Theory of Hydrogen in Semiconductors [and Discussion]

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Theory of hydrogen in semiconductors

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Hydrogen exhibits several distinct effects in semiconductors. These include: the neutralization of shallow impurities; the removal of deep states which act as recombination centres; the catalytic enhancement of oxygen diffusion; the change in the electrical characteristics of transition metal impurities. The basic theoretical methods that have been used to investigate these are described along with their principal results and outstanding problems.

1. Introduction

Hydrogen, which can be introduced into a semiconductor by a variety of methods, such as from a plasma or H_2 gas, reacts with the solid and its defects in many different ways. The isolated H-interstitial diffuses with a low activation energy – at least in the neutral and positively charged states – and hence it can reach and bind with other defects. The resulting complexes are often electrically inactive but this is not always the case. The passivation of shallow impurities is well known. Less well understood is the interaction of H with neutral impurities, extended defects and defects with deep levels such as vacancies and transition metal impurities. In some cases, gap levels are displaced or introduced whose occupancy can lead to photostructural changes or give rise to photoluminescence lines. H also has important catalytic effects on atomic processes, e.g. O-diffusion in Si and the growth of chemically vapour deposited diamond. This multitude of H related phenomena has generated extensive theoretical and experimental work. Here, we shall briefly discuss the theoretical methods that have been used in § 2 and describe their principal results and outstanding problems in later sections.

There have been several recent reviews of H in semiconductors (e.g. Myers *et al.* 1992; Van de Walle 1992), so we shall emphasize here recent work revealing the diverse nature of H interactions with non-metallic solids. Lack of space prevents a proper discussion of the disruption to the bonding on C_{60} (Estreicher *et al.* 1992) and reactions of H with the diamond (1 1 1) surface (Latham *et al.* 1993) and we shall concentrate on the effects of H on Si and GaAs.

There are several lattice sites which are important in the description of impurities in a diamond lattice. Among these are the bond-centred (BC) site which is the mid-point of the bond; the tetrahedral interstitial site, T_d, which lies at $\frac{1}{4}a(\overline{1}\,\overline{1}\,\overline{1})$; the anti-bonding (AB) site lying between the lattice site at (0 0 0) and the T_d site; the C site which is found at $\frac{1}{2}a(1\,0\,0)$. Even if the impurity is not exactly at these sites, which often happens, we still describe it by reference to the nearest high symmetry site, e.g. interstitial O is referred to as O_{BC}, even though the Si–O–Si angle is less than 180°.

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2. Theoretical methods

In treating H related defects it is essential to use a method that allows atoms to move, or relax, and permit charge to flow between atoms. This is because the energy differences between structural configurations are very sensitive to bond lengths and the charge state of the defects. This is illustrated very well by the H interstitial in Si which is bistable: the lattice location of H^+ is quite different from H^-, and in the former there is an enormous disruption to the Si lattice emphasizing the need to allow for atomic relaxation.

There are two main approaches to the study of H defects in semiconductors: a cluster method where the surface dangling bonds are themselves passivated by H and further H atoms are placed within the cluster, and a supercell method where the defect is inserted into a larger unit cell. Both methods make use of the insensitivity of bond lengths and structures to anything other than the local environment. For example, the C–C bond length in neopentane, C_5H_{12} is within 1% of that of diamond, and the calculated C–C length in $C(CH_3)_3$ is within 0.4% of the bond found in graphite. However, defect wave functions may not be localized and clusters often possess electronic gaps much larger than those observed whereas the supercell approach leads to smaller gaps. This means that the two approaches may give conflicting results for defects whose properties are critically dependent on the extent of the wave functions.

Together with the above strategies, a technique is required which solves the Schrödinger equation within the Born–Oppenheimer approximation. The usual method is to expand the wave function in terms of a basis either of plane waves or of localized functions. Then an approximate scheme for solving the many-body aspects of the electron gas is required and there are two main approaches – local density functional (LDF) and Hartree–Fock (HF) theory. Both of these average the effects of all the electrons so one ends up solving a Schrödinger equation for the single particle electronic states with the potential determined self-consistently. The self-consistent potential allows for charge transfer between atoms and is essential for a quantitative description of bond lengths, vibrational modes, etc. Although the LDF and HF treatments look superficially similar, there are important differences in the theoretical basis of the approaches and their treatment of correlation effects. The LDF theory is to be preferred as it is simpler to implement and has the tremendous advantage of including pseudo-potentials which allow an accurate description of bonding of heavy elements.

The LDF and HF are first-principles methods, but their implementation still requires an enormous computational effort. In the localized basis description, this effort lies in evaluating the four-centre integrals needed for the Hartree and exchange-correlation energies. There are then a very large number of treatments which make approximations to facilitate the evaluation of these integrals (Halgren & Lipscomb 1973; Jones & Sayyash 1986). In other cases, the various integrals are either ignored or replaced by parametrized expressions. These parameters are fitted to experiment ensuring that the method works for a certain class of problems. Examples of these methods include CNDO, MINDO, etc. (Pople & Beveridge 1970). In the plane wave basis methods, the time dominant step is the evaluation of the eigenvalues of a very large Hamiltonian. This can be achieved by using the Car-Parrinello (1984) formalism but even then the calculations are most time consuming. In early years, it was the structure of the H defects that dominated investigations, but now there are much more demanding questions to be answered such as the evaluation of the hyperfine parameters (Van de Walle & Blöchl 1993), migration energies (Buda *et al.* 1991) and the effect of H on local vibration modes (LVMs) of impurities.

The pioneering studies of H in semiconductors used semi-empirical CNDO methods (Mainwood & Stoneham 1980) to investigate the stability of H at various sites in the lattice but unfortunately overlooked the BC site. This method has continued to be used in various modifications. DeLeo (1991) used a similar technique called MNDO and a cyclic cluster method was used by Deák *et al.* (1988). In general these methods have given useful information which have often been substantiated by the more rigorous *ab initio* techniques.

We shall refer to a number of results derived using the LDF cluster method introduced by ourselves (Jones & Sayyash 1986; Jones 1992). This uses a large (*ca.* 100 atom) cluster terminated by H atoms and basis sets consisting of Gaussian orbitals to expand the wave function as well as the charge density. The self-consistent energy is evaluated for an arbitrary structure, and the forces computed for any number of atoms. These are then allowed to move, or relax, until the forces vanish, i.e. the minimum energy configuration has been found. The second derivatives of the energy can also be evaluated and yield the LVMs of the defect.

3. Interstitial hydrogen

Experimental information on interstitial H has mainly come from muon spin-polarization studies of the two paramagnetic forms, Mu* and Mu, and these have been attributed to neutral muons residing at BC and T_d sites respectively (Cox & Symons 1986; Estle *et al.* 1987; Estreicher 1987). The theory shows that H is bistable: in its positive and neutral charge states it lies at a BC site with a high gap level. When negatively charged it lies at a T_d site with a level low in the gap. These results can be understood as the propensity for the proton to be attracted to the heaped up charge density at the bond centre and for H^- to be repelled to an interstitial site in the open part of the lattice. The migration energy of H from BC to T_d or another BC site is also low: about 0.3 to 0.5 eV (Van de Walle *et al.* 1989). This is the adiabatic barrier to H motion. For H^- it is believed to be larger (Jones 1991). These low barriers cause H to rapidly diffuse to other defects or other H atoms. H°_{BC} in Si, created by proton implantation, gives an EPR signal, AA9 (Gorelkinskii & Nevinnyi 1991), which has the same (scaled) hyperfine parameters as Mu*. Recently, the AA9 signal has been observed by the Århus group (Holm *et al.* 1991). n-Si was proton implanted at low temperature and the resulting lattice damage drives the Fermi-level to mid-gap. Any H_{BC} present would be in its positive charge state and hence diamagnetic. AA9 was only observed when band gap light photoexcited H°_{BC}. The signal was also correlated with an electron trap at $E_c - 0.16$ eV (E_3') identified in DLTS. The AA9 and E_3' signals disappeared at 100 K, with an activation energy of 0.29 eV, which was interpreted as a transformation of H°_{BC} to H^- by a thermally activated jump to a T_d site followed by electron capture. It was also argued that at 200 K, H^+ moved to a trap and became converted to $H^-_{T_d}$.

The good agreement between the calculated and observed hyperfine parameters for Si:H_{BC} (Van de Walle & Blöchl 1993) confirm that the Mu* assignment is correct. An LVM has been assigned to H_{BC} at 1990 cm^{-1} by Stein (1979) which is correlated with the presence of the E_3' centre, and this frequency agrees with theoretical calculations (Van de Walle *et al.* 1989; Jones 1991; Deák *et al.* 1991).

The solubility of H in Si has been considered theoretically by Van de Walle (1994). He finds that the energy of H°_{BC} is greater than that of H in a H_2 molecule in free space by 1.21 eV, which must then be the activation energy for the concentration of H_{BC} in solution. Van de Walle was able to obtain agreement with the high-temperature experimental values of the solubility even though the dissolution energy is observed to be 1.8 eV (Binns *et al.* 1994).

4. Passivation of shallow dopants

It is well known that shallow dopants can be passivated by H (see Myers *et al.* 1992). The reduction in carrier concentration is accompanied by an increase in mobility as a consequence of the removal of ionized scatterers. Infrared (IR) absorption measurements (Stavola 1991; Pajot 1991; Newman 1994) have provided reliable models for these complexes although direct methods such as channelling studies (Bech Nielsen *et al.* 1988) have been carried out for some impurities.

Theoretical investigations for Si (DeLeo 1991; Van de Walle *et al.* 1989; Chang & Chadi 1989; Denteneer *et al.* 1990) and GaAs (Briddon & Jones 1990; Amore Bonapasta 1993) have generally led to the viewpoint that acceptors are passivated with H near a BC site, which may be closer to either the impurity as in Si:B and GaAs:C or to the host atom as group II acceptors in GaAs. Donors are passivated with H at the anti-bonding (AB) site away from the impurity as in Si:P (Denteneer *et al.* 1990; Zhang & Chadi 1990) and GaAs:S (Rahbi *et al.* 1994). In GaAs, Si_{Ga} is passivated with H at the AB site to the Si atom (Briddon & Jones 1990). The reasons for these site locations for H are not entirely clear. A remote impurity-H pair would be expected to have the stable structures consisting of H^+_{BC}–acceptor and $H^-_{T_d}$–donor but chemical bonding arguments must be used within the molecular complex. Diamond may be an exception to this rule. LDF cluster calculations (Breuer & Briddon 1994) indicate that H is bonded to a B atom near the C-site rather than the expected BC one.

The dissociation energies of shallow impurity-H complexes in Si and GaAs are of the order of 1–2 eV (Johnson *et al.* 1991). Van de Walle (1994) finds the BH and PH complexes dissociate with energies of 1.1 and 1.0 eV respectively, which are close to the observed values.

A particularly important example of H-passivation is that of C_{As} in $Al_xGa_{1-x}As$. In the case of GaAs, $x = 0$, all the LVMs have now been observed. These investigations have revealed interesting aspects of the physics of dynamical systems and especially those arising from anharmonic effects. According to the above, H should lie close to a BC site between C and a Ga atom, and theory indeed shows that this configuration is more stable than H at an AB site to C by 0.63 eV (Jones & Öberg 1991; Amore Bonapasta 1993). According to the cluster calculations, the C–H and H–Ga lengths are 1.126 and 2.253 Å. Thus C is fourfold coordinated and the Ga atom has been displaced away from its site becoming three fold coordinated. Thus the atoms of the C–H... Ga 'unit' have their normal valencies and this is enough to clear the gap from states. Uniaxial stress studies on the C–H stretch mode confirm that the defect has C_{3v} symmetry (Clerjaud *et al.* 1992) with a reorientation barrier for H among the four $\langle 1\,1\,1\rangle$ directions of 0.5 eV.

The complete sets of LVMs deduced from theory for both GaAs (Wagner *et

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Table 1. *Calculated and observed LVMs, in* cm^{-1}, *due to* C–H *in* GaAs *and* AlAs

	obs. GaAs[a]	theory GaAs	obs. AlAs[b]	theory AlAs
^{12}C–H	2635	2950	2558	2885
^{13}C–H	2628	2942	2549	2877
^{12}C–D	1969	2154	1902	2111
^{13}C–D	1958	2144	1894	2100
A_1 modes				
^{12}C–H	453	456	487	466
^{13}C–H	438	440	477	453
^{12}C–D	440	442	480	454
^{13}C–D	427	428	471	442
E^- H-like modes				
^{12}C–H	739	888	671	740
^{13}C–H	730	883	653	725
^{12}C–D	637	707	657	684
^{13}C–D	617	693	635	662
E^+ C-like modes				
^{12}C–H	563	553	ND	559
^{13}C–H	548	536	ND	551
^{12}C–D	466	495	ND	437
^{13}C–D	464	487	ND	436

[a] Wagner *et al.* 1994. [b] Pritchard *et al.* 1994*a*.

al. 1994) and AlAs (Pritchard *et al.* 1994*a*) are given in table 1 together with the observed modes found by both IR and Raman spectroscopy. The theory finds that the C–H stretch modes are very anharmonic and this is important as it can explain the anomalous isotopic shifts of the modes (Davidson *et al.* 1994). The X–H stretch mode frequency ν is often written as

$$\nu^2 = k(1/M_{\mathrm{H}} + 1/\chi M_{\mathrm{C}}).$$

Here χ is an effective mass parameter and is expected to be greater than unity in this case. However, an analysis of the experimental frequencies given in table 1 for different isotopes shows that χ is less than unity (Davidson *et al.* 1994). The reason for this is the neglect of anharmonicity. If this is included then the observed anharmonic fundamental frequency, ω, differs from ν by an anharmonic parameter B, where

$$\omega = \nu - B/M.$$

To account for the data, B must be about 176 amu cm^{-1} (Davidson *et al.* 1994) showing a strong anharmonic component and yet curiously no overtone has been reported. This is to be contrasted with the linear HCN molecule where an overtone has been observed with an anharmonic parameter of 102 amu cm^{-1} (Herzberg 1945). The anharmonic effects for both C–H in GaAs and HCN have recently been investigated in detail by us (Jones *et al.* 1994) and they show that B in the former is 156 amu cm^{-1} and 106 amu cm^{-1} in the latter. These values are close to the observed ones and the large anharmonicity in GaAs is then attributed to the effect of the close-by three-fold coordinated Ga atom. The absence of the overtone is then found to be due to electrical anharmonicity, i.e. when the dipole moment of the complex varies nonlinearly with the displacement of H, as this strongly suppresses the transition matrix element. Another curiosity of the complex, is that although the C atom is pushed towards the three back-bonded Ga atoms, which might have expected to displace upwards the C related LVMs beyond 583 cm^{-1}, the LVM due to C^{-}_{As}, the A and E modes of the C–H complex are actually pushed downwards to 453 and 563 cm^{-1}. This is due to the displacement of the three Ga neighbours outwards, away from C, so that the three C-Ga bonds actually increase in length. A similar effect does not happen in the Be_{Ga}–H_{BC}–As system (Nandhra *et al.* 1988; Briddon & Jones 1990).

The high frequency H-E modes, which are due to the movement of H perpendicular to the C–H bond, also display unusual isotopic shifts but these are due to the strong interaction between modes of the same symmetry when H is replaced by D.

Table 1 also shows that the C–H stretch mode in AlAs occurs at a slightly lower frequency than that in GaAs. Now the C–Al bond is stronger than the C–Ga one, and hence when H is introduced in the alloy, it naturally prefers a BC site between C and Ga rather than C and Al. Consequently, as x increases in the alloy, the Al_nC–H...Ga defects, with at first n equal to 1, then 2 and 3 appear, rather than those of $Al_{n-1}C$–H...Al (Pritchard *et al.* 1994*b*). Furthermore LVM spectroscopy can distinguish these defects and hence the deliberate incorporation of H can, in principle, reveal the numbers of C atoms surrounded by n Al atoms.

5. Hydrogen aggregates in silicon

Interstitial H diffuses rapidly and is expected to complex with many defects including itself. Early theoretical calculations suggested that a close-by donor–acceptor complex consisting of H_{BC}–H_{AB} was particularly stable (Briddon *et al.* 1988; Chang & Chadi 1989; Deák *et al.* 1991). Evidence has recently been found that this exists in H-implanted Si (Holbech *et al.* 1993). The four LVMs attributed to the defect occur at 2062, 1838, 1599 and 817 cm^{-1}. These anneal out together around 180°C. The weak line at 1599 cm^{-1} is an overtone of the E mode of the C_{3v} centre at 817 cm^{-1}. The 2062 and 1838 cm^{-1} LVMs represent Si–H_{BC} and Si–H_{AB} stretch modes respectively. Cluster calculations of the modes of the defect and their isotope shifts are consistent with this model and reproduce the small shifts in the H-stretch modes when the second H atom is replaced by D. This shows the distance between the H atoms, which controls their dynamical coupling, is correct and rules out earlier suggestions as to the origin of the lines (Mukashev *et al.* 1992).

Theory finds the energy of a H_2 molecule to be about 0.2 eV below H_2^*. Evidence for H_2 molecules is indirect. Annealing at 250 °C dissociates H–B complexes and yet no H effuses from the material (Stutzmann *et al.* 1991). The unobserved hydrogen defect appears to be diamagnetic and spectroscopically invisible and is attributed to molecular hydrogen. Theory gives the dissociation energy of H_2 into H_{BC} to be 1.6 eV (Van de Walle 1994) and the energy of two passivated BH complexes to be 0.5 eV below that of the molecule. Consequently, when BH dissociates, H_{BC} diffuses away until trapped by a second H which then forms an immobile molecule.

Binns *et al.* (1994), showed that introducing H by heating Si to high temperatures in H_2 gas, followed by quenching, led to the passivation of some of the B. However, a substantial amount of H was also present, presumably in the molecular form, since an anneal at 175 °C led to further B passivation. The molecular species could also be converted to H_2^* by e-irradiation perhaps by forming VH_2 or Si_iH_2 defects which subsequently captured an Si_i or V respectively. Recently, there have been reports of an EPR signal attributed to hydrogen molecules or, more likely, larger H-clusters (Stallinga *et al.* 1994).

H-plasma treatments produce (1 1 1) oriented H-platelets whose structure is uncertain. Roberson & Estreicher (1995) have suggested that the plasma etches surface Si atoms producing SiH_4, and a stream of mobile VH complexes rapidly diffuse into the bulk. Aggregation of these then leads to the nuclei for platelet formation. High resolution transmission electron microscopy studies (Muto *et al.* 1994), however, have been interpreted in terms of a model where the widely spaced (1 1 1) planes of Si are displaced apart through the formation of Si–H bonds and stabilized by H_2 gas at a pressure in excess of 1 GPa. This model is consistent with the observation of IR bands in the region of Si–H stretch modes (2000–2200 cm^{-1}).

6. Hydrogen-vacancy defects in silicon

H can complex with a Si vacancy producing four defects VH_n with n ranging from 1 to 4. In these complexes H saturates each dangling bond in turn. Thus unlike O, H does not form a bond-centred complex within a vacancy.

Our cluster calculations showed that the Si–H lengths in the neutral complexes deceased steadily as the number, n, of H atoms increased. Thus for n equal to 1 to 4, these lengths are 1.513, 1.506, 1.501 and 1.489 Å. The VH_4 defect leads to an 80% expansion in volume of the vacancy and uniaxial stress measurements on its 2222 cm^{-1} mode show directly it possesses T_d symmetry (Bech Nielsen *et al.* 1989).

Somewhat smaller lengths have been found by Roberson *et al.* (1994). They give 1.397, 1.387, 1.382, 1.378 Å respectively. The calculated values of the IR active LVMs (Hoffmann *et al.* 1994, unpublished work) range from 2319 for VH_4 down to 2248 cm^{-1} for VH. The experimental values are about 7% smaller and range from 2222 down to 2052 cm^{-1}. The highest mode of VH_4 is IR inactive. Curiously then, in mixed H, D implantation, modes are observed which possess a *higher* frequency. Theoretical investigations by Deák *et al.* (1991) give the LVMs of VH_4 to be 2109 (A_1) and 2094 (T_2) cm^{-1}.

7. Hydrogen-neutral impurity effects in silicon

H forms complexes with C in Si although as might be expected these have very low dissociation energies. Kamiura *et al.* (1994) showed that the C–H defect in Si, giving an electron trap at $E_c - 0.15$ eV, is stable to 80 °C in the dark where it dissociates with an energy of 1.1 eV in the neutral state. However, in the presence of holes generated by light, a recombination enhanced dissociation occurs at 250 K with an energy of 0.4 eV.

The thermal donors TD1 and TD2 generated by annealing O-rich Si around 450 °C can be passivated by H (Bohne & Weber 1993). The resulting defects dissociate around 300 K with an energy, which depends on the donor, of around 1.9 eV although with a very high pre-exponential factor. There have been no reports of H vibrational modes associated with the passivated donor which might give important information on their elusive structure. Photoluminescent lines, created by radiation damage followed by a 450 °C anneal in O-rich Si, arise from defects containing H, C and possibly O clusters (Lightowlers *et al.* 1994).

H_2^* complexes bound to N_P impurities in GaP have been investigated experimentally by Hahn *et al.* (1994). There are two H stretch modes detected at 2886 and 2054 cm^{-1}, both of which shift with the different N isotopes but not with Ga ones. This has led to the suggestion that both H atoms are bonded more strongly to N than to a Ga neighbour as would be expected for H_2^*. However, our cluster calculations showed that the H_{BC} atom is more strongly bonded to Ga than N in contradiction to the above assignment, even though the calculated modes, 3058 and 2213 cm^{-1}, are in reasonable agreement with those observed. The defect is interesting in that it is unusually stable and possesses a gap level whose occupancy, by photoexcitation, leads to shifts of about 100 cm^{-1} in the H related LVMS.

Photostructural changes are also expected to occur in the P...Si–H complex in Si, as it is bistable and becomes P–H–Si upon trapping a hole (Estreicher & Jones 1994).

8. Diffusion of O_i catalysed by H

Diffusion of H into oxygen rich Si leads to enhanced O diffusion jumps in a temperature region around 350 °C with an activation energy 1.7–2 eV (Newman *et al.* 1992; Stein & Hahn 1994). No stable O–H complexes have been reported and it is thought that H catalyses the movement of O. There are two theories for the enhancement in the reorientation rate of O_i in the presence of H. During the movement of O from one BC site to the next, it must pass close to the C site and is then necessarily bonded to three Si atoms, with one of the Si atoms having a dangling bond. This is the saddle point for normal O diffusion. Its energy difference from the starting configuration determines the diffusion energy of 2.8 eV. However, its energy can be lowered if the Si atom with the dangling bond is able to make a strong bond with a H atom that happens to be in close vicinity. This assumes that H in the starting structure, i.e. when O is at a BC site, is only weakly bound. Our calculations (Jones *et al.* 1992) support this picture. The lowest energy for H near O is at an AB site opposite Si–O–Si. Relative to one of these two sites, the energies of H_{BC} and the three H_{T_d} sites are 1.5 eV and 0.75 eV respectively. With H at the AB site, the energy difference between O at a BC and at a C site is only 0.2 eV. Thus the barrier of 2.8 eV for normal O-diffusion has been effectively eliminated by the presence of Si–H. Now, when O moves away from the C-site, the energy increases because the Si–H bond starts to weaken and a normal Si–Si bond starts to form. The new activation barrier is found to be 1.4 eV: somewhat lower than the observed barrier. When the O atom moves to its new bond centred site, H is now no longer in the lowest energy configuration and must jump to a new anti-bonding site. It has to move to the further one if long ranged O migration is to occur.

In contradiction with this, Estreicher (1990) found that H_{BC}–Si–O_{BC} was more stable than H_{AB}–Si–O_{BC}. The energy for a metastable configuration H_{T_d}–Si–O_{BC} was 0.66 eV higher. He then argued that when H is located near to this metastable T_d site, it is able to lower the barrier for O migrating to the C site through the formation of the Si–H bond and leaving O bonded to two atoms. This barrier, when H is initially at the T_d site, is 1.25 eV and is much lower than in the absence of H. The final configuration consists then of H and O at adjacent BC centres. This is not the starting point of the process and it is necessary to assume that H can leave the BC site after the O hop.

Further work is needed to determine the precise mechanism.

9. Hydrogen–transition metal impurity complexes

Hydrogen, introduced by in-diffusion into n-Si from a high pressure gas around 1250 °C can form complexes with Pt (Williams *et al.* 1994) It is known that substitutional Pt^- is displaced along [1 0 0] with an acceptor level at $E_c - 0.23$ eV. This leaves two Si dangling bonds which are conjectured to bond with H. IR spectroscopy revealed a near doublet at 1888.2 and 1889.5 cm^{-1} correlated with a new EPR signal, associated with Pt^+H_2 and having a level between $E_c - 0.1$ and $E_c - 0.045$ eV. Another H related doublet at 1897.2 and 1898.6 cm^{-1} is associated with the neutral or negative charge state. Thus H has not eliminated the acceptor level of Pt but displaced it and apparently introduced a donor level. The model suggested is rather like VH_4 in which two of the H atoms are replaced by Pt. However, recent calculations of the iso-electronic defect, Ni_s-H_2 (Resende *et al.* 1994, unpublished work) suggest that this model gives H LVMs strongly coupled together, contrary to the observations. The Pt–H_2 defect has also been observed by the Amsterdam group (Höhne *et al.* 1994).

Deep levels, due to electron traps around $E_c - 0.5$ eV have also been observed by DLTS for V– and Cr–H complexes in Si (Sadow *et al.* 1994). The traps are only formed in n-Si due presumably to the diffusion of neutral H to the metal impurity. In p-Si, H^+ would have to diffuse to the positively charged interstitial impurity.

10. Conclusions

Theory has progressed very far since the pioneering calculations of Mainwood & Stoneham (1980), but the ever increasing number of effects attributed to H demonstrates both the vitality of the science and the need for further theoretical investigations.

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Discussion

W. JACKSON (*Palo Alto, CA, U.S.A.*). Dr Jones mentioned that in some cases it enhances the motion of dislocation. It is also the case in Si that H suppresses vacancy motion in Si thereby increasing the recrystallization temperature. Under what conditions would one expect suppression of dislocations and vacancy motions instead of enhancement?

R. JONES. The suppresssion of vacancy motion might be attributed to the formation of strong Si–H bonds as in VH_4. These would have to be broken for the entity to move. There is no theory yet for any enhancement of dislocation motion in crystalline Si.

A. M. Stoneham (*Harwell Laboratory, Oxfordshire, U.K.*). The zero point motion is not small for the muon, and this term should surely be included in the energy when determining the atomic positions, as well as in calculating vibrational levels.

R. Jones. The anharmonicity of the C–H stretch mode in GaAs is a very large effect as already discussed. For muons, it would be even more important. However, it is not so easy to include zero-point energies into the total energy formalism as at each stage the frequencies of vibration would have to be evaluated. These, together with the internal energy, would enable the free energy to be found and the minimum of this quantity would yield the equilibrium structure. It is clear that for certain defects and atomic processes, e.g. muon diffusion, the extra terms might be essential for quantitative purposes.

R. C. Newman (*IRC Semiconductor Materials, The Blackett Laboratory, Imperial College, U.K.*). The calculations described indicated that Ni impurities in Si formed complexes with two H atoms that were bonded to Si atoms outside the nearest neighbour cage. Professor Symons thought that the latter result was surprising as the Ni atom bonded preferentially to two Si neighbours to give an off-centre defect with C_{2v} symmetry. However, at high temperatures when the complexing would take place there was likely to be a dynamic Jahn–Teller effect by comparison with the behaviour of Ni in Ge so that the hydrogen might not have sufficient space for the internal bonding arrangement.

R. Jones. It is certainly true that substitutional Ni^- in Si undergoes a Jahn–Teller effect which lifts the electronic degeneracy so that the defect has C_{2v} symmetry. This also happens for Ni^-–H_2, irrespective of whether the H atoms lie inside or outside the vacancy. However, there is less crowding and lower strain energy in the latter case, but this is partially offset by the formation of weaker Si–H bonds.

M. Symons (*Department of Chemistry and Biological Chemistry, University of Essex, UK*). I hadn't realized that metal atoms such as Ni or Pt could be incorporated into silicon, so please excuse my ignorance. However, since the Si–Si bonds are strong and since transition metal ions usually have coordination numbers greater than 4, I would have expected that $H^{\cdot}$ ($Mu^{\cdot}$) would add directly to the metal rather than bonding to silicon. In this context it may be worth noting that we have demonstrated, by ESR spectroscopy, that $H^{\cdot}$ atoms add to Ni or Pt in the complexes $Ni(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$ to give $H^-Ni(CN)_4^{2-}$ or $H^-Pt(CN)_4^{2-}$ with very high spin densities on the hydrogen as well as the metal (Symons *et al.* 1979; Wyatt *et al.* 1987). Has anyone detected hyperfine coupling to ^{61}Ni or ^{195}Pt in the silicon units that Dr Jones discussed?

R. Jones. Transition metals are important impurities in Si and other semiconductors as they often have electronic states within the band gap. They are fast-diffusing species and, for that reason, difficult to keep out!

Substitutional Ni, Pt and Pd are surrounded by four Si atoms and the gap electronic states are largely made up of Si sp^3 orbitals – there is only a small overlap with the d-orbitals on the TM. Consequently, H would be expected to bond with the Si atoms surrounding the TM and no Si–Si bonds need be broken. Hyperfine coupling between the TM and H has been discussed by Williams *et al.* (1993) as well as Höhne *et al.* (1994). The isotropic value of the hyperfine tensor, 8.7 MHz, corresponds to only 0.6% of that of a free H atom (1420 MHz). The current view is then that H is bonded to Si rather than the TM – at least in the complexes that have been seen so far. The work described by Professor Symons on H–Ni$(CN)_4^{2-}$ seems very interesting but, at the moment, irrelevant to the Si case.

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