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The nature of the hydrogen–boron complex in crystalline Si

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Abstract. We have used the complete neglect of differential overlap (CNDO) method to investigate the motion of the H atom within the Si lattice in the presence of a B impurity. Our results seem to indicate that the H atom moves in a low-energy channel in the vicinity of the B atom located at a substitutional site. However, the most stable configuration of this H–B system results when the H atom lodges itself near the bond-centred site of a Si–B bond (BM site). The B atom is displaced towards the plane of the other three neighbouring Si atoms and this displacement is calculated to be 0.28 Å, which agrees very well with the experimental value of 0.28 ± 0.03 Å.

1. Introduction

The electronic properties of Si are to a great extent influenced by impurities as well as other defect structures in the crystal lattice. Experimental observations of impurities in Si suggest that hydrogen atoms in Si are able to passivate the electrical activity of dangling or defective bonds [1]. Shallow acceptors like B, Ga and Al are passivated by reaction with atomic hydrogen. However, the nature of the structures of these impurity complexes is still very much of current interest, as knowledge of their structures will go a long way towards elucidating their properties and effects on semiconductors.

Pantelides [2] proposed that the cause of passivation of shallow acceptor impurities by H is the existence of a donor level in the gap in the diffusing H. The H-induced passivation can be represented by the following equation:



where A denotes the acceptor. Pantelides' proposal has been confirmed by local density calculations [3]. The pairing of acceptor and hydrogen ions has also been observed experimentally by SIMS [4] and Raman scattering [5].

The specific configuration and binding energy of H in relation to the acceptors is another area of interest among researchers. Experimentally, most of the data have been contributed by infra-red spectroscopy and Raman scattering [6–8] and their results will be discussed briefly in relation to our results. On the theoretical side, MNDO [9], Hartree–Fock cluster calculations [10] and pseudopotential density functional calculations [11, 12] predicted that the H atom should be situated near the bond centred site. However, X_α calculations suggest that the H atom is located at the antibonding site [13].

The criterion for a theoretical method to be able to give optimum configurations is that it should be able to calculate the total energy of the system. One such method is the

Table 1. CNDO parameters.

Element	Orbital exponent, ξ_{sp} (Bohr ⁻¹)	Electronegativity,		Bonding parameter, β (eV)
		ϵ_s (eV)	ϵ_p (eV)	
H	1.2	7.8	—	-9.0
B	1.3	9.59	4.00	-17.00
Si	1.54	6.30	4.50	-6.4
Si*	1.54	6.30	4.50	0

complete neglect of differential overlap (CNDO) method, and it is used in the present study.

2. The CNDO method

The CNDO method has been used successfully by Mainwood and Stoneham [14] to study the diffusion of H in different charge states in Si. We have also used the CNDO method to study self-interstitials in Si [15] as well as in Ge [16]. Basically, the CNDO method [17] is the approximate version of the Hartree-Fock calculation. It introduces three semiempirical parameters, namely an orbital exponent (ξ), the electronegativity (ϵ) and a bonding parameter (β). These approximations then yield self-consistent solutions analogous to Hartree-Fock solutions. The MOSES code [18] is implemented in the present calculations and the parameters we have chosen for H and the acceptor (Boron in this case) are those of Pople and Beveridge [17]. The parameters for Si are from the calculations of Harker and Larkins [19] to fit the cohesive energy, lattice parameter and valence bandwidth of a 16-atom periodic Si large unit cell (LUC). The CNDO parameters used are summarized in table 1.

The cell used to simulate the boron hydrogen complex in Si is a 59-atom cluster. This cluster is centred at a substitutional site where we place the B atom. The dangling bonds of the cluster edges are saturated by single sp^3 hybrid atoms (Si*). We have 30 of these in our 59-atom cluster. These hybrid atoms have the same parameters as Si except that their β values are set to zero.

3. Experimental background

Most of the experimental observations are performed on the hydrogen-boron complex. Pankove *et al* [20], from their infra-red experiment, suggest that the equilibrium position for the H atoms is close to the centre of a Si-B bond (hereafter will be denoted as the BM site) with the substitutional B atom pushed out towards the plane of three neighbouring Si atoms. Later measurements performed using Raman scattering [5, 8] and ion-channelling experiments [21] seem to support the proposed structure of Pankove *et al* [20]. By using channelling and lattice location, Marwick *et al* [21] have also made measurements of the displacement of the B atom from its substitutional site, and found a value of 0.28 ± 0.03 Å.

4. Results

The total energy of the cluster is calculated for the B atom at the centre of the cluster (the substitutional site) and with the H atom moving in various planes, e.g. the (001)

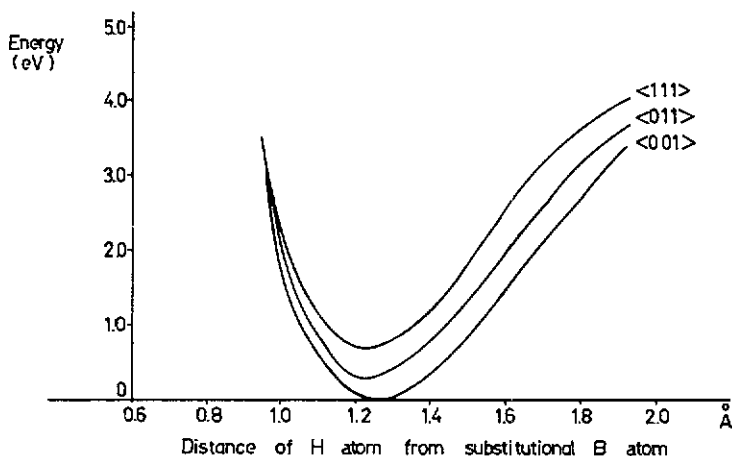


Figure 1. The variation in the total energy of the H-B complex in the Si crystal lattice along the three major axes, $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$. The equilibrium distance of the H atom from the B impurity is about 1.22 Å. This agrees well with the experimental value of 1.20 Å [21].

and (011) planes, and along various major axes, e.g. $\langle 111 \rangle$, $\langle 011 \rangle$, in the vicinity of the B atom. The variations of the total energy as the H atom is moved along the three major axes, $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$ are plotted on the same graph (see figure 1) for comparison. As can be seen, these profiles of the total energy curves along the three major axes are similar and trough-like. These suggest that the H atom confines itself to a narrow region along these three axes and possibly that it moves in a spherical shell around the B atom with a radius of about 1.22–1.25 Å. The equilibrium distance of the H atom from the substitutional B atom along the $\langle 011 \rangle$ and $\langle 111 \rangle$ axes is about 1.22 Å while along the $\langle 001 \rangle$ axis, the equilibrium distance is about 1.25 Å. These two values are in close agreement with the experimental value of 1.20 Å for the H-B terminating bond in B_2H_6 [22]. The minimum along the $\langle 001 \rangle$ axis is very close to the so called C-site of the Si lattice. This position is also the most stable along the three axes, being 0.27 eV lower than the equilibrium position for H along $\langle 011 \rangle$ and 0.72 eV lower than that along the $\langle 111 \rangle$ axis. We can deduce that if the H atom moves around the B atom in a spherical shell in the interstitial space, then a thermal activation energy of about 0.3–0.7 eV would be adequate.

Further calculations are then made for various positions of the H atom in the (011) and (001) planes with the H-B distance kept at 1.25 Å. The paths of the H atom around the substitutional B atom on these planes are shown in figure 2(a) and figure 3(a). At different positions of the H atom along the semi-circle AIQ in the (011) plane in figure 2(a), the total energy of the system (unrelaxed) is calculated, and the total energy curve along this path is illustrated in figure 2(b). Along this plane, the positions of the H atom with the lowest energy are A and Q, and these two points coincide with the minimum along the $\langle 001 \rangle$ axis (see figure 1) investigated earlier. From figure 2(b), when the H atom is moved from Q (analogous to the C site), it needs to overcome a slight barrier of about 0.7 eV before reaching I. Further movement of the H atom towards the BM site with the Si-B bond unrelaxed will result in an increase in energy as shown in figure 2(b). As the H atom proceeds from the unrelaxed BM configuration to A (another C site) the total energy drops again. If the migration of the H atom is accompanied by the relaxation of its nearest neighbours as it squeezes into the Si-B bond, then the total energy will drop till it reaches a value of about 0.19 eV below that of the C site. Here the H atom is

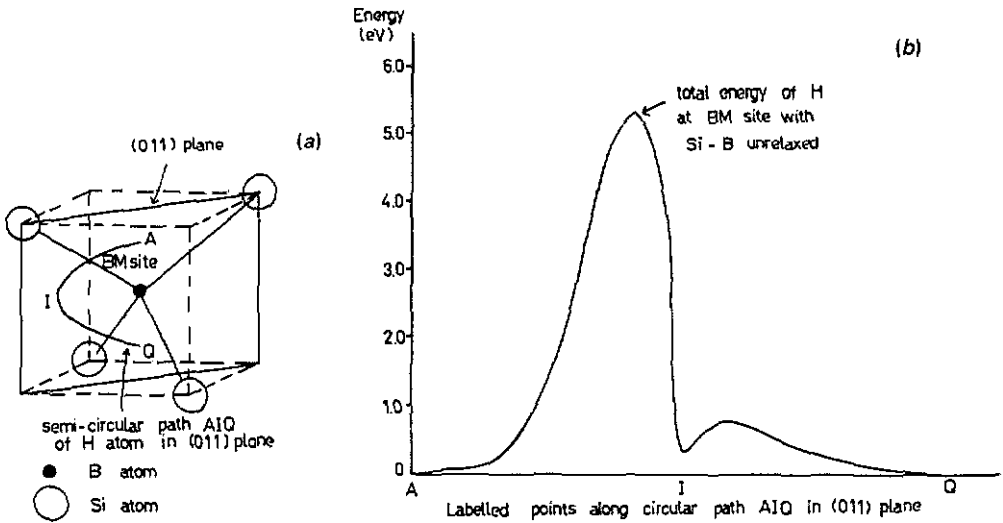


Figure 2. (a) The semicircular path of the H atom as it is moved in the (011) plane: AIQ; (b) the energy profile as the H atom is moved along the path in (a).

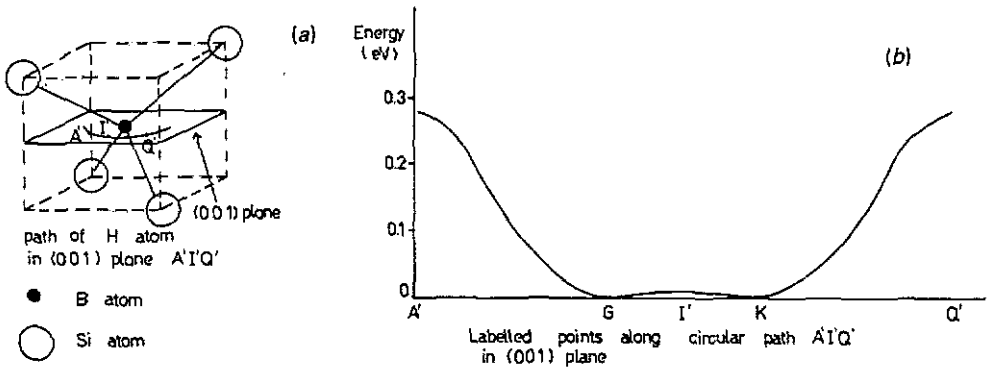


Figure 3. (a) The path of the H atom in the (001) plane (part of a circle): A'I'Q'; (b) the energy profile as the H atom is moved along the path in (a). Notice the relatively small energy barrier in this path.

in the relaxed equilibrium BM configuration. This suggests that it may be possible for the H atom to migrate from one BM site to another BM site via A or Q (a C site) accompanied by relaxation of the host crystal. The slight barrier of 0.7 eV as the H atom travels from Q to I also decreases with accompanying relaxation of the host crystal, rendering this path a low energy one. The high-energy barrier when the Si-B bond is unrelaxed implies that at any one moment, when one BM site is occupied, the other three BM sites are higher in energy and any kind of tunnelling between adjacent BM sites is highly unlikely.

On the other hand, when the H atom starts to move from one BM site via a C site (A or Q) to another BM site, adjustments and relaxations to the two Si-B bonds involved may set up a low energy channel with a barrier of only 0.19 eV. This barrier of 0.19 eV is in good agreement with the experimental value of 0.19 eV obtained using the stress-induced optical dichroism of the H-B absorption bonds technique [7]. This value also confirms the calculated value of 0.2 eV of Denteneer *et al* [12]. However, Herrero and Stutzmann [8] obtained an experimental value of less than 0.3 eV by Raman scattering. This value is on the high side compared to the value obtained by Stavola *et al* [7].

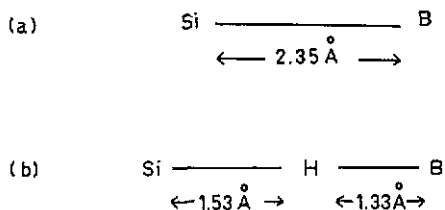


Figure 4. (a) The unrelaxed Si-B bond with both the Si and B atoms at the substitutional sites; (b) the same Si-B bond as in (a) with the H atom inserted near the middle of the bond (BM site).

For the (001) plane, the H atom is moved around the B impurity (see figure 3(a)—curve A'I'Q') with no relaxation of the crystal lattice and the energy minimum occurs at two positions, points G and K, slightly on either side of I'. I' coincides with points A and Q in figure 2(a) as well as with the minimum along the $\langle 001 \rangle$ axis. However, I' is just 0.008 eV higher than either G or K, so motion along this plane is relatively athermal except when it approaches A' and Q' (i.e. coincides with point I in figure 2(a)). A' and Q' are in the migration path of the H atom towards the BM site in the (011) plane. However, this barrier of 0.28 eV from I' to either A' or Q' will probably be much less if the movement of the H atom is accompanied by some kind of relaxation of the Si-B bonds as the H atom approaches one of them. Hence, this path in the (001) plane can also be considered as a low-energy channel or zone around the B impurity in the Si lattice where the H atom has a high degree of mobility. Changes in the H-B distance in both the (011) and (001) planes lead to an increase in energy. The global minimum of the H-B complex therefore occurs at the BM site with the Si-B bond relaxed.

With the H atom inserted in the Si-B bond, the substitutional B atom is pushed out towards the plane of the three neighbouring Si atoms. The resulting bridging bonds with the H atom in between the Si and B atoms lead to an equilibrium distance of 1.53 Å for Si-H and 1.33 Å for B-H. These values are in close agreement with the experimental value of 1.48 Å for Si-H in SiH₄ [23] and 1.34 Å for H in a bridging bond in B₂H₆ [22]. The displacement of the B atom from its substitutional site is calculated to be 0.28 Å, in excellent agreement with the experimental value of 0.28 ± 0.03 Å determined by Marwick *et al* [21] from ion-channelling experiments.

The H-induced passivation of the B impurity represented by $\text{B}^- + \text{H}^+ \rightarrow (\text{BH})^0$ can also be used to study the dissociation/binding energy of the H-B complex. It can be re-written as: $(\text{BH})^0 \rightarrow \text{B}^- + \text{H}^0 + \text{h}^+$ where h^+ denotes a free hole.

If we calculate the respective total energies of all these terms (we compute the energy of the free hole by exciting an electron out of the cluster) and find the difference of these energies on the left and right sides of the previous equation, the dissociation energy of the (BH)⁰ complex can be determined. We calculate this value to be 4.47 eV, compared to the value of 3.31 eV calculated by Denteneer *et al* [12].

5. Conclusion

Our results suggest several possibilities regarding the motion of the H atom in the vicinity of the substitutional B impurity, as well as the microscopic structure of the H-B complex for which the configuration is most stable. Firstly, along the three major axes, $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$, the H atom appears to confine itself within a narrow region or shell, with the equilibrium distance between the B atom and itself ranging from 1.22 to 1.25 Å. This suggests that the B atom restricts the movement of the H atom within the Si cluster to low-energy channels around it. Secondly, if the diffusion of the H atom towards a position near the bond-centred site of the Si-B bond via a C-site is accompanied by the corresponding adjustment of the host crystal, then a low-energy path of barrier 0.19 eV results with a global minimum at the BM site. In this configuration, the H atom is located between the Si and B atoms in the Si-B bond, with the B atom displaced slightly towards the plane of the other three neighbouring Si atoms. This calculated displacement of the B atom, 0.28 Å, is in excellent agreement with experiment [21]. Moreover, the equilibrium distances of the H atom from both the Si and B atoms in this bridging situation are also in close agreement with experiment [22, 23]. The calculated barriers for H motion along the (001) and (011) planes are relatively small compared to our calculated binding energy of the (BH)⁰ complex in the Si lattice. Therefore, if the H atom breaks away from its stable site (the BM site), it may easily move around in the vicinity of the B impurity.

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