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INTERNATIONAL WORKSHOP ON :

HYDROGEN MIGRATION AND THE STABILITY OF HYDROGEN RELATED COMPLEXES IN CRYSTALLINE SEMICONDUCTORS

HORBEN BEI FREIBURG
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Hydrogen Diffusion in Crystalline Silicon: a First-Principles Molecular Dynamics simulation

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A detailed microscopic understanding of H diffusion in crystalline silicon, in addition to its interest *per se*, is a basic step to interpret technologically important H incorporation processes [1]. Much of the earlier theoretical effort on this subject has been devoted to study the energetically favoured sites for H at zero temperature on the basis of total energy calculations. In the most notable of these investigations [2] the fully relaxed adiabatic total energy surface for an isolated H impurity was parametrized for all H locations in the unit cell. One of the important results of this study is that H^+ (H^0) prefers to sit in regions of high valence charge density (HD) rather than in interstitial low density regions (LD). All the HD configurations are characterized by a large relaxation of the neighbouring Si atoms, in contrast to the LD configurations where only small distortions are induced. In agreement with experimental findings [3], the BC site is the lowest energy configuration. A low energy path connecting adjacent BC sites through the intermediate C [4] site can be traced, lying entirely in the HD region: this was indicated in Ref. [2] as the most likely diffusion path for H in the neutral or the positively charged state. An activation energy barrier less than 0.2 eV can be estimated along this path. In these earlier calculations no attempt was made to compute the diffusion coefficient. Therefore no direct comparison with diffusion experiments was possible.

H diffusion coefficients have been measured with various techniques. At high temperatures (T > 1000 K), Van Wieringen and Warmoltz (VW) [5] found that H diffusion is characterized by a very high mobility ($D \simeq 2 \times 10^{-4} \mathrm{cm}^2/\mathrm{sec}$ at $T \simeq 1470$ K) and a thermal activation barrier of 0.48 eV within a 10% error. At lower temperatures, DLTS spectra [6] of H passivation of deep levels led to estimates of the diffusion coefficient orders of magnitude lower than the Arrhenius extrapolation of the VW data. Recently, however, diffusivity data at low T have been presented [7, 8] that agree with the Arrhenius extrapolation of the VW results. These measurements confirm the high mobility of H in Si and suggest that a single Arrhenius behaviour can be roughly traced from room up to high temperature (T > 1200 K).

The absence of dynamical simulations, in earlier theoretical studies of H in silicon, can be traced to the difficulty to accurately represent the potential energy surface of the system. We have been able to overcome this difficulty using First Principle Molecular Dynamics [9]. We report here the main results of this investigation [10].

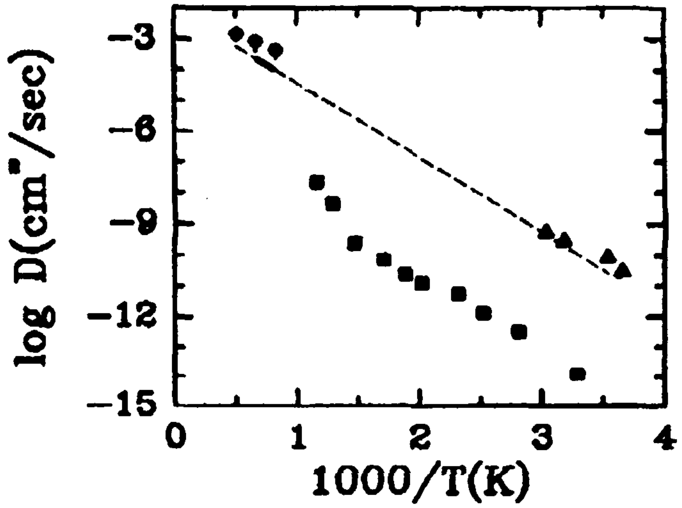

Figure 1: Diffusion coefficient for hydrogen in c-Si as a function of inverse temperature. Solid circles: present calculation for H^+. Error bars are indicated by vertical bars. Solid line: $D = 9.41 \times 10^{-3} \exp(-0.48 \text{ eV}/k_B T)$ cm² sec⁻¹ as obtained by VW (see text) in the temperature range 1240 ÷ 1480 K; extrapolation outside this range is given by the dashed line. Squares: experimental data from Ref. [6]. Triangles: experimental diffusivity values in Au Schottky barrier sample [7].

In our simulation we focused on H^+ [10] in c-Si. This charge state has been argued to be the dominant one, at least in p-doped material, both experimentally [7, 8] and theoretically [2]. We used a periodically repeated FCC supercell containing 128 Si atoms and one proton. The details of the simulation are reported in ref. [10]. As explained there we have a very accurate description of the H^+ energy surface, which is overall very similar to that of Ref. [2]. In particular, we recover the distinction between HD and LD regions in the T = 0 total energy surface. We have performed several MD runs at different temperatures higher than 1000 K. At these temperatures an H impurity in silicon can travel distances of the order of several bond lengths during a time of few picoseconds. This allows to study the diffusion process with sufficient accuracy using MD techniques. In Fig. 1 we report our results for *D* at three different temperatures, one of which would correspond to an overheated crystal. The agreement with the experimental VW data is remarkable, considering the uncertainties of both theory and experiment in addition to the fact that theory does not take into account presence of defects, possible molecular formation or other factors that could hinder the diffusion process.

An analysis of the diffusive path of the proton in the various MD runs reveals that the diffusion process proceeds via jumps between sites of high symmetry. Both high- and low-density regions are visited by the migrating particle, at variance with the predictions based on zero temperature calculations. More specifically we have detected, as the most likely, a path lying mostly in the HD region, connecting adjacent BC (or M [4]) sites, through tetrahedral (Td) site. In other segments of the trajectory, the proton has been instead observed to follow a path lying completely in the LD region. This path proceeds via jumps between near antibonding (AB) sites (about 1.6 Å from a Si atom) using Td or Hex as crossing sites. These two paths can alternate during the same simulation run and differs not only in the topology but also for the dynamical behaviour of the diffusing proton, as shown by the power spectra of the velocity-velocity correlation function of H [10]. Interestingly, the H diffusion coefficient is, within the error bars, essentially the same in the two paths.

The reason why the proton does not follow the strictly HD path resulting from T=0 calculations, can be traced to the large difference in mass between H and Si. When the H^+ motion is fast, as it is the case at these high temperatures, the heavy Si ions cannot follow adiabatically the proton. Thus the lattice may not have the time to undergo the large relaxation needed for the HD sites to become energetically favourable. When this happens the proton prefers to move through regions of low energy for the undistorted lattice.

Recently Blöchl et al. [11] used static total energy calculations to compute the H diffusion coefficient at any temperature, on the basis of a simplified rate theory approach. At high temperature their values are surprisingly in good agreement with the results of our MD simulations. Rate theory, in facts, neglects dynamical effects and is expected to be correct in the limit of low temperatures. However, the result of Blöchl et al. does not indicate that dynamical effects are not affecting the behaviour of H at high temperatures, but rather that dynamical effects do not appreciably modify the value of D. This is consistent with our finding that the two observed paths yield very similar diffusion coefficients.

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CONTENTS

Hydrogen Passivation of Carbon Acceptors in GaAs Grown from Metalorganic Sources

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ABSTRACT

For GaAs:C epitaxial layers, we have found that H_2 gas in growth and annealing ambients leads to the formation of C_x-H complexes. Up to 40% of the C acceptors are estimated to be passivated in some cases. The C_x-H centers have been shown to be stable or marginally stable at temperatures near 500°C. Hence, the unintentional passivation of C is especially likely because typical epitaxial growth and processing-related annealing steps are performed near 500°C and often in H_2 containing ambients.

Most recent work on H in semiconductors [1-3] has focussed on defect passivation in a plasma that contains atomic hydrogen. In III-V and II-VI materials, there are a few examples of H incorporation from H_2 gas of which we are aware. Svob and coworkers diffused D into GaAs [4] and II-VI materials [5] from D_2 gas and detected the indiffusion with SIMS. In more recent work, Svob et al. [6] showed with SIMS measurements that H was incorporated into II-VI materials grown by MOCVD from H_2 in the growth ambient. Defect passivation was not demonstrated in these experiments.

In our experiments on the passivation of GaAs:C, we have examined several epitaxial layers grown by MOMBE [7] and MOCVD [8] with various growth conditions and post-growth annealing treatments. Annealing experiments were performed either in an RTA oven with an ambient of forming gas or He or in a muffle furnace in sealed quartz ampules filled with H_2 (or D_2). Characterization methods include Hall effect, SIMS, and IR absorption.

IR spectra for the H-stretching region are shown in Fig. 1 for samples from a MOMBE-grown layer with $N_A = 2\times10^{20}$ cm^{-3} that had been annealed in various ambients. In Fig. 1(a) a feature at 2635 cm^{-1} that was previously assigned to the C_{As}-H center by Clerjaud et al. [9] and additional features at 2643, 2651, and 2688 cm^{-1} that also involve C and H [10] are seen in an as-grown layer. We use denotation C_x-H for these centers.

In previous work it was found that H could be introduced into the GaAs:C layers grown by MOMBE from the TMG or the AsH_3 sources.[10, 11] Fig. 1 shows that H_2 in the annealing ambient is also an important source of H in the layers. The spectrum in Fig. 1(b) shows that annealing in H_2 enhances the strength of the C-H stretching feature at 2635 cm^{-1}. This anneal was performed in a sealed ampule; spurious sources of atomic H that might result from the dissociation of H_2 on hot furnace components are unlikely. We presume that the H_2 dissociates at the sample surface and then diffuses into the epilayer where C_x-H centers are readily formed. In Figs. 1(c) and (d), samples are compared following annealing in an RTA oven in forming gas (90% N_2 and 10% H_2) and He gas. An anneal in the inert He ambient at 600°C eliminates the C-H stretching features whereas C_x-H centers remain following an anneal at 600°C in forming gas.

The presence of C_x-H centers in as-grown samples indicates that these defects are stable near the epi-growth temperature. Isochronal (5 min) annealing data are shown in Fig. 2. These anneals were performed in an RTA furnace in a He ambient. The 2635 and 2688 cm^{-1} features are annealed away at temperatures of 800 K (527°C) and 900 K (627°C), respectively. Both centers are stable or marginally stable at the epi-growth temperatures of 500 to 545°C for the MOMBE and MOCVD growths, respectively, and persist to higher temperatures when samples are annealed in H_2-containing ambients. [See Fig. 1(c)]. The stability of the C_{As}-H center (2635 cm^{-1}) is consistent with previous results due to Clerjaud et al. [12] Recent results by Pearton et al. [13] show that in a reverse biased p-n junction, C_{As}-H complexes dissociate at 145°C in a 20 min anneal. Hence the stability we measure is greatly affected by retrapping of the H^+ at C_{As} sites.

We have made an approximate calibration of the concentration of centers that include C and H by making a direct measurement of the H concentration with SIMS. Typical profiles of GaAs:C into which H and D had been diffused are shown in Fig. 3. If it is assumed that all of the hydrogen in the layers is involved in stable C_x-H complexes then the relationship between the infrared absorption strength and concentration of centers is,

$$[C_x\text{-H}]/A = 1.8\times10^{16}\ cm^{-1}$$

Here A is the integrated absorption coefficient, $A = \int \alpha(\sigma)d\sigma$, in units cm^{-2} for the total H-stretching absorption due to the C_x-H centers.

With the calibration factor given above we can estimate $[C_x\text{-H}]$ for the various epilayers from the strength of the IR absorption. The as-grown MOMBE layer in Fig. 1(a) has $[C_x\text{-H}] = 7\times10^{18}\ cm^{-3}$. Annealing in H_2 [Fig. 1(b)] increases the concentration of passivated carbon to $[C_x\text{-H}] = 1.2\times10^{19}\ cm^{-3}$ or to roughly 11% of the total [C]. The highest concentrations of C_x-H centers were observed in layers with H_2 in the growth ambient. The fraction of passivated C acceptors varies from 6% to 40% depending upon the growth method and growth conditions.

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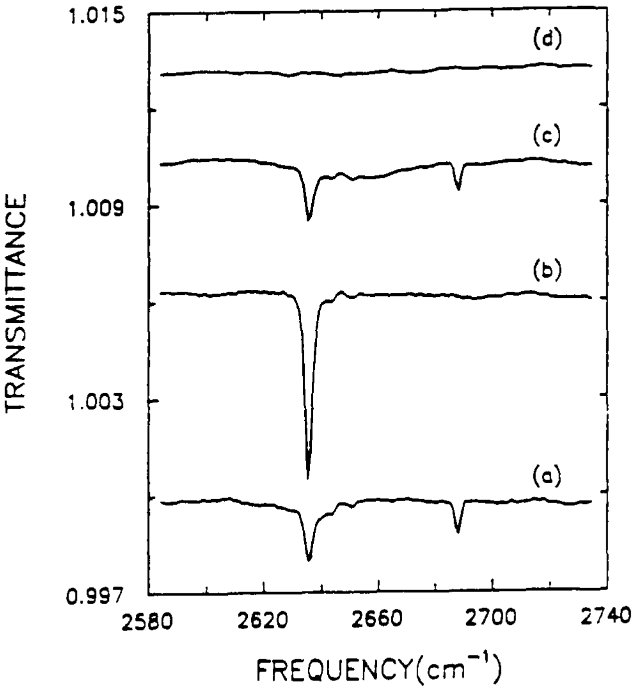

Fig. 1. IR spectra that demonstrate the effect of annealing ambient on C-H centers in GaAs:C grown by MOMBE. Samples were selected from the same wafer with N_A = 9.4×10^{19} cm^{-3}. (a) As-grown. (b) Anneal at 450°C in 0.6 atm H_2 in a sealed ampoule. (c) Anneal for 5 min in forming gas at 600°C in an RTA oven. (d) Anneal for 5 min in He at 600°C in an RTA oven.

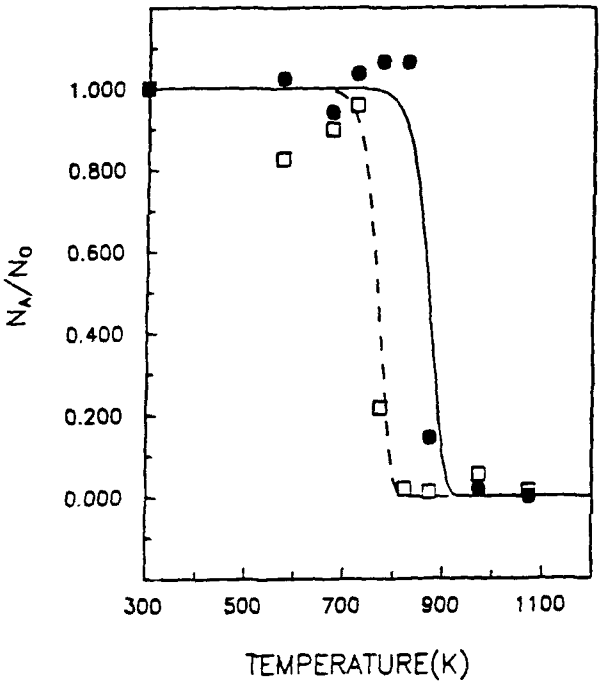

Fig. 2. Isochronal annealing data for the 2636 cm^{-1} (open squares) and 2688 cm^{-1} (closed circles) absorption signals in epitaxial GaAs:C grown by MOMBE. Anneals were performed for 5 min in a He ambient. Here, $N_A = 2\times10^{20}$ cm^{-3}.

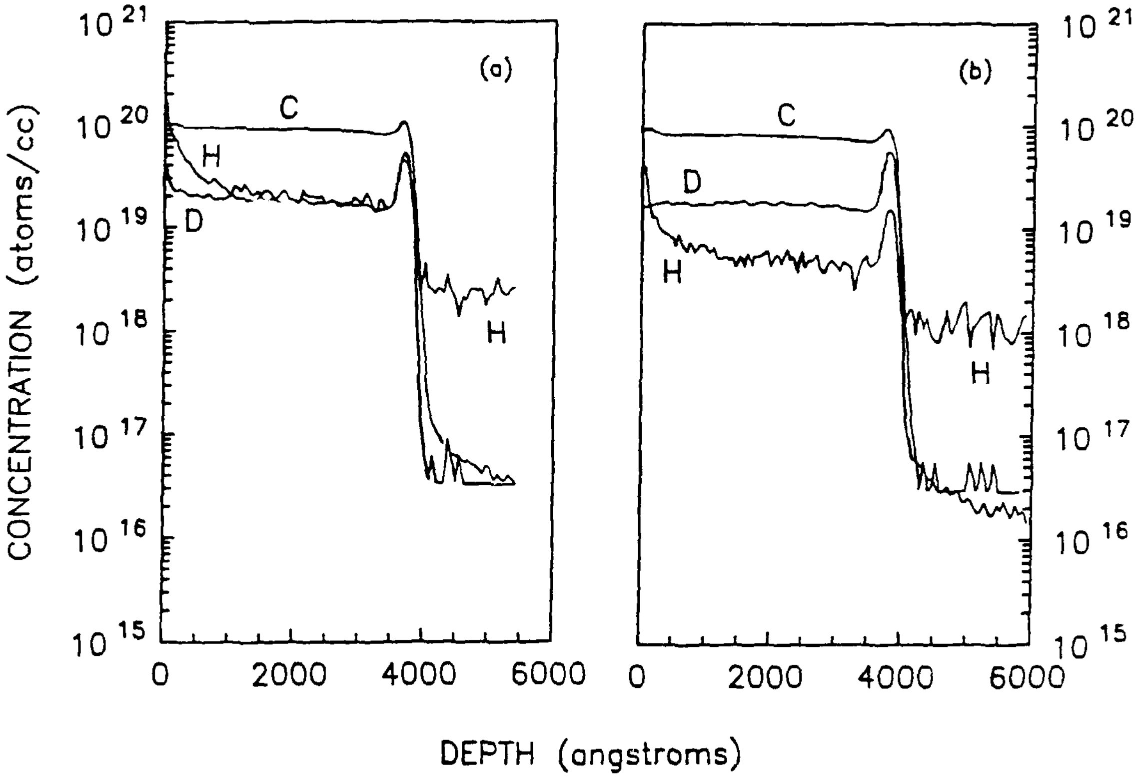

Fig. 3. SIMS profiles of H, D, and C in epitaxial GaAs grown by MOMBE (a) annealed in H_2/D_2 and (b) annealed in D_2. Anneals were performed in sealed ampules at 500°C for 20 min with a gas pressure of 2/3 atm. In (b) the hydrogen was present in the as grown sample.

Raman spectroscopy of localized vibrational modes from carbon-hydrogen pairs in heavily carbon doped GaAs layers grown by metal organic vapor phase epitaxy

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There is considerable current interest in doping GaAs with carbon during epitaxial growth (see, e.g., Refs. 1-3). As an impurity significantly lighter than the host lattice atoms carbon produces a localized vibrational mode (LVM) which is at 582 cm^{-1} for ^{12}C incorporated on an arsenic lattice site ($^{12}C_{As}$) [4]. LVM absorption spectroscopy has been successfully used to study the incorporation of carbon in epitaxial layers [5-7]. One of the results of this work is that carbon-hydrogen (C-H) pairs can be formed in such layers not only after intentional hydrogen treatment but also during the layer growth by metalorganic molecular beam epitaxy (MOMBE)[5] and by metal organic vapor phase epitaxy (MOVPE)[7].

Here we report on a Raman spectroscopic study of the LVM produced by carbon and C-H pairs in as-grown heavily carbon doped GaAs layers grown by MOVPE using trimethylarsine and trimethylgallium[8]. The Raman spectroscopic work was complemented by secondary ion mass spectroscopy (SIMS), to assess the total carbon concentration [C], and by Hall effect measurements.

Fig. 1 shows a sequence of Raman spectra from samples doped with carbon to concentrations [C] of $1.2\text{x}10^{19}\text{cm}^{-3}$ and $6\text{x}10^{19}\text{cm}^{-3}$, respectively. For reference purposes the spectrum of undoped GaAs is also displayed. All spectra were excited at 2.71 eV, which is below the E_1-band gap resonance. Besides second order phonon scattering with a broad band centered at 540 cm^{-1}, the $^{12}C_{As}$ LVM is resolved at 582 cm^{-1}. For excitation at 3.00 eV in resonance with the E_1-band gap of GaAs the $^{12}C_{As}$ LVM is masked by intrinsic scattering from two longitudinal optical phonons (2LO) occuring at the same frequency (Fig. 2). For carbon concentrations $\geq 6\text{x}10^{19}\text{cm}^{-3}$ an additional peak appears at 454 cm^{-1} (labelled X) which becomes the most intense feature for concentrations [C] exceeding 10^{20}cm^{-3}. This peak is strongest in intensity for the polarization of the incident and scattered light parallel to each other, indicating that the vibrational mode causing this peak has A_1 symmetry. Along with line X a high frequency mode can be resolved at 2642 cm^{-1} (Fig. 3). This mode is superimposed on a photoluminescence background arising from the recombination of non-thermalized electrons[9] which is by an order of magnitude more intense than the Raman signal. From a comparison with recent LVM absorption data on hydrogen treated carbon doped GaAs layers[6,7] the 2642 cm^{-1} Raman line can be assigned to the stretch mode of the $^{12}C_{As}$-H pair and the line X to a carbon mode of that pair.

For the two less heavily doped samples the concentration of free holes equals, within the experimental accuracy, the total carbon concentration [C]. In the most heavily doped sample, however, the hole concentration amounts to $1.2\text{x}10^{20}\text{cm}^{-3}$ which is less than the carbon concentration of $1.8\text{x}10^{20}\text{cm}^{-3}$. It is not clear at present whether the formation of C-H pairs, which is evident from the above Raman spectroscopic data, can account for this discrepancy quantitatively. Thus the question remains open, whether the incorporation of hydrogen does limit the maximium achieveable hole concentration in the present MOVPE process.

We would like to thank K. Winkler and T. Fuchs for valuable technical assistance as well as R.C. Newman for helpful discussions and for communicating results prior to publication.

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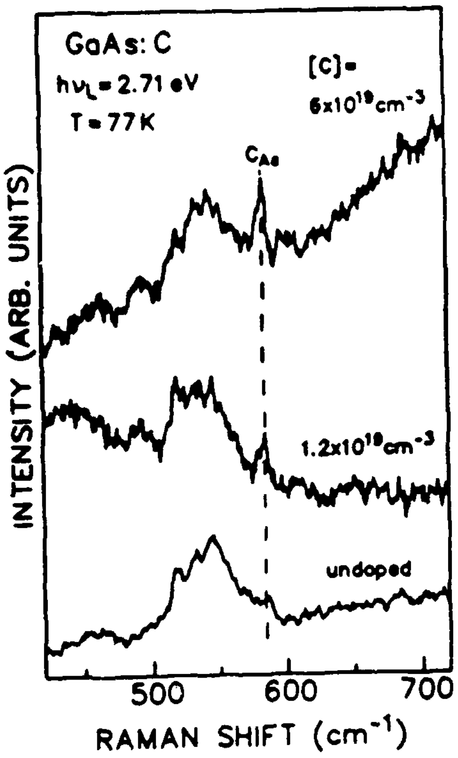

Fig. 1 Low-temperature Raman spectra of MOVPE grown GaAs:C showing the $^{12}C_{As}$ LVM and of undoped GaAs. The total carbon concentrations [C] are given in the figure.

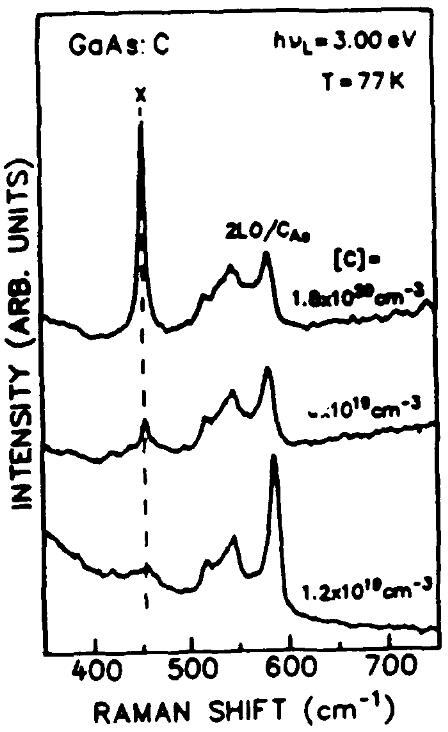

Fig. 2 Low-temperature Raman spectra of MOVPE grown GaAs:C for different total carbon concentrations [C] given in the figure. X denotes a carbon mode of the $^{12}C_{As}$-H pair.

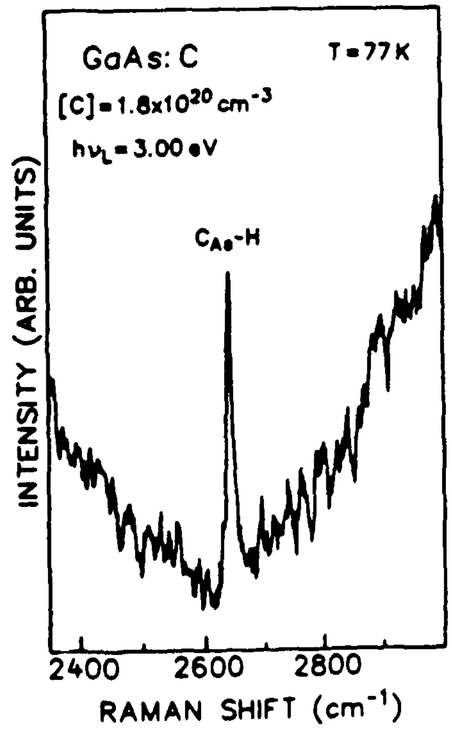

Fig. 3 Low-temperature Raman spectrum of MOVPE grown GaAs:C showing the C-H stretch mode of the $^{12}C_{As}$-H pair.

H-ENHANCED OXYGEN DIFFUSION IN SILICON

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Hydrogen is known to enhance the diffusion of O through silicon, reducing its activation energy from 2.5 eV to 1.6 eV [1, 2]. An understanding of this effect can come from carrying out calculations of the most stable site for H close to an O interstitial, and investigating how the energy required to displace the oxygen atom from its interstitial site to an adjacent one is affected by this hydrogen

We have carried out this programme [3] using a first-principles local density functional pseudopotential method applied to a cluster of 72 atoms. The method allows us to move atoms until an equilibrium structure is found and then to compute the energy necessary to distort the structure and determine saddle point energies.

We found that the isolated O atom has Si-O bonds of about 1.6 Å and Si-O-Si angle around 160°. The energy necessary to pull the cluster into a *ylid* saddle point configuration where the O atom changes from being bonded to atoms 1 and 3 (fig. 1) to 1 and 4 is 2.8 eV and is in reasonable agreement with observation.

In this *ylid* configuration the Si atom 1 is only 3-fold coordinated and has bonds 1.54 Å with the O atom 2 and 2.26 Å with the other two Si atoms (not 3 and 4). The bonds with 3 and 4 are 2.86 Å.

An extra H atom placed successively at an anti-bonding site (along the continuation of the line starting at 2 and passing through 1) , a bond centred site (between 1 and 4) and one of the three equivalent tetrahedral sites all led to stable configurations when the cluster was relaxed. The energies of the latter two relative to the first (H at the anti-bonding site) are 1.5 and .75 eV respectively. Thus we believe the most stable site for H near O is at a anti-bonding configuration. If O traps H in this manner, then the solubility of H in Si should be dependent on the O concentration.

If O is now displaced into the *ylid* configuration, and the rest of the cluster including H, allowed to relax, the energy difference is now only .2 eV. This is because as the Si bond 1-4 weakens, the Si-H bond strengthens. Thus the Si atom always has 4-fold coordination and this leads to a reduction in the distortion energy.

When O moves from the *ylid* configuration towards the centre of the bond 1-4, the energy continues to increase reaching a maximum of 1.4 eV. The H atom being progressively pushed towards the tetrahedral site opposite O in fig.1 .

The final configuration then has an energy .75 eV above the original. The activation barrier along this path is then 1.4 eV. H must then hop to another anti-bonding site to O for a further motion of O to occur with a low barrier. This is likely to be an easy process and we conclude that the activation energy for O reorientation in the presence of H is 1.4 eV.

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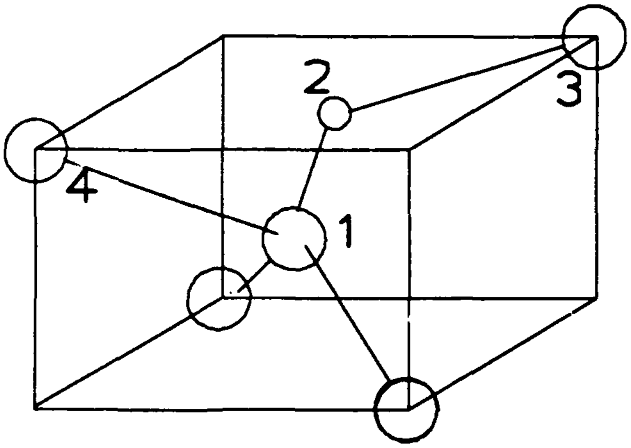

CARBON-HYDROGEN COMPLEXES IN GALLIUM ARSENIDE

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Infra-red absorption studies show that H-passivated C-rich GaAs has absorption lines due to C-H stretch at 2635 cm^{-1} [1, 2, 3, 4], X^H at 452 cm^{-1}, and Y at 563 cm^{-1} [3, 4] as well as C_{As} at 582 cm^{-1}.

We have carried out [5, 6] local density functional cluster calculations on models of defects giving rise to these lines. The calculations give the structures of the defects as well as their vibrational modes and effective charges. The latter control the intensity of the infra-red absorption.

We find:

1) The charged acceptor, C^-_{As}, has four C-Ga lengths of 2.03 Å and a triplet mode at 544 cm^{-1} to be compared to the observed mode at 582 cm^{-1}.

2) The charged donor, C^+_{Ga}, has C-As lengths of 2.08 Å and a triplet mode at 538 cm^{-1}. The donor has not been positively identified but the closeness of this frequency to that of the Y line is not inconsistent with the view that donors are present in the material [4]. It is not clear, however, whether the line Y is independent of H [8].

3) The bond centred H-C_{As} complex has three rather longer C-Ga bonds of 2.18 Å , a very short C-H bond of 1.12 Å and a weak H-Ga bond of 2.05 Å.

The longer C-Ga bonds probably arise in response to the very short C-H bond. The C-H entity behaves as an 'atom ' isoelectronic with As and makes long bonds with Ga which drive the C-related local modes downwards, below those of the isolated substitutional impurity.

Table 1 gives the local modes and their effective charges. The small effective charge renders the H-bend modes infra-red invisible.

The highest A mode related to C is close to line X^H and has similar isotope shifts.

Table 1: Frequencies, cm^{-1}, and Effective Charges, ϵ, of Local Modes of the Bond Centred C-H-Ga Complex and the C_{As}-C_{Ga} Pair

Mode	η	$^{12}C\ ^1H$	$^{13}C\ ^1H$	$^{12}C\ ^2H$
C-H-Ga Complex				
H. stretch	.96	2605	2598	1905
H. bend	.04	730	729	540
		707	704	528
C. *A*	1.66	413	399	402
C. *E*	1.15	392	379	376
		367	355	355
Observed [1, 2, 3, 4]				
H. stretch		2635	2628	1969
X^H		452		440
C_{As}-C_{Ga} pair				
E	.55	556	534	
		551	530	
A	.48	425	410	
E		383	370	
		381	367	

The C related *E* modes fall bellow that of the *A* mode and have about 50% of the absorption intensity of the *A* mode.
4) The reorientation energy of the H is calculated to be .67 eV and observed 7 to be .5 eV.
5) H at an anti-bonding site has an energy .5 eV greater than the bond centred configuration above and the bond centred complex is then the most stable one. This is consistent with the assignment [1] of the 2635 cn^{-1} line to the bond centred defect.
6) The pair defect C_{As}-C_{Ga} has C-Ga, C-C, C-As bonds of lengths 2.12, 2.27 and 1.83 Å, and the local modes (table 1) are below those of the isolated defects. It also has a mid-gap empty level whose wave-function is made up of anti-bonding combination of sp^3 orbitals on the C atoms.

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The Hydrogen-Carbon Complex in Silicon: Tunneling Effect of Electrons

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The properties of hydrogen (H) in crystalline silicon (Si) have been studied extensively [1]. It is now well established that H can passivate shallow acceptor and shallow donor impurities and forms H-acceptor [2,3,4] and H- donor complexes [5,6] which have been studied in detail. However, hydrogen can also be bound to isoelectronic group IV impurities in Ge [7] and Si [8] where it forms *electrically active* centers. H bound to substitutional carbon (C) in Si is known to form a hydrogen-carbon (H-C) related deep donor level [8]. Due to the isoelectronic behaviour of C in Si, this H-C complex is well suited for studying the possible charge states of H in silicon, i.e., it reflects the principal electronic properties of hydrogen. Ab initio calculations [9] even lead to the result that such an H-C complex has an energy level that is virtually identical to the level of an H atom at the same atomic site but *without* the C impurity. The most important electronic and kinetic properties of the H-C complex are already available [8,10]. The defect is a deep donor because it is visible in the C-V-profile [11] and a Poole-Frenkel effect should therefore exist.

In order to measure the Poole-Frenkel effect quantitatively the emission time constants of the H-C complexes are determined as a function of the electric field strength. This information is obtained from "double correlation deep level transient spectroscopy" (D-DLTS) transients which are measured at a fixed temperature. A systematic variation of the electric field strength E at the trap position finally permits a quantitative analysis of the Poole-Frenkel effect. In Fig. 1 the emission time constant of the H-C complex is plotted as a function of $\sqrt{E}$ for two different temperatures.

The measurement in Fig. 1 shows that for electric fields $\leq 2 \times 10^4$ V/cm the electric field dependence of the H-C emission time constant is much weaker than predicted by a three-dimensional Coulomb potential model [12] showing clearly that the potential of the H-C complex is not exactly coulombic. For electric fields $E \geq 4 \times 10^4$ V/cm, however, the data appear to have a stronger electric field dependence than predicted. This effect could possibly be due to an emission process that is superimposed to the Poole-Frenkel effect like a (phonon-assisted) tunneling process of electrons through the barrier. With increasing field strength the height as well as the width of the barrier would decrease and the rate of tunneling would therefore increase — quite independently of temperature [13].

In order to test the possibility of electron tunneling out of the H-C complex, DLTS transients are recorded in the temperature range from 45 K to 90 K with a fixed electric field strength of $\approx 1 \times 10^4$ V/cm at the trap position. The time constant τ of the

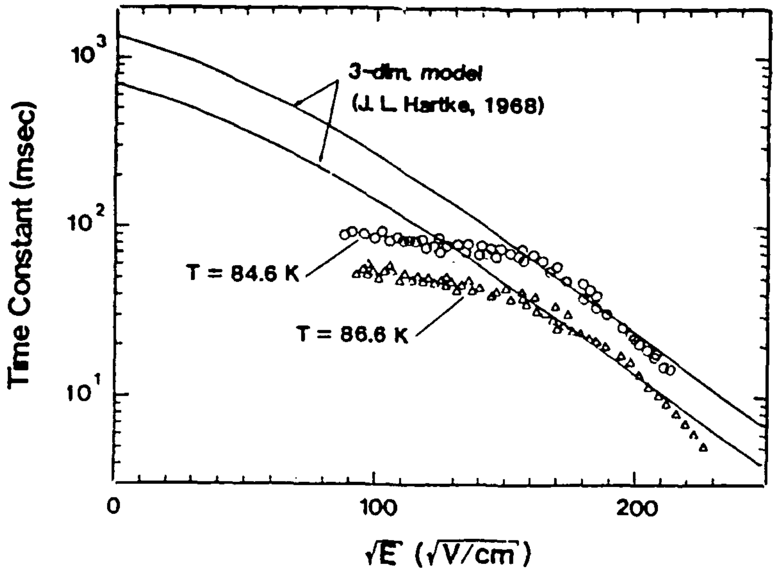

Figure 1: Emission time constant τ of the H-C complex as a function of electric field strength E at two different temperatures. The dependence that is predicted from a 3-dimensional Coulomb potential model is plotted as a solid line.

transients is evaluated and is shown in Fig. 2 as a function of the inverse temperature in an Arrhenius plot. Fig. 2 clearly reveals that the measured emission time constants (triangles in Fig. 2) follow the usual Shockley-Read-Hall (SRH) behaviour $\tau_{SRH} \sim \exp(E_A/kT)$ only for temperatures T higher that 70 K. For lower temperatures the emission time constant becomes completely independent of temperature with a constant value of 38 sec. The amount of this effect cannot be explained with the Poole-Frenkel effect (dashed line in Fig. 2) alone. Only if an additional tunneling effect is taken into account (solid line in Fig. 2) via a temperature independent time constant $\tau_T = 38$ sec the rates add according to

$$\frac{1}{\tau} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_T}$$

and the experimental data can be explained. Phonon-assisted tunneling should not contribute significantly since the phenomenon is observed at low temperatures and is practically temperature independent. The effect is therefore contributed to pure tunneling.

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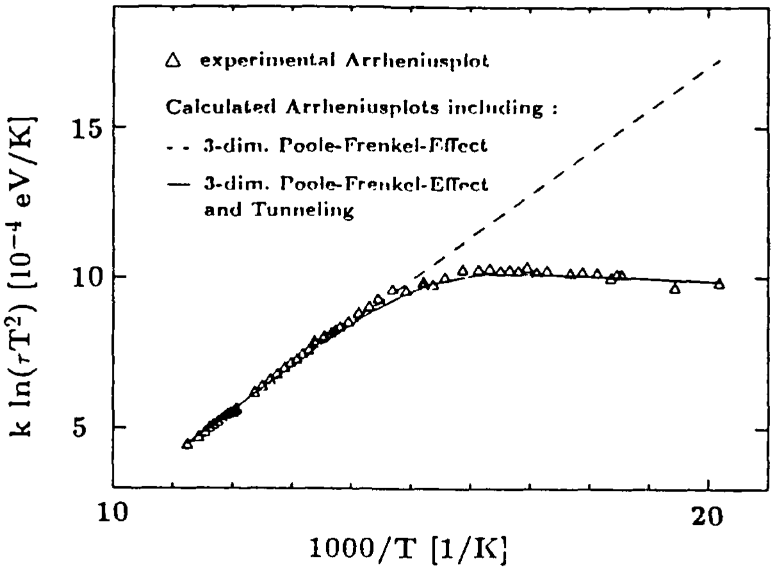

Figure 2: Emission time constant τ of the H-C complex as a function of temperature T in an Arrhenius form.

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Hydrogen ion-implanted into crystalline silicon.

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Hydrogen in crystalline silicon has been studied intensively during the last decade by a large number of experimental techniques[1]. In addition remarkable progresses in the theoretical description have been achieved by large-scale total-energy calculations[2]. Consequently, our knowledge about the properties of hydrogen in silicon has grown significantly.

Hydrogen may be introduced into silicon crystals in various ways, the one most widely used is to expose the surface at moderate temperatures to a hydrogen plasma. Ion-implantation is an alternative technique, which will be in focus in this talk. The major advantages offered by ion-implantation is the possibility to introduce well-controlled amounts of hydrogen at a given temperature. Moreover ion-implantation often leaves the impurities in a non-equilibrium state, a fact which makes the technique interesting for studies of defect-metastability[3]. The major disadvantage is that the creation of defects accompanies the implantation process. At a first glance this seems to represent a serious limitation for applications in studies of isolated hydrogen-defects. However, for typical implantation energies 50-500 KeV and at low temperatures a large fraction of the implanted hydrogen atoms may still end up in "semi-isolated" configurations, even for local concentrations up to ~10^{19} H/cm^3, corresponding to doses in the range 10^{14}-10^{15} H/cm^2. This point will be discussed further in the following.

Theoretical calculations[2] showed that hydrogen in silicon may exist in three charge states H^+, H^0 and H^-, where H^+ and H^0 occupy the bond-center site BC while H^- has minimum in energy at the tetrahedral site T (see fig. 1). The existence of neutral hydrogen at the BC site finds strong support in the EPR experiments by Gorelkinskii et al.[4]. They observed a hydrogen-related EPR-center, denoted AA9, after proton implantation at 80 K (~5x10^{17} H/cm^3). The AA9-center is trigonal, involves two equivalent silicon atoms, and the hyperfine parameters are consistent with those found for anomalous muonium, for which the BC configuration has been confirmed[5].

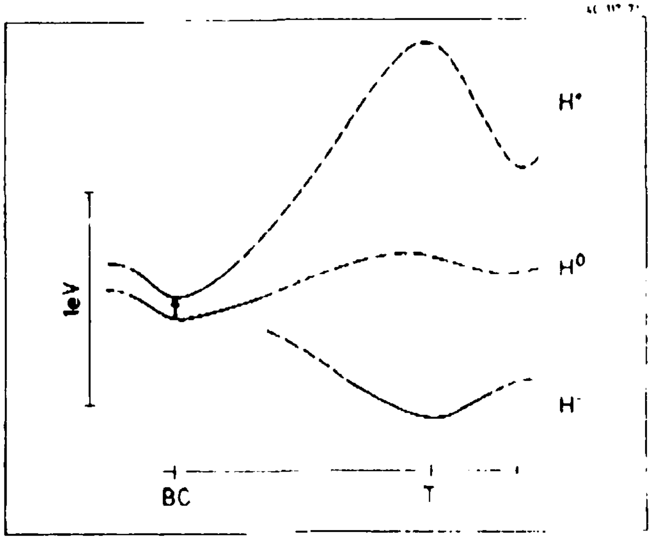

Fig. 1: Sketch of total-energy curves for H^+, H^0, and H^- in n-type silicon based on the calculations in ref. [2]

As pointed out by Watkins[6] isolated hydrogen is expected to be a bistable defect. Recently, we have carried out DLTS experiments[3] in p⁺n diodes after implantation of about 10^{10} H/cm^2 (~3x10^{14} H/cm^3) at low temperatures (40 K). A hydrogen-related deep donor E3′ with the ground state located at E_c-E_t = 0.16 eV was observed. The E3′-defect transforms into a DLTS-invisible component at about 100 K (or 210 K) during zero-bias (or reverse-bias) annealing, and the decays of the E3′-signal are consistent with first-order processes, υ = 3.0x10^{12} s^{-1} exp[-0.29eV/k_BT] (or υ = 1.3x10^8 s^{-1} exp[-0.44eV/k_BT]). The E3′-center is metastable, since the DLTS-signal can be regenerated by forward-bias injection at low temperatures. Very recent measurements of capacitance versus temperature indicate that the reverse-bias annealing of the ionized E3′-center occurs without any change in the charge state. However, as soon the bias is removed two electrons are captured. Thus in n-type silicon the DLTS-invisible component contains one additional electron compared with the non-ionized E3′-donor. On this basis it is suggested that the E3′-signal originates from the H^0 at the BC site. The zero-bias annealing stage at 100 K is ascribed to the transformation from H^0(BC) to H^-(T), and the reverse-bias annealing stage is believed to reflect a jump from H^+(BC) to H^+(near-T), from which it relaxes into H^-(T) when electrons become available. In this context it is important to note that although H^-(T) represents the global minimum in energy (see fig 1), hydrogen may very well be trapped in the metastable configuration H^0(BC) when it comes to rest in the crystal.

The assignment of E3′ made above is consistent also with the EPR data of Gorelkinskii et al.[4]. In their case high-resistivity silicon was applied, and the local hydrogen concentration was about 5x10^{17} H/cm^3. Thus the Fermi-level may be expected to have been close to mid-gap, and consequently the E3′-donor would have been ionized. This explains why the AA9-center was observed only during illumination[4]. In fig. 2 the lifetime τ for annealing of the AA9-center (in the dark[4]) is shown as a function of inverse temperature together with the τ-values from reverse-bias annealing of the E3′-defect. As can be seen from the figure the two sets of data are consistent, supporting that E3′ originates from H^0(BC).

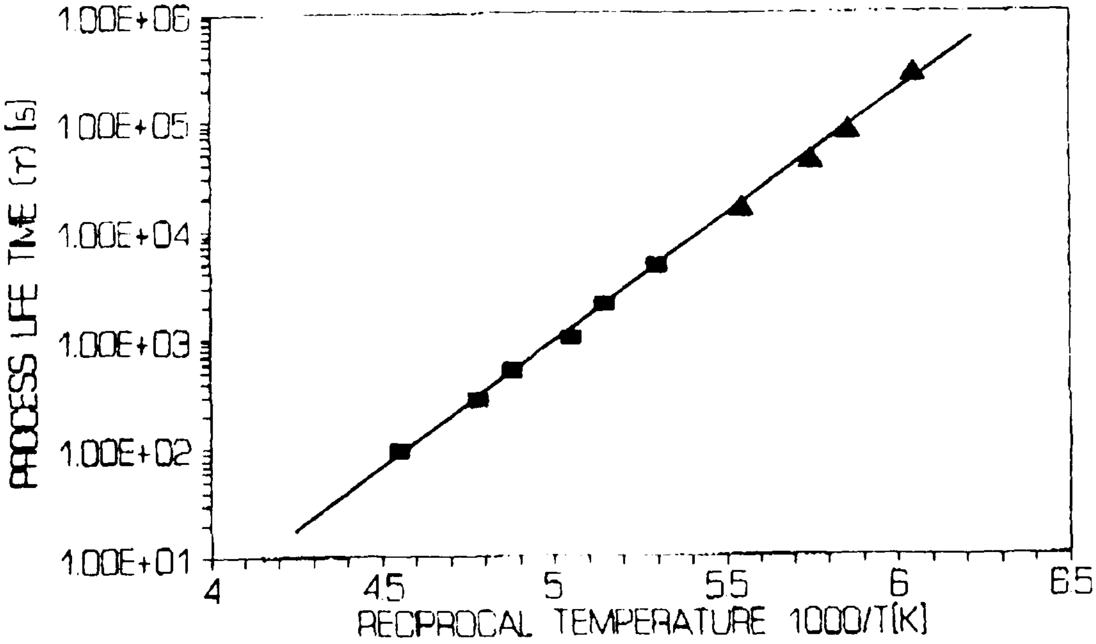

Fig. 2: The lifetimes τ for the annealing of the AA9-center (■) (from ref.[4]) and the E3′-center (▲) (from ref. [3], reverse-bias annealing) shown as a function of inverse temperature.

Channeling measurements[7] was carried out after implantation of deuterium at 30 K (~7×10^{19} H/cm^3) into intrinsic silicon (see fig. 3). The results showed that 80 % of the deuterium atoms occupies near-BC sites while the remaining 20% is located at near-T sites (see fig. 3). After annealing at 140 K the population of near-BC sites decreased and there was a corresponding growth of the near-tetrahedral component. Stein found a major Si-H stretching mode[8] at 1990 cm^{-1} after implantation at 80 K (~4×10^{20} H/cm^3) which annealed out at about 140 K with an activation energy of 0.36 eV. Since the implantation conditions in these experiments were rather similar the 1990 cm^{-1} line was assigned to a local vibrational mode of hydrogen located at a near-BC site[7]. Stavola and Pearton suggested[9] that the 1990 cm^{-1} may be associated with either H^0(BC) or H^+(BC). The frequency agrees with the theoretical estimates for H^0(BC) which is 1945±100 cm^{-1}, whereas the value 2210±100 cm^{-1} calculated for H^+(BC) seems a little high. Since the implanted doses were rather large the Fermi-level was close to mid-gap and the E3'-donor was therefore ionized, i.e. hydrogen at the BC site should have been positively charged. The activation energy for annealing of the 1990 cm^{-1} line is apparently too low compared with that for the annealing of the AA9- or the ionized E3'-center. However, with a local concentration at about 10^{20} H/cm^3 the average separation distance between hydrogen and the nearest defect will be less than 13 Å, and the BC configuration has to be distorted. Under such circumstances deviations should be expected. Never the less, the observations indicate that the dominant hydrogen-related complex formed during low temperature implantation may be described as "semi-isolated" BC site hydrogen.

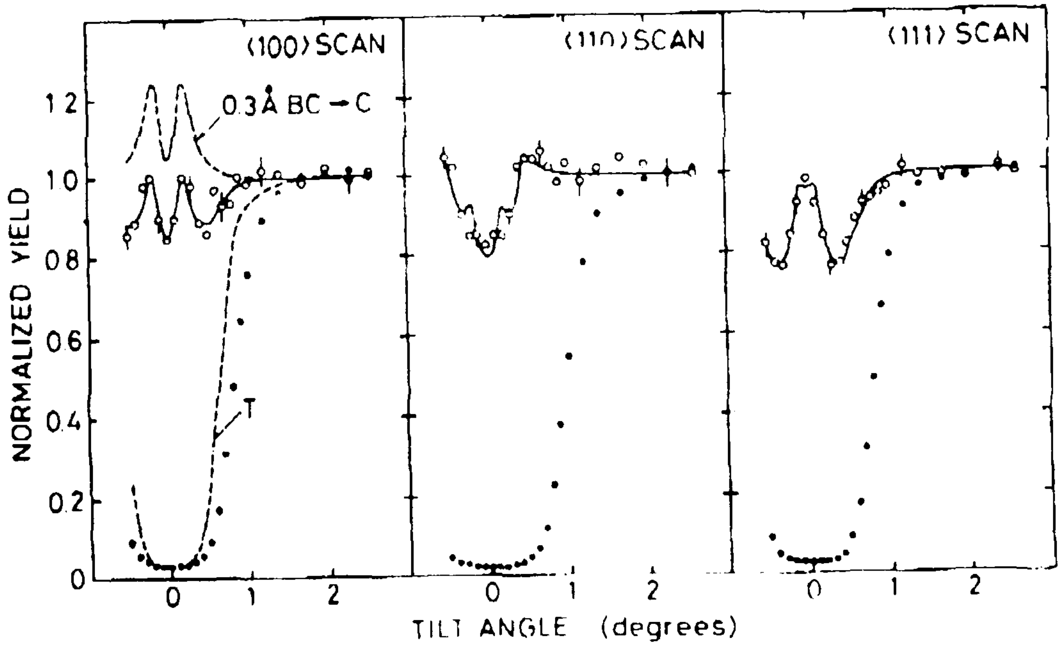

Fig. 3: Channeling scans for deuterium around the major axes in silicon. The solid line represents the best fit to the data, obtained with 80% of the atoms at near-BC sites and 20% at near-T sites.

As mentioned in the introductory remarks damage may represent a problem in application of ion-implantation. Hydrogen implanted at energies in the range 50-500 KeV creates 10-19 vacancy-interstitial pairs according to a TRIM calculation. However, due to recombination with migrating defects the actual number will be smaller. CV measurements on low-temperature hydrogen-implanted samples[3] (480 KeV) showed that about 1-2 electrically active defects were created per ion. In addition with a displacement energy of 20.4 eV a hydrogen atom will have an average energy of about 150 eV just after its last collision. With this energy the hydrogen atom will be able to move about 200 Å away from the last vacancy-interstitial pair it created. This implies that for damage concentrations below $\sim 10^{16}/cm^3$ (about 10^{11} H/cm^2) the hydrogen atom will come to rest 200 Å away from the nearest defect. When the damage level is above $\sim 10^{16}/cm^3$ we may assume that the hydrogen atoms come to rest in a region with a Gaussian distribution of defect traps. When the local hydrogen concentration is below 10^{18} H/cm^3 ($\leq 2 \times 10^{19}$ defects/cm^3) the fraction of hydrogen atoms which end up being trapped to defects is $\leq 5\%$, if the defect-hydrogen trapping radius is 10 Å. This estimate is of course based on the assumption that hydrogen is immobile and does not recombine with migrating intrinsic defects. At low temperatures, below 60 K, only self-interstitials are believed to be mobile and most of these will recombine with vacancies. Thus a substantial part of the implanted hydrogen atoms may end up in a "semi-isolated" configuration, even for doses comparable to those applied in FTIR and channeling measurements.

Stein[8] found that the annealing of the 1990 cm^{-1} line at about 140 K is correlated with the growth in intensity of two other Si-H modes at 1839 cm^{-1} and 2062 cm^{-1}. These two lines are observed also after implantation at room temperature[10], and they disappear together after annealing at about 200°C. The annealing behavior of the lines are consistent with that of the near-T component observed with channeling[7], indicating that at least one of them is associated with hydrogen at a near-T site. However, in the same temperature range a strong near-BC component is also present[7]. In our view it is unlikely that hydrogen at a near-BC site should not give rise to a Si-H mode. On that basis it was suggested that the line at 1839 cm^{-1} (or 2062 cm^{-1}) is associated with hydrogen at a near-BC site while the other at 2062 cm^{-1} (or 1839 cm^{-1}) originates from hydrogen at a near-T site. Uniaxial stress measurements[10] demonstrated that both lines are associated with trigonal centers, and the stress-splitting could be analyzed with just one free parameter $f_{//}$ which describes the change in the effective Si-H force constant per unit stress applied parallel to the bond. The values obtained was $f_{//} = -0.58$ N m^{-1} GPa^{-1} for the 1839 cm^{-1} line and $f_{//} = 3.30$ N m^{-1} GPa^{-1} for the 2062 cm^{-1} line. Thus the stress dependence of the two centers are opposite and quantitatively very different, supporting the view that these lines reflect Si-H bonds in two different environments. Deák et al. suggested[11] that the two lines may originate from (the theoretical) H_2^*[11,12] so that the 1839 cm^{-1} and 2062 cm^{-1} lines correspond to vibrations of hydrogen at a near-BC site and at a near-T site, respectively. This assignment is seemingly consistent with the experimental findings mentioned above. However, one crucial check would be to see whether the lines split into two, in samples implanted both with hydrogen and deuterium. Such splitting was not observed in our previous work[10], but recently this result was disputed (see ref. [11]).

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Hydrogen related complexes in neutron transmutation doped FZ silicon grown at a hydrogen atmosphere

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Hydrogen is one of the most important impurities in semiconductor materials. The study of the state and behavior of hydrogen and hydrogen-related defects in silicon is an interesting and noticeable area[1-4]. But still a great deal of confusion exists. In this paper, many obvious characters and new phenomena due to existence of hydrogen, the effect of hydrogen on electrical and optical properties of neutron irradiated and transmutation doped FZ silicon grown at a hydrogen atmosphere - NTD FZ(H_2) Si, the hydrogen passivation of radiation defects, the behavior of hydrogen impurity, the interaction of hydrogen with radiation defects and other impurities, and the action of hydrogen as an indicator of some radiation defects and secondary defects were studied by Hall - coefficient - resistivity and minority carrier lifetime measurements, infrared (IR) absorption and deep level transient spectroscopy (DLTS) as well as positron annihilation technique(PAT).

Our main conclusion is as follows:

1. Hydrogen passivation effect

Hydrogen influences strongly the electrical properties of NTD FZ(H_2) Si during annealing. A high concentration hydrogen-defect shallow donor (up to about $2x10^{15}$ cm^{-3}) produces in NTD FZ(H_2) Si annealed at 300 - 600 °C[4]. Its maximum concentration, appearing and disappearing temperature depend on the starting silicon, thermal neutron doses and annealing parameters.

There is another big lifetime peak from 350 to 600 °C except a peak at about 850 °C on the minority carrier lifetime isochronal annealing curve.

Because of hydrogen the production rate of some radiation defects such as (V-V) and (V-O) decreases, the recovery temperature of the electrical properties such as free carrier concentration and mobility, and the annealing temperature of radiation defects lower [4, 5]. And hydrogen can prevent from the formation of the secondary defects related to vacancies (e.g., V_4 cluster: about 435 ps from positron annihilation lifetime measurements).

Hydrogen atoms begin to participate actively in the interaction with radiation defects above 200 °C. They diffuse into defects and saturate silicon dangling bonds to passivate the defects.

2. Hydrogen-related deep centers

We first measured many deep centers in as-grown, neutron and γ-ray irradiated FZ(H_2) Si, and studied their annealing behavior by DLTS, found several hydrogen-related deep centers although hydrogen in silicon has no energy level in energy gap, and suggested their possible structure models[4, 6]:

1). E_c- 0.20 eV, Z center, (V+2H), observed in low dose neutron irradiated n- and p-type FZ(H_2) Si,γ-ray irradiated n-type FZ(H_2) Si and annealed NTD FZ(H_2) Si irradiated with $3x10^{17}$ neutrons/cm^2.
2). E_c-0.35 eV, E_4 center, (V-O+H), observed in low dose neutron irradiated n - type FZ(H_2) Si and annealed NTD FZ(H_2) Si.

3). E_v+0.23 eV, H_7 center, (V_4+nH), observed in low dose neutron irradiated p-type FZ(H_2) Si.

4). E_c- 0.22 eV, HD center, related to formation of the hydrogen-induced defects, observed in FZ(H_2) Si and NTD FZ(H_2) Si annealed in 500-650 °C.

5). E_c- 0.54 eV wide DLTS peak, WB center, corresponding to the 4000 cm^{-1} wide IR band (WB band) in NTD FZ(H_2) Si [7] due to electron transition from neutron radiation disordered region to hydrogen - defect shallow donor complexes or conduction band.

3. Si-H IR absorption bands

We have found about 20 new IR bands caused from the stretching vibration of Si-H bonds[7, 8], shown in Fig. 1.

In NTD FZ(H_2) Si cooled for 6 years at RT, the 1832 and 2054 cm^{-1} strong neutron-induced Si-H IR peaks disappear, but the 1980 and 2065 cm^{-1} IR peaks become still stronger, e.g., the strength of 1980 cm^{-1} peak increases by 11 times. The change indicates that at RT the simple point defects can diffuse and interact, and hydrogen atoms may trap the vacancy and vacancy cluster [7].

We measured the formation and annealing activation energy, estimated the optical absorption cross sections and concentration for some important IR peaks. Comparing with the IR results of γ-ray irradiated and H^+ implanted silicon as well as the DLTS and PAT results, based on their annealing behavior and activation energy as well as their dependence on neutron fluence and starting silicon, we identify them[7]:

1832 and 2054 cm^{-1} (V+H)
1980 cm^{-1} (V+2H) (Z center: E_c- 0.20 eV)
1970 and 1984 cm^{-1} (V_2+nH) (SiH_1)
2016 cm^{-1} (splited V_2+nH) (SiH_2)
2162[9] and 1836 cm^{-1} (V_3+mH) (SiH_3)
1894 cm^{-1} (V_4+nH) (H_7 center: E_v+0.23 eV)
2066 cm^{-1} (V-O+2H)
2050-2150 cm^{-1} wide IR band (disordered region +nH)

Among them, the identification of the 1832 and 2162 cm^{-1} IR bands is basically in agreement with that in [10].

4. Hydrogen-defect shallow donor

The hydrogen-defect shallow donor in NTD FZ(H_2) Si is very different from the oxygen donor in CZ Si. It is the hydrogen and point defect complexes because there is no this shallow donor in as-grown, only fast neutron irradiated FZ(H_2) Si, or NTD FZ(H_2) Si kept for a longer time at RT.

It has been proposed that the 2162 cm^{-1} IR absorption peak is due to the stretching vibration of the Si-H bond of hydrogen-defect shallow donor complex in the proton implanted silicon[9]. Indeed, we have observed the 2162 cm^{-1} IR peak in NTD FZ (H_2) Si irradiated by 2.9×10^{17} neutrons/cm^2. This work has found that within the temperature range of the hydrogen-defect shallow defect, a new IR peak at 1836 cm^{-1} appears and its annealing behavior is similar to that of the 2162 cm^{-1} peak. In NTD FZ (H_2) Si irradiated with 1.13×10^{18} neutrons/cm^2, the concentration of the above donors increases, but the 2162 cm^{-1} peak does not appear, and another new peak at 2016 cm^{-1} appears. In addition, a new peak at 1954 cm^{-1} appears in both kinds of NTD FZ(H_2) Si. These show that hydrogen- defect shallow donors do not correspond to only one Si-H peak(2162 cm^{-1}) and only one kind of Si-H vibrational center and defect structure.

The formation of hydrogen-defect shallow donor is because some weaker Si-H bonds break, and released hydrogen atoms diffuse and bind with the point defects. After the silicon dangling bonds are completely saturated by hydrogen atoms, or the Si-H bonds break and these vacancy-type defects anneal out, the donor property disappears.

5. Disordered region- related wide IR band

A 2050- 2150 cm^{-1} wide IR band in NTD FZ(H_2) Si annealed at 650 °C has first been found[7]. Its appearance is due to hydrogen and neutron radiation defects, and is an evidence and hydrogen indication for the disordered region.It is the stretching vibrational mode of Si-H bonds formed because some weaker Si-H bonds break, hydrogen atoms diffuse into neutron radiation- induced disordered region defect clusters to saturate the silicon dangling bonds, and is similar to the wide IR band in a-Si:H[11]. The vibration frequence shift has been explained[12].The hydrogen concentration in FZ(H_2) Si used in this study is estimated to be 1- 2x$10^{17}cm^{-3}$ on the basis of the strength of this wide IR band. It is in a good agreement with the value 1- 1.5x10^{17} cm^{-3} measured with the melt- gas chromatography method. This supports the amorphous silicon- like model of the disordered region.

6.Hydrogen- indued defect

The Si-H bond break and hydrogen aggregate in disordered region can cause the hydrogen- induced defects. We propose that the disordered region could be the nucleating centers of *hydrogen and oxygen precipitation*[7]. We also point out that a E_c-0.21 eV deep center (500- 650 °C), 250 ps positron lifetime component (650 °C) and minority carrier lifetime valley are all related to formation of the hydrogen-induced defect.

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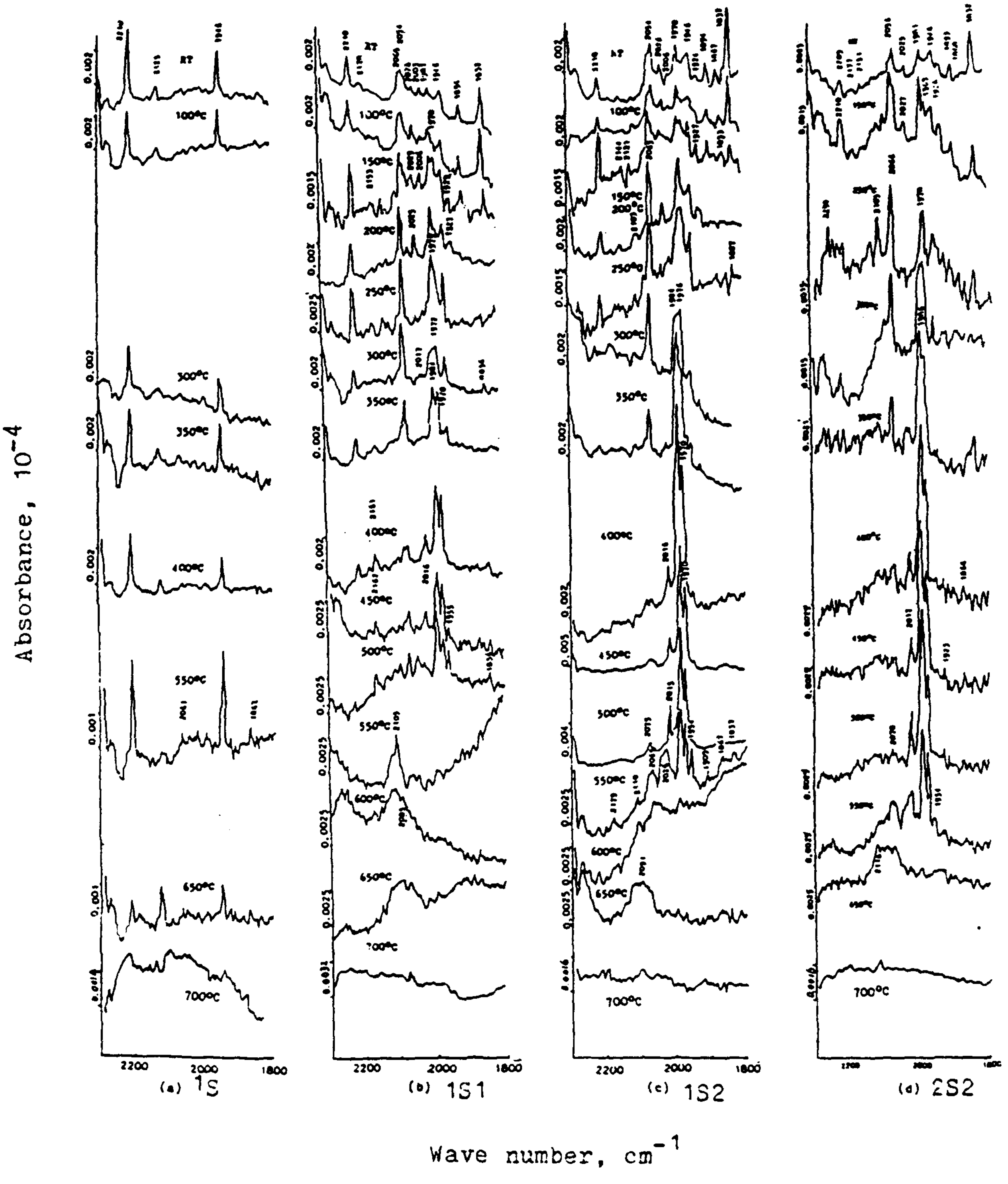

Fig. 1 Si-H stretching vibration IR absorption spectra of FZ(H_2) Si and NTD FZ(H_2) Si

1) 1S: FZ(H_2) Si- 1

2) 1S1: NTD FZ(H_2) Si- 1, 2.9×10^{17} neutrons / cm^2

3) 1S2: NTD FZ(H_2) Si- 1, 1.13×10^{18} neutrons / cm^2

4) 2S2: NTD FZ(H_2) Si- 2, 1.13×10^{18} neutrons / cm^2

VIBRATIONS OF HYDROGEN COMPLEXES IN SILICON

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Infrared spectra of crystalline silicon grown in hydrogen or irradiated with protons exhibit a rich variety of hydrogen related bands.[1,2] Various centers have been proposed as the origin of these bands based on their behavior under heat treatment, uniaxial stress, isotope substitution, irradiation, or on their correlation with channeling results.[3,4] Using this information alone, a unique assignment has not yet been possible.

Si-H vibrations observe well defined trends in substituted silanes depending on the the nature and the environment of the bond. This can be well reproduced in a semi-empirical molecular orbital theory. Since the alternative structures proposed to explain the origin of a given band are very different (as far as the local environment of the Si-H bond is concerned), decision between them can be facilitated by properly scaled frequencies obtained from such calculations. As in our earlier calculations on hydrogen in silicon,[5,6] the MINDO/3 (modified intermediate neglect of differential overlap)[7] approximation has been employed to calculate the normal mode vibrations of defects involving a vacancy (V) or self-interstitial (I) and/or hydrogen atoms. Details has been described earlier.[8]

We have found four basically different types of bonding with characteristic frequency regimes. The calculated (scaled) frequencies allow us to comment on the assignments proposed earlier. V(nH) and $V_2(nH)$ complexes with $n>1$ should give rise to vibration frequencies higher than 2055 cm^{-1}, which is the frequency assigned to VH (or V_2H). Our scaled frequencies for the hydrogen decorated split self-interstitial, $I_{sp}HH$, complex agree very well with the electron-irradiation sensitive double band at 1980 cm^{-1}. Other self-interstitial related hydrogen complexes are also in this region. The calculated frequency of the negatively charged isolated hydrogen (in antibonding position) is close to the one observed at 1835 cm^{-1} (such an assignment has been suggested as an alternative for this band).[4] Other possible assignments are also discussed.

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HYDROGEN NEUTRALIZATION OF DOUBLE ACCEPTOR CENTERS IN SILICON

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Energy levels in Zn-, Be- or Cd-doped Si samples

Zinc, beryllium, and cadmium form isolated substitutional centers in silicon and a variety of complexes containing further extrinsic atoms or intrinsic defects. The chemical nature of such complexes is usually not identified. The isolated substitutional centers act as double acceptors [1,2,3,4,5].

The investigated elements are incorporated in Si by diffusion (Zn, Cd) [2,4], by standard implantation (Be) [2], or by implantation of radioactive probe atoms which are transmuted into stable daughter nuclei, e.g. stable Cd according to

$$^{111}\mathrm{In}^{*} \xrightarrow{T_{1/2}=2.83d} {}^{111}Cd \qquad [4,5]$$

The generated defect levels are analyzed by deep level transient spectroscopy (DLTS), Hall effect and IR *absorption* measurements. The implantation damage is annealed in a Rapid Isothermal Annealing (RIA) system [6]. Be- and Cd-related centers are thermally unstable at relatively low temperatures as demonstrated in Figs. 1 and 4a,b; the investigated centers can be generated or annihilated depending on the annealing temperature, annealing period or ramp down velocity of the diffusion temperature. This thermal instability is responsible for the complicated experimental situation with respect to the hydrogen neutralization of Zn-, Be and Cd-related defects. The following levels are determined:

a) **Si(Al) : Zn** [2] (see Fig. 2)

$Zn^{0/-} = E_V + 319$ meV, $Zn^{-/2-} = E_V + 698$ meV (double acceptor)
$Zn(x1) = E_V + 277$ meV
$Zn(x2) = E_V + 345$ meV

b) **Si(B) : Be** [2] (see Fig. 3)

$Be^{0/-} = E_V + 190$ meV, $Be^{-/2-} = E_V + 440$ meV (double acceptor)

c) **Si(B) : Cd** [4,5] (see Fig. 4b)

$Cd^{0/-} = E_V + 485$ meV, $Cd^{-/2-} = E_C - 450$ meV (double acceptor)
($Cd^{-/2-}$ is observed in P-doped Si samples, not shown in Fig. 4, see [4])

$Cd(B1) = E_V + 200$ meV
$Cd(B2) = E_V + 400$ meV

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Hydrogen neutralization of double acceptors

The hydrogen passivation of Zn-, Be- or Cd-doped Si samples was performed by a remote microwave plasma and exposed to monatomic hydrogen at sample temperatures of 200°C for 1h. All the observed levels were completely neutralized by the hydrogenation process (see Figs. 2 (dotted line), 3 (dashed line), and 4 (solid line)). The following additional levels appear after the hydrogenation process:

a) **Si(B) : Be** [2]

$Be(H) = E_V + 101$ meV

b) **Si(B) : Cd**

$Cd(H1) = E_V + 135$ meV
$Cd(H2) = E_V + 260$ meV

These new levels could not be identified yet. We suggest that these complexes are H-related and contain at least one hydrogen atom [7,8].

Subsequent heat treatments of the neutralized defects result in DLTS spectra as given in Figs. 2,3, and 4c. The spectra demonstrate that the double acceptors recover simultaneously during the thermal anneal. The evaluation of the reactivation energy of the Zn double acceptor results in $Ea=2.2\pm0.3$eV (see Fig.5)

It appears that a single hydrogen atom bonded at the defect site is sufficient to remove both energy levels of the double acceptor center. However, it is still an open question whether levels Be(H), Cd(H1), and Cd(H2) represent such an H-related complex. In order to obtain additional information on their chemical compositions, we plan to investigate the hydrogenated defects by IR absorption. This optical method becomes now applicable because of a new hydrogenation technique [9] that achieves the hydrogenation of defect centers throughout the bulk of a Si wafer. In a first run, we have tested this new technique and succeeded in passivating the total concentration of Zn-related levels in a Si sample of 400 μm thickness.

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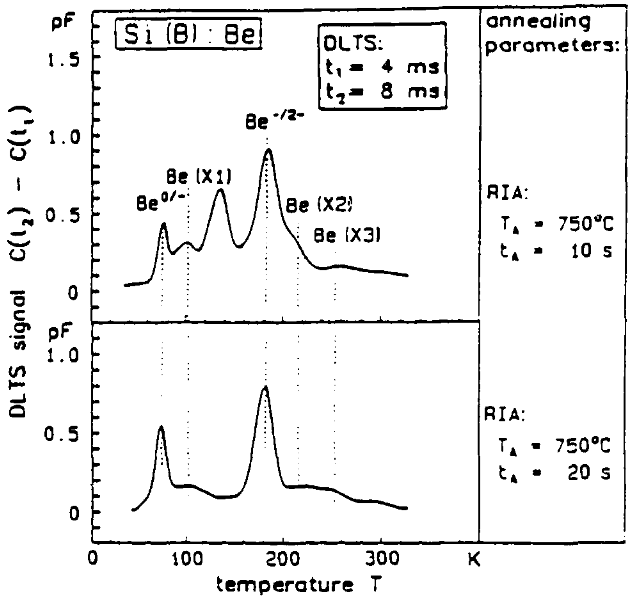

Fig.1. DLTS spectra of a Be-implanted Si sample recorded after various heat treatments in a RIA system.

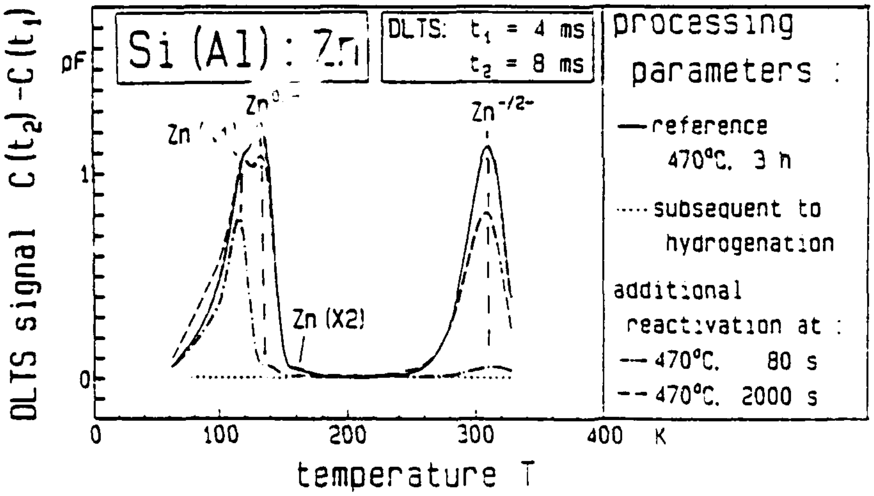

Fig.2. DLTS spectra of a Zn-diffused Si sample taken after different processing steps.

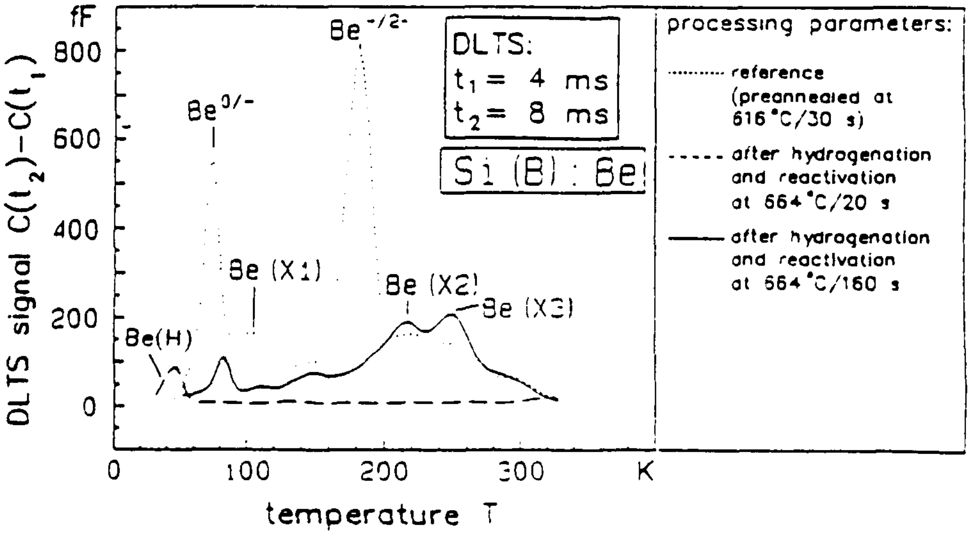

Fig.3. DLTS spectra of a Be-implanted Si sample taken after different processing steps.

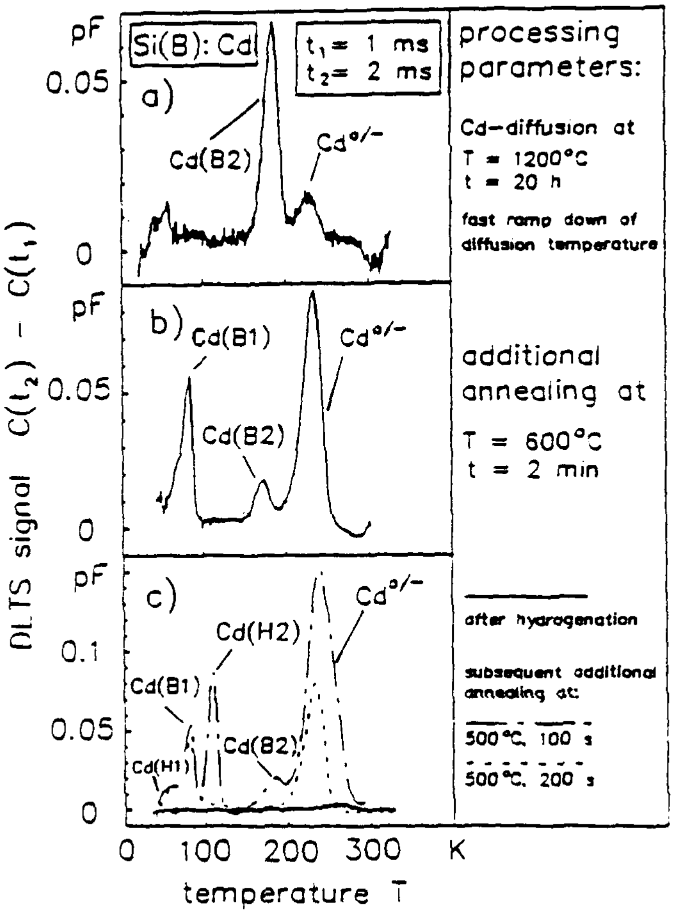

Fig.4. DLTS spectra of a Cd-diffused Si sample taken after different processing steps.

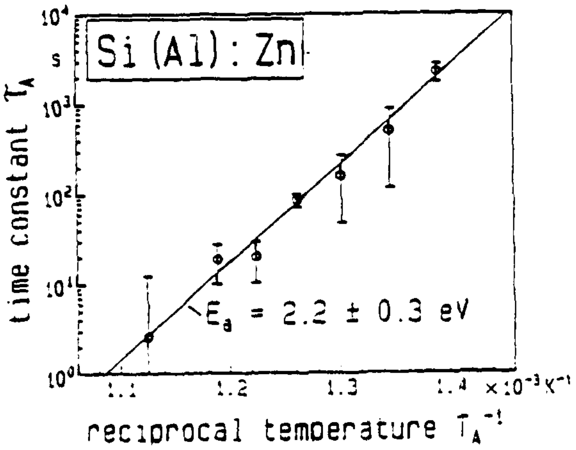

Fig.5. Time constant τ_A vs. reciprocal anneal temperature T_A^{-1}; the reactivation energy E_a of H-passivated Zn double acceptors is determined from the slope of the straight line.

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1. STABILITY OF HYDROGEN COMPLEXES IN SEMI-INSULATING (SI) INDIUM PHOSPHIDE GROWN BY THE LIQUID ENCAPSULATED CZOCHRALSKI (LEC) METHOD.

In order to obtain highly doped InP samples which can be used for piezo-spectroscopic measurements after hydrogenation, relatively thick (1.5 mm) transparent SI InP substrates are required on which thin (≈ 3 µm) epilayers are deposited. Now, SI LEC InP is known to contain hydrogen-related complexes[1] and their absorption have to be determined to differentiate it from the absorption of the active layer. Moreover, the growth of the epilayers by MOVPE is performed near 650°C so that the effect of such an annealing has to be studied on the substrate.

Oriented substrate slices and reference samples were cut from an as-grown SI InP:Fe cone kindly provided by J.P. Farges from L.E.P. The lines observed at 6 K in the reference samples are listed in Table 1. It shows in the as-grown sample the PH,Zn line[3] at 2288 cm^{-1}, the strong 2316 cm^{-1} line, related to an intrinsic H defect[4] and three new weak lines at 2306.8, 2307.2 and 2311 cm^{-1}. After annealing for 3 hours at 600°C in a sealed ampoule

Table 1

Lines observed at 6 K in LEC-grown SI InP:Fe #184 for characteristic heat treatments

Line position (cm^{-1})	As-grown	Annealed 3 hours at 600 °C	Annealed 3 hours at 650 °C
2202.39*	NO	YES	YES
2250.74*	"	"	"
2254.7*	"	"	"
2273.42*	"	NO	"
2282.8	"	YES	NO
2287.71*	YES	"	YES
2306.82	"	"	"
2307.17	"	"	"
2311.28	"	"	"
2315.62*	"	"	"

* Reported in Ref. 2

with a phosphorus overpressure, the lines at 2202, 2251 and 2255 cm^{-1} emerge from the background at the expense of the intensity of the 2316 cm^{-1} line. This can be interpreted as a partial dissociation of the complexes responsible for that line followed by the trapping of hydrogen by more stable defects or by the partial transformation of the 2316 cm^{-1} defect into other defects. For non cumulative annealing for 3 hours at 650 °C, the intrinsic 2202 cm^{-1} line still grows at the expense of the 2316 cm^{-1} line and a very weak and sharp line is also observed at 2273 cm^{-1}. After this annealing, the Zn,H line is only reduced by a factor of 2, indicating a relatively high stability of this complex at low concentration ($\approx 2 \times 10^{14}$ at/cm^3).

The structure of the defects related to the lines at 2202 and 2316 cm^{-1} have been discussed in ref. 4. It is clear from the spectroscopic measurements under a uniaxial stress that the centres associated with these lines and with the new lines at 2306.8, 2311 cm^{-1} have a trigonal symmetry. A comparison with the spectra of the InP:Zn/InP:Fe structures shows the presence of the 2202 cm^{-1} line indicating that the corresponding center has also been formed during the growth of the epilayer.

2. OH AND NH COMPLEXES IN SEMI-INSULATING GALLIUM ARSENIDE

OH- and NH-related lines have been observed at 6 K in as-grown LEC SI GaAs in the 2945-3500 cm^{-1} range. Oxygen has been identified to be involved in the strongest line at 3300 cm^{-1} because of the ^{18}O isotope effect. The intensity of some of these lines is photosensitive in the samples where EL2$^+$ is present at thermal equilibrium (Fig. 1).

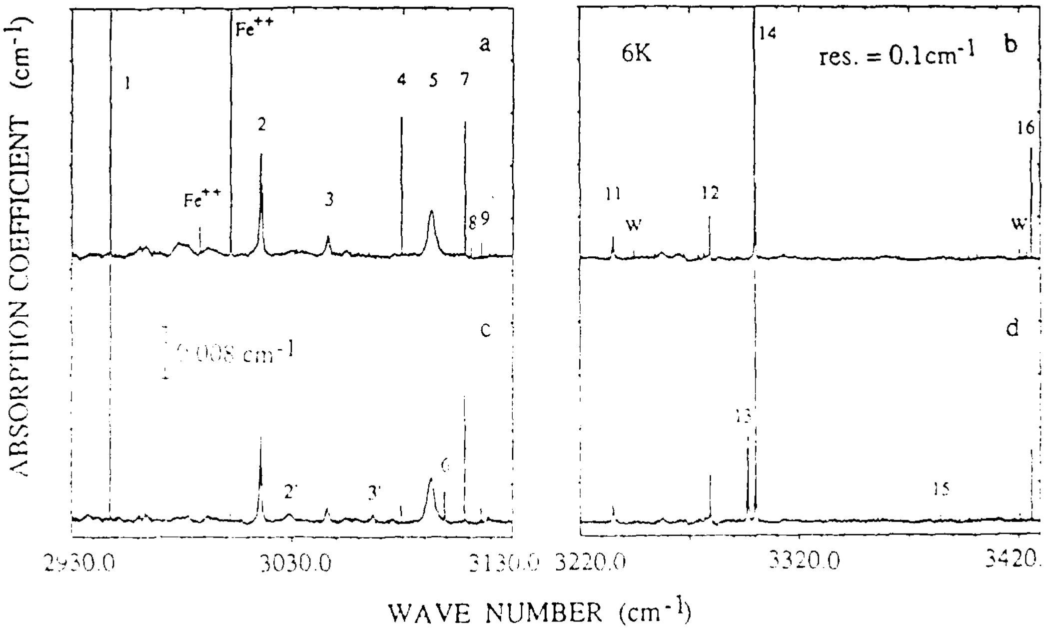

Figure 1. a and b: Absorption of GaAs sample #1 under thermal equilibrium. The labelling is that of Table 1. Line 10 is not observed in this sample and line 17 (not shown) is about 2 times larger than line 15. Line 14 is truncated at 16% of its peak absorption. c and d: Same as a and b after 150 minutes illumination with 1.25 eV photons. Line 14 is truncated at 20% of its peak absorption. Residual water vapor lines are noted W.

There is proof that it is due to the trapping of free holes by these H complexes which can exist under at least two charge states[5,6].

The properties of the OH bond related to the 3300 cm^{-1} line has been specially investigated. It seems to be weakly bonded to the lattice and the splitting behaviour of the line under uniaxial stress indicates that the OH bond can reorient at low-temperature.

These XH centres seems to be relatively stable under electron irradiation, but after such an irradiation, a new XH line is however observed which must come from the dissociation of existing complexes. The stability of these complexes after annealing under different atmospheres is presently investigated.

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What did we learn from PAC Experiments about Hydrogen in Semiconductors ?

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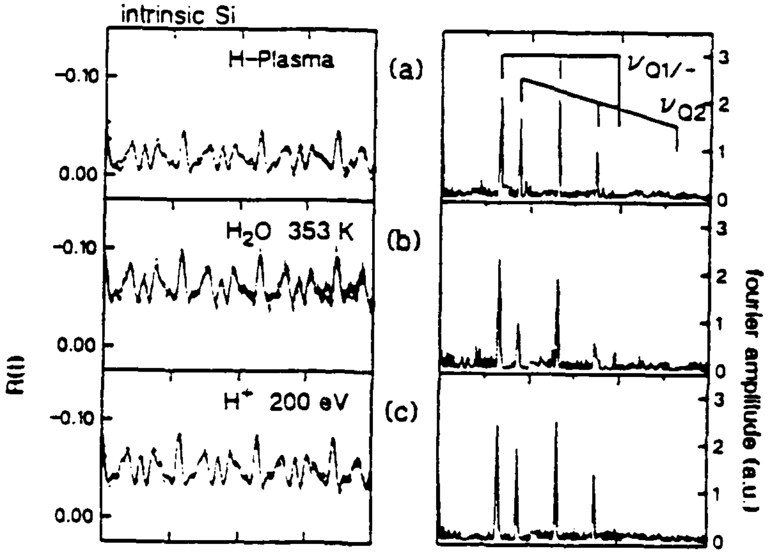
Using the radioactive probe atoms ^{111}In or ^{111m}Cd the Perturbed Angular Correlation technique (PAC) is able to investigate the formation of acceptor-H complexes in elemental semiconductors as well as in III-V compound semiconductors. PAC is sensitive to the direct vicinity of the probe atom, any impurity or point defect in next neighborhood creating an electrical field gradient (efg) at the probe nucleus site is dedected via the modulation of the spatial anisotropy of two subsequently emitted gamma quanta. More information on the technique and its application in semiconductors is given by Wichert et al. (1). The total number of probe atoms necessary to perform PAC experiments is in the order of 10^{11}, allowing experiments with local concentrations well below 10^{17} cm^{-3} after implantation of the probe atoms and subsequent annealing of irradiation damage.

Unfortunately the chemical nature of the defect could not be extracted from the observed modulation. To use this technique to obtain general information on the passivation process, an unquestionable identification of the chemical nature of observed defects is necessary. This is achieved by combination of different passivation procedures, especially the use of low energy hydrogen implantation (about 150 eV implantation energy), and the application of electrical measurements. Knowing the chemical nature of the complex PAC reveals information on the amount of formed complexes, its symmetry and dynamic behavior.

To investigate a possible acceptor-hydrogen complex formation an intrinsic Si sample was doped with ^{111}In and exposed to a hydrogen plasma (13.56 MHz, 320 V). In Fig. 1a the PAC spectra and its corresponding Fourier transform taken from this sample at 300K are shown. Pronounced oscillations indicating the formation of two well defined complex configurations around about 50 % of the probe atoms are seen. Each complex is characterized by a frequency triplett in the Fourier transform. The efg's are labeled $\nu_{Q1/-}$ = 349 MHz and ν_{Q2} = 463 MHz. The same efg's are observed after boiling an identical sample in water for 100 min in darkness (Fig. 1b) and after low

Figure 1

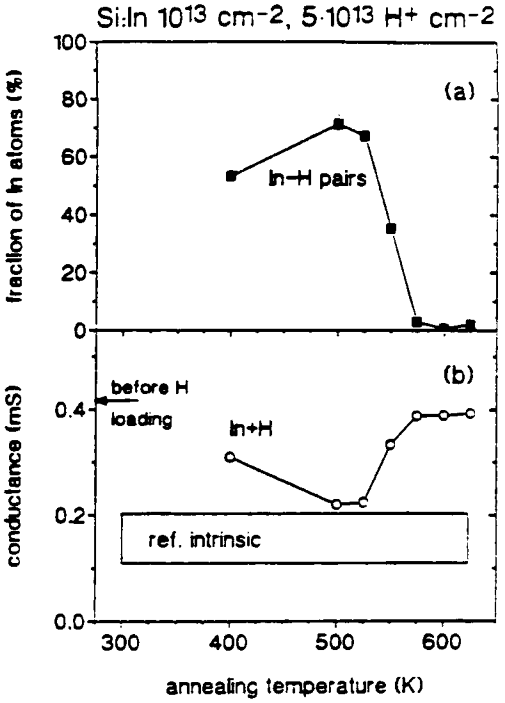


energy hydrogen implantation with 200 eV and a total dose of 10^{14} cm^{-2} (Fig. 1c) (2). An additional configuration labeled $\nu_{Q1/0}$ = 270 MHz is observed in highly B-doped Si. Because no or very few intrinsic defects are created in case of the H_2O treatment or during low energy implantation, complexes formed between In and intrinsic defects can be ruled out. Because of mass selected implantation nothing but hydrogen was introduced into the sample verifying that hydrogen has been trapped at the ^{111}In probe atoms (3). Isochronal annealing experiments reveal the same stability for all three observed configurations, indicating, that only one In-H complex is formed.

The PAC result reveals the symmetry of the complex after the decay from ^{111}In to ^{111m}Cd. Therefore, from measurements with different sample orientations we can only determine the symmetry and dynamic behavior of the resulting Cd-H complex, which should now act as a single acceptor in Si. All efg's are oriented along <111> lattice directions. The occurrence of different defect configurations as a function of electronic parameters was investigated in more detail (4, 5, 6) and is well understood for the transition between the two complex configurations labeled $\nu_{Q1/-}$ and $\nu_{Q1/0}$. It is described in terms of different charge states of the Cd-H acceptor according to the position of the fermi level (4, 6).

Having undoubtedly identified the chemical nature of the observed complex PAC can be used to investigate more general aspects of hydrogen passivation. The correlation between electrical deactivation deduced from electrical measurements and acceptor-H pair concentration measured by PAC in the same sample, clarifies the question whether every deactivated acceptor atom is involved in an acceptor-H pair. In other words,

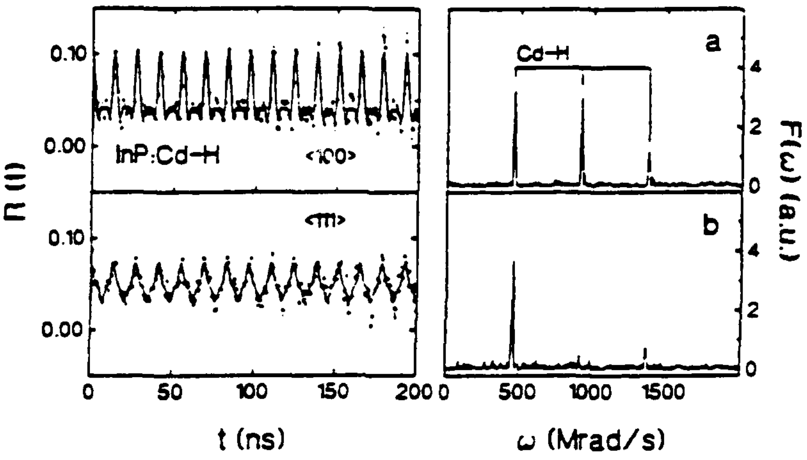
Figure 2



whether the passivation process and not compensation is the only relevant deactivation mechanism. For this purpose four point resistivity measurements were performed parallel to the PAC experiment. In order to achieve a detectable electrical conductivity intrinsic Si was implanted with stable ^{115}In (10^{13} cm^{-2}, 350 keV) in addition to the implanted radioactive ^{111}In (10^{11} cm^{-2}). After annealing of implantation damage (1173 K, 10 min, furnace) an electrical conductivity of about 0.4 mS was observed (Fig. 2b), indicating that about 80% of the implanted In was electrically active after this procedure. Subsequently the sample was loaded by low energy hydrogen implantation (200 eV, $5\cdot10^{13}$ cm^{-2}, implantation temperature 400 K). A drop of electrical conductivity to 0.2 mS (Fig 2b) and the formation of In-H pairs at 60 % of the In atoms was detected by PAC (Fig 2a). Annealing of this sample above 500 K is leading to a reduction of the amount of In-H pairs accompanied by an increase of electrical conductivity (Fig. 2a,b). A quantitative analysis of this experiment proved that the amount of In-H pairs seen by PAC follows directly the fraction of deactivated In in the sample. This direct correlation proves that passivation is the only deactivation mechanism (3).

In III-V compound semiconductors we have used the probe atom ^{111m}Cd, an excited state of ^{111}Cd, which could be produced and implanted (60 keV) at the ISOLDE facility in Geneva. Since no elemental transmutation takes place in this case, the PAC results reveal directly the properties of the formed complexes. The implantation damage after implantation in InP and GaAs was removed by rapid thermal annealing. In Fig. 3 a,b the PAC signal after hydrogenation with low energy ion implantation (150 eV, 3 10^{14} cm^{-2}, implantation temperature 370 K) proves the formation of Cd-H. The efg is symmetric along <111> lattice directions and the corresponding hyperfine coupling constant is ν_Q = 484 MHz. The same signal was observed after hydrogen plasma treatment (7,9). Additional to the investigation of the thermal stability of this complex,

Figure 3



which is reported by Baurichter et al. (7,9) we have also investigated the formation efficiency of Cd-H pairs as function of the achieved electrical activation of the acceptor Cd controlled by the annealing temperature and with variation of the hydrogen implantation temperature. The efficiency of pair formation reflects directly the activation of Cd, indicating that the Cd atom must be in a negative charge state to attract the hydrogen atom. Therefore hydrogen should be most probably in a positive charge state during diffusion. The efficiency of pair formation is increased with higher implantation temperature reflecting the higher mobility of hydrogen.

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Structure, Stability and Internal Dynamics of Cd-H Complexes in Semiconductors

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Information on hydrogen decorated acceptors in elemental and compound semiconductors is obtained from the interior of the complexes by analyzing the perturbed angular correlation (PAC) of gamma quanta emitted by radioactive acceptor atoms. Since the PAC spectroscopy detects the electrical field gradient at the site of a probe nucleus via hyperfine interaction, it enables the study of structure and stability of impurity-hydrogen pairs, as well as the investigation of dynamical processes like charge fluctuations inside and around these complexes in the time range from nanoseconds to microseconds. Examples for each of these observables will be given.

The structure and stability of Cd-defect complexes formed in H-plasma exposed GaAs, InAs, GaP, InP, and InSb samples have been studied through the PAC probe atom ^{111m}Cd, which decays into the ground state of ^{111}Cd via a γ-γ cascade. Undoped III-V-compound samples were implanted by 60 KeV ^{111m}Cd^{+} ions to doses of $10^{11}...10^{12}$ cm^{-2} at the on-line mass separator ISOLDE of CERN. After rapid thermal annealing (GaAs, InAs, GaP, InP) or furnace annealing in sealed quartz ampoules (InSb), most of the probe atoms (50-80%) were located on lattice sites with vanishing electrical field gradients, indicating substitutional lattice positions. Finally, the specimens were exposed to a parallel plate dc H_2 glow discharge (30 min. at 400...500 K), with the implanted surface in direct contact with the plasma. This treatment yields in the formation of at least one Cd-defect complex per compound, as revealed by PAC analysis [1,2]. The formation of two complexes is observed in GaAs and InAs. All defect configurations are characterized by axially symmetric field gradients. The orientation of the electrical field gradients in <111> lattice directions can be extracted from the spectra, except for one of the complexes in InAs, and the complex in InSb. The data are insufficient for the determination of the orientation in the latter cases. The quadrupole coupling constants vary between ν_Q = 357 MHz (InSb) and ν_Q = 581 MHz (InAs) and scale approximately with the inversed cube of the lattice constants. A simple point charge model approach indicates, that the same defect species is trapped at the Cd acceptors. Since experiments on low energy proton implantation (E = 150-

400 eV) yield in the same PAC results [3], this species can be identified with hydrogen. The observed symmetry reflects the symmetry of the structural model proposed for acceptor hydrogen pairs in III-V-compounds, based on results from IR spectroscopy on GaAs and InP with various acceptors [4]. The assignment in terms of Cd-H pairs is supported by annealing experiments. Figure 1 and figure 2 display the results of isochronal (10 min.) annealing experiments on hydrogenated GaAs, InP and InAs samples. A first order dissociation reaction is fitted to the GaAs and InP data, assuming a value of $\upsilon = 7 \cdot 10^{13}\ s^{-1}$ for the attempt frequency, which was found for Zn-H pairs in GaAs [5], and which can also be related to the stretching mode of the As-H bond [4]. The fits yield a dissociation energy of E_D = 1.3(0.1) eV for GaAs (for both complexes) [2,3]. This values agree quite well with those obtained recently from electrical measurements in GaAs:Zn (E_D = 1.33 eV) [5]. The Cd-H pairs in InP are more stable compared to the Cd-H pairs in GaAs. This observation has also its analogy to Zn-H pairs in these two compounds [6]. The fit to the annealing data obtained by PAC exhibits a dissociation energy of E_D = 1.6 eV. The similarities in the dissociation energies for Zn and Cd acceptors can also be related to IR measurements. These experiments indicate, that hydrogen is bonded to the group V atom rather than to the adjacent acceptor in the bond center configuration. Hence the dissociation should be governed by the bond between hydrogen and the group V atom. A metastable annealing behaviour is observed for the complexes in InAs (fig. 2). Here, one complex dissociates between 300 K and 350 K, accompanied by an increase of the population of the other configuration. The more stable configuration then anneals at approximately the same temperature as the complexes in GaAs. This phenomenon indicates, that the same defect species is involved in both complexes, most likely hydrogen.

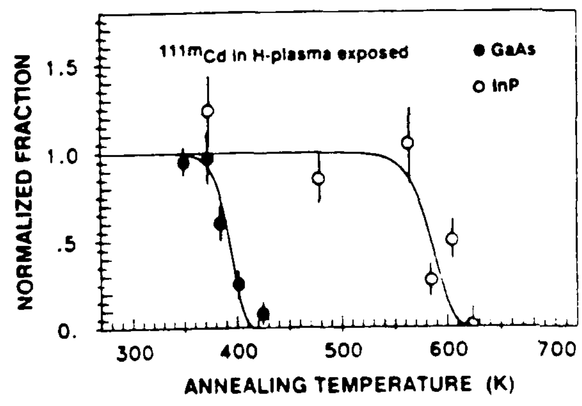

Figure 1 (see text)

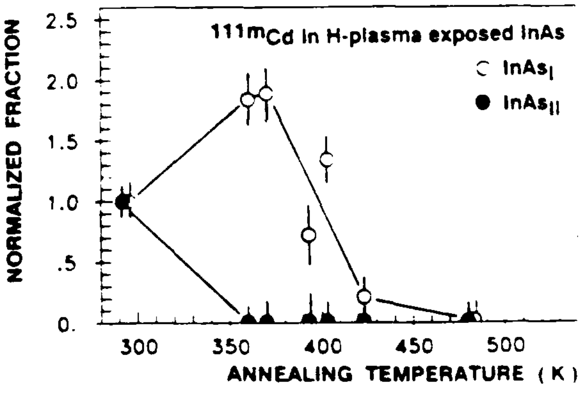

Figure 2 (see text)

Another example for thermal metastability of acceptor hydrogen complexes was observed in silicon on Cd-H pairs. Boron doped silicon crystals have been implanted by radioactive $^{111}In^{+}$ ions with an energy of 400 KeV to a dose of $10^{11}...10^{12}$ cm^{-2} at the IONAS implantor of the Göttingen University. The samples were subsequently sealed in quartz ampoules and the radiation damage was annealed in a furnace at 800...1200 K. After annealing the radiation damage, the specimens were hydrogenated in an atomic hydrogen atmosphere, originating from a remote H-plasma. PAC measurements performed after these treatments reveal the formation of two to three distinct defect complexes, depending on the boron concentration and the measuring temperature. The hyperfine interaction is again observed at ^{111}Cd, the decay product of ^{111}In. The configurations are all axially symmetric and oriented in <111> lattice directions. All three configurations have been previously identified to be In/Cd-H pairs [7,8]. The discussion of the experimental situation will be focussed on the thermal metastability of the two complexes characterized by quadrupole coupling constants $\nu_Q = 350$ MHz (at T=295K), and $\nu_Q = 270$ MHz (at T=100K). They can be assigned to two different charge states of an electrically active Cd-H complex [8]. A set of PAC data has been recorded under variation of the Fermi energy with respect to the energy level of the Cd-H state in the band gap by varying the boron concentration (between 10^{15} and 10^{18} cm^{-3}) and the measuring temperature. These experiments permit the time resolved study of charge carrier recombination processes [9,10]. This charge carrier recombination results in fluctuating electrical field gradients, which is described by the dynamical PAC theory. The analysis reveals the hole emission time constant for the Cd-H center as a function of temperature (figure 3), and permits the determination of the Cd-H energy level to $E = E_V + 80(20)$ meV (fit in figure 3).

The pronounced fluctuation of electrical field gradients in Si material with high boron concentration ($> 10^{18}$ cm^{-3}) cannot be due to the carrier recombination of the Cd-H center. This dynamic behaviour can be explained by the localized motion of hydrogen in the complexes

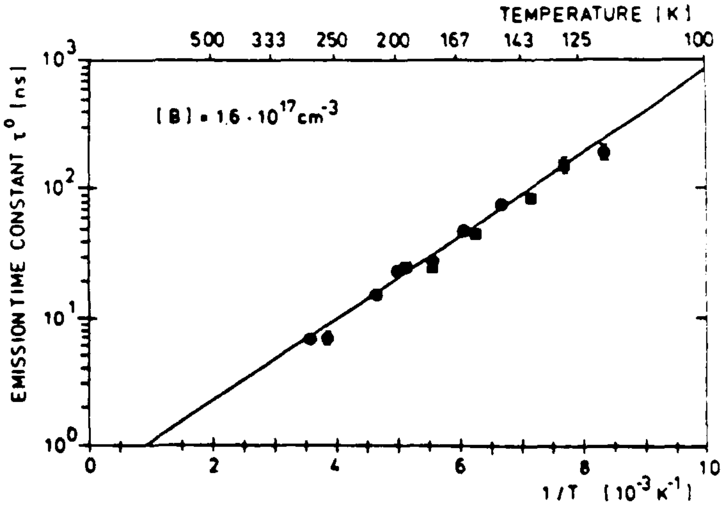

Figure 3 (see text)

as it is observed in other acceptor-hydrogen pairs [11,12]. The impact of the detailed understanding of the Cd-H system on previously published PAC data on the annealing of In-H pairs will be discussed [13].

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Structure and energy of interstitial hydrogen and hydrogen-related complexes in crystalline semiconductors

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I will present a number of recent results, interpreting them in the context of what we already know about the atomic and electronic structure of hydrogen in semiconductors, and highlighting directions for future work.

For hydrogen in silicon, I will discuss results for energies of hydrogen in various configurations, expressed with respect to hydrogen in free space. The configurations include hydrogen on the surface, isolated interstitial hydrogen, hydrogen at dangling bonds, and hydrogen in various complexes with shallow impurities. These results shed light on issues of solubility, stability, and reactivity.

For the compound semiconductors, I have carried out first-principles calculations of hyperfine parameters for isolated interstitial hydrogen in GaAs, in the configurations that were determined by Pavesi *et al.*[1] The values for the two types of tetrahedral interstitial sites are quite close, and close to the experimental value obtained from muon spin rotation.[2] The calculated values for the bond-center site also agree with experiments for "anomalous muonium".[3]

Finally, for hydrogen in ZnSe, I will discuss the relative stability of various sites, show results for hyperfine parameters, and comment on the stability of hydrogen-impurity complexes. The latter issue may be of great importance in light of the recent successes in p-type doping of ZnSe and fabrication of blue laser diodes.

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HYDROGEN IN SILICON: ASPECTS OF SOLUBILITY DIFFUSION AND CATALYZED ENHANCED OXYGEN DIFFUSION

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The earliest estimates of the solubility and diffusion of hydrogen in silicon were obtained by Van Wieringen and Warmoltz [1] from permeation measurements made in the limited temperature range 967°C to 1200°C. They obtained $[H_s] = 4.96\times10^{21}\exp(-1.86\text{eV}/kT)\text{cm}^{-3}$ (Figure 1) so that at 1200°C $[H_s]\sim2\times10^{15}\text{cm}^{-3}$. By extrapolating these results, a vanishingly small solubility of $6\times10^{3}\text{cm}^{-3}$ would be expected at 250°C. However, measurable effects believed to be due to the presence of mobile hydrogen have been found at these low temperatures [2-6], implying that the real concentration is significantly higher. Subsequent work by Ichimiya and Furiuchi [7], involving the use of tritium, yielded $[H_s]=6.61\times10^{19}\exp(-1.39\text{eV}/kT)\text{cm}^{-3}$, and also gave $[H_s]\sim1\times10^{15}\text{cm}^{-3}$ at 1200°C but larger values compared with those of Van Wieringen and Warmoltz, at low temperatures because of the smaller heat of solution. More recently, Peale et al [8] showed that hydrogen diffused into Si at 1280°C from a gas source was retained in the solid during a quench to room temperature and led to the formation of H-S complexes.

We have quantified the heat and quench procedure by using silicon doped with boron in a concentration in the range $6\times10^{16}\text{cm}^{-3}$ to $4\times10^{17}\text{cm}^{-3}$ and measuring the concentration of [H-B] pairs, deduced from the strength of the localized vibrational (stretch) mode (LVM) of the paired hydrogen atoms [9,10]. We showed that pairing occurred in both Cz and FZ Si, that D-B pairs were produced if the diffusion was carried out in deuterium gas, the distribution of H-B pairs was uniform throughout samples up to 1mm in thickness and [H-B] saturated for the highest values of [B]. The IR absorption (Figure 2) was converted to concentrations of [H-B] pairs by establishing calibrations made on passsivated boron doped layers prepared by MBE or ion implantation into CVD epitaxial layers [9]. The concentration [H-B] increased as the heating temperature was increased and we obtained values of $[H_s]=3.7\times10^{19}\exp(-1.2\text{eV}/kT)\text{cm}^{-3}$ for the range 900-1300°C, by assuming that all the dissolved hydrogen was trapped. We then found an extrapolated value of $[H_s]\sim10^{8}\text{cm}^{-3}$ at 250°C, which appears to be reasonable in relation to other observations. Similar measurements have been obtained by other workers [11], and there is a common view that pairing of hydrogen with phosphorus does not occur in such heated and quenched samples.

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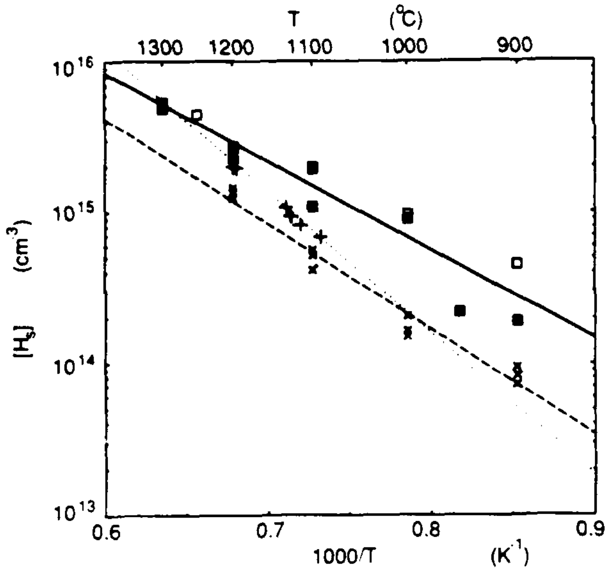

Fig. 1. The solubility of hydrogen in Si: ■ present results; ❑ our previous values; + and dotted line from [1]; x and dashed line from [6].

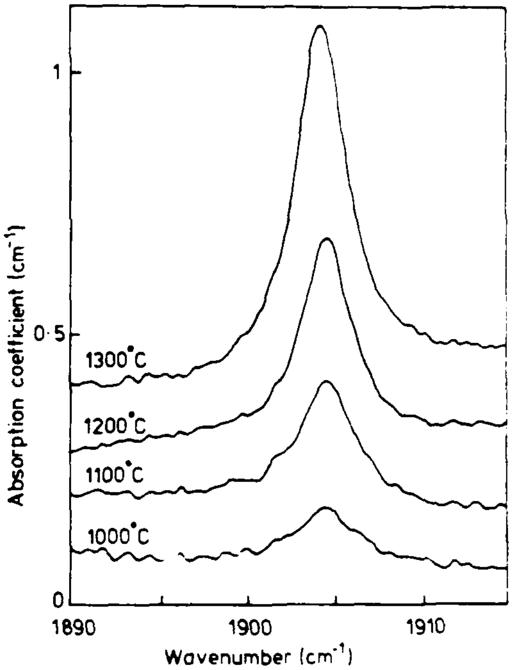

Fig. 2. Absorption (20K) from H-B stretch mode in CZ Si with [B] ~ $9 \times 10^{16} cm^{-3}$ after annealing in H_2 and quenching to 300K.

We measured the diffusion coefficient of oxygen (D_{oxy}) in our heated and quenched samples by the method of relaxation of stress-induced dichroism. D_{oxy} was enhanced at low temperatures (225°C to 350°C), compared with D_{oxy} (Equil) = 0.11 exp (-2.51eV/kT)cm^2s^{-1}, and D_{oxy} (Enh) has an activation energy close to 2.0 eV; however, the pre-exponential factor increased as $[H_s]$ increased, for the higher quench temperatures in the range 600°C to 800°C (Figure 3). We proposed a model in which diffusing hydrogen atoms collided with oxygen atoms to form a transient complex which subsequently dissociated [3,4,5,10]. Such interactions have been modelled by two different first principles calculations [13,14].

The dichroism measurements related only to a limited number of diffusion jumps but it is implied that there would be enhanced long-range oxygen diffusion unless the hydrogen concentration was depleted by out-diffusion, by trapping of diffusing atoms at defects, or the formation of hydrogen molecules or larger clusters. In fact, we have now observed enhanced rates of thermal donor formation in heated and quenched n-type samples, confirming the enhancement of D_{oxy} for times up to 100h at 430°C. Our results confirm the early observation of Fuller & Logan [15] who found that the rate of TD-formation at 450°C in Cz Si grown in a hydrogen atmosphere was ten times greater than that measured for ingots grown in helium.

We now consider heat treatments of samples in the temperature range 225°C - 350°C in a hydrogen (or deuterium) plasma (13.56 MHz, 40W, 2 Torr). It is known that hydrogen diffuses into a surface layer to a depth ~0.1μm in a concentration of $\sim 10^{20}cm^{-3}$. SIMS profiles indicate that [H] becomes smaller than 10^{15}-10^{16} at depths greater than a few microns. Nevertheless, stress dichroism measurements of aligned oxygen impurities reveal enhancements in D_{oxy} that extend from the surfaces of the samples to depths in excess of 0.5mm. By measuring the time dependence of the critical depth for the loss of the dichroism, we obtain a rate of diffusion for hydrogen of $1.7x10^2exp(-1.2eV/kT)cm^2s^{-1}$ (Figure 4). It is unclear whether this expression for D_H corresponds to a trap limited process of atomic hydrogen (our samples contained [B] $\sim 10^{15}cm^{-3}$) or whether the molecular species is involved. Similar profiles with an abrupt interface have been found by spreading resistance measurements [6] for the formation of TD-centres. Thus, there is a greatly enhanced rate of TD-formation in a surface region which is n-type, whereas our samples were p-type.

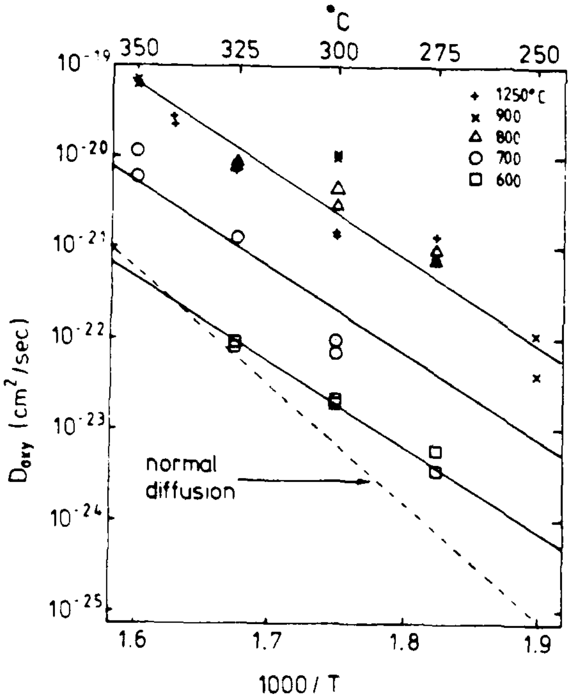

Fig. 3. Arrhenius plot of enhanced D_{oxy} (Enh.) as a function of pre-anneal temperature in H_2 (g).

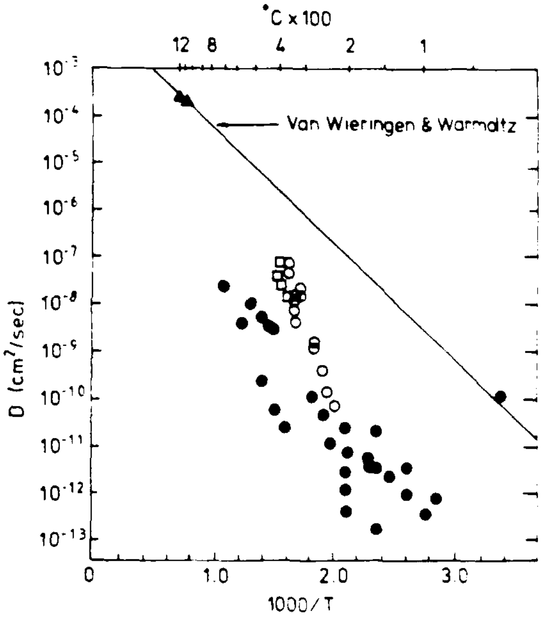

Fig. 4. Arrhenius plot of the hydrogen diffusion coefficient: ▲ and solid line from [1]; ● other previously published data; □ result from [6]; O present results

We have also reported that the total TD-concentration may rise to a value as high as $10^{17}cm^{-3}$ in samples heated in a plasma at a temperature of 350°C and that there are enhanced rates of formation of carbon-oxygen complexes in magnetic Czochralski Si [4]. A set of auxiliary experiments has demonstrated that self-interstitials, vacancies, fast diffusing metals etc are not involved in these various effects. The conclusion is that hydrogen is responsible for the enhancement of the oxygen diffusion. There may be technological applications in view of the extensive use of plasma processing and the passivation of samples in forming gas (hydrogen-nitrogen mixtures).

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The stability of hydrogen complexes in Si and GaAs

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A summary of our capacitance measurements on Si and GaAs samples containing various hydrogen complexes is presented. The stability of these complexes is studied under thermal annealing, optical excitation, or in an electric field.

In Si, the thermal dissociation of electrically neutral, shallow acceptor-hydrogen complexes (AH with A = B, Al, Ga, and In) is found to follow first-order kinetics over the entire annealing process, provided the isothermal anneal is performed with a reverse bias applied to the Schottky diode [1,2]. An example of the $C(V)$-profile is presented in Fig. 1. A boron-doped hydrogenated sample is annealed at a temperature $T_a = 80°C$ with a reverse bias $V_R = 60$ V. The active acceptor profiles are shown for different annealing times t_a(crosses). As t_a increases, the dopant is progressively reactivated in the region $x \leq 7\,\mu m$, while the neutralization becomes more pronounced in the region 7 $\mu m < x < 12.5\ \mu m$. The dopant passivation results from the formation of a neutral BH complex which can be thermally dissociated. The positively charged atomic hydrogen released, drifts under the electric field present in the space charge region and accumulates in the low field region, where new BH complexes are then able to form. The profiles $N_I(x, t_a)$ are almost flat in the region $x < 3\ \mu m$. A quantitative analysis of the acceptor

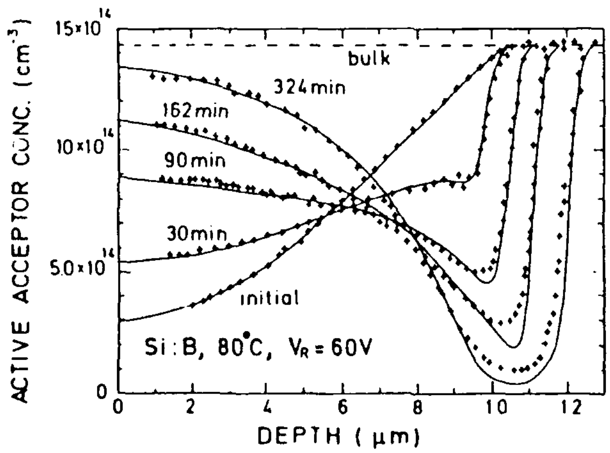

Figure 1: *Evolution of the active boron concentration profile as a function of the reverse-bias annealing time ($V_R = 60$ V, $T_a = 80°C$). Prior to the anneal, the sample is treated in a H plasma (120°C, 2 h), and the 2-μm-thick surface layer is removed. The solid lines represent the profiles calculated.*

reactivation in the high-electric field region ($x < 3$ μm) is established by plotting the electrically inactive acceptor concentration $A(t_a) = N_{A0} - N_I(2\ \mu\mathrm{m}, t_a)$ *vs* t_a (Fig. 2). N_{A0} is the uniform acceptor concentration in the nonhydrogenated control sample. The reactivation of the acceptor follows the equation for first-order kinetics, characterized by $A(t_a) = A(t_a = 0)\, exp[-\nu(T_a)t_a]$, and the dissociation frequencies ν follow an Arrhenius law

$$\nu(T_a) = \nu_0\, exp(-E_d/kT), \tag{1}$$

where ν_0 and E_d are the attempt frequency and the dissociation energy, respectively.

A corresponding study of the behavior of the different impurity hydrogen complexes has been carried out for GaAs, using both n- and p-type material [3,4,5]. The drift of hydrogen in an applied electric field convincingly demonstrates the existence of negatively charged hydrogen in n-type GaAs and positively charged hydrogen in p-type GaAs as the mobile species. Table I summarizes the dissociation energies and attempt frequencies in Si and GaAs, determined by the $C(V)$ method described above.

A dramatic enhancement of the reactivation of the inactive donors and acceptors occurs for above band gap illumination of the sample [5,6,7,8]. A careful analysis of the reactivation kinetics reveals a second order process, due to the formation of stable hydrogen centers which contain at least two hydrogen atoms [6].

The $C(V)$ profiling technique allowed us to determine the diffusion constant for hydrogen. In p-type Si the hydrogen diffusion was studied in the temperature range 60°C-140°C for different boron concentrations. Reverse bias annealing of the samples for long periods generates a step-like profile of the inactive acceptor concentration. Annealing

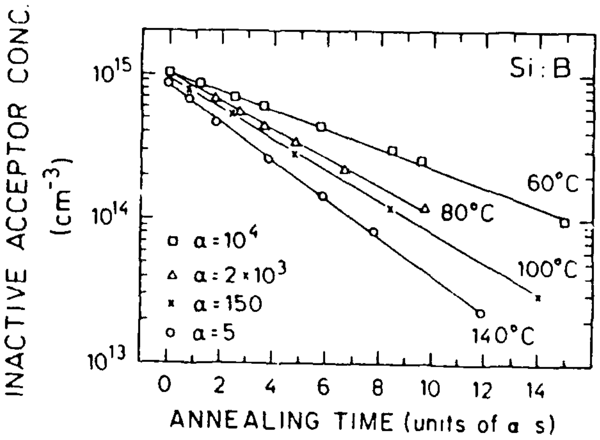

Figure 2: *Inactive boron concentration vs annealing time, measured in the high-field region ($x = 2\mu m$) of a reverse-biased diode. A reduced time scale is used to clearly reveal the first-order kinetics in the entire annealing temperature range*

	Silicon				GaAs	
	BH	AlH	GaH	InH	ZnH	SeH
E_d	1.28 ± 0.03	1.44 ± 0.02	1.40 ± 0.03	1.42 ± 0.05	1.33 ± 0.03	1.52 ± 0.05
ν_0	2.8×10^{14}	3.1×10^{13}	6.9×10^{13}	8.4×10^{13}	7×10^{13}	2×10^{13}
Ref.	[1]	[1]	[1]	[1]	[3]	[4]

Table 1: *Dissociation energies E_d (eV) of acceptor and donor-hydrogen pairs and attempt frequencies ν_0 in Si and GaAs.*

without applied bias leads to a levelling out of the step due to the diffusion of hydrogen (Fig. 3). An analysis of the profiles after different annealing times and temperatures allows us to evaluate the hydrogen diffusion constant. Under our experimental conditions the diffusion of hydrogen appears to be entirely trap limited [9].

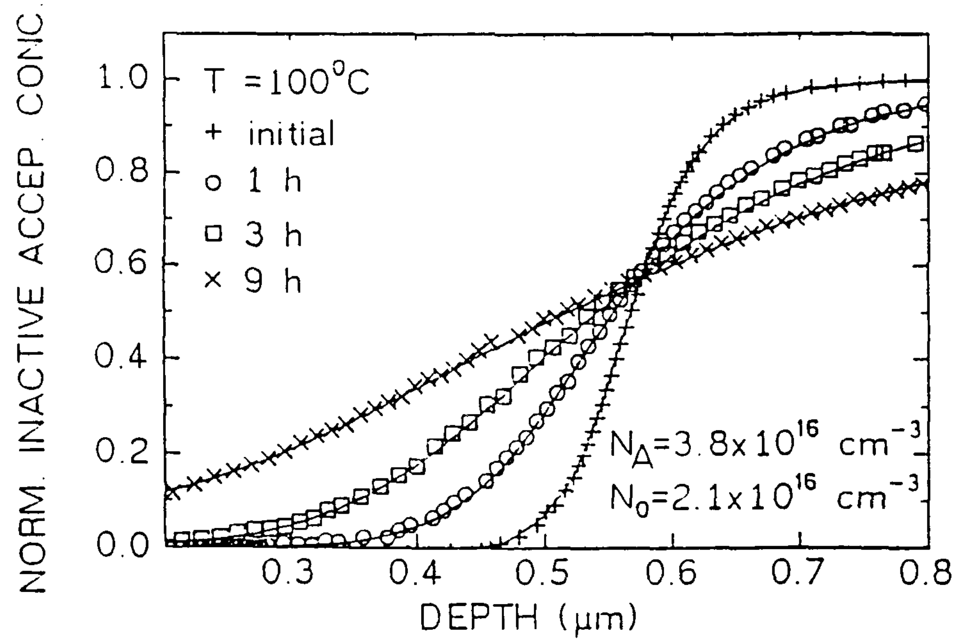

Figure 3: *Normalized inactive boron profiles after zero bias annealing for increasing times t_D at 100°C. The symbols N_A and N_0 denote the total boron concentration and the normalization factor.*

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RECENT STUDIES OF HYDROGEN IN SILICON AND III-V SEMICONDUCTORS

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Summary

Given below are summaries with highlights of several recent studies performed at the Xerox Palo Alto Research Center on hydrogen in crystalline semiconductors. The references at the end of the summary identify the individual contributors and where the full-length papers have been or will be published.

Migration of the H_2^* Complex and its Relation to H^- in *n*-type Si:[1]

Thermally-induced depth redistribution of the H_2^* complex was determined from SIMS. The activation energy for migration was found to be 0.81 ± 0.06 eV. However, the data do not determine whether the migration involves dissociation. Both the migration kinetics and direct measurements on reverse-bias-annealed Schottky diodes show that for annealing times up to 25 h at temperatures near 60°C there is no detectable redistribution or dissociation of H_2^*, contradicting a currently-ambiguous claim that such annealing produces a large redistribution due to dissociations yielding H^-. The effect of the presence of H_2^* on the evolution of the neutralized-donor profiles at such temperatures is negligible.

H-induced Platelets in Silicon--Separation of Nucleation and Growth:[2]

It has been demonstrated that the growth of hydrogen-induced platelets in *n*-type single-crystal silicon can be controlled independently of the nucleation process. The results demonstrate that the suppression of platelet formation at high hydrogenation temperatures (e.g., >250°C) is a consequence of the suppression of platelet nucleation and that platelets nucleated at lower temperatures (e.g., 150°C) grow markedly at the higher temperatures. The kinetics of platelet formation are qualitatively explicable by classical nucleation theory. The platelets, though somewhat reminiscent of the Guinier-Preston zones long familiar in certain metallic alloys, have novel traits that suggest that short-range interatomic forces are sufficiently anisotropic to produce the two-dimensional silicon-hydride phase.

Thermal Dissociation Energy of the Si-H Complex in *n*-type GaAs:[3]

The thermal dissociation kinetics of the Si-H complex in *n*-type GaAs:Si were determined from bias-temperature anneals on hydrogenated Schottky diodes. The anneal kinetics are approximately first order and yield a thermal dissociation energy of 1.2±0.1 eV. Depth redistribution of the Si-H complex both within the depletion layer of biased diodes and in the field-free region of unbiased diodes suggests that hydrogen in *n*-type GaAs can migrate as a negatively charged species.

Hydrogen Passivation and Reactivation of Se Dopants in AlGaAs:[4]

The reactivation kinetics of Se-H complexes in *n*-type $Al_xGa_{1-x}As$ ($x=0.25$) were determined in the space-charge layer of reverse-biased Schottky diodes. The thermal dissociation energy for recovery of Se shallow donors was found to be 1.48±0.15 eV. The observed redistribution of Se-H complexes in the depletion layer strongly suggests that hydrogen migrates in *n*-type AlGaAs as a negatively charge species.

Hydrogen Passivation of Si and Be Dopants in InAlAs:[5]

Hydrogen passivation and thermal reactivation of Si donors and Be acceptors were investigated in InAlAs. The alloy was grown by MBE, lattice matched on InP, and passivated by exposure to monatomic hydrogen at 250°C (1h) from a remote hydrogen plasma. In both Si and Be doped samples, the dopants were passivated by over two orders of magnitude to a depth of ~2 µm (the epilayer thickness). Furthermore, DLTS revealed essentially complete passivation of three known deep donor levels, which are commonly designated EA1, EA3, and EA4. A subsequent anneal at 500°C (2 min) completely reactivated the passivated shallow donors. In addition, SIMS was performed on deuterated samples to determine the distribution of hydrogen. In both Si and Be doped material, the deuterium profiles were essentially identical to the dopant profiles throughout the epilayers. This behavior resembles the situation of H in B-doped Si and suggests that hydrogen migration in InAlAs is limited by dopant trapping.

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Multitrapping of atomic Hydrogen in doped crystalline silicon.

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The multitrapping of H atoms near boron or phosphorus sites in doped crystalline silicon has been investigated in the framework of pseudopotential-density-functional methods. Although both dopants give rise to metastable complexes containing several H atoms, only the P dopant has the capability to trap H ions by Coulombic attraction. This is due to the peculiar electronic structure of the metastable configurations of the Si-H-P complex. The different properties shown by the phosphorus- and boron-containing complexes may explain the different diffusion behaviour shown by the H diffusion in boron- and phosphorus-doped silicon.

Modeling of Hydrogen Diffusion in Semiconductors

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We present a theoretical model for the diffusion of hydrogen in semiconductors. This model was initially developed to describe the diffusion of H in Si [1-4], but has been shown later convenient in the case of GaAs [5]. In fact, due to the generality of the equations used, it is believed that this model can likely be used for any semiconductor, with a suitable choice of the model parameters.

In this analysis, it is considered that hydrogen can have both an acceptor (E_a) and a donor (E_d) level in the band gap, and thus exists in the three charge states H^+, H^0, and H^-, the relative concentrations of which depend on the local Fermi level position :

$$[H^-] = (n/n_a)[H^0] \tag{1a}$$

$$[H^+] = (n_d/n)[H^0] \tag{1b}$$

where n is the local concentration of free electrons, and n_a and n_d reflect the position of the E_a and E_d levels in the gap,

$$n_a = N_c \exp[-(E_c-E_a)/kT) \tag{2}$$

and the corresponding relation for n_d. The isolated hydrogen atoms can react with the ionized acceptors (A^-) or donors (D^+) to form neutral complexes :

$$H^+ + A^- \rightleftharpoons AH \tag{3a}$$

$$H^- + D^+ \rightleftharpoons DH \tag{3b}$$

In addition to these neutralization reactions (dopant passivation), the possible formation of H_2 complexes is also taken into account, either by reaction between two H^0 atoms, or by reaction between H^0 and H^+ :

$$H^0 + H^0 \rightleftharpoons H_2 \tag{4a}$$

$$H^0 + H^+ \rightleftharpoons H_2 + h^+ \tag{4b}$$

Finally, the high H concentration in the damaged surface region is described by trapping on plasma-related unidentified traps T :

$$T + H^0 \rightleftharpoons TH \tag{5}$$

Assuming that the only mobile species are the free hydrogen species in their various charge states, the evolution of the various concentrations is given by the following set of differential equations :

$$\frac{\partial[H]^{tot}}{\partial t} = -\frac{\partial J_H}{\partial x} \quad (6a)$$

$$\frac{\partial[H_2]}{\partial t} = k_{H_2}[H^0]^2 + k^+_{H_2}[H^0][H^+] - k'_{H_2}[H_2] \quad (6b)$$

$$\frac{\partial[AH]}{\partial t} = k_{AH}[A^-][H^+] - k'_{AH}[AH] \quad (6c)$$

$$\frac{\partial[DH]}{\partial t} = k_{DH}[D^+][H^-] - k'_{DH}[DH] \quad (6d)$$

$$\frac{\partial[TH]}{\partial t} = k_{TH}[T][H^0] \quad (6e)$$

where the total hydrogen flux is given by:

$$-J_H = \left(D_{H^0} + \frac{n}{n_a} D_{H^+} + \frac{n_d}{n} D_{H^-}\right) \frac{\partial[H^0]}{\partial x} \quad (7)$$

The local density of free carriers is obtained by the simultaneous resolution of Poisson's equation.

In Equs.(6), the rate constants for the reactions (3) to (5) are calculated from the values of the diffusivities, assuming purely diffusion limited reactions. The corresponding capture radii are either 5 Å, or the Coulombic radius for reactions (3).

Fits on numerous experimental profiles, covering experimental results obtained on substrates with different starting doping levels, allow the determination of the unknown parameters. Examples of fitted profiles, and the corresponding extracted diffusivities, are given in the two pages of figures, in the case of n- and p-type Si, and for semi-insulating and p-type GaAs(Zn).

It is emphasized that the fits on the experimental profiles led us to rule out the possibility of H_2 formation at the diffusion temperature.

Acknowledgements

This work has been performed in close collaboration with the groups of the Laboratoire de Physique du Solide of CNRS Bellevue. The author is particularly grateful to M. Aucouturier, D. Ballutaud, P De Mierry, and R. Rizk for the Si results, and to J. Chevallier and R. Rahbi in the case of GaAs.

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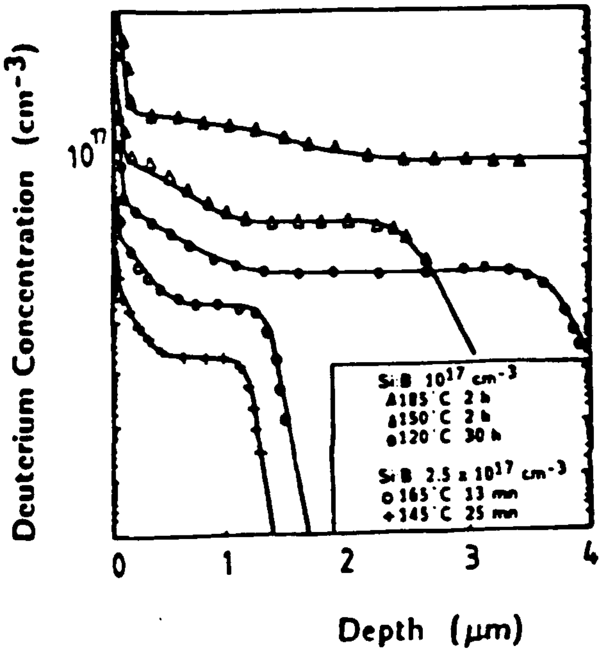
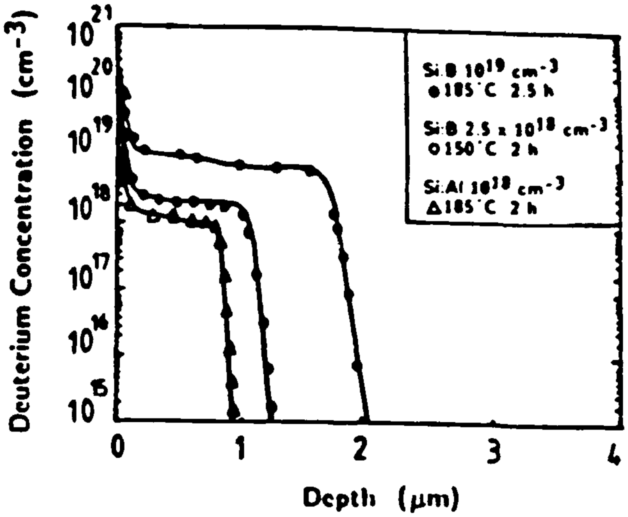
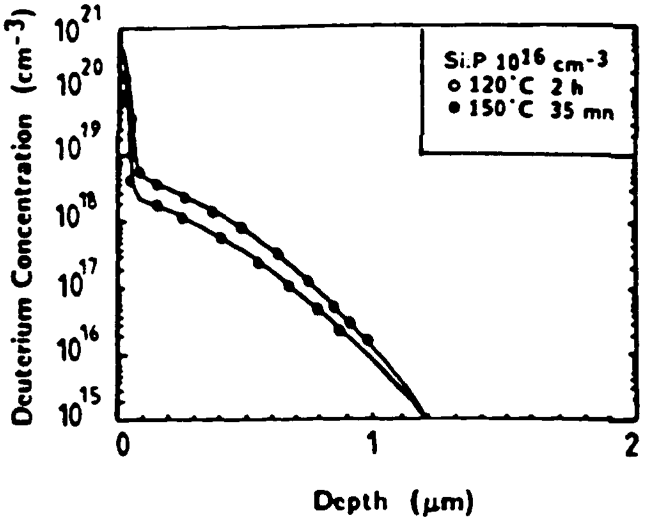
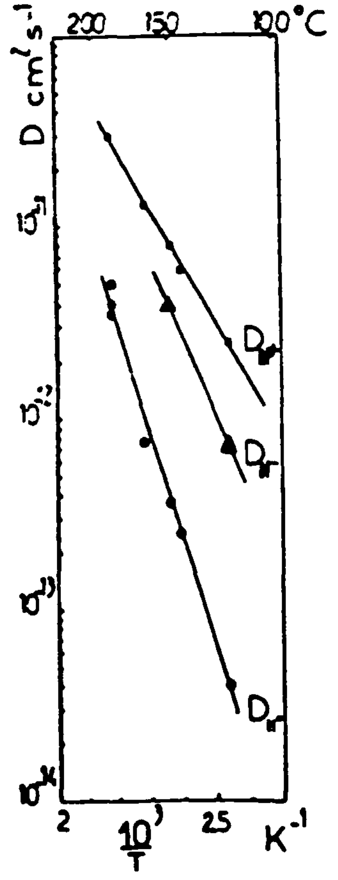
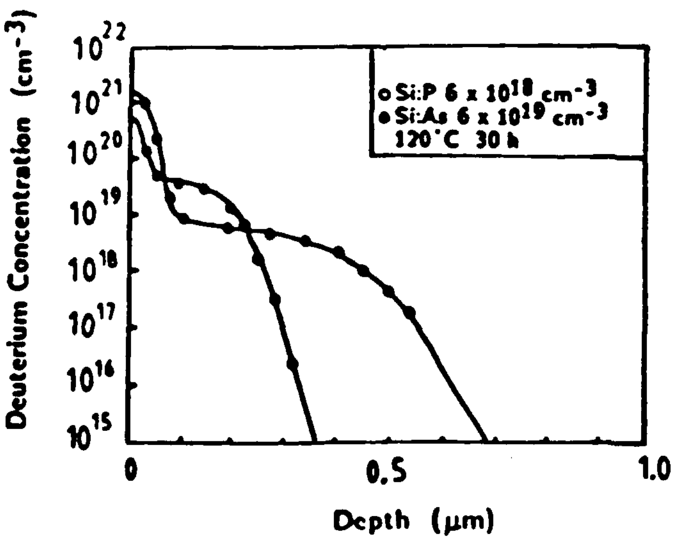
H in Si : Simulated Profiles and Extracted Diffusivities.



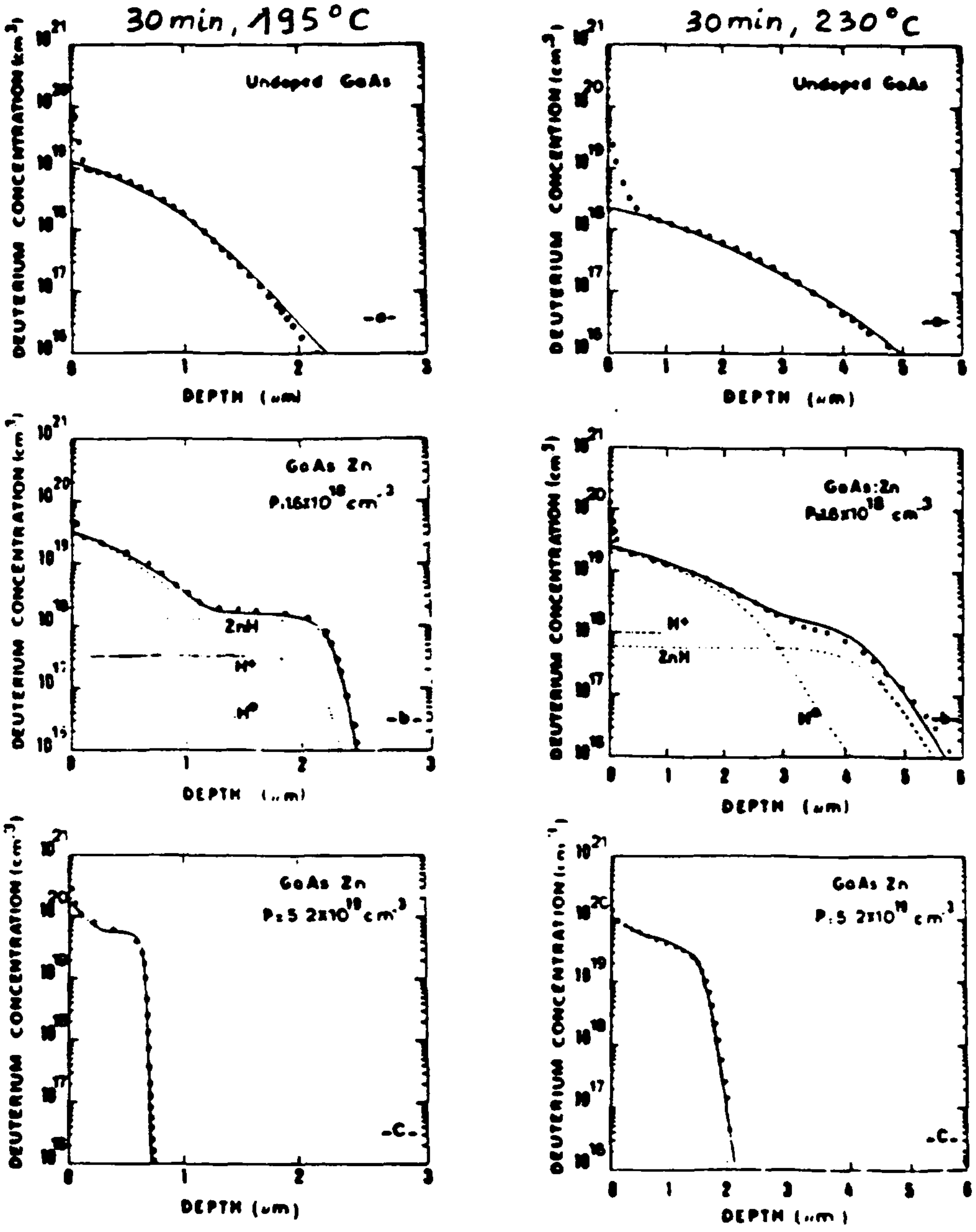


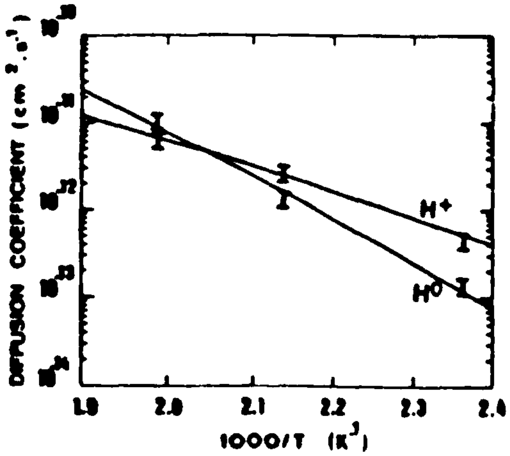






H in GaAs : Simulated Profiles and Extracted Diffusivities.





(Extended Abstract for the Workshop on Hydrogen Migration and the Stability of Hydrogen Related Complexes in Crystalline Semiconductors, Horben bei Freiburg, Germany, 3-6 November 1991).

"DIFFUSION AND ELECTRONIC STATES OF HYDROGEN IN n-GaAs: Si and n-$Al_xGa_{1-x}As$: Si".

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Among the different problems raised by the behaviour of monatomic hydrogen in crystalline semiconductors, one is related to its charge states and its interactions with impurities as it migrates in the lattice.

From drift experiments of hydrogen under electric field it has been recently established that H^- is a migrating species in hydrogenated n-GaAs doped with tellurium [1] or selenium [2] and also in n-GaAs and n-AlGaAs doped with silicon [3]. Based on the evolution of the hydrogen diffusion profiles with the alloy composition and with the silicon donor concentration, we bring information on the dominant diffusing species in Si doped $Al_xGa_{1-x}As$ alloys. To explain the data we propose a model based on the alloy composition dependence of the hydrogen acceptor level position with respect to the conduction band of the materials.

Deuterium diffusion experiments have been performed on a series of MBE grown $Al_xGa_{1-x}As$ epilayers doped with silicon. The alloy composition ranges from $x = 0$ to $x = 0.30$. Two silicon doping levels have been used: $1.5x10^{18}cm^{-3}$ and $2x10^{17}cm^{-3}$. All these samples have been exposed to a R.F. plasma at T = 190-240°C for t = 30 min.

Figures 1 and 2 present the deuterium diffusion profiles in the series of highly doped samples. In GaAs, we find a deuterium distribution very close to a complementary error function (erfc). As the aluminum content increases, the erfc function is progressively replaced by a diffusion profile characterized by a plateau followed by an abrupt decrease of the deuterium concentration. This shape is characteristic of a strong trapping mechanism. This situation occurs above $x \gtrsim 0.06$ for this doping level of $1.5x10^{18}cm^{-3}$. For all studied compositions above this critical value, the diffusion profiles are very similar with the same diffusion depths.

The solubility of deuterium in the plateau region of alloys with $0.035 < x < 0.15$ is markedly close to the active dopant concentration. For $x > 0.22$, DX centers governed the electrical properties of AlGaAs: Si alloys. For $x = 0.30$, a freeze-out of the free carriers occurs at 300K but, at 513K, which is the hydrogen diffusion temperature, most of the DX centers are ionized and the exhaustion regime occurs. Then, the solubility of deuterium in $Al_{0.30}Ga_{0.70}As$ alloys is still equal to the active dopant concentration at the diffusion temperature and deuterium species interact with the positively charged DX^+ centers. This interaction is at the origin of the neutralization of the silicon donors observed in deuterated $Al_xGa_{1-x}As$: Si alloys with $0 < x < 0.37$ [4, 5, 6].

For the series of alloys containing $2x10^{17}cm^{-3}$ silicon donors, we qualitatively have the same change of diffusion profiles as the aluminum content increases, but the appearance of profiles exhibiting trapping characterictics occurs above $x \gtrsim 0.25$ (instead of $x \simeq 0.06$ for the high doping level).

From vibrational absorption spectroscopy it is known that the neutralization of silicon donors by hydrogen in GaAs: Si and AlGaAs: Si proceeds through the formation of Si-H bonds. It has been established that the wagging modes of Si-H in GaAs and AlGaAs are very close to each other ($896.8cm^{-1}$ in GaAs: Si and $896.4cm^{-1}$ in $Al_{0.2}Ga_{0.8}As$: Si) [7, 8] and that the dissociation energy of Si-H bonds is basically independent on the aluminum composition [3]. For these reasons, we rule out the possibility that the above changes of deuterium profiles with alloy composition are associated with a change of the thermal dissociation probability of Si-H complexes.

Instead, we propose an explanation in terms of hydrogen diffusing with different charges states. In other words, we assume that hydrogen behaves as a deep acceptor level which is slightly resonant in the conduction band of GaAs and which merges as a localized state in the forbidden gap of $Al_xGa_{1-x}As$. As a consequence, for samples where the Fermi level is well above the hydrogen acceptor level, H^- is the dominant diffusing species and the hydrogen diffusion profile will result in a trapping of H^- by the positively charged donors, by a long range interaction. For samples where the Fermi level is close to or somewhat below the hydrogen acceptor level, hydrogen diffuses in two different charge states H° and H^-. However, in this case, the high effective diffusivity of neutral hydrogen governs the experimental hydrogen diffusion profile.

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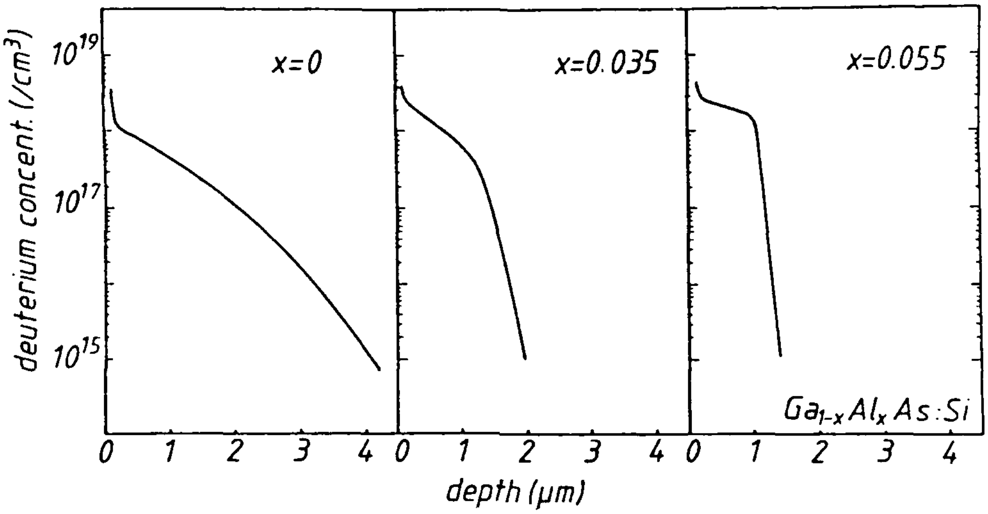

Figure 1 : Deuterium diffusion profiles in n-type GaAs: Si and $Al_xGa_{1-x}As$: Si alloys with low amounts of aluminum. The plasma conditions are T= 240°C, t = 30 min. and P = 0.04W/cm^2.

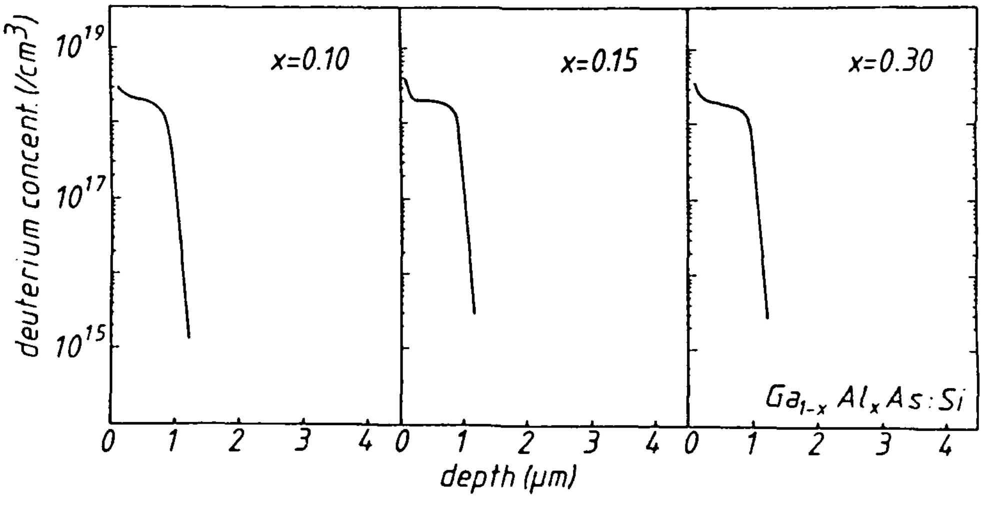

Figure 2 : Deuterium diffusion profiles in a series of n-type $Al_xGa_{1-x}As$: Si alloys with different values of x. Same plasma conditions as figure 1.

THE EXPERIMENTAL EVIDENCE FOR VARIOUS CHARGE STATES OF HYGROGEN IN SILICON

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The question of the preferred charge states of interstitial hydrogen in the silicon lattice has generated increasing controversy in the past few years. Theoretical investigations[1-3] of the minimum free energy of H^0, H^+, and H^- by Local Density Functional methods, Molecular Orbital techniques, and Hartree-Fock calculations have not generated the unanimity of results that experimentalist find comforting. In addition, while recent experimental results have been interpreted as supporting the existence of H^0 and H^+, the evidence for H^- is controversial. In this talk I will attempt to review the available experimental data for various charge states of hydrogen; I will also point out some caveats that should be kept in mind when interpretation of these measurements is attempted.

Recently Herring[4] and others[5] have presented a Schockley, Read, Hall analysis of the fractional occupation of various H charge states as a function of the local electron and hole populations. I will review these briefly because they should guide us in anticipating the charge states expected in neutral and depleted regions. I say "should" because the complications of charge dependent lattice positions, Franck-Condon shifts, and negative U phenomena have not really been addressed and may well complicate the picture. In addition to the simple equilibrium case, where the position of the Fermi level with respect to the +/0 and 0/- demarcation energies determines the H charge occupation, this analysis also predicts that the charge state ratios in depletion depend only on emission rates and thus should be independent of the dopant type.

Early work by Tavendale et al[6] and Johnson[7] established that electric fields applied during annealing of p-type Schottky diodes or during hydrogenation of n^+/p junctions strongly affected the resultant evolution of H bonded to acceptors. The first group suggested that these data were strong evidence for field-induced drift of H^+, while Johnson cautioned that they might only prove that holes were necessary for the H•acceptor bonding process. A later, more complete study of the thermal dissociation of H from acceptors by Zundel and Weber[8] established that, under reverse diode bias, all debonded hydrogen (within the error limits of the measurement) was driven deeper into their diodes and rebonded to acceptors. This conservation of H proved that all of the released H moved under the influence of the applied field and is strong evidence for the existence of H^+ in depletion. Studies of H penetration and debonding[5,9] by our own group at Sandia have also shown that: 1. room temperature motion of H is accelerated by increasing depletion layer electric fields, and 2. the debonding rate of H from acceptors is strongly dependent on the local population of majority and minority carriers. We find that it is difficult to explain the detailed functional dependence of our results without supposing that H is usually neutral but positive ~1/10 of the time in depletion and almost always positive in equilibrium.

The evidence for H^- is more problematic. Work by Johnson and Herring[10] showed that SIMS-determined densities of H (D) in n-type Si deuterated at 300 C increased with donor density in the 10^{17} - 10^{19} cm^{-3} range. This was even true when a lightly n-doped epitaxial layer covered a more heavily doped substrate. They interpreted these results by suggesting that $H^- > H^0$ at 300 C, and that the population of H^- became larger as the Fermi level approached the conduction band bottom. However, it seems unlikely that mobile H^- would remain in their samples between treatment and analysis; thus the form of H detected by these SIMS analyses is likely some other trapped species. This clouds the interpretation of these results. More recently, work by Tavendale et al[11], Zhu et al[12], and our group[13] has shown that **some, but not all** of the H thermally released from donors rebonds deeper in the sample when n-type Schottky diodes are reverse-bias-annealed. By analogy with data seen in p-type diodes, the first two groups cited these data as evidence for the field-induced motion of H^-. However, our group has offered the explanation that depletion enhances the thermal debonding rate, and this causes the transfer of some of the debonded H to donors located deeper in the diode. Other data[13] showing the influence of the electron and hole density on the debonding rate clearly shows that interpretation of these types of debonding measurements must be approached with caution. Perhaps the most serious objections to supposing that H^- exists in depletion are: 1. From the SRH analyses we anticipate that the same admixture of charge states exists in a depletion region regardless of doping type, but no evidence of H^- can be found in any data from reverse biassed p-type samples[8,9]. 2. Penetration of H in reverse biassed n-type diodes at temperatures where H•donor pairs are stable has been shown to be consistent with the same mixture of H^0 and H^+ seen in p-type diodes[9]. We conclude that, unless H^- is a long lived, metastable byproduct of donor•H dissociation, its existence in silicon is doubtful.

Finally I shall review the evidence that the introduction of hydrogen gives rise to trapped positive charge in a form that appears to be quite distinct from mobile H^+. Support for this assignment comes directly from H penetration studies on n-type diodes[9] and, indirectly, from p-type penetration and debonding measurements. This trapped charge decays slowly (hours to days) and appears to be the primary reason for the large impedance changes seen in hydrogenated Schottky diodes. One interesting consequence of this charge is that it eventually establishes fields which repel H^+ back toward H exposed surfaces; this may contribute to the very slow, non $t^{1/2}$-like, dependence of H penetration that is almost always observed in capacitatve and SIMS profiling work on H exposed samples.

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NITROGEN-HYDROGEN COMPLEX AND HYDROGEN CHARGE STATES IN GaP

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In the case of GaAs, the donor level of hydrogen has been located within the bandgap by monitoring the type of complexes formed as function of the Fermi energy.[1,2] The complex used for probing H^+ was the C-H complex which is formed according to the reaction : $C^- + H^+ \rightarrow (C\text{-}H)^0$. On the other hand, the complexes used for probing H^0 were involving lattice defects and in particular a gallium vacancy having one of its dangling bonds saturated with hydrogen.[3,4] The formation of this type of complexes is not well understood and it is possible that in fact, the vacancy and neutral hydrogen do not exist independently, but that the presence of neutral hydrogen itself is at the origin of the hydrogenated defect. In order to avoid this ambiguity, a hydrogen related complex involving an impurity would have been a more suitable probe for H^0.

The few results available[5,6] concerning the passivation of impurities in GaP by hydrogen seem at first sight contradictory. Singh and Weber[5] report on the passivation of carbon and nitrogen impurities, whereas Mizuta et al.[6] claim that carbon is not neutralized in n-type GaP and isolated nitrogen not passivated in p-type material. Having in mind the concept developped in Ref. 1 and 2, these two types of results are not necessary in contradiction, but can be due to Fermi energy effects. The neutralization of carbon in p-type GaP having been recently demonstrated,[7] we have investigated the passivation of nitrogen in GaP using infrared spectroscopy.

In semi-insulating GaP grown by the liquid encapsulated Czochralski (LEC) technique containing nitrogen (in low concentration in order to avoid the formation of nitrogen pairs) and unintentional hydrogen as it is always the case in this type of material,[8] we have observed an intense absorption line at 2885.5 cm^{-1} (at 6 K). This line is always accompanied by an other one at 2879.7 cm^{-1} whose intensity is 3.6 ± 0.5 ‰ of the 2885.5 cm^{-1} one as shown in Fig.1. This ratio matches exactly the ratio of the natural abundances of ^{15}N and ^{14}N ; moreover, the 5.8 cm^{-1} shift between the two lines is very close to the isotopic shift calculated for the stretching mode of an imaginary N-H diatomic molecule having an energy of vibration of 2885 cm^{-1} (for ^{14}N) : 6.4 cm^{-1}. This demonstrates that the two lines observed correspond to the vibration of ^{14}N-H and ^{15}N-H bonds. One can safely conclude that unpaired nitrogen is passivated by hydrogen in semi-insulating GaP.

In all the samples investigated, an other line at 2054.0 cm^{-1} is always present; the ratio of the integrated intensities $I(2885) / I(2054) = 9.5 \pm 0.5$ is sample independent. We are therefore tempted to attribute the 2054 cm^{-1} line to one of the vibration modes of the N-H complex. In all of our samples, the intensity of the 2054 cm^{-1} line was unfortunately not strong enough for observing the corresponding mode involving ^{15}N.

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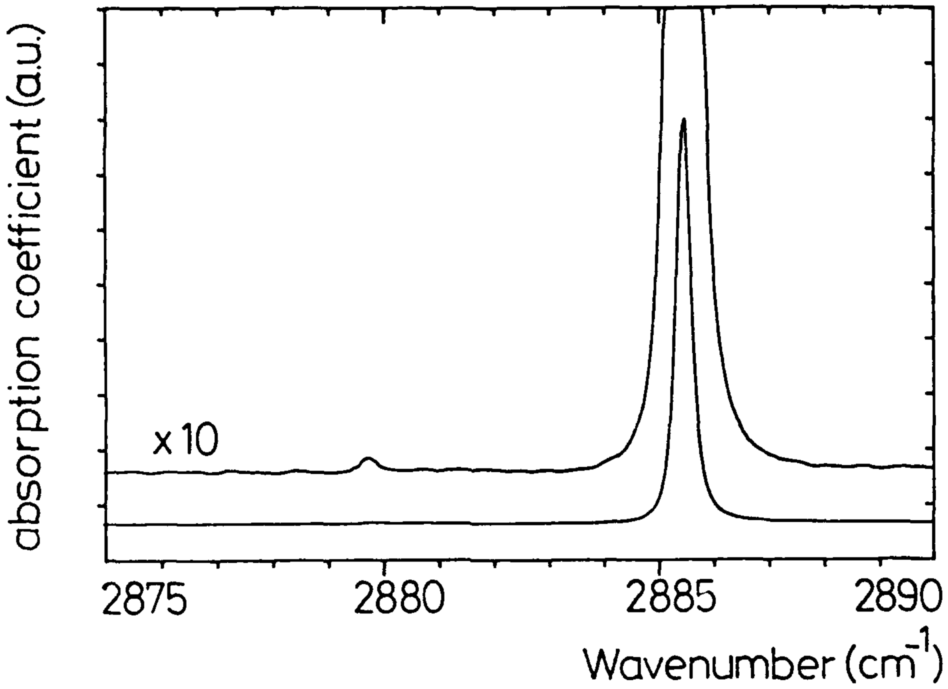

FIG. 1. Absorption of the N-H stretching modes of vibration. Both ^{14}N- and ^{15}N-related modes can be observed.

We have performed experiments under uniaxial stress on both modes of vibration at 2885 and 2054 cm^{-1} in order to have a deeper insight into the miscroscopic structure of the N-H complex. The effects of stress on the 2885 cm^{-1} line correspond to what is expected for a non degenerate mode of vibration of a center of trigonal symmetry[9] (with equal populations of the four equivalent configurations). Therefore this mode of vibration corresponds to a streching mode of N-H bonds aligned along the four trigonal axes. In order to know whether the complex is able to reorient among its four equivalent configurations, we have undertaken stress-induced dichroism experiments.[9] In fact, applying uniaxial stress for one hour at room temperature, we have not been able to induce any dichroism. This means that the complex is not able to reorient among its four equivalent configurations at room temperature.

We have also performed uniaxial stress experiments on the 2054 cm^{-1} local vibrational mode. Very surprisingly, this LVM does not split for any direction of the applied stress; it is just shifted independently of the stress direction. Such a behavior for this LVM is not understandable without assuming a motion of the complex which averages the stress effects.

In order to explain the stress measurements on both LVMs, we propose that the 2885 cm^{-1} and 2054 cm^{-1} LVMs are respectively the stretching and wagging modes of the N-H complex. The complex precess around a trigonal axis in such a way that the precession averages out the stress effects on the wagging mode and gives a trigonal impression on the stretching one. The precession is supposed to occur around an antibonding position for the following reasons : i) this location leads to high energy wagging modes (in contrast with the bond center one) ii) reorientation among the four equivalent configurations is difficult in this location. The proposed microscopic structure is schematized in Fig.2.

In order to have an insight into the formation of the N-H complex, we have looked at its existence in various samples containing carbon and nitrogen (and of course hydrogen) with various Fermi energies. There is practically no coexistence of the C-H and N-H complexes. This means that different hydrogen charge states are involved in the formation of the two complexes. H^+ being involved in the formation of the C-H complex, H^0 is responsible of the formation of the N-H one. Isoelectronic impurities are therefore the most suitable probes for H^0.

We have used the same procedure as the one used previously in GaAs[1,2] for locating the hydrogen donor level in GaP. We have observed that in the few very small samples in which both the C-H and N-H complexes were observed (most probably in different parts of the samples), two charge states of the vanadium impurity could also be observed : $V^{(+)}$ and $V^{(0)}$. This means that the donor level of vanadium almost coincide with the hydrogen one. This would be strictly true if the complexes were formed at zero temperatures; in fact, they are formed during the cooling stage of the LEC growth at temperatures below 400 °C. At this temperature, the decrease of the Fermi function extends over about 0.2 eV and therefore, we can say that the vanadium and hydrogen donor levels coincide within 0.1 eV.

Several values of the vanadium donor level have been given : 0.35 ± 0.1,[10] 0.2 ± 0.05,[11] 0.33 ± 0.03,[12] and 0.25 ± 0.02[13] above the top of the valence band. All these values seem to converge around 0.25-0.30 eV above the top of the valence band. Therefore the hydrogen donor level in GaP is located at 0.3 ± 0.1 eV above the top of the valence band.

It had been assumed[14] that, among the III-V compounds, the hydrogen donor level is pinned to an absolute energy with respect to the vacuum level; the comparison between GaAs[1,2] and GaP shows that this assumption is not relevant.

We have shown that the nitrogen-hydrogen complex only forms if the Fermi level is higher than 0.3 eV above the valence band maximum. This explains why several attempts[6] of nitrogen passivation have been unsuccessful : at high nitrogen doping level, nitrogen pairs are formed; the pairs act as shallow acceptors and the samples become p-type with a Fermi level too low for the unpaired nitrogen to be passivated.

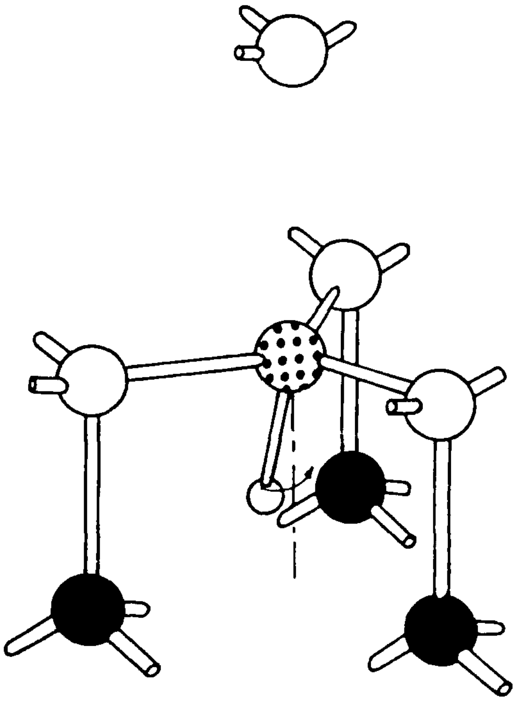

FIG. 2. Schematic representation of the N-H complex.

Acknowledgements

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HYDROGEN STABILITY AND PASSIVATION OF SHALLOW AND DEEP CENTERS IN GaSb AND InSb

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Abstract

Spreading resistance and C-V measurements show that hydrogen can passivate shallow acceptors and to some extent, shallow donors in GaSb and InSb. Deep levels, as revealed using DLTS and photoluminescence, have also been passivated. The hydrogen-defect complexes are destroyed by heating at 250 to 300°C. SIMS has been used to determine the physical location of the hydrogen atoms and the doping densities of impurities.

INTRODUCTION: Hydrogen passivation of defects and impurities in some III-V materials (GaAs, InP, AlGaAs, InGaAs) is documented, and understood to some degree.[1-3] Recently, studies have begun on InSb,[4] InGaP,[5] and GaP.[6] A common concern is whether there are general trends in the behavior of H in these III-V materials, and whether this behavior can be utilized in the fabrication of devices in these materials, which have less mature processing technologies. In this paper, we report the effects of H treatment on GaSb, and to a lesser degree, on InSb. One application for GaSb is with quaternaries to produce lasers and photodetectors in the 2-μm wavelength range.[7,8]

EXPERIMENTAL APPROACH: Hydrogen treatment studies were carried out on p^+-GaSb samples doped with either Si or Zn (10^{18}-10^{19} cm^{-3}), on n-GaSb samples doped with Te ($2x10^{17}$-$2x10^{18}$ cm^{-3}), on undoped GaSb samples with native acceptors of about 10^{17} cm^{-3}, on Be-doped GaSb layers (~1μm) grown on SI-GaAs using MBE, on InSb, and on AlGaSb. Hydrogenation or deuteration was performed in a parallel plate capacitor reactor at 30 kHz between 100 and 250°C for times between 0.5 and 1 h.[9] Deuterium profiles for hydrogen diffusion and defect-complexing location studies were measured using SIMS (14.5-keV Cs primary ions and negative secondary ions).[10,11] Resistivity and free carrier density profiles were measured using the two-probe spreading resistance profiling (SRP) method.[12] The measured SRPs are converted to densities using calibration curves from n- and p-type samples with known densities.[12,13] On the more lightly doped n-GaSb(Te) samples, electron density was also determined from C-V measurements on Au/n-GaSb Schottky diodes.[14] The influence of H on deep centers in GaSb was studied using DLTS on Au/GaSb(Te) Schottky diodes and room temperature PL. DLTS spectra were obtained in the range from 100 to 300K using a SULA-1 spectrometer and a cooled Ge photodetector with sensitivity between 0.8 and 1.8μm.

RESULTS AND DISCUSSION: We found that H diffusivity in GaSb depends on the conductivity type and doping density. In Fig. 1, four deuterium (^2H) profiles that correspond to 100, 150, 200, and 250°C are shown for the p^+-GaSb(Zn) sample with hole density $2x10^{18}$ cm^{-3}. These profiles can be approximated by an erfc-type function, and the apparent diffusion coefficient can be expressed as $D = 1.5x10^{-6}exp(-0.45eV/kT)$. The ^2H density near the surface is much higher than that of acceptors for temps below 250°C (presumably because of preferential formation of H_2 pair formation), and approaches the density of acceptors at

250°C. In n$^+$-GaSb, the surface density of ^{2}H was significantly lower than in p$^+$-GaSb. The depth of the ^{2}H profile is greater, and the form of the decay is better described by an exponential (Fig. 2). This behavior was previously observed for H in InP and explained by supposition that H readily complexes with acceptors, but that its interaction with donors is inefficient.[16] Such an explanation also seems plausible for GaSb. The effective diffusion coefficient for n$^+$-GaSb can be described by: $D = 3.4\times10^{-5}\exp(-0.55\mathrm{eV}/kT)$.

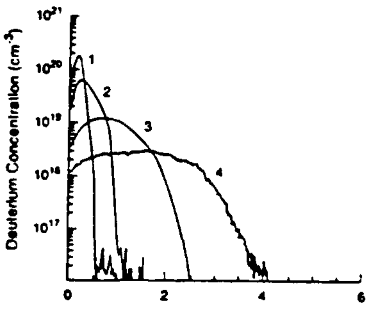

Fig. 1. ^{2}H profiles (SIMS) in p$^+$-GaSb(Zn); 1-100, 2-150, 3-200 4-250°C; exposure time 0.5h

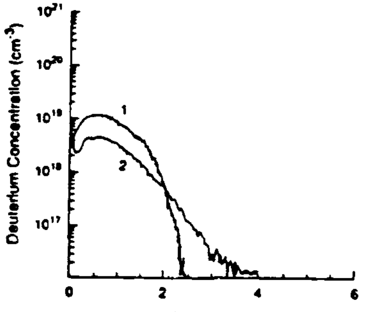

Fig. 2. ^{2}H profiles (SIMS) in p$^+$-GaSb (Zn) (1) and in n$^+$-GaSb(Te) (2); treated at 200°C

In undoped p-GaSb, the H density is approx. three times less than in p$^+$-GaSb and is close to the density in n- and n$^+$-GaSb (which do not differ). One explanation is that H in GaSb is a donor with energy level close to the valence band edge. In p$^+$-GaSb, H is positively charged at the temperatures of hydrogenation, whereas in undoped GaSb and in n-GaSb, it is neutral. If this is true, the H donor level should lie at $\sim E_v$+0.1eV, the position that coincides with that of Fermi level pinning at the surface of GaSb.[14,16,17] The H level in GaSb is within 0.2eV of the position that is calculated using the vacuum reference level pinning model.[18] Electrical measurements indicate that there is a symmetry in acceptor and donor passivation in GaSb. As shown in Fig. 3, there is more than a two-fold decrease in the hole density in the first 0.5μm of the heavily Si-doped p$^+$-GaSb sample, whereas in the n$^+$-GaSb sample, the concentration profile before and after H treatment remains constant. From the amount of passivation observed for the heavily doped p$^+$-GaSb sample in Fig. 3, it would be expected that more lightly doped samples would be rendered highly resistive. However, measurements on the lightly Be-doped epitaxial sample (Fig. 4) show that the density decrease is not large; rather the density changes in lightly doped GaSb are comparable with those in lightly doped n-GaSb(Te), in which a decrease from

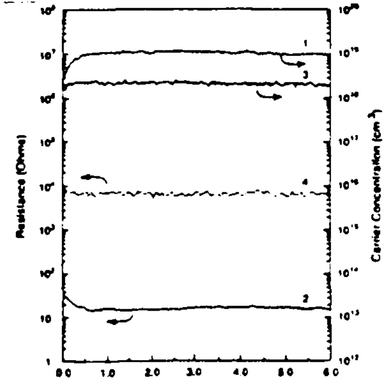

Fig. 3. Carrier density (1,3) and SRP (2,4) in p$^+$-GaSb (1,2) and n$^+$-GaSb (3,4) after H treatment at 150°C

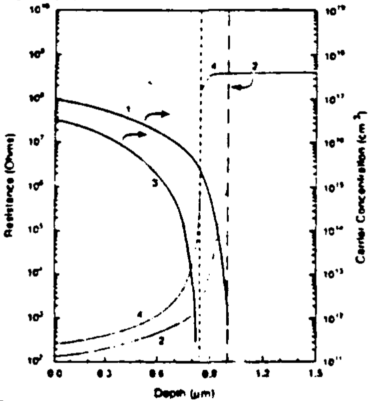

Fig. 4. Carrier density (1,3) and SRP (2,4) in p-GaSb/SI GaAs before (1,2) and after (3,4) H treatment at 150°C

2 to 1×10^{17} cm^{-3} was measured using C-V, possibly because H in n- and lightly doped p-GaSb is neutral and the passivation efficiency is not so high as in the case of Coulombic attraction between charged acceptors and H ions.

The effect observed in the case of p^+-GaSb is probably passivation and not compensation, as confirmed by van der Pauw measurements on the p^+-GaSb(Be)/SI GaAs epitaxial structures, which have shown a density decrease from 1 to 0.6×10^{19} cm^{-3} and mobility increases from 100 to 180 cm^2/Vs as a result of H treatment at 150°C. DLTS shows the presence, in n-GaSb, of an electron trap with an apparent ionization energy 0.25eV and density near 10^{15} cm^{-3}. As a result of H treatment at 150°C, the density of this trap decreases by six. From measurement of the PL band in p^+-GaSb at room temperature, H treatment causes a five-fold increase in the intensity of this band, presumably because of passivation of the nonradiative recombination centers. Similar changes were measured for n^+-, n-, and p-GaSb. Annealing of a passivated Au/n-GaSb Schottky diode at 250°C for 0.5h caused the complete recovery of the free electron density and to the nearly total recovery of the density of deep electron traps. In, p^+-GaSb, complete recovery of the hole density occurred after a 300°C, 0.5h anneal, and that anneal also restored to a large extent the density of nonradiative centers in p-type material.

The lifetime in n-InSb was measured before and after hydrogenation at 150°C, using a contactless method in which the sample is excited by a CO_2 laser and the diffraction pattern for 10.6-μm light is measured. Depth profiles were obtained by varying the excitation laser wavelength and therefore the absorption depth. The results indicate that passivation is occurring to a depth of about 9 μm. However, SIMS depth profiling of these samples indicates that H has not penetrated more than 0.5 μm (with a density greater than 3×10^{16} cm^{-3}). Therefore, we tentatively conclude that the H at the surface provides a sink for defects (or that H at a density less that 3×10^{16} cm^{-3} in the bulk produces the observed effect). These observations are under further study. In separate experiments, ^2H was implanted into GaSb at room temperature and into InSb at 80K (liquid nitrogen temperature), and the depth profiles of ^2H were measured using SIMS for samples unannealed and annealed at temperatures from 100 to 350°C. Figure 5 shows H redistribution toward the GaSb surface through the layer damaged by the implant and deeper into the GaSb not damaged by the implant. Figure 6 shows redistribution of H deeper into the bulk of the InSb sample. Redistribution deeper into the bulk is greater for InSb (~50μm for the 175°C anneal) than for GaSb (~5μm).

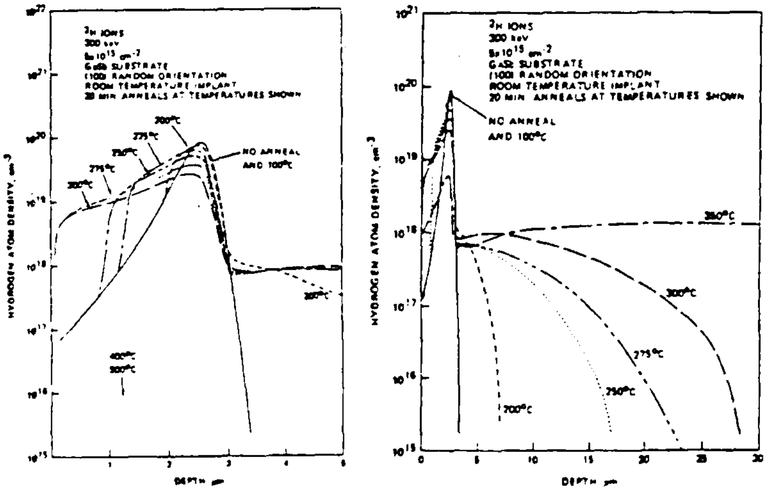

Fig. 5. SIMS depth profiles for ^2H implanted into GaSb and annealed

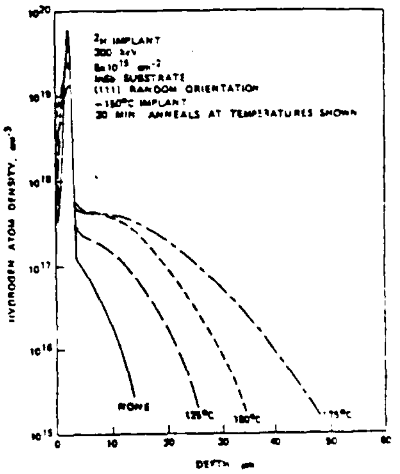

Fig. 6. SIMS depth profiles for ^2H implanted into InSb and annealed

DISCUSSION AND CONCLUSIONS: Passivation of GaSb seems to be of less practical importance because the degree to which shallow acceptors can be passivated is not so high as in InP,[19,20] making it difficult to use H passivation to produce high resistivity GaSb layers. There does not exist a wide window in the annealing temperatures of deep and shallow defects that would make it possible to improve recombination characteristics of GaSb without changing the density of free carriers necessary for the operation of electronic devices, as is the case for GaAs.[3] The extrapolation schemes for the behavior of H in III-V materials proposed in ref. 16, crude as the may seem, do give an estimate of H behavior in unmeasured materials. One implication is that in AlGaAsSb quaternaries lattice matched to GaSb and used for optical confinement in DH lasers,[8,9] higher resistivities should result from H treatment because the H^+ level would lie near the middle of the gap and because the gap is near the band gap of InP,[8,9] making it possible to use these passivated layers for current confinement as in AlGaAs[21] or in InGaAsP.[22]

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INCORPORATION OF HYDROGEN IN II-VI EPITAXIAL LAYERS GROWN BY MOCVD

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Some properties of hydrogen in II-VI compounds (CdTe, ZnTe) have been previously studied using proton implantation and annealing under H_2 as hydrogenation techniques [1]. We report here several observations about the hydrogen incorporation which occurs during the growth of epitaxial layers by MOCVD.

In common MOCVD techniques the source of hydrogen is twofold : first the carrier gas H_2 which is the main gaseous component in the reactor, second the hydrogen liberated by the pyrolysis of organometallic molecules. It is often difficult to separate these two effects.

The first experiments we report concern the growth of $Cd_xHg_{1-x}Te$ alloys (x 0.3) by the Interdiffused Multilayer Process at 365°C. The substrate was GaAs (100) covered by a CdZnTe-ZnTe buffer layer. The precursors were Dimethylcadmium, Diisopropyltellurium and elemental mercury. The SIMS profile of Fig. 1 shows a uniform concentration of hydrogen (1.5×10^{17} cm^{-3}) in the CdHgTe layer. At least a part of this hydrogen comes from the carrier gas as demonstrated in a subsidary experiment : another sample was grown using a mixture $H_2 + D_2$ as the carrier gas during a fraction of the growth time ; SIMS analysis shows the corresponding incorporation of deuterium in the material (Fig. 2).

The hydrogen incorporation rate depends on temperature and material doping. Fig. 3 shows that the concentration of hydrogen in CdTe increases by about seven times when the growth temperature decreases from 250°C to 200°C. The effect of doping was revealed by growing an As-doped CdTe layer at 365°C on an undoped CdTe/ZnTe buffer layer and a GaAs substrate. Arsenic was introduced during growth through the decomposition of AsH_3. The SIMS profiles in Fig. 4 yield a higher hydrogen concentration in the doped layer compared to the undoped one. The formation of As-H complexes might be anticipated.

The incorporation of hydrogen from the metalorganic precursors was established by performing the growth of ZnTe at 400°C under either H_2 or He carrier gas. The precursors were Diethylzinc and Diethyltellurium. The comparison of the SIMS profiles in Fig. 5 reveals a higher hydrogen concentration in the material when He is used as the carrier gas. Under these conditions a larger carbon incorporation also occurs. The parallel evolution of C and H points out to the introduction of C-H complexes originating from the decomposition of organic molecules.

At last hydrogen effusion experiments have been carried out on CdTe and ZnTe layers grown in H_2 or He carrier gas. Preliminary results yield additional information on the relative quantity of hydrogen incorporated in these different samples.

[1] L. SVOB, A. HEURTEL, Y. MARFAING, J. Crystal Growth 101 (1990) 709 and references therein.

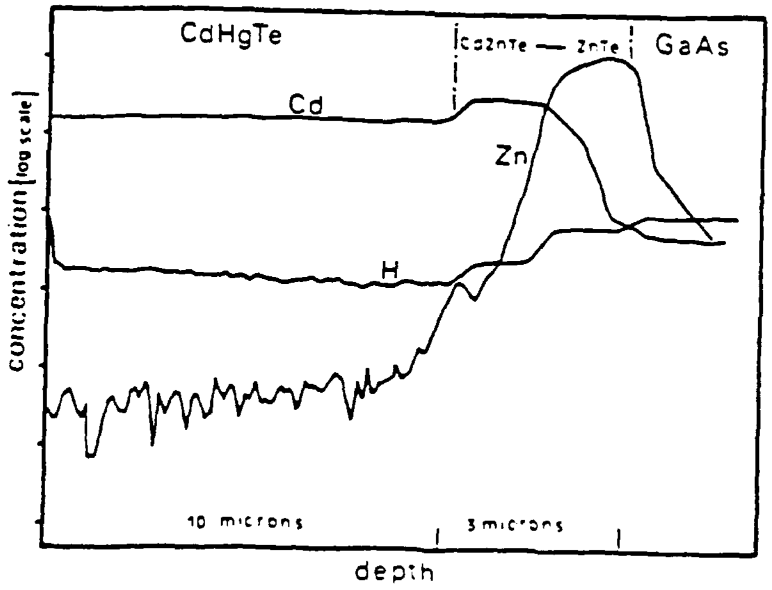

Fig. 1 - The hydrogen concentration profile in a $Cd_{0.29}Hg_{0.71}Te$ layer grown by the IMP method at 365°C on a CdZnTe-ZnTe graded buffer.

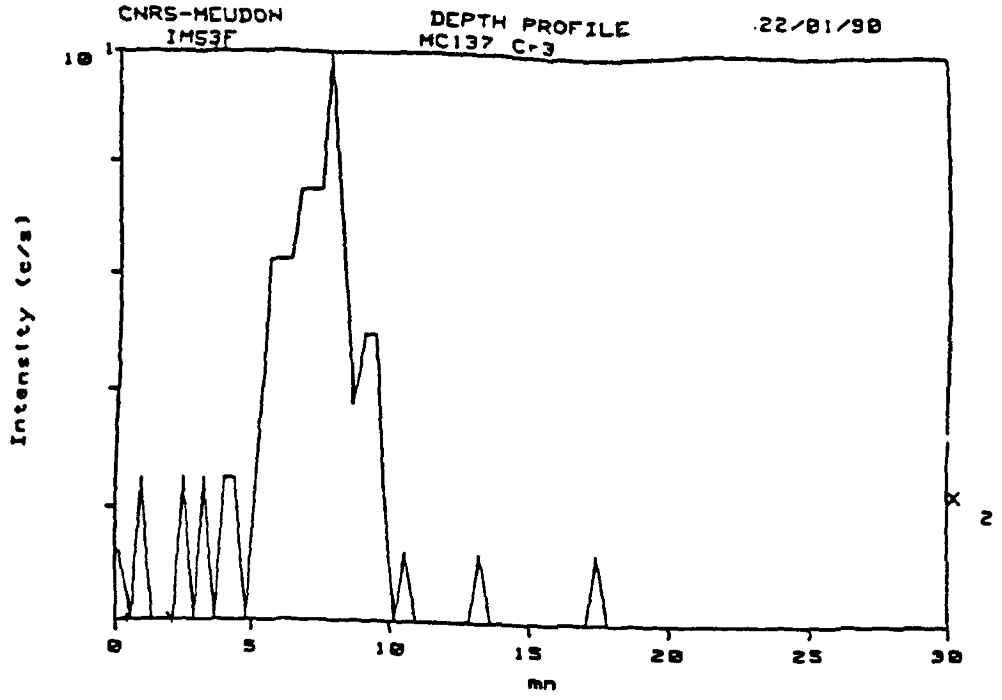

Fig. 2 - SIMS profile of deuterium in a CdHgTe layer grown by MOCVD using a carrier gas containing D_2.

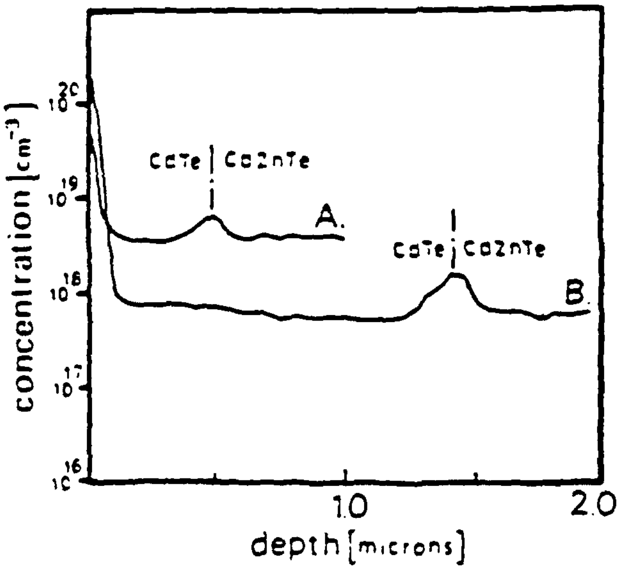

Fig. 3 - Influence of the temperature of growth on the hydrogen concentration in MOCVD grown CdTe layers : A.T = 200°C ; B.T = 250°C.

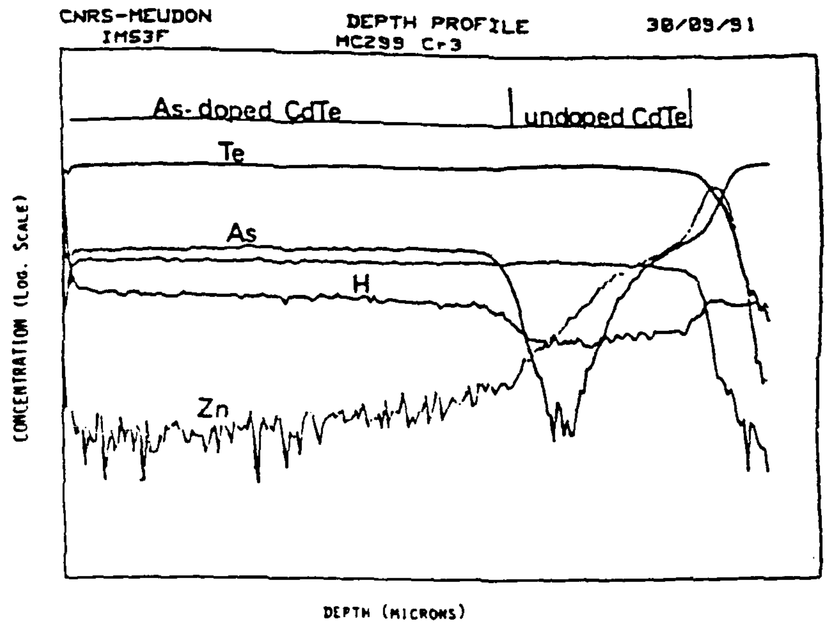

Fig. 4 - SIMS profiles of the constituting elements in an As-doped CdTe layer grown by MOCVD on a undoped CdTe layer and a GaAs substrate with ZnTe buffer.

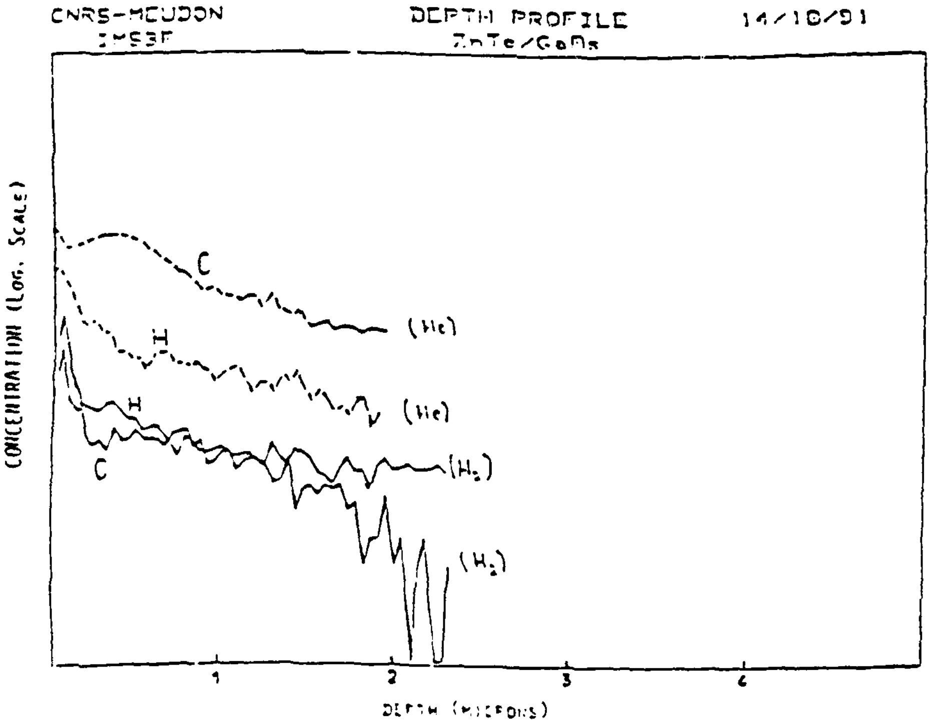

Fig. 5 - SIMS profiles of hydrogen and carbon in two ZnTe layers grown by MOCVD using H_2 and He as carrier gas respectively.

Comments on Hydrogen in Natural Diamond

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Hydrogen or muonium in diamond has been the subject of experimental [1,2] and theoretical [3] investigations. It is now established that hydrogen and anomalous muonium occupy the bond-centered interstitial (BCI) site in diamond [3]. Eight years ago, when the first detailed infrared absorption spectra were published [1,2], several exceptional features in the spectra were noticed but the natural interpretation by the special properties of the BCI site could not be given at that time. In figure 1 and in table I results from the literature [1,2] are reproduced. In the infrared absorption spectrum broad bands from the first (< 1333 cm^{-1}), second (< 2666 cm^{-1}), and third (< 4000 cm^{-1}) order lattice phonon absorption can be seen on which five sharp local vibrational mode (LVM) absorption lines (see table I) are superimposed. An interesting feature is a weak shoulder on the 3107 cm^{-1} line, located at 3098 cm^{-1} and arising from ^{13}C-H [2].

It is reported that some 50 type Ia diamonds all showed the hydrogen LVM spectrum [2]. Detailed measurements showed good correlation between the intensities of the five lines, which evidently arise from a single center [1]. Two exceptional features were noticed for the hydrogen LVM lines in diamond [1]: (i) The frequencies are 5 % higher than expected for (sp^3) C-H vibrations [4,5]. (ii)The intensities of the overtone and combination lines are very high (up to 15 % of the fundamental !) and the anharmonic frequency shifts are relatively large (0.3 to 1.1 %).

The BCI site of hydrogen in diamond provides a natural explanation for the unusual spectrum: (i) The C-H bond length is shorter than in molecules and larger force constants can be expected. (ii) The energy potential surface on which the inerstitial hydrogen can move is known to be complex and not of the harmonic type [3]. It should be emphasized that only one bending vibration is observed. This indicates C_{3v} symmetry and an on-axis position of the hydrogen along the C-H-C bond in contrast to an off-axis position with C_{2v} symmetry and two bending vibrations. The observed line widths (see table I) are larger than for hydrogen in other crystals (0.015 - 1.0 cm^{-1}). They show very little temperature dependence in the range $4 < T < 500$ K [1]. This is indicative of inhomogeneous broadening which is expected because the large lattice relaxation around the BCI site [3] makes the center sensitive to nearby lattice imperfections. Note that in a-C:H the hydrogen lines have a temperature independent width of 75 cm^{-1} [4].

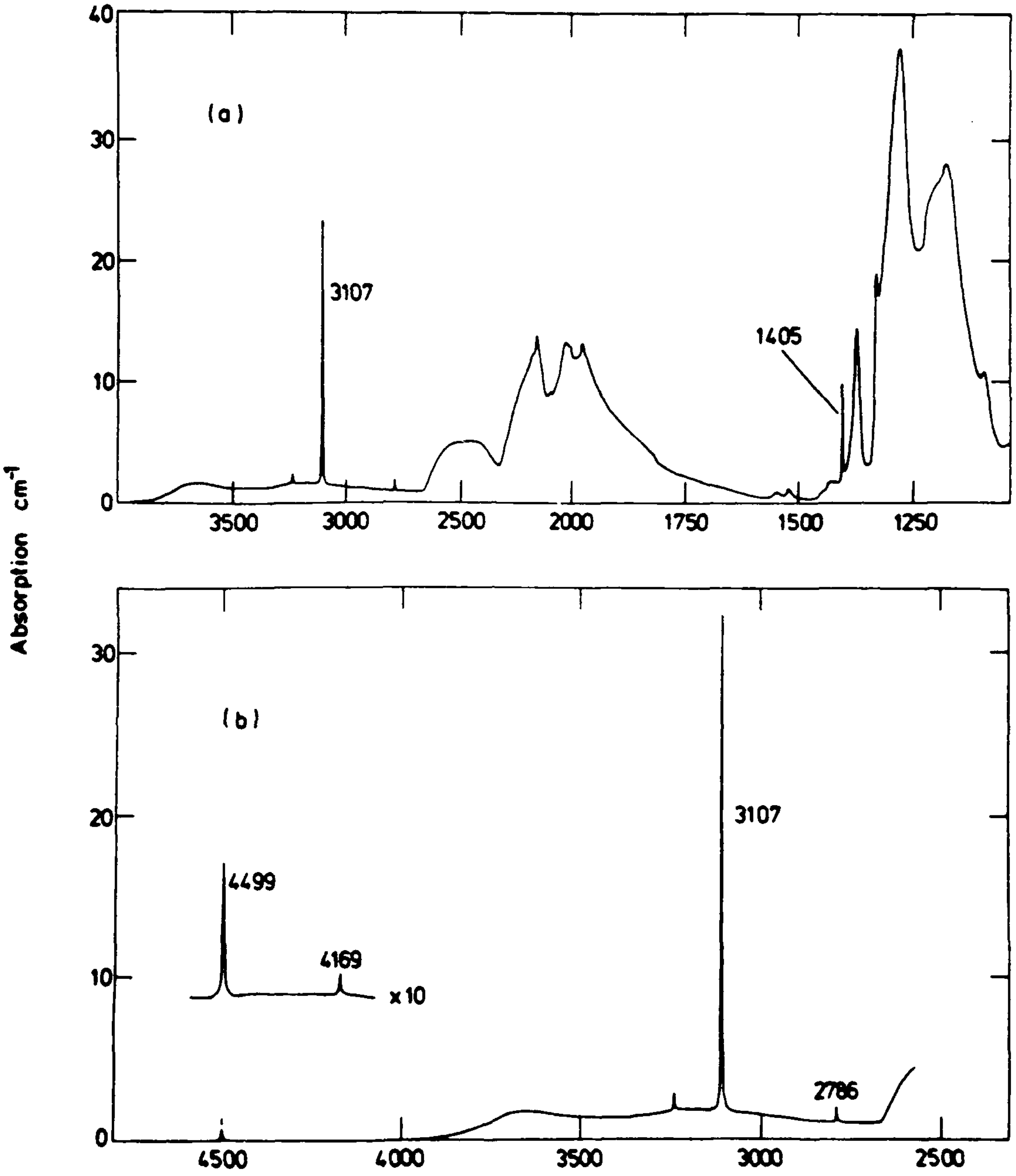

Fig. 1. Absorption lines from hydrogen in diamond measured at 300 K with (a) a standard double beam spectrometer and (b) with a monochromator [1].

Table I

Hydrogen LVM lines observed in natural diamond [1,2] and comparison with amorphous hydrogenated carbon (a-C:H) [4] and a molecule [5].

frequency (cm^{-1})	width (cm^{-1})	intensity (%)	assignment	corresp. frequency (cm^{-1}) a-C:H	corresp. frequency (cm^{-1}) CHD_3
1405	1.5	20	ω_{bend}	1370	1299
2786	2.5	3	$2\ \omega_{bend}$	—	—
3098	-	1.4	$\omega_{stretch}(^{13}C\text{-}H)$	—	—
3107	2.9	100	$\omega_{stretch}(^{12}C\text{-}H)$	2920	2992
4169	4.4	0.6	$3\ \omega_{bend}$	—	—
4499	4.8	5	$\omega_{stretch}+\omega_{bend}$	—	—

Table II

Analysis of ^{13}C-H versus ^{12}C-H isotopic shift in diamond using Eq.(1)

model	α	k ($10^6 cm^{-2} amu$)	rel. intensity (%)
C-H-C (BCI)	0.24	8.9	2.2
C-H	0.99	8.2	1.1

The frequency and intensity of the shoulder at 3098 cm^{-1} have been reported and it was assigned to the ^{13}C-H bond (1.1 % isotopic abundance) [2]. The isotopic frequency shift can be calculated by the familiar formula for LVM vibrations [6,7]:

$$\omega^2 = k \, [\, (1/m) + (1/\alpha M) \,]. \qquad (1)$$

Here k is the force constant, m the impurity mass, M the nearest neighbour mass and α is an adjustable parameter. Most of the empirical α values for LVM are between 0.5 and 3.0 [8], while the "ideal" value is $\alpha = 1$ (diatomic molecule or lattice TO mode). Inserting the experimental frequencies (3107.1 and 3097.8 cm-1) into Eq. (1) yields the α values and force constants listed in table II. The first line applies to the BCI hydrogen with ligand masses of 24 and 25 while the second line applies if the hydrogen is bonded to one carbon only, as assumed previously [2]. Small α values are indicative of a ligand relaxation away from the impurity [8], therefore the value 0.24 in table II appears very reasonable for BCI hydrogen. The relative intensity of the shoulder is difficult to determine [2] but the calculated value of 2.2 % is compatible with the observed spectrum. It is interesting to compare the force constants in table II: For the BCI model it is 8.5 % higher because of the larger ligand mass.

During the last years great activities to grow chemical vapour deposited (CVD) diamond have developped [9]. These CVD diamonds contain several percent of hydrogen but the LVM lines from BCI hydrogen are completely missing [10]. Instead C-H stretch absortion spectra similar to those from a-C:H [4] are observed. The question arises whether the different sites for hydrogen in natural or CVD diamond are caused by the different growth conditions or by the different time scales involved.

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^{2}D INTERACTION WITH ION IMPLANTED AND ANNEALED GALLIUM ARSENIDE

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A detailed study of ^{2}D diffusion from a ^{2}D plasma into semi-insulating undoped and bulk Si-doped GaAs, and Si$^+$, Mg$^+$ and Be$^+$ implanted/annealed GaAs was conducted. The GaAs samples were exposed to a ^{2}D plasma at 300 °C for 15 minutes in a PlasmaTherm system. The samples experienced an additional heat treatment at 300°C for 15 minutes while the plasma chamber was being flushed with N_2. The following summarises our observations.

Bulk GaAs : Figure 1 shows ^{2}D profiles in semi-insulating undoped, 2×10^{17} cm^{-3} and 2×10^{18} cm^{-3} Si-doped GaAs. The doped samples showed ^{2}D levels in proportion to the doping concentrations to depths of $\simeq 0.2 - 0.3$ μm extending from the the surface. The ^{2}D level in the undoped sample was $\lesssim 3 \times 10^{16}$ cm^{-3} near the surface and decreased gradually to SIMS detection limit at 0.3-0.4 μm.

Implanted But Unannealed GaAs : Figure 2 shows the SIMS profiles of ^{2}D in GaAs samples implanted with 30 keV Si in the dose range of $1 - 10 \times 10^{13}$ cm^{-2}. High concentrations ($\simeq 10^{20}$ cm^{-3}) of ^{2}D accumulated in the implanted region. Deeper diffusion of the ^{2}D occurred in the low dose implanted ($\lesssim 10^{13}$ cm^{-2}) samples compared to that in the high dose samples. Similar ^{2}D diffusion behavior was observed for Si$^+$ and Mg$^+$ implantations conducted at higher energies (upto 150 keV). Above a certain threshhold implant dose which depended on the implant energy, ^{2}D profiles in all the implanted samples became identical and looked similar to that shown in Fig 2c. In other words, the ^{2}D distribution had no correspondence with the damage distribution in the implanted region. Similar dose dependence of the ^{2}D diffusion was further confirmed in Be$^+$ implanted GaAs samples which were implanted at 5-60 keV in the dose range of $10^{13} - 5 \times 10^{14}$ cm^{-2}. It should noted that none of the implants produced any amorphous layer in the GaAs. The anomaly between the expected damage and observed ^{2}D distributions in the high dose implanted samples (such as those in Fig 2) occurs because the samples experience $\gtrsim 30$ minutes anneal at 300 °C during the ^{2}D plasma experiment. During this time, partial recrystallization of the implantation induced damage can occur. The ^{2}D distribution in Figs 2b presumably represents the residual damage distribution in the high dose implanted samples.

Implanted and Annealed GaAs: Strong n but weak p-carrier passivation was observed when Si$^+$ and Mg$^+$ implanted/rapid thermally annealed (850 °C/10s) GaAs samples were exposed to the ^{2}D plasma. Based on the Hall data from 30 keV / 4.5×10^{13} cm^{-2} and 120 keV / 1.0×10^{14} cm^{-2} Si$^+$ implanted samples, the passivation effect was more pmounced ($\gtrsim 80\%$) for the shallow implant compared to the deep implant ($\simeq 50\%$). In contrast, in the 120 keV / 1.0×10^{14} cm^{-2} Mg$^+$ implanted/RTA samples no significant passivation occurred after the plasma exposure. In both the Si$^+$ and Mg$^+$ implanted/annealed samples XTEM revealed a similar damage distribution, i.e., a discrete layer of dislocation loops centered around the mean projected range of the ion (Figs 3 and 4). The ^{2}D interaction with the loops was also found to be anomalous. The concentration of the ^{2}D in the implanted region in the case of Mg$^+$ was an order of magnitude higher than that in the the case of Si$^+$ (Fig 4b). The ^{2}D distribution in the Si$^+$ implanted sample closely resembled with that of the n-carrier profile of the sample (Fig 3ii). In the Mg$^+$ implanted sample ^{2}D profile showed no resemblence with the p-carrier profile. Furthermore, $\gtrsim 80\%$ of the ^{2}D diffused away from the Si implanted/RTA samples during a heat treatment at 350 °C after the plasma exposure and this was accompanied by reactivation of the n-carriers. However, the ^{2}D in the Mg implanted/RTA samples remained pinned in the implanted region even after a heat treatment of 850 °C/10s.

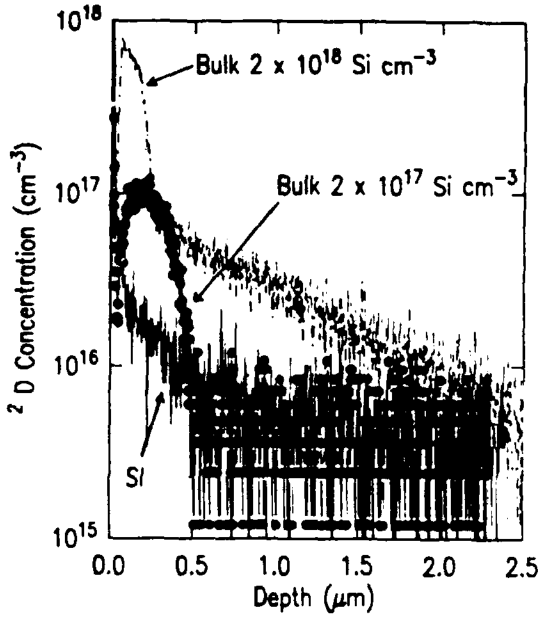

FIG. 1. ^{2}D SIMS profiles in undoped and bulk Si-doped GaAs after the ^{2}D plasma exposure.

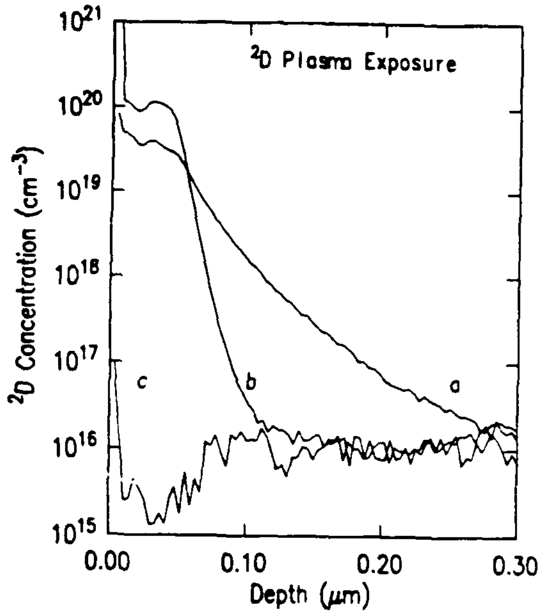

FIG. 2. ^{2}D SIMS profiles in the GaAs samples with (a) Si^{+}, 30 keV, 1.0 x 10^{13} cm^{-2}, (b) Si^{+}, 30 or 120 keV, 1.0 x 10^{13} cm^{-2}, and (c) no implant (virgin). All samples were unannealed.

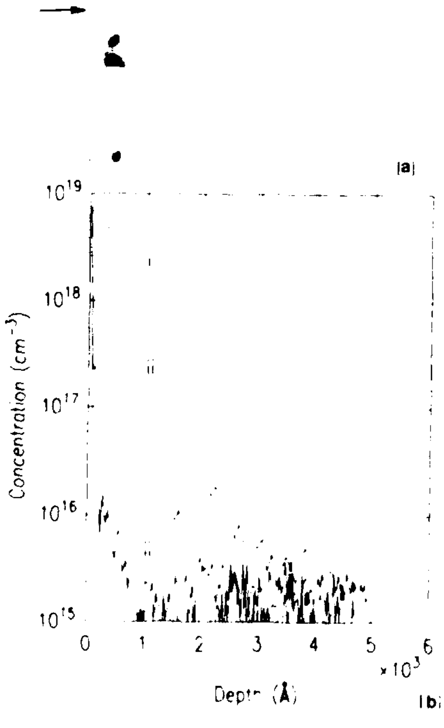

FIG. 3. GaAs sample implanted with ^{29}Si, 30 keV, 4.5 × 10 cm and subsequently annealed at 850 °C/10 s. (a) an XTEM micrograph showing the distribution of dislocation loops, (b) the corresponding SIMS profiles of ^{29}Si (i) and ^{2}D (ii) from the sample, and D profile after a 350 C 10 min anneal (iii).

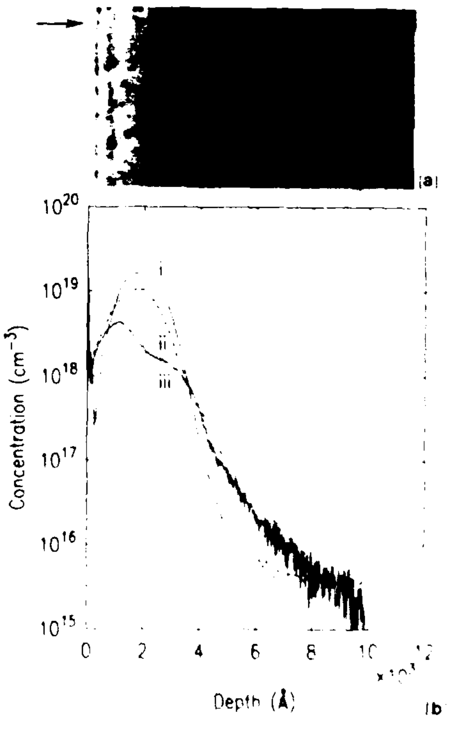

FIG. 4. GaAs sample implanted with Mg, 120 keV, 1.0 × 10 cm and subsequently annealed at 850 °C/10 s. (a) an XTEM micrograph showing the distribution of dislocation loops and (b) the corresponding SIMS profiles of ^{2}D (i) and Mg (iii) from the annealed sample. Also included in (b) is the Mg profile (ii) from the unannealed sample.

OPTICAL WAVEGUIDES in GaAs CRYSTALS FORMED BY HYDROGEN INTERACTIONS

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In general, the effect of charge carriers in a semiconductor crystal is to lower the refractive index and to increase the optical absorption at frequencies below the absorption edge of the material. Optical waveguides based on carrier reduction have been studied for a number of years and experiments have shown good agreement with models based on a Drude term for the carrier contribution to the refractive index. Garmire et al. reported the use of proton implantation in bulk, Si-doped, n-type GaAs crystals to form such optical waveguides [1]. They observed that after implantation optical losses were very high, in excess of 200 Db/cm, and attributed these losses to damage effects. These losses could be reduced by thermal annealing to levels on the order of 3 Db/cm. However, the damage caused by ion implantation has been a major concern in the formation of carrier reduced waveguides and thermal annealing procedures have not always been reproducible.

Several years ago Chevallier et al. reported that atomic hydrogen in n-type GaAs can passivate Si donors leading to measurable electrical changes [2]. Since then a number of experiments have established that either atomic hydrogen (H) or atomic deuterium (D) is able to passivate a variety of shallow donors and acceptors in crystalline GaAs and other III-V semiconductors [3]. Attempts have been made to utilize this passivation technique in the processing of field effect transistors as well as laser structures. The changes in the optical properties of doped semiconductors due to the introduction of atomic hydrogen are not as well established.

Plasma hydrogenation of GaAs wafers is a relatively simple process that is compatible with conventional masking techniques. The damage to the GaAs crystal as a result of plasma exposure is expected to be significantly less that that due to ion implantation. Consequently, plasma hydrogenation of GaAs crystals may be a useful method for fabricating optical waveguides provided that appropriate optical effects can be achieved.

In this presentation we describe the results of several experiments concerning the changes produced in the refractive index of Si doped, p-type GaAs epilayers after exposure to a deuterium plasma. The epilayers used in these experiments were grown on n^+-GaAs crystal substrates using conventional, slow-cooling, liquid phase epitaxy (LPE). Under such growth conditions, material grown below a certain critical temperature is p-type. The total concentration of Si atoms in the epilayers was approximately 2 x 10^{19} cm^{-3} and the conductivity at the surface was p-type with the carrier level at 7 x 10^{18} cm^{-3}. Due to the LPE growth technique, the surfaces of the epilayers were not very smooth and subsequent efforts were required to remove the surface imperfections.

Two attempts were made to passivate the surface regions through plasma treatment. In the first case, the epilayer samples were polished prior to plasma treatment using a mechanical technique to obtain a smooth surface for the optical measurements. The resulting surface had good optical quality but microscopic damage and defects could not be avoided. Three such samples were exposed to a capacitive RF deuterium plasma with a power density of 0.18 W cm^{-2} for a period of ninety minutes. Processing temperatures were chosen to produce passivated layers similar to those that had been previously investigated using SIMS and electrical measurements [4]. This attempt was not successful and the samples failed to show the existence of passivated surface regions. In the second case, the epilayer samples were treated with a chemical etch to remove the surface imperfections. While the overall surface smoothness of these samples was not as good as in the first case, these samples did exhibit passivated surface regions.

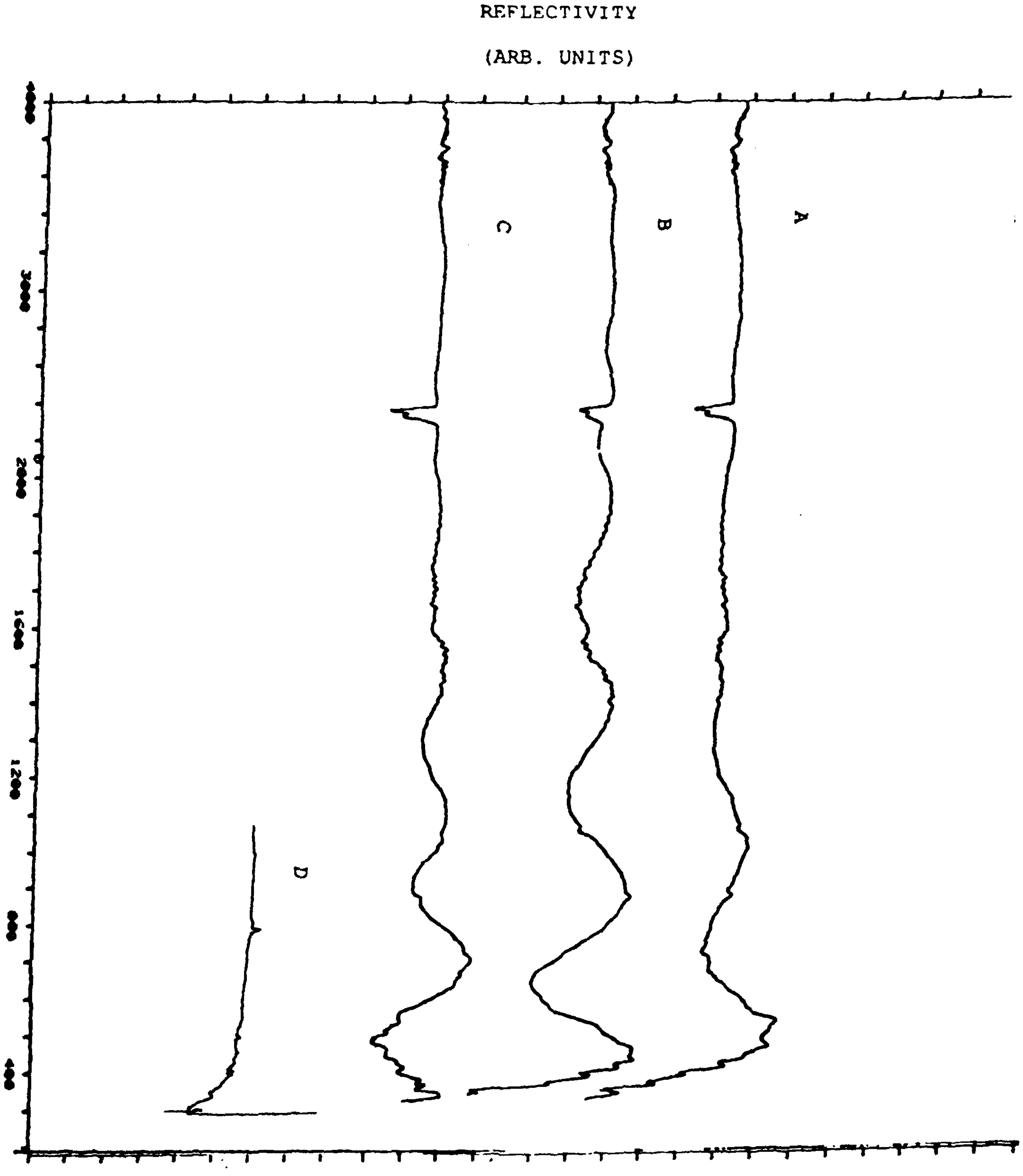
Infrared reflectivity measurements were made on both sets of samples. With the first set of samples, the ones polished using a mechanical method, no regular fringe pattern could be discerned in the spectra. Based on these measurements, it was concluded that the passivation of the acceptors was weak and did not extend very deep into the samples.

The second set of samples (A, B, C), the ones treated with a chemical etch, provided a definite set of fringes, as shown in Fig. 1. From the fringe patterns the thicknesses of the passivated layers in the three samples were calculated to be 2.7, 2.9 and 4.0 µm. The degree of passivation in these samples was estimated by comparing the spectra with a computer simulation. The fringe amplitudes in the plasma-treated samples were about half of the corresponding ones in the simulation indicating that nearly 60% of the acceptors had been passivated.

Secondary ion mass spectrometry (SIMS) analyses were performed on the samples after the reflectivity measurements. The SIMS D depth profiles for the first set of samples showed that there was a large accumulation of D at the surface. Apparently, the mechanical polishing introduced numerous microscopic surface defects which formed trapping centers for the migrating atomic D and impeded the atoms from penetrating deeper into the epilayer. Deuterium that did pass through the surface damage region formed a plateau at a concentration comparable to the carrier level.

The SIMS D depth profiles for the samples prepared with the chemical etching method did not display any major accumulation at the surface and the depth of their plateaux are in good agreement with prior results [4]. The plateau concentrations were at the carrier level in these samples and the measured depths were 2.15, 2.80 and 3.80 µm. These depths compare reasonably well with the thicknesses determined by infrared reflectivity, except for sample A. This sample, which had the poorest surface quality, showed very few fringes in its reflectivity spectrum.

The samples of the first set were below the cut-off condition and no attempt was made to couple laser radiation into these epilayers.


REFLECTIVITY
(ARB. UNITS)
4000
3000
2000
1600
1200
800
400
A
B
C
D

Following the reflectivity measurements, samples from the second set were cleaved to provide specimens with smooth end-faces for laser coupling experiments.

Waveguide losses were measured at wavelengths of 1.15 and 1.523 µm for both TE and TM polarizations, using low power, stabilised HeNe lasers. Each of the samples in the second set provided light confinement at the shorter wavelength of 1.15 µm. While both TE and TM modes were observed, waveguide losses were high. As expected, these losses were observed to decrease with increasing processing temperatures due to an associated increase in the passivated layer thickness. Losses in sample C, which contained a 4 µm thick passivated layer, were on the order of 35 dB/cm for either the TE or TM mode which is considerably less than that reported for unannealed, proton implanted samples [1].

These experiments represent the first successful effort to form optical waveguides in III-V compound semiconductors using plasma passivation of dopant atoms. The D plasma treatment of Si-doped, p-GaAs has been shown to yield passivated surface regions of sufficient thickness and with large enough increases in the refractive index to guide laser radiation at wavelengths of 1.15 and 1.523 µm. The optical changes can be measured by infrared reflectivity and correlate well with SIMS D depth profiles. The data from these two measurements can be effectively utilized to predict the waveguide characteristics of the passivated regions.

ACKNOWLEDGEMENTS

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HYDROGEN PLASMA DEVICES FABRICATION AND PERFORMANCE

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ABSTRACT

When n-type GaAs and AlGaAs are exposed to a hydrogen plasma, the free carrier concentration drops down and this is accompanied by an increase in resistance. In this paper we will describe the use of these phenomena in the technological process of field-effect-transistors : MESFET, TEGFET and MISFET, and also for the realization of IMPATT and Avalanche diodes. In the first part, the use of hydrogen passivation in the realization of these devices will be described and the performances will be discuss. In the second part, we will show the perspective of hydrogen plasma in circuit design. Lastly, the different problems that still have to be solved will be presented.

(Extended Abstract for the Workshop on Hydrogen Migration and the Stability of Hydrogen Related Complexes in Crystalline Semiconductors, Horben bei Freiburg, Germany, 3 - 6 November 1991)

Thermal Effusion as an Analytical Tool for Hydrogen Bonding in Crystalline Silicon and Germanium

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Thermally programmed desorption of hydrogen (or deuterium) from hydrogenated semiconductor surfaces or hydrogenated thin films of amorphous semiconductors has been widely used to study the different thermal stability of hydrogen in these materials. Thus, hydrogenated Si(111) surfaces as a function of hydrogen coverage show two effusion maxima at $\approx$350°C and $\approx$500°C assigned to di- and monohydride bonding configurations, respectively [1]. Also, a quite detailed understanding of hydrogen binding and diffusion energies in hydrogenated amorphous silicon has been obtained via effusion studies [2]. Here, we apply this technique to hydrogen-plasma-treated crystalline silicon and germanium with different doping levels and types of dopants, exposed to a D or H plasma at different temperatures.

Thermal desorption of deuterium from plasma-exposed crystalline silicon occurs at three distinct temperatures: $\approx$350°C, $\approx$450°C, and $\approx$500°C. The corresponding bonding states of H or D have been assigned to surface dihydrides, interstitial molecules, and surface or bulk monohydrides [3]. The relative fractions of the different bonding states are found to depend strongly on a number of parameters [3,4]: (i) bulk doping level and type of dopant (ii) sample temperature during plasma treatment (iii) post-passivation anneals (iv) pre- and post-passivation surface etching (v) pre-existing defects (e.g. dislocations, ion bombardment). Figures 1 – 3 show the dependence of the effusion spectra on the plasma-passivation temperature for *p*-type, intrinsic, and *n*-type silicon. The main features are the increase of the monohydride peak with increasing temperature for *n*-type Si, the changes in the effusion peak position of *p*-type Si for temperatures above 200°C, and the decrease of the total amount of evolved deuterium in intrinsic material with increasing temperature.

Apart from the characteristic temperature, T_{M}, of the effusion peaks for a fixed heating rate, information about the thermal stability of the different hydrogen configurations can be obtained from the dependence of the peak temperature on the linear heating rate, $\beta = dT/dt$, which is commonly used in effusion experiments. An example of this dependence for p-type silicon is shown in Fig. 4. Quantitative estimates for the desorption activation energy, E_D, can be deduced from a plot of $\ln(\beta/T_{\mathrm{M}}^2)$ versus $1/T_{\mathrm{M}}$, giving values of $\mathrm{E}_D = 0.75$ eV and $\mathrm{E}_D = 1.4$ eV for the low and high temperature effusion peaks in Fig. 4.

Fig. 5 summarizes the effects of chemical etching on the effusion spectra of undoped c-Si which was treated in a D_2– plasma at 300°C. Without chemical etching, the effusion of D_2–molecules (m=4) occurs in a single peak at about 450°C. Chemical etching after plasma passivation greatly reduces this effusion peak, showing that most of the deuterium was concentrated in a thin surface layer, in agreement with SIMS depth profiles. Etching prior to passivation, on the other hand increases the solubility of D, most likely because of the creation of additional surface defects capable of forming strong Si–D bonds. Also shown in Fig. 5 is the effusion of HD (m=3) molecules. These are formed when evolved deuterium atoms react with residual hydrogen and can be used to address the question of atomic deuterium desorption.

Finally, we present in Fig. 6 the effusion spectra of D_2 from plasma-treated p–type germanium, which occurs at lower temperatures compared to silicon (100–400°C versus 300–600°C). Contrary to p–type silicon, the total amount of deuterium desorbed from p–type germanium decreases strongly with increasing plasma treatment temperature, and resembles more the behavior observed for undoped silicon. This finding will be discussed in comparison to the low efficiency for shallow acceptor passivation in p–type germanium.

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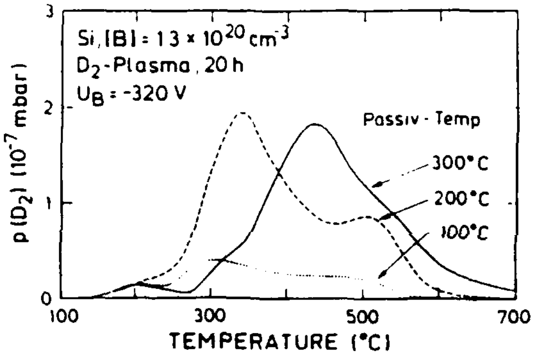

Fig.1: Deuterium effusion spectra for p-type silicon plasma-passivated at different temperatures.

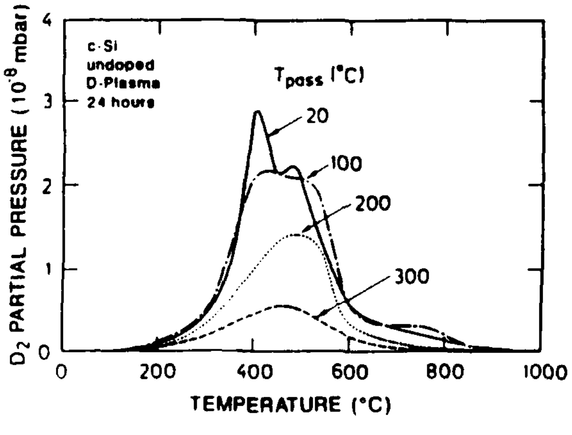

Fig.2: Same as Fig.1, but for undoped Si.

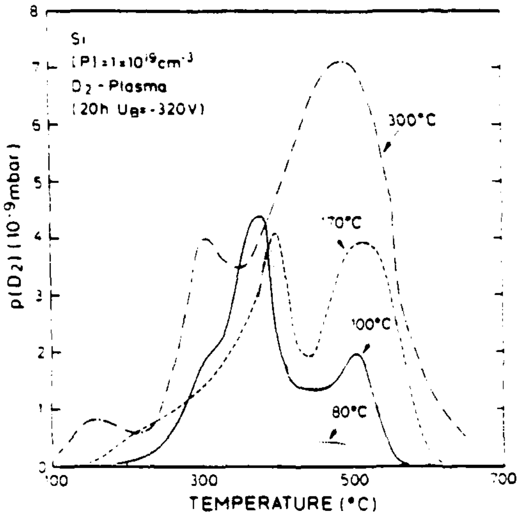

Fig.3: Same as Fig.1, but for n-type silicon.

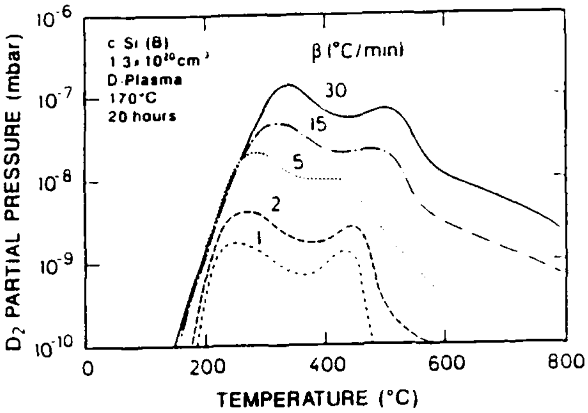

Fig.4: Deuterium effusion spectra of p-type Si measured with different heating rates,β.

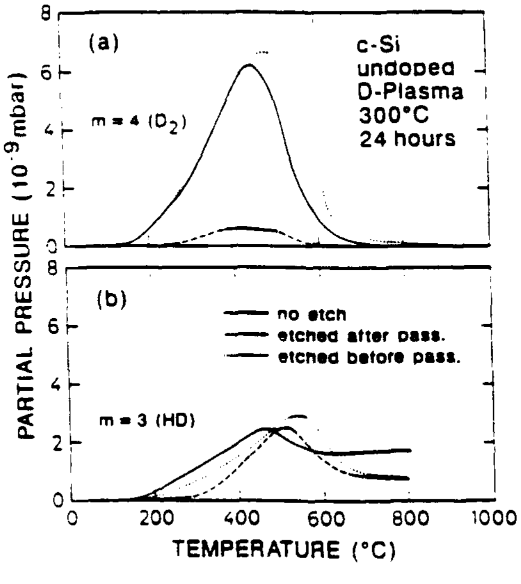

Fig.5: Influence of chemical etching on the effusion spectra of D_2 and HD molecules in undoped Si.

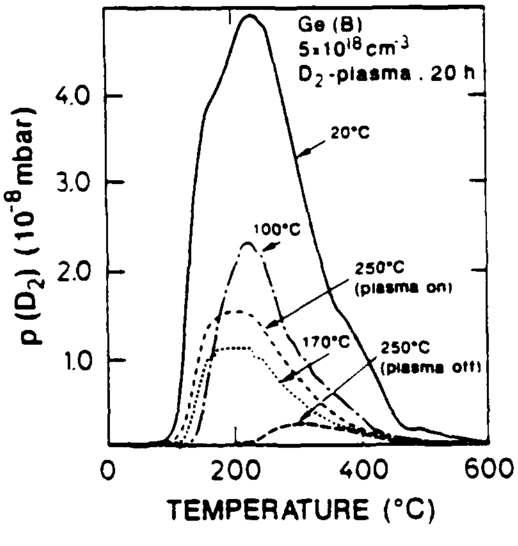

Fig.6: Deuterium effusion of p-type germanium.

Hydrogenation of SiGe/Si Layered Structures

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Summary

Hydrogenated Si_mGe_n Superlattices

The concept of zone folding in 1974 by Gnutzmann et al. [1] indicates that the minimum of the conduction band of an indirect bandgap semiconductor can be folded back to the Γ point through the use of an artificial periodicity. However, with the growth of alternate Si and Ge layers to form a superlattice (SL), no experimental evidence of direct band gap transitions has been demonstrated. At UCLA, we have investigated the effect of hydrogen passivation on the photoluminescence (PL) spectra of Si-rich SL's. These SL's were grown at low temperature by molecular beam epitaxy (MBE). The structure consists of a 2 μm thick $Si_{1-x}Ge_x$ relaxed buffer layer on which the SL is grown. The SL is made of 80 periods of m Si monolayers and n Ge monolayers and is symmetrically strained with the average Ge concentration in the superlattice matched to that in the buffer layer. Transmission electron micrographs (TEM) show layered SL's with a low dislocation density. However, due to its strain relaxation, the buffer contains a high density of misfit dislocations located near the $Si/Si_{1-x}Ge_x$ interface. A typical PL spectrum of a 16×4 (m×n) SL is shown in Fig. 1, along with the PL spectra of the passivated sample under different hydrogenation conditions. For the as-grown sample, we observe the transverse optical (TO) phonon assisted boron bound exciton luminescence line at 1.093 eV, a sharp peak at 1.023 eV and a broad spectrum or background luminescence at lower energies attributed to point defects and dislocations in the buffer layer [2]. After passivation, only two well defined peaks remain from the original spectrum. The broad background luminescence almost completely disappears and a new line at 0.962 eV, a 61 meV lower in energy than the narrow line, emerges. This line corresponds to the phonon replica of the 1.023 eV peak. The main peak is seen to have its apparent intensity slightly reduced upon hydrogenation. Nevertheless, after subtracting the background PL signal from the as-grown spectrum, the relative intensity of the sharp peak is in fact increased. It can be seen more obviously on Fig 2 where we show the PL spectra of a 12×4 SL for both the as-grown and H-annealed cases. The phonon replica with an energy difference of 58 meV (12×4) from the main feature is well resolved following the hydrogen treatment. The increase in PL intensity upon passivation is attributed to a reduction of the density of recombination centers due to defects, leading to an improved yield or intensity of the superlattice peaks. In order to investigate the re-activation of the passivated defects, we annealed the samples in N_2 at 350°C, 450°C, and 550°C for time periods of 30 min. The spectra are shown in Fig. 3 for the 16×4 SL. For the three temperatures, we observe a decrease in the PL intensity peak at 1.023 eV. The resurgence of the background luminescence does not permit the identification of the phonon replica. The broad background luminescence signal does not completely recover after annealing. However, N_2 annealing has probably a dominant effect on the luminescence even if most of the passivated defects are reactivated after N_2 annealing above 400°C.

This result demonstrated that hydrogenation is selective means in distinguishing defect- and band gap-related luminescence signals.

Hydrogenation of δ-doped Si Layers

The hydrogen compensation and the neutralization of acceptors by atomic hydrogen have been exploited for new device applications. Towards this goal, the effect of hydrogen passivation on intersubband absorption of boron δ-doped Si layers was also investigated. The samples used in this study consist of a sequence of 35 Å heavily boron doped Si layers followed by a 300 Å undoped Si spacers, repeated ten times [3]. The structures are grown in a Si MBE chamber on a p^- substrate which is used in order to reduce free carrier absorption from the substrate. Two samples, A and B, are doped to the densities of 4×10^{20} cm^{-3} and 7×10^{19} cm^{-3}, respectively. The measured absorption spectra of sample A versus the photon energy after several different hydrogenation time periods (10, 30, 60, and 90 min.) are shown on Fig. 4. The absorption peak originates from transitions between the holes subbands in the δ-doped potential well. After a H plasma exposition for 60 min, the peak intensity decreases by approximatively 30 %. In addition, the absorption spectra shifts to lower energies as the hydrogenation time period is increased. The shift to the lower energy side is due to a decrease of the active dopant density in the δ-layers, resulting in a shallower potential well. This assertion is supported by the observation of the absorption spectra of sample B with a lower doping density shown on Fig. 5. After only ten minutes of H exposition, the absorbance decreases considerably. These observations suggest that the H atoms are trapped with the acceptors and neutralize the holes, effectively reducing the doping concentration, and that the transition energy is a function of the density of only those acceptors which are not bounded to H atoms in the potential wells. After a hydrogenation for 90 minutes, no detectable absorption is measured for both samples but a new peak at about 230 meV (or 1870 cm^{-1}) emerges . This peak may be ascribed to the Si-H streching motion of the B-H complex [4] and thus confirms the passivation of the boron atoms. This statement was directly supported by SIMS analysis where perfect correlation between H and B atoms was observed. In order to study the re-activation of the passivated acceptors, we annealed the samples in a N_2 backfilled standard furnace at 300 ^{0}C for several time periods. The resulting spectra are shown on Fig. 6. Upon annealing, the absorption peak increases and the energy transition shifts to the higher energy side, towards its initial value. The dissociation of the B-H complexes occurs during the annealing and the H atoms subsequently outdiffuse from the sample. The dissociation activation energy was estimated using a simple first order kinetics model. We obtained an activation energy of 1.9 ± 0.1 eV, about 0.2 eV higher than those reported for 3-dimensional (3-D) systems. The 2-D system in our case may account for the difference from the 3-D case. More work needs to be done to assess the difference in activation energy between the δ-doped Si layers and bulk Si.

In conclusion, atomic hydrogen is shown to alter the effective dopant density in δ-doped Si mutiple quantum wells. These results may be used to tailor intersubband absorption process. In addition, the deactivation of specific layered regions may be of interest for the isolation of quantum devices.

Acknowledgement: The work was in part supported by ARO.

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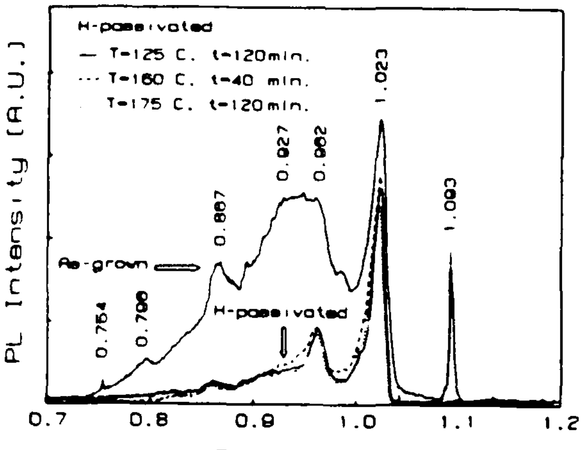

FIG 1. As-grown and hydrogenated photoluminescence spectra of a 16×4 superlattice. Hydrogenated spectra for three different temperatures and times are represented: 125 °C for 20 min, 160 °C for 40 min, and 175 °C for 120 min.

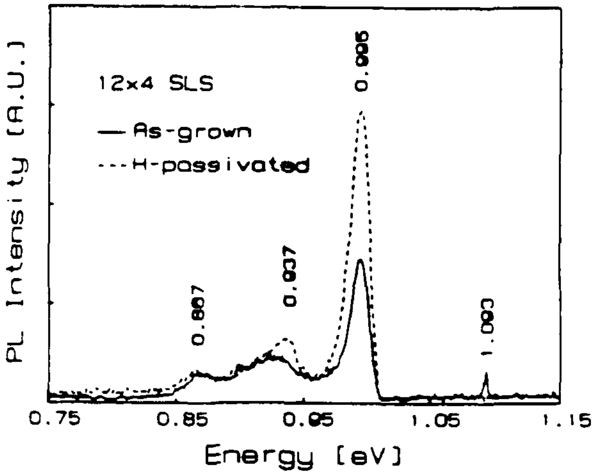

FIG 2. As-grown and hydrogenated photoluminescence spectra of a 12×4 superlattice. The superlattice was passivated for 120 min at 175 °C.

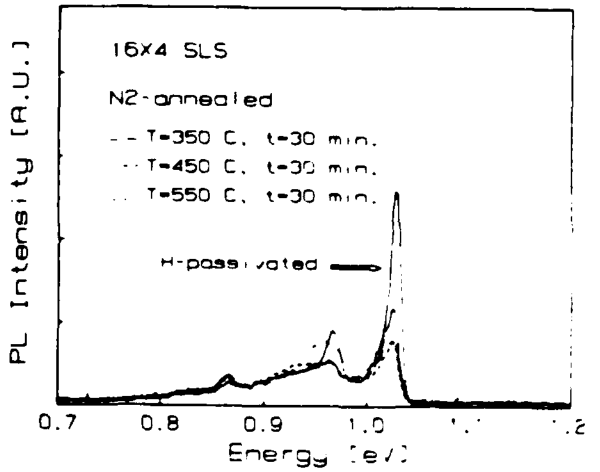

FIG. 3 Annealed spectrum of a 16×4 superlattice to remove H. Three different annealing conditions are used: 350 °C for 30 min, 450 °C for 30 min, and 550 °C for 30 min. Also, the passivated spectrum is plotted for comparison.

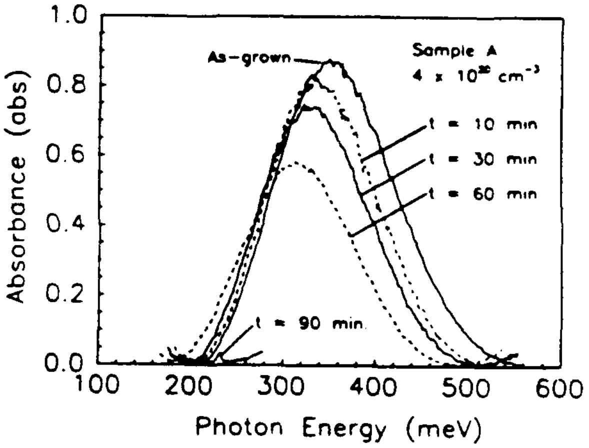

Fig. 4 Absorption spectra for sample A taken after different hydrogenation time periods.

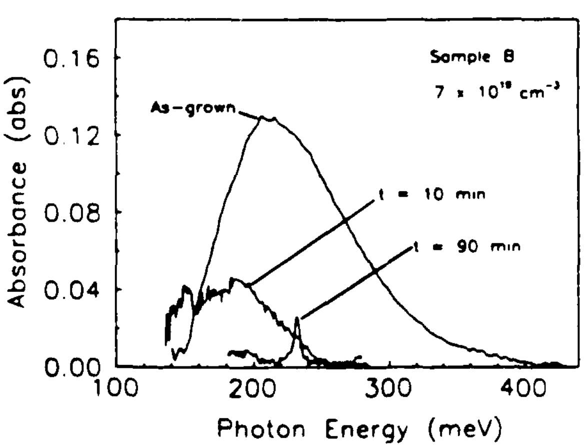

Fig. 5 Absorption spectra for sample B taken after different hydrogenation time periods.

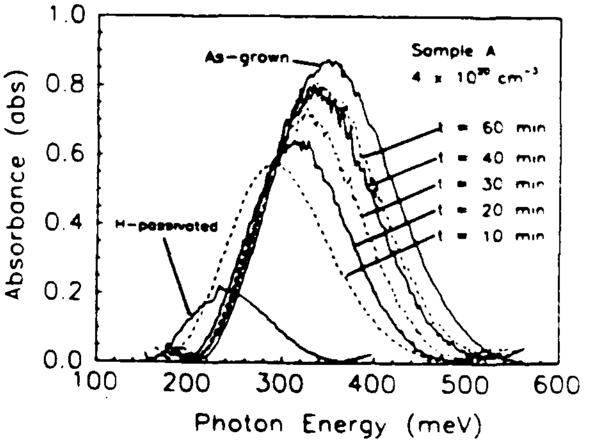

Fig. 6 Absorption spectra for sample A taken after different periods.

EFFECTS OF HYDROGEN ON THE PHOTOLUMINESCENCE OF Si-DOPED GaAs/AlGaAs MULTIPLE QUANTUM WELLS

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By now it is well known that atomic hydrogen is able to passivate shallow impurities in crystalline semiconductors [1]. Hydrogen neutralization of donor and acceptor atoms has been exploited for new device applications including field effect transistors and solid state lasers. Passivation of deep levels by hydrogenation has also been observed and leads to an increase in luminescence efficiency in InP compounds [2]. However, the effects of hydrogen on the electronic and optical properties of two dimensional systems, such as multiple quantum wells (MQW) and superlattices (SL), has received attention only recently. Studies on the photoluminescence properties of GaSb/AlSb MQW [3] and SiGe SL [4] have been made and indicate a similar improvement in the luminescence signal. The purpose of the present work is to extend these results by investigating the effect of hydrogen on the optical properties of Si-doped GaAs/AlGaAs MQW structures.

In these experiments a set of GaAs/AlGaAs MQW samples grown by molecular beam epitaxy (MBE) have been studied. Here we report the results from two samples in this set. Each sample was grown on a semi-insulating GaAs substrate beginning with an undoped GaAs epilayer about 250 nm thick. The MQW structure consisted of alternated layers of AlGaAs barriers, with Al mole content of 0.3, and GaAs wells. The thickness of the barriers Lb was 12.5 nm and that of the wells Lz was 15 nm. The cycle was repeated 63 times to produce a MQW region approximately 1.73 μm thick and capped with a GaAs layer. A Si doping spike was introduced during MBE growth in the wells for sample #324 and both in the wells and barriers for sample #325. The doping spike was about 5 nm thick with a doping level of 5×10^{15} cm^{-3}.

The photoluminescence (PL) characteristics of similar samples have been previously reported by Shanabrook and Comas [5]. They found that the binding energies of the donor impurities increased due to the spatial confinement and reached a maximum when the dopant spike was located at the center of the well. PL measurements that were made of the current samples showed good agreement with the prior results.

Each sample was broken into smaller pieces and specimens were exposed to a RF deuterium plasma operating at low power density (0.04 W cm^{-2}) in order to limit irradiation damage. Two different hydrogenation conditions were studied. The first one, D1193, was for 90 min exposure with the samples at 240°C, the second, D1189, for 360 min exposure with the samples at 200°C.

Photoluminescence (PL) measurements on the hydrogenated samples and on their untreated partners were made at 4.2 K using the 700 nm line of a pyridine II dye laser that was pumped by an Ar cw laser operating at 514 nm. The luminescence was dispersed by a 0.85 m double spectrometer at a spectral resolution of 0.4 meV and detected by a cooled GaAs cathode PMT. The excitation power was varied from 20 mW cm^{-2} to 20 W cm^{-2}.

Typical spectra before and after the two hydrogenation treatments for samples #324 are shown in Fig.1. The excitation power was changed to separate the effect of hydrogen on the impurity related line, that saturates at high excitation power, from the free exciton line that does not. In most of the samples, some changes in the peak position were observed, probably due to inhomogeneity either in the average well thickness or the Al content in the barriers. In some cases, Fig. 1b, we observed the exciton lines of the GaAs buffer layer which indicates that deuterium has reached the buffer layer and has improved its optical quality too.

One of the main results from the PL measurements is that there is a decrease in the FWHM of the free exciton line from 9 meV to 5 meV at high excitation power. This effect is due to a reduction in the low energy side of the peak, which is particularly noticeable at low excitation power where the contributions of the free exciton and the impurity related peaks are more clearly separated. There is also an inversion of the ratio of the free exciton line to the impurity related line, which again is more visible at low excitation power. Furthermore, we observe an increase in the intensity of the exciton line after hydrogenation. This effect is much larger in the case of the D1189 hydrogenation which was done at a lower temperature.

Secondary ion mass spectrometry (SIMS) measurements of the MQW samples were made following the PL measurements. A CAMECA IMS-3f machine was used and D, Al, Si depth distributions were obtained. The absolute D concentration was determined using a D^+ implanted GaAs sample as a standard. The error on the D concentration is estimated to be about 20% and the incertitude in the micro-profilometer measured depth is 7%. SIMS depth profiles for sample #324 are shown in Fig. 2. For the low temperature hydrogenation, D1189, the D level is almost constant throughout the MQW region at a level of 4 x 10^{18} cm^{-3}. The D profile in the substrate is similar to those generally observed in diffusion of hydrogen in GaAs [1] except for a large accumulation of D at the buffer layer/substrate interface. Such an accumulation of diffusing D has been previously observed in D implanted MQW structures [6]. With the high temperature hydrogenation, D1193, we observe a diffusion profile for D, at a lower concentration, in the MQW region as well as in the GaAs buffer. An accumulation of D is also found at the buffer/substrate interface in this sample.

In conclusion, we have observed in our GaAs/AlGaAs MQW samples optical changes similar to those reported in the GaSb/AlSb MQW and SiGe SL studies. There is an increase in the luminescence efficiency and a diminution of impurity related peaks. This process could be used as a method to improve the quality of the MQW structures for device applications. After hydrogenation there is a large, narrow free exciton PL peak which is generally regarded as the signature of a good quality sample material. Our experiments also point out the problem of proper hydrogenation conditions. Changes in these conditions can drastically alter the D diffusion profiles. So, while initial concentrations and location of impurities are important parameters, the time and temperature of hydrogenation, as seen in our results, need to be selected carefully.

ACKNOWLEDGMENT

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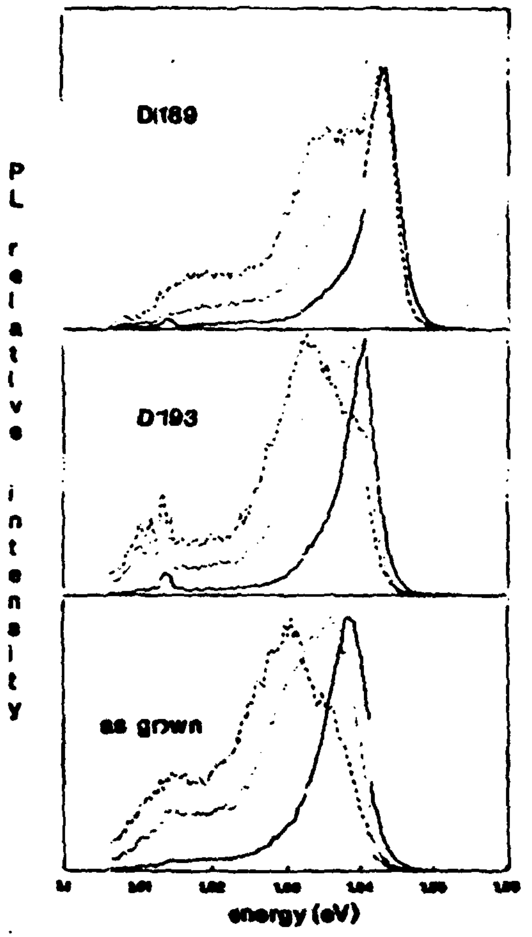

Figure 1

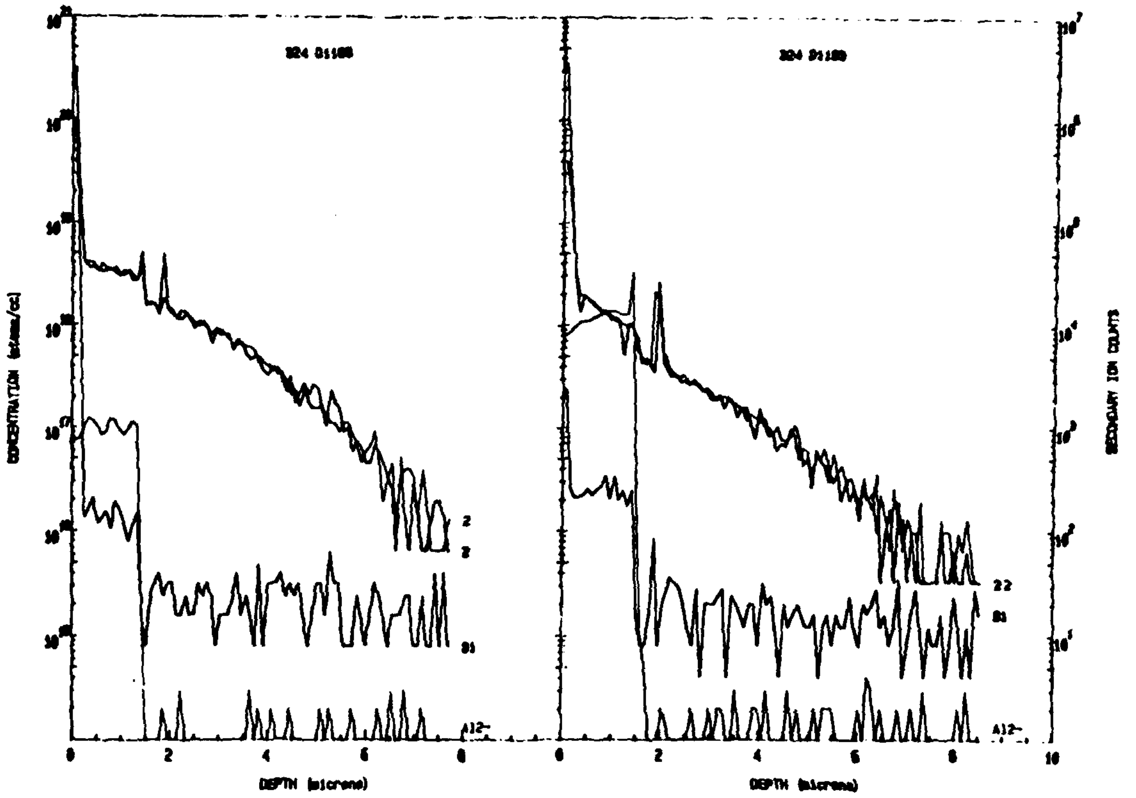

Figure 2

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