in n-type silicon which act as double
donors. Their activation energies have been determined by
Hall effect -,DLTS -, and IR absorbtion measurements /1/.
The electrical activity of all these double donors can be
completely removed by hydrogen passivation /2,3/. The hydro-
genation was performed by a remote microwave plasma e.g.
at 150°C for 30 min. The reactivation of the donor activity
was studied for the neutralized sulfur double donors by
the rapid isothermal annealing technique. The reactivation
energies for the isolated S-impurity and for the pure S-pair
have approx. the same values; they result in

$$E_a(S^{0/+}) = E_a(S_2^{0/+}) = 2,1 \pm 0,15 \text{ eV} \qquad /3/.$$

From the annealing kinetics, it appears that a single hydrogen
atom bonded at the defect site is sufficient to remove both
energy levels of the double donor center. The large reactivation
energies suggest that the hydrogen is strongly bonded at the
defect site.

Yapsir and coworkers /4/ have recently performed cluster
calculations of isolated sulfur-hydrogen-complexes in silicon.
They predict two stable configurations containing one and
two hydrogen atoms, respectively. The hydrogen atoms bond to
the nearest silicon atoms and interact only weakly with the
sulfur. Already the inclusion of one hydrogen atom moves the
ground levels of the double donor complex below the valence
band edge. DLTS investigations are therefore not suited to
decide which of the two stable configurations is advantageously
formed by the hydrogenation process. Optical investigations
are in preparation to clarify this open question.

Oxygen-related defects in Si

In Cz-grown silicon, the oxygen content may reach concentrations between $5 \cdot 10^{17}$ and $2 \cdot 10^{18}$ cm^{-3}. The oxygen is mainly incorporated into the Si lattice on electrically inactive interstitial sites. During heat treatments, oxygen forms clusters or precipitates which act as donor traps. "Thermal Donors" (TD's) and "New Oxygen Donors" (ND's) are generated in the temperature range of 350 - 500°C and 550 - 800°C, respectively. The TD's appear as discrete peak in the DLTS spectrum at approx. T = 55 K. Hydrogenation at 120 - 300°C for 30 min leads to a maximum reduction of the TD concentration by a factor of approx. 5 /5/. This amount of TD passivation is not a drastic effect and does not support those TD models which explain the TD activity by broken Si bonds.

The DLTS spectra of ND traps indicate the presence of deep levels that are continuously distributed in energy. Intensive DLTS studies have been performed on the passivation of ND traps /5,6/. It has been demonstrated that energy levels with $E_C - E \gtrsim 200$ meV (E_C = conduction band edge) can be completely removed and that energy levels with energies $E_C - E \lesssim 200$ meV are only partially reduced. This behavior supports our suggestion that the continuous energy distribution of the ND traps is composed of two different types of energy states. We suggest that interface states at the surface of SiO_x-precipitates as well as bound states in the Coulombic wells of fixed positive charges which reside in the SiO_x-precipitates contribute to the ND traps.

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HYDROGEN PASSIVATION OF DOPANTS AND
DEFECTS IN III-V COMPOUNDS AND THEIR ALLOYS

Extended and point defects

J. H. Neethling and H. C. Snyman (University of Port Elizabeth): "TEM study of the extended crystal defects in hydrogen-implanted GaAs". Invited talk.

P. Hautojärvi (Helsinki University of Technology) and C. Corbel (C.E.N. Saclay): "Positron annihilation spectroscopy of defects in as-grown and irradiated GaAs". Invited talk.

J. M. Zavada (E.R.O. London), H. A. Jenkinson (US Army ARDEC Dover), R. G. Wilson (Hughes Malibu) and S. J. Pearton (A.T.&T. Bell Labs Murray Hill): "Dopant neutralization and defect decoration in hydrogen-bombarded gallium arsenide". Invited talk.

TEM STUDY OF THE EXTENDED CRYSTAL DEFECTS IN HYDROGEN IMPLANTED GaAs

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Proton bombardment of GaAs has become a standard technique in the fabrication of various optoelectronic devices. Because the point and extended defects introduced during bombardment critically influence the electrical properties of the device, the knowledge of the nature and distribution of the implantation damage is important.

Cross-sectional transmission electron microscopy was used to investigate the crystal structure at and near the end of the projected range of 300 keV protons implanted at 7° off the GaAs [001] to total doses of $5x10^{15}$, $1x10^{16}$ and $1x10^{17}$ H^+ cm^{-2}.

In the low dose (10^{15}-10^{16} H^+ cm^{-2}) samples, no visible defects were observed without annealing. After a 15 minute anneal at 500°C, defects in the form of black dots became visible. With further increase in temperature (500 to 700 °C), these black dots grew in size and were analysed to be hydrogen platelets (i.e. hydrogen filled vacancy loops) on the {110} planes of GaAs.[1,2]

In the $5x10^{15}$ H^+ cm^{-2} samples annealed at 800 °C and above or the 10^{16} H^+ cm^{-2} samples annealed at 55 °C and above, the damage precipitation was heterogeneous consisting not only of platelets but also containing damage rafts (i.e. three dimensional dislocation - void clusters).[3] The damage rafts were found to consist of planar arrays of voids on the {110} planes and were elongated along the <110> directions. It was proposed that damage rafts originate at microsplits on the {110} cleavage planes of GaAs following the cracking open of small hydrogen filled platelets when the internal gas pressure exceeds that which is necessary for crack propagation.[3]

The damage rafts were found to act as dislocation sources with the generation of glissile dislocations, of the type $(a/2) <110>$ on the $\{111\}$ slip planes intersecting the rafts on the $\{110\}$ planes, in a similar manner as usually demonstrated for a Frank-Read source. The glissile dislocations generated at the rafts were found to glide over distances of about $1\mu m$ during the 15 minutes of anneal at temperatures in the range of 500 to 800 °C.[3]

In the high dose samples (10^{17} H^+cm^{-2}) the radiation damage was detectable in the TEM without annealing. Upon annealing the diffuse damage structure changed quite markedly with increasing temperature and at 580 °C hydrogen platelets, voids, line diclocations and extrinsic Frank loops became visible.[4]

In conclusion it is suggested that upon implantation the hydrogen atoms diffuse interstitially until trapped at lattice vacancies created during implantation. Upon subsequent annealing, at temperatures of 200 °C and above, the hydrogen atoms become mobile and leave the vacancies. At 500 °C, the temperature where vacancy coalescence starts to take place, the platelets are formed by the cooperative coalescence of vacancies and hydrogen atoms.[2]

Models will be presented to explain the absorption of hydrogen atoms at platelets and to calculate gas pressures in platelets.

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Positron Annihilation Spectroscopy of Defects in As-Grown and Irradiated GaAs

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Positron lifetime spectroscopy give information on vacancy-type defects in the bulk. No positron trapping is observed in as-grown Si, whereas in III-V compounds positrons have revealed high concentrations ($>10^{16}$ cm^{-3}) of native vacancy defects. In LEC-grown GaAs positron trapping in monovacancy defects is seen in n-type, but not in p-type nor in semi-insulating crystals. The defects are removed by annealing above 700 K. They are identified as As vacancies. Two Fermi-level controlled transitions have been found in positron lifetime spectra at 0.032 eV and 0.10 eV below the conduction band. They have been attributed to (2-1-) and (-/0) ionisation levels of the As vacancy.

A beam of low-energy positrons can be used to profile vacancy-type defects in near-surface regions. This technique combined with ion beam methods (NRB and RBS) has been applied to characterize damage and hydrogen profiles in n-type Si(100) implanted with 10^{16} 35-100 keV H$^+$ ions/cm^2. The damage distributions do not correlate with the deposited energy distribution. A vacancy-type defected overlayer is seen close to the surface well above the range of H atoms. Similar experiments are going on in hydrogen-implanted semi-insulating GaAs(100) and preliminary results will be discussed in the workshop.

DOPANT NEUTRALIZATION AND DEFECT DECORATION IN
HYDROGEN-BOMBARDED GALLIUM ARSENIDE

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Recently, considerable interest has focused on the effects of hydrogen
(H) in GaAs since it has been established that H can passivate various
shallow and deep impurity dopants in the crystal. Experiments have been
performed to introduce H into device structures to improve electronic
performance and into crystal growth procedures to produce higher quality
GaAs epilayers. Implantation of H into n-type or p-type GaAs is a related
processing technique that has been useful for electrical device isolation,
surface passivation, and optical index definition. However, most implant-
ation studies have centered on damage defects induced by the implantation
and not on the additional effects due to the chemical activity of H in the
crystal.

In a prior study, we have examined the post-implantation behavior of H
in n+ GaAs(Si) using secondary ion mass spectrometry (SIMS) and infrared
reflectance measurements. It was shown that implanted H is redistributed
with post-implantation furnace annealing and produces optical effects
associated with carrier removal [1].

Here we first report on the properties of H implanted into p+ GaAs(Zn)
crystals and the subsequent behavior with post-implantation annealing.
Depth profiles for both H and Zn atoms, as a function of anneal temper-
ature, have been determined using SIMS. Infrared reflectance measurements
indicate little, if any, change neutralization associated with H migration
into the substrate. Results of these experiments with p+ GaAs(Zn) are
compared with data obtained for H in n+ GaAs(Si) and with related studies
involving plasma hydrogenation.

The second part of our presentation concerns the redistribution of
implanted H ions in GaAs multilayer structures due to post-implantation
annealing. Several different multilayer structures have been investigated
including GaAs-on-Si samples and GaAs/AlAs superlattices. In each experi-
ment, SIMS measurements show that post-implantation annealing causes the H
atoms to undergo a redistribution and to accumulate at interface regions
within the crystal.

For the GaAs-on-Si samples, a major accumulation of migrating hydrogen
has been measured at the GaAs/Si hetero-interface [2]. This accumulation
reaches concentrations in excess of 10^{20} H cm^{-3} and is stable even at a
temperature of 700°C. With materials having such a large lattice mismatch
(4%), it can be expected that the interface region would contain a high
density of defects and dangling bonds leading to trapping of H atoms.
However, the experiments with the GaAs/AlAs superlattices show that even a
homo-epitaxial interface can produce similar effects [3]. While the

effects [3]. While the numerous material interfaces in these multilayer structures affect the migration of the atoms, the GaAs buffer layer/GaAs substrate interface appears to be the most important. This interface impedes the migration of atoms into the substrate and retains them at concentrations of about 10^{18} H cm^{-3}, even after annealing at 500°C. In either experiment, the accumulation of H appears to be due to the bonding of H with dislocations and crystal imperfections created during the initial stages of epitaxy.

These findings are used to form a qualitative model for the behavior of H implanted into GaAs. Initially, the majority of H decorates crystal damage within the implanted region. During post-implantation annealing, H atoms are released from the damage centers, migrate to other regions of the crystal, and are trapped either by different damage centers or by impurity atoms. Charge neutralization is due to ion irradiation effects, as well as to trapping of H at impurity dopant locations. The redistribution of implanted H is a complicated process depending on many parameters including damage concentration, dopant level and dopant species. Further experiments are needed to clarify the relative importance of these parameters.

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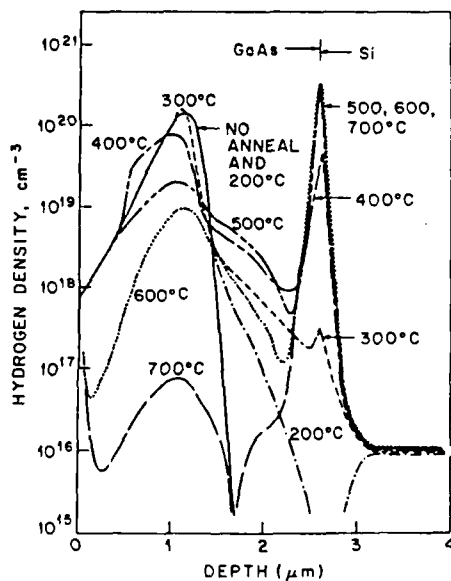
HYDROGEN PASSIVATION OF DOPANTS AND
DEFECTS IN III-V COMPOUNDS AND THEIR ALLOYS

Vibrational spectroscopy

R. C. Newman (University of Reading) and B. Pajot (Université Paris 7): "Localised modes of impurities anu their complexes with hydrogen in gallium arsenide". Invited talk.

B. Clerjaud, D. Côte, M. Krause, C. Porte (Université Pierre et Marie Curie Paris) and W. Ulrici (Zentralinstitut für Elektronenphysik Berlin): "Spectroscopic studies of H-related complexes in bulk III-V compounds". Invited talk;

B. Pajot (Université Paris 7): "Spectroscopic investigations of the neutralization by hydrogen of dopants in III-V compounds".

W. Ulrici (Zentralinstitut für Elektronenphysik Berlin), R. Stedman (University of Lund), B. Ulrici (Zentralinstitut für Elektronenphysik Berlin), B. Clerjaud and M. Krause (Université Pierre et Marie Curie Paris): "Hydrogen in LEC-grown GaP and possible relations to oxygen".

C. P. Herrero and M. Stutzmann (MPI-FKF Stuttgart): "Infrared and Raman studies of hydrogen passivation in silicon".

J. Tatarkiewicz and M. Stutzmann (MPI-FKF Stuttgart): "Hydrogen vibrations in semiconductors".

LOCALISED MODES OF IMPURITIES AND OF THEIR COMPLEXES
WITH HYDROGEN IN GALLIUM ARSENIDE

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The lattice locations of isolated substitutional dopant atoms with a low mass in GaAs can be determined by measurements of their infrared localized vibrational mode (LVM) absorption using high resolution Fourier transform spectroscopy. It is a good approximation to assume that second nearest neighbours are stationary so that the angular frequency of a mode may be written as $\omega^2 = k[M_{imp}^{-1} + (\chi M_{nn})^{-1}]$, where M_{imp} is the mass of the impurity, M_{nn} is the mass of the nearest neighbours and the parameter χ depends on the local bending and stretching force constants[1]. There is a large impurity isotope shift, (e.g. between say ^{28}Si and ^{29}Si and ^1H and ^2D but there are also measurable frequency changes when nearest neighbour isotopes are changed. Atoms occupying Ga lattice sites (As neighbours : ^{75}As, 100% abundant) produce sharp lines, whereas broadened lines with structure occur for atoms occupying As lattice sites (Ga neighbours: ^{69}Ga, 60% abundant and ^{71}Ga 40% abundant).

When impurity hydrogen pairs form the symmetry is reduced from T_d (to say C_{3v}) so that the impurity will have a longitudinal mode $\omega_{\parallel}$ along the pair axis and a doubly degenerate transverse mode $\omega_{\perp}$. The modified local bonding will change the local force constants : a reduction in the frequency of an LVM indicates a corresponding reduction in the force constants. It should be remembered that stretching force constants are about ten times greater, and are therefore more important, than the bending constants[1]. If the frequency is lowered too much, the mode will become incorporated into the lattice continuum and will not be detected. The impurity modes will also be lowered in frequency when hydrogen is replaced by deuterium. In general the presence of a static charge on an impurity in a covalent host should not change the strength of the IR integrated absorption appreciably compared with that produced by a neutral impurity[2]. Thus reasonable conservation of integrated absorption is expected when hydrogen-impurity pairs are formed, and the strength of $\omega_{\perp}$ should be about twice that of $\omega_{\parallel}$.

For the paired hydrogen, longitudinal and transverse modes are also expected. The ratio r of a hydrogen frequency ω_H to that of the corresponding deuterium mode ω_D gives information about the mass of the atom to which the hydrogen is bonded. Although most of the kinetic energy will be in the H-mode, the impurity can also move and transfer energy to other neighbours. It follows that the value of r will be smaller than the value calculated for a diatomic molecule. Finally, the application of a uni-axial stress along certain directions will remove the double degeneracy of both the impurity and the hydrogen transverse modes.

These topics are illustrated for the systems $Be_{Ga}-H$[3] and $Si_{Ga}-H$[4] in GaAs.

MBE GaAs doped with Be to a concentration of $3.7 \times 10^{18} \text{cm}^{-3}$ was fully compensated by 2MeV electron irradiation. The $^9\text{Be}_{Ga}$ impurities gave a symmetrical LVM line at 482.4cm^{-1} with a half width Δ of 0.5cm^{-1} as expected for an impurity on a Ga lattice site. The integrated absorption was characterized by an apparent charge of $\eta = 1.1 \pm 0.1 e$, in agreement with previous measurements on LPE material. However, as-grown material containing Be_{Ga}^9 appeared to show a much stronger LVM line with $\eta = 1.7 e$. The line was shifted to a lower energy by 0.3cm^{-1} and most unexpectedly the value of Δ increased to 1.0cm^{-1}. These differences have now been resolved by recognizing that the line shape is an asymmetric Fano profile. Following hydrogen diffusion from a plasma the Be LVM is reduced in strength and a new line appears at 555.7cm^{-1} for Be-H and at 553.6cm^{-1} for Be-D. Only one line is found, implying that either $\omega_\perp$ or $\omega_{//}$ has been lowered into the continuum. Taking account of the Fano effect the new line has about 2/3 the absorption lost from the isolated $\text{Be}(T_d)$. Only one high frequency LVM line from hydrogen is found for Be-H at 2037.1cm^{-1} and Be-D at 1471.2cm^{-1}, giving $r = 1.38$ which implies that the hydrogen is bonded to a host lattice atom and not a ^9Be impurity ($r = 1.386$ for Zn-H). This is undoubtedly a stretching mode and so the transverse mode must be soft, i.e. at a frequency less than about 300cm^{-1}. Recent calculations[5] support these interpretations and will be discussed in a separate paper. It is also concluded that the 555.7cm^{-1} mode should be identified with $\omega_\perp$ rather than $\omega_{//}$. Thus the Be is tri-co-ordinated, while the H atom bonds to an adjacent As neighbour. It appears that re-orientation of the Be-H pair may occur as Δ for the Be-H (2037cm^{-1}) mode is greater than that for Be-D.

For Si_{Ga}-H, there is again only one mode from the paired Si at 409.95cm^{-1} (and 409.45cm^{-1} for Si-D). As there is evidence for direct bonding of the hydrogen to the Si_{Ga} atom, it was thought at first that the local force constants might increase so that both $\omega_{//}$ and $\omega_\perp$ would be greater than $\omega = 384 \text{cm}^{-1}$ for isolated $\text{Si}_{Ga}(T_d)$. Recent theory indicates however that one of the Si_{Ga} bonds to an As neighbour breaks, in which case $\omega_{//}$ would occur at a low frequency and would not be observed. Both $\omega_{//}$ and $\omega_\perp$ are observed for the paired hydrogen, and silicon isotope effects are evident on $\omega_{//}$. Recently it has been shown that the line ascribed to $\omega_\perp$ is indeed doubly degenerate indicating that the defect has C_{3v} symmetry.

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SPECTROSCOPIC STUDIES OF H-RELATED COMPLEXES
IN BULK III-V COMPOUNDS

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All the GaAs, InP and GaP materials grown by the liquid-encapsuled Czochralski technique show series of infrared absorption lines in the 2000 cm^{-1} range for GaAs and in the 2200-2300 cm^{-1} range for InP and GaP. These lines are due to local modes of vibration of hydrogen related complexes, involving As-H or P-H stretching modes of vibration [1]. In indium phosphide, some of the complexes involve dopant impurities |2| whereas some others involve lattice defects [3]. In gallium arsenide, no correlation could be found with any dopant and probably most of the observed lines are related with complexes involving hydrogen and lattice defects [4]. The acceptor impurity related complexes are believed [1] to be of the bond center type first proposed by Pankove et al. [5] for the boron-hydrogen complex in silicon. In order to learn more about the complexes involving lattice defects, we have performed infrared measurements under uniaxial stress. The results of these experiments together with the other properties of the center suggest that the 2001 cm^{-1} line observed in GaAs is due to the binding of an hydrogen atom by an As dangling bond in a gallium vacancy [6]. The same type of defect involving an indium vacancy in indium phosphide has a local mode of vibration at 2202.4 cm^{-1} [7]. The microscopic structure of the other complexes involving lattice defects is not fully understood yet.

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Spectroscopic investigations of the neutralization by hydrogen of dopants in III-V semiconductors.

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At GPS, we have primarily studied the infra-red absorption of the hydrogen-related modes in III-V semiconductors plasma-treated or implanted with hydrogen. The frequencies where absorption is observed, eventual natural isotope effects and the ratio of the frequencies when ^{1}H is replaced by ^{2}H (the r-factor) provide information enabling to identify the atom(s) to which hydrogen is bonded. Once done, it is generally possible to establish the structure of the complex involving hydrogen and to relate it to the neutralization of the dopant atom. The structure can be also deduced or confirmed by measurement of the absorption of polarized radiation by the sample under uniaxial stress.

We summarize here the main results obtained using low-temperature infra-red absorption with Fourier transform spectroscopy.

1) *Silicon donors in GaAs*

a) Neutralization by hydrogen of n-type GaAs:Si

High-resolution measurements have shown that H was bonded to Si on the Ga sublattice. From these results was proposed the location of the hydrogen atom on the anti-bonding site and the neutralization of the electrical activity by localization of the donor electron on the Si-H bond. Uniaxial stress measurements proved to be in agreement with the trigonal symmetry expected from this centre in the GaAs lattice.

b) Proton implantation in n-type GaAs:Si

The Si-H bending mode already observed in H-plasma neutralized material is also found in H⁺ implanted material at ambient. The co-existence of this mode with modes of H-related defects

show that in H^- implanted GaAs:Si, a small part of the carrier removal already arises from direct neutralization of dopant by hydrogen. This fraction increases under annealing up to a point where carrier removal comes only from dopant neutralization.

c) Silicon donors in $Ga_{1-x}Al_xAs$

Substitution of Al to Ga atoms usually lowers the symmetry of the close environment of the trigonal centre, hence removing the two-fold degeneracy of the Si-H bending mode. This and the different splittings from the different arrangements of the Al atoms produce many lines near the position of the single line in pure GaAs. Analysis of the structure informs on the actual probability to find a given configuration as compared to the one derived from the Al concentration alone.

2)   Acceptors in Gallium Arsenide and Indium Phosphide

a) The formation of hydrogen-dopant complexes in p-type III-V complexes is a two-step process resulting from i) compensation of acceptors by hydrogen and ii) complexing of hydrogen with acceptor dopant driven by coulombic interaction. Spectroscopy shows that this pairing is achieved by covalent bonding with hydrogen in a bond-centred configuration.

b) Silicon in p-type GaAs

The lines observed in p-type GaAs:Si neutralized with hydrogen are ascribed to the stretching mode of hydrogen bonded to Si in the As sublattice. The r-factor indicates however some coupling between hydrogen and the nearest neighbour Ga atom. No interaction is found between hydrogen and the residual Si donors, showing that in GaAs, the formation of complexes with dopant atoms is possible only when these atoms are electrically active.

c) Acceptors in the cation sublattice

The observations for Zn in GaAs an in InP as well as for Be in GaAs are explained by the binding of hydrogen to the group V atom nearest neighbour of the acceptor. The interaction between hydrogen and the acceptor seems so weak that it can be thought of as tri-coordinated.

d) Temperature effects and line width

No temperature-dependent structure is found for hydrogen lines with all the acceptors when temperature is raised. This could be interpreted as a consequence of an "on-line" geometry of the H bond along the <111> direction. The dependence of the width and position of the lines on temperature reflects the coupling between the complex and the lattice and a part of it can be explained by steric effects. An interpretation of the results is on the way.

Hydrogen in LEC-grown GaP and possible relations to oxygen

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By FT-IR-spectroscopy we studied LEC-grown GaP doped in the
melt with Sc, Ti, V, Cr, Co, or Ni. In GaP:Ti 3 sharp lines have
been found around 2200 cm^{-1} (Fig. 1) which are local vibrational
mode (LVM) lines as proved by their temperature dependence. These
lines are interpreted as due to P-H centres [1] in analogy to the
As-H centres investigated in LEC-grown GaAs [2, 3]. However,
these H-related lines could be detected only in GaP:Ti.

In GaP doped with Sc, V, Cr, Co, or Ni on the other hand
several LVM absorption lines in the region 1000 cm^{-1} to 1400 cm^{-1}
were measured (Fig. 2) not detectable in GaP:Ti samples. These
lines have been assigned to centres containing oxygen on inter-
stitial sites (O_i) [1]. There is no correlation of the lines with
the kind of transition metal doping. The large number of lines is
possibly due to different centres of O_i bonded to P or Ga and
complexed with typical residual impurities (C_P, B_{Ga}, Si_{Ga}) or P_{Ga}
anti-site defects (all of them present in the samples $\approx 10^{16}$
cm^{-3}). The absence of all of these lines in GaP:Ti supports their
assignment to oxygen-related centres as Ti is known to be a very
effective getter material for oxygen. A first quantitative argu-
ment in favour of O_i is the detection of a weak line at 1199.2
cm^{-1} accompanying the most intense line at 1275.3 cm^{-1}. The ratio
of their frequencies $r = 1.0635$ is very close to the expected $r =$
1.0607 for the corresponding ^{18}O line, and their ratio of inten-
sities (0.0026) is in good agreement with the natural abundance
of ^{18}O (0.0020).

The inset of Fig. 1 shows 2 LVM lines at 2285.3 cm^{-1} and 2054.0 cm^{-1} occurring always together with the oxygen-lines and their ratio of intensity is $\alpha(2085)/\alpha(2054) = 10 \pm 1$ for all samples. Also the ratio of the intensities of these high-frequency lines to those of the most dominant oxygen lines has been found to be quite constant ($\alpha(2085)/\alpha(1007) = 0.3 \pm 0.1$, $\alpha(2085)/\alpha(1275) = 0.4 \pm 0.2$). The high frequency of these lines together with its correlation to the oxygen centres suggests their interpretation as due to O-H centres, where the 2885.3 cm^{-1} line would be the stretching mode of the O-H molecule. The reduction of its frequency compared with O-H centres in alkali halides can be caused by covalent bonds. The inverse temperature shift of the line position of the 2885.3 cm^{-1} line (dE/dT > 0) in contrast to that of LVM lines (dE/dT < 0) also indicates a specific kind of vibrating centre. The proposed assignments are speculative yet and have to be checked by experiments with ^{18}O- and D-doped GaP.

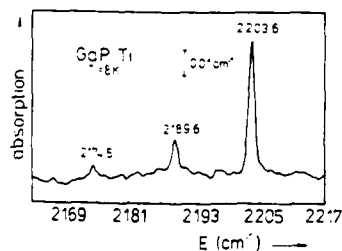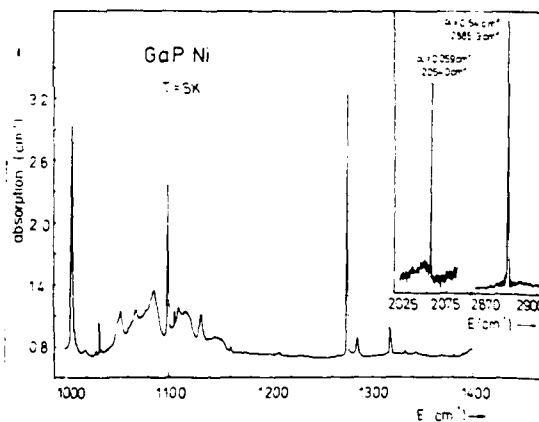
Fig. 1

Fig. 2

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Hydrogen Vibrations in Semiconductors

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The possibility of passivating many points defects in a large variety of different semiconductors by introduction of atomic hydrogen has spurred new interest in this simple impurity and its bonding properties. However, no general approach to hydrogen bonding in crystals has been developed so far. In our recent paper [1] we have shown that a simple model of a harmonic oscillator embedded in a dielectric medium enables us to predict hydrogen vibrational frequencies in semiconductors as well as in ionic crystals. Here we present the next logical step in the extension of our model: instead of using molecular hydrogen vibrational frequencies ω_m to predict corresponding hydrogen frequencies in crystals ω_c, we estimate (cf. e.g. [2]) the force constant k of the harmonic potential $V = kx^2$ from the dissociation energy D [3] and the bond length a [3] of the corresponding free diatomic molecule: $k \sim D/a^2$. In the previous paper [1] we used a correction due to the depolarizing field produced by the vibrating dipole in a cavity inside the solid. However, in the case of semiconductors this correction is smaller than the error of the estimate. Hence in the present model we plot (see also Table I, where $\Delta\omega$ indicates hydrogen band width)

Table I

| Crystal	Bond	D kcal/mol	a Å	$\sqrt{D}/a$ √eV/Å	ω_m cm⁻¹	ω_c cm⁻¹	$\Delta\omega$ cm⁻¹	Ref.
Si	SiH	71.4	1.520	1.158	2042	1996	200	[4]
SiC	SiH	71.4	1.520	1.158	2042	2090	150	[5]
	CH	80.0	1.120	1.664	2861	2920	25	
Ge	GeH	66.8	1.588	1.072	1834	1886	125	[6]
GaAs	GaH	68.0	1.663	1.033	1604	1711	100	[6]
	AsH	65.0	1.534	1.094	2130	1998	100	
ZnSe	ZnH	19.5	1.595	0.577	1608	1315	150	[7]
	SeH	73.0	1.470	1.210	2400	2150	50	
ZnTe	ZnH	19.5	1.595	0.577	1608	1215	100	[8]
	TeH	48.2	1.520	0.951	2250	1655	25	
ZnS	ZnH	19.5	1.595	0.577	1608	1680	100	[9]
	SH	81.4	1.346	1.396	2200	-	-	
CdTe	CdH	16.5	1.780	0.475	1337	1205	100	[10]
	TeH	48.2	1.520	0.951	2250	1730	25	
CdS	CdH	16.5	1.780	0.475	1337	1285	150	[11]
	SH	81.4	1.346	1.396	2200	2450	100	
GaP	GaH	68.0	1.663	1.033	1604	1849	25	[12]
	PH	82.0	1.422	1.326	2365	2204	25	[13]
InP	InH	59.0	1.838	0.870	1476	-	-	
	PH	82.0	1.422	1.326	2365	2204	25	[14]
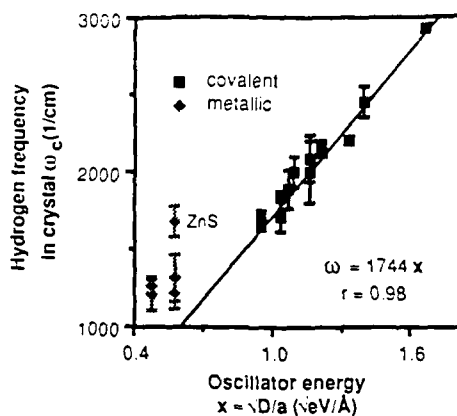
Fig. 1
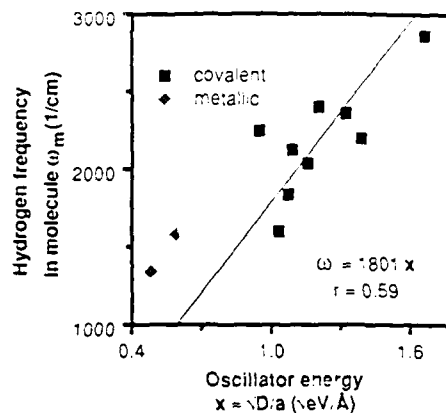
Fig. 2

the observed hydrogen vibrational frequencies in crystals ω_c as a function of the square root of k. As shown in Fig. 1 this procedure gives an excellent fit, except for the group IIa metals (Zn and Cd). On the other hand, if we plot hydrogen molecular vibrational frequencies ω_m vs. $\sqrt{k}$ (Fig. 2) we get a much worse fit. We also notice that the molecular frequencies in zinc and cadmium hydrides are much higher than they should be if calculated from the simple model of the harmonic oscillator. We explain this fact by the metallic character of these bonds, as opposed to the covalent character for other bonds considered here. Finally, let us note that experimental data for ZnS has been obtained for a crystal grown in hydrogen atmosphere [9], whereas in all other materials hydrogen was introduced by implantation.

We conclude that our simple model applies to all covalent semiconductors, permitting easy predictions of hydrogen vibrational frequencies in these crystals. This can be of some help for future studies of hydrogen in various semiconductors (see e.g. [15]), where the vibration energies are still unknown.

Acknowledgement

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INFRARED AND RAMAN STUDIES OF HYDROGEN PASSIVATION IN SILICON

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We have studied the hydrogen passivation of B-doped Si by means of infrared reflectance and Raman scattering. The samples used were bulk doped with boron concentration between 1×10^{19} and 1.2×10^{20} cm^{-3}.

The IR reflectance of the doped and passivated samples was measured in the region of the free-carrier plasma edge. After passivation, a shift of the plasma edge to lower wavenumbers is observed, corresponding to a decrease of the free hole concentration. The interference pattern observed in the IR spectra of the hydrogenated samples allows us to deduce the thickness of the passivated region. Moreover, the decay of this interference pattern is directly related to the steepness of the H-profile in the passivated samples. With these three variables (hole concentration in the surface, depth of the passivated region and steepness of the H-profile) we can fit the experimental reflectance spectra for different B-concentrations and times of exposure to hydrogen. A typical experimental spectrum together with a calculated fitting is presented in Fig. 1. The calculated profiles agree well with those obtained by means of SIMS[1]. So, IR reflectance provides a direct and nondestructive way to obtain depth profiles in passivated samples. The correlation found between B-concentration and H-depth indicates that the H-diffusion is basically controlled by an impurity trapping mechanism. For a boron concentration of 1×10^{19} cm^{-3}, the diffusion coefficient obtained at 150°C is about 6×10^{-13} cm^2 s^{-1}.

Direct information about the free hole concentration can also be obtained by looking at the Raman active silicon zone-center optical phonon, which in doped-Si appears shifted and asymmetrically broadened in comparison to the undoped semiconductor, showing the so-called Fano profile. The narrowing of this profile after hydrogenation can be used as a direct test to obtain insight into the remaining hole concentration[2].

From a more microscopic point of view, the localized vibrations of boron and hydrogen in the Si-lattice are direct probes for the bonding structure of these atoms. Moreover, the H-mode observed at 1905 cm^{-1} can be used to obtain information about the symmetry of the B–H complex in the lattice. For this purpose, we have analyzed the Raman scattering due to H-vibrations under uniaxial stress along different lattice
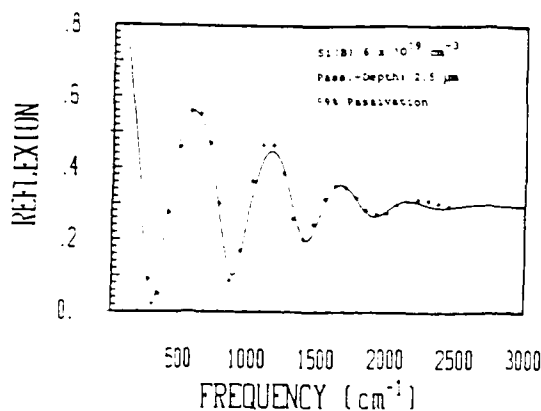
Fig. 1. Infrared reflectance spectrum of a passivated B-doped Si sample. Points correspond to the experimental data and the continuous line is calculated using the indicated parameters.
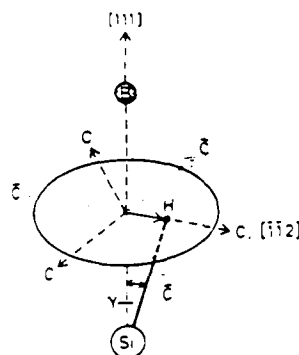
Fig. 2. Off-bond-center hydrogen displacements along $[\bar{1}\bar{1}2]$ (towards C-points) and along $[11\bar{2}]$ (towards $\bar{C}$-points).

directions. From our results, and mainly from the line splitting observed for stress along a [100] direction, we find at 100K a non-trigonal symmetry for the B–H complexes. This corresponds to off-bond-centered interstitial sites for hydrogen, which can be modified under stress. The stress dependence observed for the line intensities indicates a stress-induced hydrogen redistribution among non-equivalent positions around a B-impurity[3]. In Fig. 2 we present a scheme corresponding to the H-displacements along $[\bar{1}\bar{1}2]$ directions deduced from the analysis of the Raman results. Hydrogen can move between different energy minima with barriers of less than 300 meV, in agreement with theoretical calculations[4].

The discrepancy between our results and the trigonal symmetry found by Bergman *et al.*[5] at 4K may be due to the strong T-dependence of the H-mode, as well as to different internal strain in the samples (ion implanted vs. bulk doped).

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HYDROGEN PASSIVATION OF DOPANTS AND
DEFECTS IN III-V COMPOUNDS AND THEIR ALLOYS

Advanced nuclear methods

T. L Estle (Rice University) and R. F. Kiefl (TRIUMF Vancouver): "Isolated hydrogen and anomalous muonium in semiconductors". Invited talk.

Th. Wichert (Universität Konstanz): "Detection of hydrogen in semiconductors by nuclear methods". Invited talk.

A. D. Marwick (I.B.M. Yorktown): "Ion beam studies of hydrogen in semiconductors".

Isolated Hydrogen and Anomalous Muonium in Semiconductors

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E. J. Ansaldo, and others.

Over the last five years much has been learned about muonium impurities in semiconductors and it now appears very likely that most of this information will be directly applicable to the understanding of hydrogen impurities. Muonium may be formed when positive muons (μ^+) are implanted into nonmetallic samples. They may be studied by techniques closely related to magnetic resonance and collectively referred to as muon spin rotation or μSR. Muonium is a neutral atom formed by an electron bound to the μ^+ and may be regarded as a very light isotope of hydrogen ($m_\mu \cong m_p/9$). In semiconductors muonium is quite different from muonium in free space. Two distinct forms of muonium are seen[1], one with an isotropic hyperfine interaction ranging from 83% of the vacuum value (in diamond) to 27% (in CuCl). This normal muonium or Mu has a hyperfine interaction which is about 50% of the vacuum value in Si and Ge but about 65% in GaAs and GaP. One can visualize this as a neutral muonium impurity covalently-bonded to atoms in the crystal so that about half (for Si and Ge) the spin density is on the muonium and about half is on the host atoms. The experimental and theoretical evidence supports the view that for normal muonium the μ^+ is centered at the tetrahedral interstitial site. In addition, a highly-anisotropic form of muonium is observed. It is called anomalous muonium or Mu* and has a trigonally-symmetric hyperfine interaction whose angular average is only a few percent of the vacuum value. Recent studies by muon level-crossing spectroscopy, augmented by resolved nuclear hyperfine structure in the muon precessional frequencies, have shown that for anomalous muonium in silicon the electron spin density and the muon are centered on a covalent bond[2]. Similar observations have been made on GaAs[3,4] and GaP[4] and presumably in all cases of Mu* the muon is near the center of a covalent bond.

The recent report of an electron paramagnetic resonance (EPR) spectrum (AA-9) in hydrogen-implanted silicon[5] was the first example of EPR for isolated hydrogen in a semiconductor known to these authors. Comparison of the scaled hydrogen and

muon hyperfine parameters and those of the nearest ^{29}Si for the AA-9 center and Mu* in silicon indicate that the hyperfine parameters are the same to within about the uncertainty of the less accurate EPR results (the hydrogen values must be multiplied by the ratio of the muon to the proton magnetic dipole moments, i.e. scaled). We may therefore conclude that this muonium center has a corresponding hydrogen center which exists with nearly the same structure, and this is quite likely true for most other muonium centers as well. The principal effect of the large mass difference should occur in the dynamics of the two types of systems. In that regard, metastable forms of muonium have been observed in many materials. This includes Si, Ge, diamond, SiC, GaAs, GaP, CuCl, and CuBr. For some of these systems (Si, diamond, CuCl, CuBr) there is evidence of a thermal conversion of one form to another.

At present one may conclude with considerable confidence, based on the measurements described and upon theoretical studies which support these conclusions, that the stable structure of neutral, isolated, interstitial hydrogen in silicon is one in which the proton is at the bond center and the spin density is primarily on the two nearest silicons. A similar model can also be inferred for GaAs and GaP although it has not been demonstrated that this is the stable structure.

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Detection of Hydrogen in Semiconductors by Nuclear Methods

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The impact of nuclear methods, like the ion channeling or blocking technique, perturbed $\gamma\gamma$ angular correlation (PAC) and Mössbauer spectroscopy (MS), on the detection of hydrogen interacting with dopant atoms in semiconductors is discussed. In particular, the recent results for H(D)-acceptor interactions in Si obtained by ion channeling and PAC are be presented and their interpretations are compared. In addition, the possibility of transferring these experiments to studies of dopant atom-hydrogen interactions in GaAs are outlined.

There exist several ion channeling experiments on p-type Si doped with B and D atoms of equal concentrations. It is concluded that the majority of D atoms is situated at near-bond centre sites at 30 K and at 295 K; however, the possibility of an antibonding site of D at 295 K has to be considered, as well. The interpretation of the ion channeling results is affected by two experimental facts: The high D (and B) concentration (10^{19} cm^{-3}), required for this type of experiment, and the introduction of the D atoms from a plasma, which might create additional lattice defects being capable of interacting with D atoms, as well. Recent results on the lattice location of radioactive interstitial impurities, like Li atoms in GaAs, using the blocking technique, will be presented because this type of experiment is sensitive to much lower impurity concentrations than the ion channeling technique.

The formation of acceptor-H complexes, involving the radioactive probe atom ^{111}In, was identified with help of the PAC technique. This type of experiments yields information on the chemical and structural identity of the formed complexes. Using the H specific electric field gradient, the formation and dissolution of the In-H complexes was pursued under a variety of different conditions, such as sample temperature, dopant atom concentration and position of the Fermi level. By additionally doping the samples with a second type of acceptor atom the stability of other acceptor-H complexes, here of B-H complexes, was determined. In order to complement the investigations on H, experiments on Li atoms and an interstitial X defect, produced during wafer polishing, were performed. The X defect bears close resemblance to the H defect in some respects, but is different from H because of its mobility and stability at the acceptor atoms. For a transfer of this type of experiments to GaAs radioactive atoms are needed which act as acceptor or donor atoms and at the same time are suited for either PAC or MS spectroscopy. In case of PAC, Cd is a possible candidate, in case of MS, Sn, Sb, and Te can serve as probe atoms. Thus, experiments on H in GaAs, being similarly detailed as in Si, should become feasible in the near future.

Ion Beam Studies of Hydrogen in Semiconductors

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Ion beam analysis techniques, including nuclear reaction analysis, channeling, and Rutherford backscattering are being applied to several aspects of the behavior of hydrogen in crystalline semiconductors and simple device structures.

Nuclear reaction profiling of hydrogen in MOS capacitor structures with Al and Au gates was used to show that most of the hydrogen in such structures is localized in a layer at the gate-oxide interface [1]. This hydrogen, whose amount in the samples studied varied between 10^{15} and 3×10^{15} atoms/cm^2, is probably the source of the hydrogenic species believed to diffuse towards the oxide/Si interface during hot electron injection or after exposure to ionizing radiation. The results suggest that the source of the H in the samples was air exposure of the oxide before metallization.

The lattice location of hydrogen (^2H) and boron atoms in boron-hydrogen complexes in silicon was determined using ion channeling combined with nuclear reaction analysis. [2, 3]. The boron atom was found to be slightly displaced off a lattice site, by $0.28\pm0.03\text{Å}$, while the majority of the hydrogen atoms occupied bond-center positions. THe samples were characterized by SIMS and Monte-Carlo modelling was used in the analysis of the channeling data. The results are in qualitative agreement with theoretical models of the structure of the B-H center.

Present work includes investigation of damage induced by high hydrogen concentrations in silicon, channeling studies of other solute-hydrogen complexes, and annealing studies on solute-hydrogen complexes.

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HYDROGEN PASSIVATION OF DOPANTS AND DEFECTS IN III-V COMPOUNDS AND THEIR ALLOYS

Theory

P. Briddon, R. Jones and G. M. S. Lister (University of Exeter) "The Structure and properties of H complexes in GaAs, a-Si and Diamond". Invited talk.

C. G. Van de Walle (Philips Briarcliff Manor): "Theory of hydrogen diffusion and reactions in crystalline semiconductors". Invited talk.

G. G. DeLeo (Lehigh University): "Theory of interstitial hydrogen and hydrogen-containing aggregates in silicon: Recent semiempirical caculations". Invited talk.

J. M. Baranowski (University of Warsaw): "Activity of atomic hydrogen in a-Si and c-Si".

The Structure and Properties of H Complexes in GaAs.a-Si and Diamond.

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We have calculated /5,6,7/ the structure and properties of H in clusters of atoms simulating the solid state. These have contained 30-90 atoms and have surfaces saturated with H. We use a self-consistent local density functional method with s- and p- Gaussian orbitals as a basis for the wave-functions and s- Gaussian orbitals as a basis for a fit to the charge density /1,2,3,4/ . Bond centred orbitals are used in addition to atom centred ones.

The cluster and bases are sufficiently large that bond lengths and angles are accurately found to within a few per-cent. Dynamical properties are given to within 10%. The cluster size is , however, inadaquate to give the theoretical band gap, but we feel the method can distinguish deep from shallow levels.

We have found the GaAs,Si and diamond bond lengths to be within 2%,1.5%, 1% of experiment respectively . Calculating the energies of distorted central atoms of the cluster allowed bond stretching and bending force constants to be found which , in the case of Si and C, yield bulk phonon dispersion curves within 10% at the zone-edges. For GaAs , a Coulomb potential must be added to give phonon frequencies within 20% at the zone edges.

1.   H in GaAs, GaAs:Be, GaAs:P /7/

56 or 57 atom clusters revealed there is a marginal (.2eV) tendency for neutral H to lie at a T-interstitial position over a BC-(bond centred) site. Furthur calculations on larger clusters are necessary to confirm the stability of the T-site. BC H has a singly occupied level high up in the gap; T-sited H has a level in the middle of the gap. Thus in p-GaAs , BC- sited H is likely to be preferred over T-sited H and vice-versa in n-GaAs.

Be/Ga is an off-centred defect which is displaced along [-1,-1,-1] and bonded to 3 As atoms. The As atom along [1,1,1] is also 3-fold coordinated and is the centre for the acceptor wave-function . A H atom prefers to sit at a BC site between the As and Be where it's wave function strongly overlaps that of the acceptor.
This structure and the LVM of H (2083 cm^{-1}) are in good agreement with experimental values (2037 cm^{-1}).

Conversely H in Si/Ga prefers to lie along [-1,-1,-1] where the Si is 4-fold coordinated. The Si-As bond along [1,1,1] is broken and the low lying filled state has appreciable overlap on this As atom and the H. The calculated H stretch mode frequency for an 87 atom cluster is 1805 cm-1 . The observed one is 1717cm-1 .

2.   H in a-Si /5/

A 34 atom cluster of Si and H atoms containing a central Si-H bond adjacent to a strained Si-Si bond simulates a-Si:H. The energy of this cluster was evaluated as a function of the strain in the Si-Si bond. At around 40% strain , the Si-H bond spontaneously breaks and the H atom forms a bond centred H defect in the middle of the strained Si-Si bond leaving a dangling bond behind.To move the H atom furthur away from the bond - centred site adjacent to the Si dangling bond costs ~1eV. This calculation supports a model of the Staebler-Wronski effect introduced by Stutzmann, Jackson and Tsai. Light of energy 1.2-1.5e V creates e-h pairs at strained bonds which either promote Si-H dissociation (the first step above) or cause a furthur Si-Si weakening allowing spontaneous Si-H dissociation .

3.   H in Diamond. /6/

A 57 atom cluster showed BC -sited H is 1.9eV more stable than T-sited H. This is consistent with muon spin rotation experiments. The BC H has a level close to E_c and thus there is a strong tendency for it to pair with acceptors or other defects. The wave function is built up of antibonding p-orbitals on adjacent C atoms and has lobes which point along [-1-1-1] and consequently there is strong overlap with H placed at an anti-bonding site. This structure of H2 is more stable by 3.32 eV over a H_2 molecule placed near a T site. Accordingly H2 should should have a deep trapped state in diamond.

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Theory of hydrogen diffusion and reactions
in crystalline semiconductors

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State-of-the-art theoretical techniques can provide a first-principles description of the behavior of hydrogen in crystalline semiconductors. Using density-functional theory and *ab initio* pseudopotentials, a comprehensive picture can be obtained of stable configurations, migration paths, charge states, etc., for H in pure and in doped semiconductors. Hydrogen interacts strongly with the crystalline network, and relaxation of the lattice around the impurity must be included to obtain the correct minimum-energy positions. Total-energy surfaces, in which the position of the H atom in the crystal is the coordinate, provide *immediate insight into the relevant* properties. Silicon, as the prototypal semiconductor, has been the first material for which we have performed the calculations[1]; recent work on H in Ge[2] indicates similar behavior.

The study of H as an impurity in the semiconductor provides information about its charge state, and allows us to predict the reaction mechanisms through which it will interact with other impurities. For instance, H in p-type Si is most stable in the positive charge state; its electron causes compensation of free holes. Such an H^+ impurity diffuses very fast through the crystal, and will readily be attracted by negatively charged acceptors. Formation of neutral hydrogen-acceptor pairs is a result of this process. Our calculations of boron-hydrogen complexes in Si show that the global energy minimum occurs for H at the center of a Si-B bond. H can move on a spherical shell around B with an energy barrier of only 0.2 eV. In n-type Si, we predict H to be negatively charged. The deep donor and acceptor levels associated with the amphoteric H impurity are close in energy; the possibility that H in Si is a negative-U impurity can not be excluded.

In Si, isolated hydrogen atoms in the positive and neutral charge state prefer the bond-center site as the stable location; in the negative charge state, the tetrahedral interstitial site is favored. In the absence of other defects, H_2 molecules are the most stable state for H in the Si crystal. The binding energy (compared to two isolated neutral H atoms inside the crystal) is 2 eV per molecule. If one of the H atoms that forms the molecule is positively charged (as suggested by Johnson and Herring[3]) the binding energy becomes smaller, and is Fermi-level dependent.

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Theory of Interstitial Hydrogen and Hydrogen-Containing
Aggregates in Silicon: Recent Semiempirical Calculations*

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The results of recent semiempirical computations on
hydrogen-related defects in silicon are summarized. Total
energies and single-particle electronic structures are produced
by the MNDO (modified neglect of diatomic overlap) method using a
finite-cluster framework. Equilibrium geometries, migration and
reorientation barriers, and vibrational frequencies are inferred
from the atom-position dependence of the total energies.
Specifically, interstitial hydrogen, hydrogen-acceptor (B, Al)
pairs, and a hydrogen-donor (P) pair are treated.

The impurities and environment are simulated in these
treatments by finite fragments of the solid, or "clusters." The
primary cluster used in these studies is XSi_8H_{18}; this is bond
centered. Also, we use the clusters $XSi_{10}H_{16}$ and XSi_4H_{12} to
simulate interstitial and substitutional environments,
respectively. The hydrogens serve to terminate the cluster.

In its simplest application, the host atoms are kept at
their rigid-lattice sites and the total energy is monitored as a
function of the impurity positions. A somewhat more elaborate
procedure involves the simultaneous displacments of the impurity
atom(s) and the neighboring silicon(s). When the outer silicons
are relaxed, they are connected to springs with parametrized
spring constants for parallel (to bond) and perpendicular (to
bond) displacements; we refer to this as the hybrid approach.
The H-terminators follow the outer silicons with the
corresponding bond angles and lengths preserved (taken here to be
109.47^b and 1.48 Å, respectively). We note that allowing
silicons to fully relax for each hydrogen position may not be
appropriate when considering the dynamics of a light element such
as hydrogen.

The most decisive statement which can be made on the basis
of our computational results for isolated interstitial hydrogen
is that a bond-centered (BC) configuration is the stable geometry
for the neutral and positive charge states.[1] This supports
other computational results [2] and recent μSR [3] and EPR
studies of anomalous muonium and hydrogen in silicon,
respectively. We find neutral hydrogen to be asymmetrically
located along the bond, with a barrier for reorientation of about
0.2 eV. This barrier is sufficiently small, however, that
motional averaging would cloud an inequivalence of the
neighboring two silicons. Such an asymmetric configuration might
be distinguished from the corresponding symmetric one in an
infrared experiment by the anharmonic H/D isotope shift of 1.7
which we predict.

Since the neighboring silicons relax by about 0.4 Å each to accommodate the hydrogen, migration between neighboring BC sites would require substantial silicon participation. Therefore, we compute a migration barrier by determining the energy required to displace the neighboring silicons so that the hydrogen may spontaneously move between adjacent BC sites. We find the migration barrier to be $\leq$ 1.0 eV.

There also appears to be an athermal motion which is associated with the migration of normal muonium. Here it is most appropriate to determine the migration barrier in the absence of silicon displacement; the hydrogen would tunnel before the silicons could fully respond.[4] We find a hydrogen-motion barrier for migration between adjacent M-sites of $\sim$0.1 - 0.2 eV. Another way of expressing such athermal motion may involve a Bloch representation of the H or muonium atoms; this is currently being explored.

In some recent treatments of the hydrogen-acceptor pairs, we have taken up the problem of the low frequency ($\sim$70 cm^{-1}) sideband, which was revealed experimentally by Stavola, et al.[5] We have considered the hydrogen off-axis motion (wagging, or E mode) as a candidate for this sideband. We compute these vibrational frequencies to be in the 700-800 cm^{-1} range, much too high to explain the observed sideband. Furthermore, they appear to be relatively insensitive to the locations of the near-neighbor silicons and whether or not the hydrogen is forced off the axis by reducing the Si-acceptor distance. Hence, it is not clear that these wagging modes can explain the low-frequency sideband. Also, more complicated motions involving the hydrogen are not likely to exhibit an isotope shift so close to 1.41. This remains a problem of interest and controversy.

In some very preliminary work, we have explored the energy surface appropriate to hydrogen motion in a hydrogen-phosphorous pair. Current models locate the hydrogen along the <111> axis in an antibonding position to the silicon neighboring the phosphorous.[6] We have seen indications that the hydrogen may be stable as well at a bond-centered site. These studies are continuing with larger clusters.

* Work done in collaboration with W. Beall Fowler.

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A tight binding   total energy calculation indicate a high
chemical   activity of hydrogen in a Si lattice. Atomic hydrogen
is   not stable   in an unbound interstitial form in a Si lattice
and   reacts with the Si-Si bond. As the result of such reaction
an   H-center is created whitch consist a σ type Si(p)-H(s) bond
and   one unsaturated p—like dangling hybrid. The hydrogen atom
may   be bound   outside or   inside the   bond region depending on
the   occupancy of   the adjacent dangling hybrid. The calculated
activation   energy of   the diffusion   of H—centers   is 1.23 eV.
Interactions   between   H-centers   and   D-centers   lead   to
annihilation   of dangling   hybrids in   the lattice, in spite of
the   fact that   the number   of Si-H bonds remains unchanged. On
the other hand,   collisions between   diffusing   H-centers   may
lead   to two   types of   effects: 1) formation of an H_2 molecule
in   the Si   lattice, or 2) formation of a stable defect contain
two   Si(p)-H(s) bonds. The first of the predicted effects gives
fresh   microscopic   insight . into   the   mechanism   of   low
temperature   evolution   of   hydrogen   from α-Si:H.   The   second
effect   is responsible   for the   damage induced   by hydrogen in
crystalline Si.

AUTHORS INDEX