PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Hydrogen Atoms and Complexes in Monocrystalline Semiconductors [and Discussion]

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Hydrogen atoms and complexes in monocrystalline semiconductors

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Infrared (IR) measurements of the concentrations of H–B pairs formed in boron-doped silicon heated in H_2 gas and quenched from a temperature in the range 900–1300 °C have led to a new determination of the hydrogen solubility $[H_s] = 9.1 \times 10^{21} \exp(-1.80\,\mathrm{eV}/kT)\,\mathrm{cm}^{-3}$ and there is evidence that H_2 molecules are also formed. The presence of hydrogen leads to the enhancement of the diffusivity of oxygen impurities at temperatures below 500 °C. Indications that hydrogen is present in as-grown Czochralski silicon have been supported by the observation of H–C complexes using the photoluminescence technique. The analysis of the structure of a hydrogen complex by IR vibrational spectroscopy is illustrated for the H–C_{As} pair in GaAs.

1. Introduction

An electron paramagnetic resonance spectrum labelled AA9 has been found at 77 K in high purity silicon following proton implantation at a temperature of 80 K (Gorelkinski & Nevinnyi 1991). The centre responsible was identified as a hydrogen atom in the neutral charge state (H°) occupying a bond-centred (BC) lattice site. To observe the spectrum it was necessary to photo-excite samples, implying that only diamagnetic H^+ or H^- centres were present in the dark. The anneal of the AA9 centre at temperatures above 200 K (in the dark) occurred with second order kinetics and an activation energy of 0.48 eV. With the assumption that this process was due to hydrogen migration the pre-exponential factor D_0 of the diffusion coefficient D_H was estimated to be 10^{-2}–$10^{-3}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. Values of the product $D_H\,[H_s]$, where $[H_s]$ is the solubility of hydrogen, had been deduced previously from the rates of permeation of hydrogen atoms through silicon in contact with H_2 gas at atmospheric pressure at temperatures in the limited range 1092–1200 °C (Van Wieringen & Warmoltz 1956, henceforth referred to as VVW). By introducing temperature or pressure transients, the two quantities were determined separately to give $[H_s] = 4.8 \times 10^{21} \exp(-1.87\,\mathrm{eV}/kT)\,\mathrm{cm}^{-3}$ and $D_H = 7.9 \times 10^{-3} \exp(-0.48\,\mathrm{eV}/kT)\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, the same as for the proposed annealing process for the AA9 defect. It is then implied that the only defects incorporating hydrogen that are stable above 200 K involve other impurities, lattice defects or two or more hydrogen atoms. Such a conclusion is consistent with measurements and appears also to be valid for hydrogen impurities in GaAs.

Confirmation of the value of D_H or $[H_s]$ for hydrogen in silicon, was clearly de-

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sirable. New measurements of [H_s] involving determinations of the concentration of [H–B] pairs formed in boron-doped silicon heated to 900–1300 °C in H_2 gas followed by a rapid quench have therefore been made. These data will be shown to be consistent with parallel measurements of [H_s] made by secondary ion mass spectrometry (SIMS) (Binns *et al.* 1993) (§ 2) and with the early work of VVW. Hydrogen in a form that is not infrared (IR) active was also present in the as-quenched silicon, but was converted to H_2^* defects by 2 MeV electron irradiation. It has been proposed that the 'hidden' hydrogen H_h was present initially as H_2 molecules.

Such heated and quenched material has been compared with silicon heated in the range 225–450 °C in a hydrogen plasma (Brown *et al.* 1988; Newman *et al.* 1991). Greatly enhanced rates of diffusion of grown-in interstitial oxygen impurities (O_i) have been found during low temperature anneals of both types of material and the process has been attributed to a catalytic interaction of fast diffusing H-atoms with O_i atoms (§ 3) (McQuaid *et al.* 1991). Other studies of oxygen diffusion have indicated that hydrogen could be present in as-grown silicon and might also be introduced during low temperature heat treatments of material in air. These ideas have received considerable support from recent photoluminescence (PL) measurements which revealed hydrogen complexed with carbon impurities in samples annealed at 450 °C (§ 4) (Lightowlers *et al.* 1994).

There have been many studies of hydrogen complexes with the aim of determining their local bonding and geometry. One of the best characterized defects is now the H–C_{As} pair produced by hydrogen passivation of carbon acceptors occupying As-lattice sites in GaAs. Pairing of either H or D with either $^{12}C_{As}$ or $^{13}C_{As}$ has led to the detection and assignments of all four localized vibrational modes (LVM) of the complex for each of the four isotopic combinations (§ 5) (Davidson *et al.* 1993; Wagner *et al.* 1995). These results illustrate the value of IR LVM absorption measurements in the study of hydrogen complexes in monocrystalline semiconductors.

2. Hydrogen solubility in silicon

Samples of boron-doped silicon were heated for 2 h at a temperature in the range 900–1300 °C in H_2 gas at a pressure of one atmosphere and then quenched rapidly. The boron concentration [B] = $10^{17}\,cm^{-3}$ was chosen to be greater than the value of [H_s] ≈ $10^{16}\,cm^{-3}$ at 1300 °C extrapolated from the data of VVW. H–B pairs produced during the quench were revealed by an IR absorption line at 1904 cm^{-1} (figure 1) due to the vibrational mode of the paired hydrogen. The integrated absorption coefficient (I_a) of this line was converted to a concentration [H–B] using a previously established calibration (McQuaid *et al.* 1991) for which $I_a = 1\,cm^{-2}$ corresponded to [H–B] = $3.0 \times 10^{15}\,cm^{-3}$. Values of [H–B] for the quenched samples (figure 2) were in close agreement with independent measurements of Veloarisoa *et al.* (1991). It was argued that the data points of Binns *et al.* (1993) represented only lower limits for [H_s] since H–H interactions during the quench might also have led to the formation of H_2 molecules or larger hydrogen aggregates. In fact, anneals of samples at 175–200 °C led to an increase in the concentration of [H–B] pairs which reached a maximum value before decreasing more slowly. The samples clearly contained 'hidden' hydrogen and this hydrogen became mobile and was trapped by boron

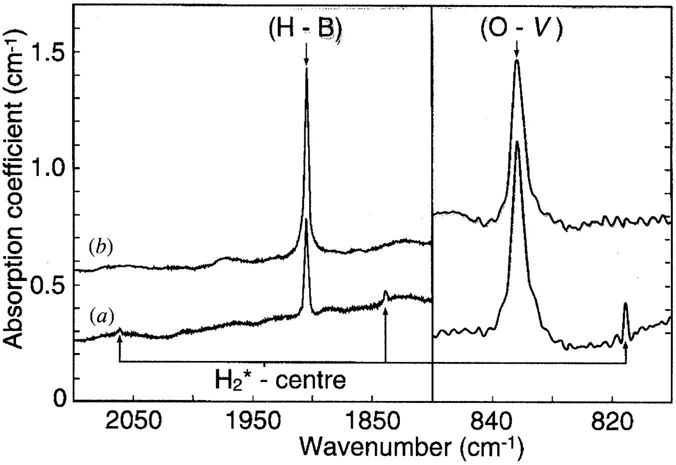

Figure 1. IR spectra following 2 MeV electron irradiation (dose: 2×10^{17} cm^{-2}) at room temperature of boron-doped ([B] = 10^{17} cm^{-3}) Si hydrogenated at 1300 °C for 30 min and quenched. Spectrum (*a*) is for an irradiated as-quenched sample and (*b*) is for an irradiated sample given a post-quench anneal at 200 °C for 30 min to produce $[\mathrm{H{-}B}]_{\max}$. The LVM line at 836 cm^{-1} is due to an oxygen-vacancy complex formed during the irradiation.

acceptors during the anneal. A least squares fit of $[\mathrm{H{-}B}]_{\max}$ (figure 2) yielded $[\mathrm{H{-}B}]_{\max} = 9.1 \times 10^{21} \exp(-1.80\,\mathrm{eV}/kT)\,\mathrm{cm}^{-3}$ for both pure float zone silicon and Czochralski silicon that contained oxygen impurities with $[\mathrm{O_i}] = 10^{18}\,\mathrm{cm}^{-3}$. The assumption that $[\mathrm{H{-}B}]_{\max}$ is equal to $[\mathrm{H_s}]$ therefore led to concentrations in close agreement with those derived by VVW and with the same value of the heat of solution.

The concentrations of deuterium, $[\mathrm{D_s}]$, present in samples heated at various temperatures in deuterium gas at a pressure of one atmosphere, followed by a quench, were then determined by SIMS analyses. Samples implanted with deuterons were used to calibrate the SIMS data and the detection limit was found to be 10^{14} atom cm^{-3}. These points (figure 2) all fall between the line determined for $[\mathrm{H_s}]$ using the IR method and that reported by VVW. The overall agreement must be considered to be excellent when the errors of calibrations of the various measurements are taken into account.

IR measurements showed that $[\mathrm{H_s}]$ varied with the partial pressure of the H_2 gas (mixed with argon) as $p^{0.57}$ following diffusion treatments at 1300 °C (Binns *et al.* 1994), again in agreement with data of VVW and it is concluded that values of $[\mathrm{H_s}]$ refer to neutral H° atoms. The present results give considerably added confidence to the values of D_{H} given by VVW, which had to be separated from $[\mathrm{H_s}]$ because their basic measurement was of the rate of hydrogen permeation.

Irradiation of as-quenched material by 2 MeV electrons to doses up to 2×10^{17} cm^{-2} led to no detectable change in the concentration [H–B] but there was formation of the H_2* defect revealed by very weak IR absorption lines due to vibrational modes of H–Si at 2062, 1839 and 817 cm^{-1} (figure 1): similarly irradiated n-type quenched silicon shows the same IR lines, implying that H_2^* is electrically neutral. This defect, previously produced in silicon irradiated with protons at room temperature, has trigonal symmetry and incorporates two hydrogen atoms, one atom in a BC site and the other in an antibonding (AB) site,

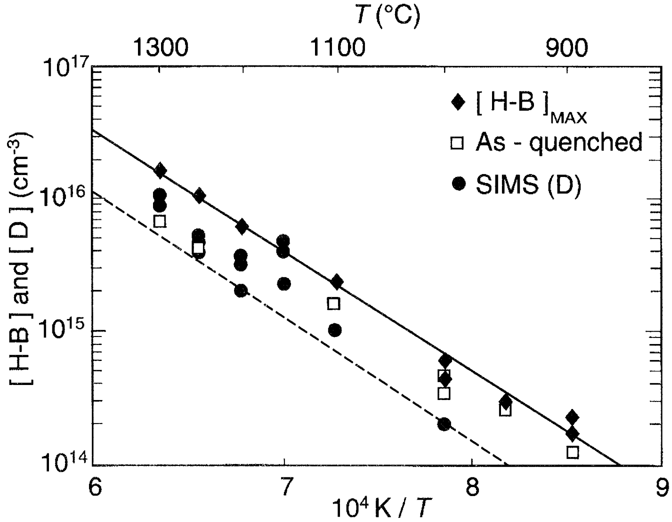

Figure 2. Arrhenius plots of [H–B] pairs versus the hydrogen in-diffusion temperature for as-quenched boron-doped Si samples (□) and $[\mathrm{H{-}B}]_{\max}$ obtained following sample anneals at 175 °C for 5 h (♦). $[\mathrm{H_s}]$ set equal to$[\mathrm{H{-}B}]_{\max}$ (the solid line) may be compared with the results of Van Wieringen & Warmoltz (1956) (dashed line). The solid circles (•) are values of $[\mathrm{H_s}]$ determined from SIMS measurements of in-diffused deuterium.

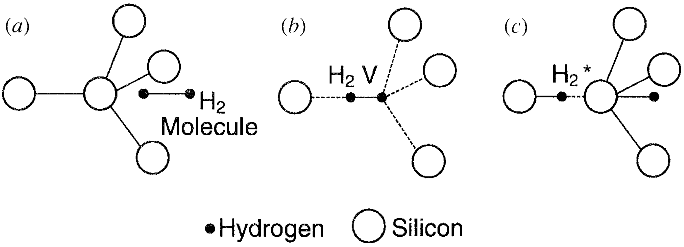

Figure 3. Proposed model for the formation of the H_2^* defect in electron irradiated as-quenched silicon. It has been inferred that the precursor is an interstitial H_2 molecule (*a*) that traps a mobile vacancy (*b*) and the VH_2 defect then traps a mobile self-interstitial (*c*).

straddling a common silicon lattice atom (Holbech *et al.* 1993) (figure 3). The H_2^* defect was not however generated (figure 1) in irradiated boron-doped samples that had been pre-annealed at 200 °C to the stage when [H–B] had reached its maximum value, about double that measured in samples quenched from 1300 °C (figure 2). It was inferred that the irradiation caused the locations of 'hidden' hydrogen atoms to be modified but that two atoms were always in adjacent sites: because [H–B] did not change, there was no evidence for long range hydrogen diffusion. The consequence is that H_2 molecules were likely to have been present in interstitial sites in as-quenched samples. A large proportion of the vacancies and self-interstitials produced by electron irradiation of silicon recombine rapidly and the process is catalysed by oxygen impurities that first trap a vacancy and then a self-interstitial (Davies 1989). If a H_2 molecule also acted as such a catalyst a final metastable configuration could be the H_2^* structure (figure 3).

If the increase in the concentration of [H–B] produced by annealing is equated to that of $[H_2^*]$ produced by irradiation, the IR dipole moment of the former centre would have to be larger than that of the latter by a factor of five to explain the difference in the relative strengths of the IR absorption lines (figure 1). This requirement is consistent with the experimental data reported by Stein *et al.* (1993) who showed that the effective charge η (dipole moment per unit displacement) of H–Si modes is in the range $\eta = 0.15 - 0.8e$, where e is the charge of an electron, whereas $\eta = 1.5e$ for the H–B mode. It should be noted that the I_a of an LVM line is proportional to η^2.

When boron-doped samples were over-annealed at 200 °C to the stage where [H–B] had been reduced from its maximum value, the lost hydrogen was again converted to a form that was not IR-active but this 'hidden' hydrogen could not be revealed by subsequent electron irradiation. It was concluded that this hydrogen, still detectable by SIMS, was present as clusters of three or more atoms that were not present in a significant concentration in the silicon immediately after a quench from 1300 °C.

3. Enhanced oxygen diffusion in silicon

O_i atoms in silicon are electrically neutral and occupy off-axis bond-centred sites. Measurements of the 'normal' diffusion coefficient, given by

$$D_{\mathrm{O}xy} = 0.15\exp(-2.53\,\mathrm{eV}/kT)\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1},$$

extend over 13 decades for a temperature range from 300 °C to 1400 °C (Mikkelsen 1986): there is no evidence that the process involves intrinsic defects or other impurities. However, if samples are heated to a temperature below 500 °C while they are exposed to atomic hydrogen in a radio frequency plasma or if similar low temperature treatments are carried out on samples pre-annealed in H_2 gas at a temperature above 900 °C and then quenched, the oxygen diffusion jump rate is enhanced (Newman *et al.* 1992).

To make low temperature measurements, rectangular bars of Czochralski silicon (containing grown-in oxygen) with the long direction parallel to a [1 1 1] axis are subjected to a uni-axial stress along this axis while they are held at a temperature of 420 °C for 30 min and they are then cooled to room temperature before the stress is removed (Newman *et al.* 1992). Oxygen diffusion jumps occur leading to a depletion of the population n_1 of O_i atoms occupying the [1 1 1] bonds but with corresponding enhancements of the populations n_2 in the bonds with the three other $\langle 1\,1\,\bar{1}\rangle$ axes. Consequently, the IR absorption coefficient $\alpha_\perp$ of the oxygen antisymmetric LVM at 9 µm with the electric vector of the incident radiation polarized perpendicular to [1 1 1] is then greater than $\alpha_\parallel$ for the orthogonal polarization. On reheating, equilibrium is restored when diffusion jumps again lead to equal populations of O_i atoms in all four $\langle 1\,1\,1\rangle$ bonds. The exponential decay of the normalized dichroism $(\alpha_\perp - \alpha_\parallel)/\alpha_\perp$ has a time constant $\tau^* = (a_0^2/64D_{\mathrm{O}xy})$, where $a_0 = 5.42$ Å is the lattice spacing of silicon. For samples annealed in a plasma, enhanced diffusion jumps occur first at the surface and the depth of this region increases with increasing periods of heating, due to in-diffusion of a species identified with atomic hydrogen (Newman *et al.* 1991). There is no direct correlation with the values of D_H given by VVW but this is not expected as trap-limited diffusion would almost certainly occur in relatively impure Czochralski silicon. For samples first given high temperature anneals, the alignment process is carried out as the second step followed by a third treatment at a lower temperature when the time constant τ^* is measured. Enhanced oxy-

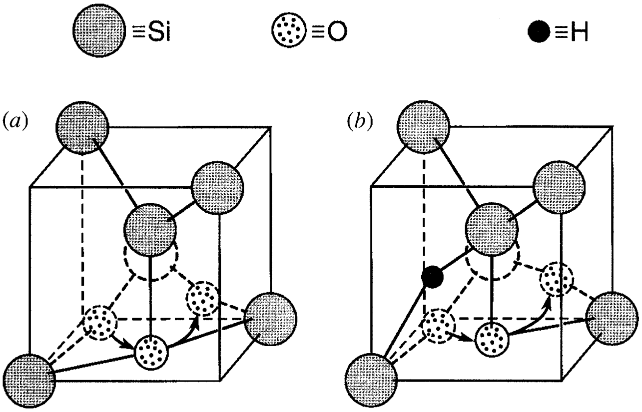

Figure 4. Diagram showing (*a*) the trajectory of an interstitial oxygen atom in Si making a single diffusion jump from one bond to the next. The proposed enhancement of the process shown in (*b*) results from the presence of a hydrogen atom (after Estreicher 1990).

gen diffusion jumps then occur uniformly throughout samples. Enhancements of $D_{\mathrm{O}xy}$ were also evident in both types of sample from the measured rates of loss of isolated $\mathrm{O_i}$ atoms from solution due to the formation of oxygen aggregates. Enhancement factors are about 5, 30 and 300 for temperatures of 450, 400 and 350 °C, leading to an activation energy of 1.8–2.0 eV The enhancement of $D_{\mathrm{O}xy}$ has been investigated using two different theoretical models which imply that the proximity of a hydrogen atom to an $\mathrm{O_i}$ atom in silicon leads to the lowering of the barrier for it to make a diffusion jump (figure 4) (Estreicher 1990; Jones *et al.* 1991). The H-atom then diffuses away until it encounters another $\mathrm{O_i}$ atom, and so on, so that the hydrogen is only a catalytic agent in the process. Experimentally, there is no evidence from IR spectroscopy for the formation of stable H–$\mathrm{O_i}$ pairs during this process, while the concentration of diffusing H-atoms remains unknown.

Heat treatment of Czochralski silicon below 500 °C leads to the formation of thermal donors (TD), and electron nuclear double resonance measurements made on samples containing enriched $^{17}\mathrm{O}$ show that oxygen atoms are incorporated in these centres (Michel *et al.* 1989). Newman *et al.* (1991) then found that the ratio of oxygen atoms lost from solution to the number of donors formed is always close to 10, irrespective of whether or not the oxygen diffusion rate is enhanced. The results of Brown *et al.* (1988) relating to enhanced rates of TD-formation therefore explain the similar observations of Fuller & Logan (1957) for Si crystals grown in a hydrogen atmosphere. It is clear that it is the presence of hydrogen in a crystal that leads to the enhancement of $D_{\mathrm{O}xy}$. Finally, it has to be noted that measurements made on as-grown samples annealed in air, particularly at temperatures below 400 °C, have revealed small enhancements of the oxygen diffusivity, implying that hydrogen impurities may have been present in a low concentration.

4. Hydrogen as an inadvertent impurity in silicon

Self-interstitials produced in silicon irradiated by 2 MeV electrons at 300 K or higher temperatures are mobile and are trapped by neutral substitutional carbon atoms, whereupon the two atoms exchange their lattice sites. The carbon interstitials then diffuse rapidly and form complexes with remaining undisplaced carbon atoms, oxygen atoms or additional self-interstitials to form complexes that are detected with the greatest sensitivity as sharp lines in high resolution PL spectra (Davies 1989). These lines frequently show small shifts in their energies when samples contain ^{13}C rather than ^{12}C or ^{18}O rather than ^{16}O. Likewise, it has now been demonstrated that certain complexes also incorporate a hydrogen atom since similar isotopic shifts have been observed when ^{1}H is replaced by ^{2}H(D) (Safonov & Lightowlers 1994). Self-interstitials are also produced in silicon crystals to accommodate the local increase in volume when grown-in O_i atoms precipitate to form SiO_2 particles, even at 450 °C, and there is again formation of carbon related complexes. The defects of primary interest here are the I-centre (PL line at 0.9650 eV) and the T-centre (PL line at 0.9351 eV), both of which have now been shown to incorporate a carbon atom and a hydrogen atom, while the I-centre may also contain an O_i atom (Lightowlers *et al.* 1994).

Most samples were cut from a crystal with $[O_i] = 1.8 \times 10^{18}\ \mathrm{cm}^{-3}$ and $[C] = 3.4 \times 10^{17}\ \mathrm{cm}^{-3}$ and heated at 450 °C for 15 h in pure argon, air, H_2 gas, D_2 gas, argon containing D_2O vapour or a hydrogen plasma: the effect of 'soaking' oxidised samples in HF acid diluted with D_2O was also studied. PL lines from the T and I-centres (and other defects) were present in all these samples but their strengths relative to the emission from excitons bound to grown-in phosphorus donors varied according to the sample treatments. The lines were stronger after heat treatments in air rather than in pure argon and were much stronger after pre-treatments at 450 °C for 15 h in a hydrogen plasma. The T and I-lines for samples heated in argon containing a small partial pressure of D_2O vapour both appeared as close doublets (figure 5). The higher energy components are due to complexes incorporating a D atom rather than an H atom. After polishing to remove a surface layer 27 μm in thickness, the concentrations of the T(D) and I(D) centres were reduced by a factor close to 8 compared with those of the T(H) and I(H) centres (figure 5), due to the limited diffusion depth of the deuterium. Similar in-diffusion occurred from D_2 gas and from a surface oxide layer which had been soaked in D_2O for 1 h. These observations are clearly consistent with the inference that a small concentration of hydrogen is present in as-grown silicon and that hydrogen in-diffusion occurs during post-growth heat treatments and could lead to enhancements of $D_{\mathrm{O}xy}$ (§ 3).

5. The H–C_{As} complex in GaAs

The structures of the T and I complexes discussed in § 4 are not known and hydrogen modes have not so far been detected by IR LVM spectroscopy. Such absorption has however been observed from various deep defects, shallow donors and acceptors paired with hydrogen in silicon and several III–V compound semiconductors. For carbon acceptors C_{As} in GaAs, theory indicates that the H-atom should occupy a BC site and be strongly bound to the carbon atom: there is only a weak interaction between the H-atom and its collinear Ga neighbour (figure 6) (Jones & Öberg 1991). Two modes, each with A_1 symmetry, have been detected by LVM spectroscopy. The antisymmetric A_1-mode clearly corresponds to the high frequency H–$^{12}C_{As}$ stretch mode at 2635 cm^{-1}, while the symmetric A_1^+ mode with a much lower vibrational frequency of 453 cm^{-1} has been identi-

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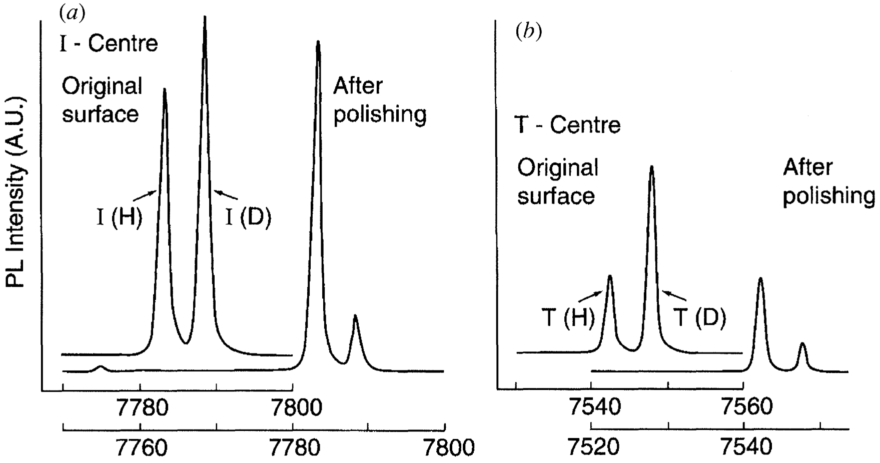

Figure 5. Photoluminescence due to (*a*) the I-centre and (*b*) the T-centre formed in Si after an anneal at 450 °C in argon containing D_2O vapour. The limited diffusion depth of the D atoms is indicated by the reduction in the strengths of the higher energy components of the doublets due to I(D) and T(D) centres after removing a surface layer 27 μm in thickness.

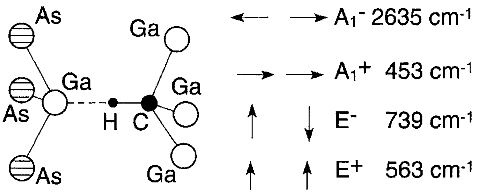

Figure 6. The model of the H–C_{As} pair in GaAs, together with the directions of the displacements of the two atoms for the two A_1 modes and the two E modes. The frequencies shown are for the modes of H–$^{12}C_{As}$ pairs.

fied with the motion of the almost rigid H–^{12}C ‘molecule’ along the trigonal axis (Davidson *et al.* 1993). Assignments of the transverse E^+ and E^- modes were not obvious, as these two modes were predicted by theory to lie in the same spectral region. In initial experiments only one E-mode of H–$^{12}C_{As}$ and one E-mode of D–$^{12}C_{As}$ pairs were detected, with the latter mode having the higher frequency. It was then recognised that the two types of mode could be distinguished if ^{12}C were replaced by ^{13}C since ‘carbon-like‘ modes would exhibit an isotopic shift of some 20 cm^{-1}, whereas H-wag modes would show only much smaller shifts. Conversely, replacing D by H would in general produce a huge shift in the ‘H-like’ modes but only a small change in the frequency of a ‘C-like’ mode.

Crystals containing ^{13}C were characterized, initially by IR measurements and very recently by Raman scattering measurements: comparisons were also made with local density functional (LDF) theory (Davidson *et al.* 1993; Wagner *et al.* 1995). Knowledge of the frequencies of the A_1^- modes of both H–$^{13}C_{As}$ and D–$^{13}C_{As}$ allowed estimates to be made of anharmonicity but the significant new advance was the analysis of the E-modes by a ‘mass and spring’ model to yield the level crossing diagram shown in figure 7. It became clear that the E-modes detected originally from H–$^{12}C_{As}$ and D–$^{12}C_{As}$ belong to the lower and upper branches respectively, explaining the apparent enigma. H–$^{12}C_{As}$ and H–$^{13}C_{As}$ wag (E^-) modes, initially not detected by IR absorption measurements, were

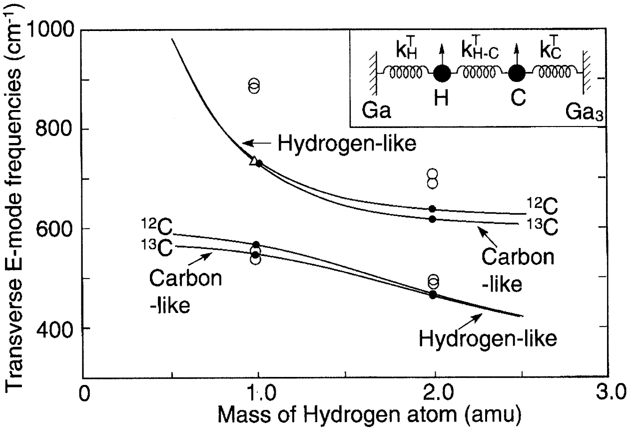

Figure 7. Level crossing diagram for the E modes of H(D)–^{12}C(^{13}C) pairs in GaAs. Measured (IR and Raman) energies are shown as full circles and an open triangle: open circles are the results of LDF theory. The solid lines were obtained from the model shown in the inset with $k_{\mathrm{H}}^{\mathrm{T}} = 9.2\ \mathrm{N\ m^{-1}}$, $k_{\mathrm{H-C}}^{\mathrm{T}} = 20.0\ \mathrm{N\ m^{-1}}$ and $k_{\mathrm{C}}^{\mathrm{T}} = 244.6\ \mathrm{N\ m^{-1}}$.

predicted to occur close to 745 $\mathrm{cm^{-1}}$. LDF theory had indicated that these modes had a small dipole moment but that they should be Raman active. The lines were found subsequently by both Raman and IR measurements at 739 $\mathrm{cm^{-1}}$, while Raman measurements using various polarization configurations have confirmed all the mode symmetries.

6. Conclusions

Measurements of the hydrogen solubility in silicon at high temperatures have led to agreement with early work and so give support to the values D_{H} determined from permeation measurements. The new work also demonstrated the existence in quenched silicon of hidden hydrogen that was revealed following 2 MeV electron irradiation. The available evidence supports the view that this hidden hydrogen is present as $\mathrm{H_2}$ molecules. Nevertheless, other types of hidden hydrogen can exist, possibly in the form of larger aggregates, and this hydrogen cannot be detected after electron irradiation.

The presence of hydrogen in silicon leads to enhancements in the diffusivity of interstitial oxygen atoms at temperatures below about 500 °C, and the process has been attributed to catalytic interactions with fast diffusing hydrogen atoms. Other work had implied that small enhancements of $D_{\mathrm{O}xy}$ can occur in samples not deliberately contaminated with hydrogen. PL measurements then revealed carbon–hydrogen complexes in heated Czochralski silicon with the inference that hydrogen was present in the as-grown material. The structures of these defects are still unknown but other types of complexes are now well characterized. As an example, the analysis of the H–$\mathrm{C_{As}}$ complex in GaAs by IR and Raman LVM spectroscopy was described.

A central feature of all this work has been the synergy between experiment and first principles theory. This is an exciting development that is likely to lead to further significant advances in the future.

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R. Davidson, R. Jones, T. B. Joyce, E. C. Lightowlers, S. A. McQuaid, R. E. Pritchard, J. H. Tucker and J. Wagner. The Science and Engineering Research Council, U.K., are thanked for their financial support.

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Discussion

W. Jackson (*Palo Alto, CA, U.S.A.*). What is the activation energy of conversion from hidden H to B–H?

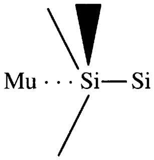
R. C. Newman. The process occurs in a narrow temperature range from 170 to 200 °C and an activation energy close to 1.5 eV is indicated. Further work involving isothermal anneals is in progress.

M. Symons (*Department of Chemistry and Biological Chemistry, University of Essex, U.K.*). I would have expected that some form of Raman spectroscopy would have been best for studying H_2 in silicon?

R. C. Newman. The silicon samples discussed in this paper have not so far been examined by Raman scattering. However, as the maximum concentration of H_2 molecules is no greater than 10^{16} cm^{-3}, even in samples quenched from the highest temperatures of 1300 °C, it is thought to be unlikely that they would be detected by this technique.

M. Symons. I was very interested in the 'anomalous hydrogen' model, which, if I understood correctly, comprises one H in the normal bond-centred site, and one on the back-side of one of the silicons. The latter site is exactly the one that I have postulated for the major (H^0_T or Mu^0_T) centre. Am I right in saying that the site is made more favourable by the presence of the bond-centre hydrogen?

I expect that my model (Symons 1984) for the caged muonium has long since been forgotten, so maybe I should give a brief résumé. It seems that the idea of bond-centred muonium unit is accepted, at least for the moment. However, in my view, it is the other centre (Mu^0_T) that is the puzzle, although most people seem happy with the concept of an atom in a cage. My problem as always been, how can there by a loss of 50% of the expected electron density? Simple cage compression should cause an increase, so it must be a result of delocalization. My model was a locally bonded unit, closely similar to the bond-centre unit, but with $Mu^{\cdot}$ outside rather than inside:



The absence of anisotropy then requires rapid migration between the four equivalent sites, which in turn, requires relatively little distortion. An alternative is to have the atom in the centre of the cage but experiencing some transfer into the conduction band. The problem with this is that the more the unit comes to resemble Mu^+ (H^+), the more this will need to interact with the s-electrons of the silicon cage, which brings us back to the original model or to the bond-centre model!

R. C. Newman. The following ideas are now generally accepted. Isolated hydrogen atoms in silicon crystals may be present in three different charge states, namely, H^+, H^0 and H^-, dependent on the position of the Fermi level. H^- is located along a crystallographic $\langle 1\,1\,1 \rangle$ axis in an antibonding (AB) site, where the electron density is 'low'. The hydrogen atom is therefore in some sense a 'caged' interstitial but bonded to one silicon atom. H^+ is located in a bond-centred (BC) site, where the electron energy is high. As a consequence, the H_2^* defect $\text{Si–H}^+ \ldots \text{Si–H}^-(\text{AB})$, in which an H^- atom occupies an AB site collinear with an H^+ (BC) complex, would be a neutral defect and all the bonding would be satisfied. According to theory, this is a metastable arrangement only slightly higher in energy than an interstitial H_2 molecule and there is substantial experimental evidence to support the model (Holbech *et al.* 1993).

Recent experiments have implied that the isolated H atom is a negative-U defect (Johnson *et al.* 1994): hydrogen atoms may be present as H^- or H^0 species in BC sites, while H^- and H^0 species may be present in AB sites. However, H^0 is not an equilibrium charge state and it has been proposed that there is disproportionation of $2H^0$ into H^+ and H^-. The formation of H_2^* paired defects would then further lower the total energy.

These various ideas would appear to be consistent with the models proposed for Mu and Mu*, but the effect of the higher zero point energy would have to be taken into account.

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