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Abstract. The total energy profile or surface for Al–H complexes in a large silicon cluster has been calculated using a self-consistent semi-empirical method. The diffusion path of hydrogen appears to be confined to a low-energy channel in the vicinity of the Si atom which is bonded directly to the Al atom at a substitutional site. The most stable configuration of this Al–H system results when the H atom is located at the bond-centred (BC) site. The system probably contains a Si–H–Al three-centre bond structure of bridging nature. This finding is compared with the Al–H pair assignment based on infrared experiments given by Stavola and co-workers which is based on the Al–H frequency calculated by DeLeo and Fowler.

1. Introduction

The study of hydrogen-related defects in silicon is of current research interest because of its importance in electronic device technology. The presence of hydrogen atoms in p-type Si containing Group III shallow acceptors, like B and Al, can cause the passivation of these acceptors. Although the hydrogen passivation of these acceptors in silicon is well known, the structure and properties of the acceptor–H complexes, as well as the mechanism for the passivation, are still controversial. Basically, there are two schools of thought in explaining the passivation. One view advocates the formation of acceptor–H complex [1, 2]. Another view emphasizes that such passivation effects are due to the compensation by a supposed deep donor level associated with the atomic H, and hence the formation of the acceptor–H complex is not a necessity [3, 4]. However, it is generally believed that compensation alone without complex formation cannot explain the passivation effect [5].

Among the H-containing complexes in Si, the B–H complexes in Si are supposed to have the best-understood structure. All the available theoretical and experimental studies consistently show the existence of B–H pairing [6, 7]. In contrast, in the case of the Al–H complexes, only a few studies have been carried out. DeLeo and Fowler [8], by using the modified neglect of diatomic overlap (MNDO) method have found that H is situated at the bond-centred (BC) site. This result has been supported by Estreicher *et al* [9] by using a more sophisticated Partial Retention of Diatomic

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Table 1. The CNDO parameters used.

Atom	Orbital exponent ξ_{sp} (Bohr^{-1})	Electronegativity		Bonding parameter β (eV)
		ε_s (eV)	ε_p (eV)	
H	1.20	7.18	—	−9.00
Al	1.17	6.63	2.73	−7.35
Si	1.54	6.30	4.50	−6.40
Si*	1.54	6.30	4.50	0

Differential Overlap (PRDDO) method in an *ab initio* Hartree–Fock approach, where large clusters were used.

DeLeo and Fowler [8] also predicted an H-stretching frequency of 2220 cm^{-1} for the Al–H complex. To test this prediction, Stavola *et al* [10] used the plasma treatment technique and a Fourier-transform spectrometer (Nicolet, 60 SX) to study the vibrational spectroscopic data of the Al–H complex in silicon. They identified a frequency of 2201 cm^{-1} for the Al–H complex at He temperature, which is in good agreement with the calculated value of DeLeo and Fowler. However, besides these, little is known about the structure and properties of the Al–H complex. Hence, it prompts us to conduct this study.

2. Method and calculations

We use a 65-atom molecular cluster [7] to simulate the crystalline Si. (The dangling bonds at the edges of this cluster are saturated by single sp^3 hybrids of silicon (Si*).) Then we employ the complete neglect of the differential overlap (CNDO) method and perform our calculations on the molecular cluster [7]. The CNDO method is a semi-empirical self-consistent molecular method. Approximations are made to Hartree–Fock–Roothaan equations via the introduction of three semi-empirical parameters, namely, (1) the orbital exponent ξ, (2) the electronegativity ε and (3) the bonding parameter β. The CNDO parameters used are summarized in Table 1. The parameters for Si are from Harker and Larkins [11], whereas the H and Al parameters are from Pople and Beveridge [12]. The calculations of CNDO are implemented in the Harwell MOSES code [13]. The code involves the computation of routines in which equations are solved by a self-consistent iterative technique until convergence of the total energy minimum is achieved. This method has been used successfully to study the B–H complex in Si [7], as well as related systems, e.g. hydrogen in diamond and silicon [14], hydrogen in germanium [15] and self-interstitials in silicon and germanium [16,17].

3. Results and discussion

In our calculations, we move the H atom in the vicinity of the substitutional Al atom (X_{Al}) (see figure 1(a)), along the three major axes, namely the $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$, on the (110) plane. The total energy for the H atom along all these axes are calculated and the profiles of the total energy curves are shown in figure 1(b). As can be seen, along the $\langle 111 \rangle$ axis, the interstitial H atom appears to be localized at a distance of 1.75 Å from the Al atom. This Al–H distance is in good agreement with the experimental value for Al–H bond of 1.6 Å in compounds containing directly bonded Al and H, e.g. AlH [18]. This value is also comparable to the Al–H separation

of the Al–H pair defect (1.78 Å) found by DeLeo and Fowler [8]. Comparing this result to that of Mainwood and Stoneham [14] for interstitial H diffusion along the ⟨111⟩ direction in perfect crystalline Si, the mobility of the interstitial H appears to be affected by the presence of the substitutional Al atom.

However, this position along the ⟨111⟩ axis is not the most stable, and the binding energy calculated for this site is only 0.29 eV. For the three major axes, the location with the lowest energy is a site along the ⟨110⟩ direction at a distance of 2.23 Å from the substitutional Al atom. The three curves suggest that the H atom is weakly bound to Al and prefers to move away rather than stay near it. Moreover, the equilibrium distance of the interstitial H at this site to the nearest Si atom is found to be 1.39 Å, which is even shorter than the experimental value of 1.48 Å for Si–H in SiH_4 [19]. This position is 1.83 eV and 0.32 eV lower than the minima along the ⟨111⟩ and ⟨100⟩ axes, respectively. The minimum position along the ⟨100⟩ axis is very close to the C-site of the silicon lattice.
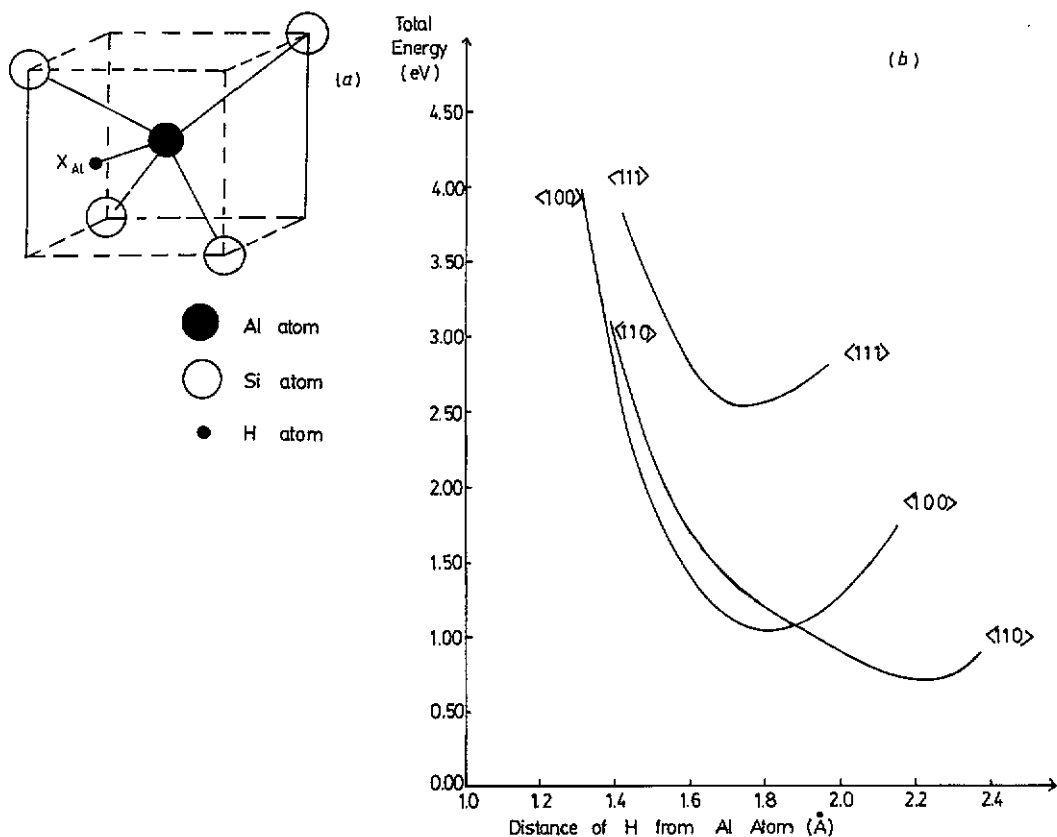

Figure 1. (*a*) Diagram showing the location of the H atom (X_{Al}) in the vicinity of the substitutional Al atom in a silicon crystal lattice on the (110) plane. (*b*) The variation in the total energy of the Al–H complex in the silicon crystal lattice shown in figure 1(*a*) along the three major axes.

Another set of calculations is then made at the various positions of the H-atom along a circular path AIQ on the (110) plane as shown in figure 2(a). As can be seen, before relaxation, the movement of the H atom into the bond-centred (BC) position of the Al–Si bond is not favoured because the total energy increases to about 40 eV as the H atom approaches from either A or Q, two positions close to the C-sites of the crystal lattice along the ⟨100⟩ axis.

However, if relaxation of the Al–Si bond takes place, the energy barrier of about 40 eV will disappear. Then the most stable configuration of this H–Al system results when the Si atom relaxes by 0.33 Å and the Al atom by 0.54 Å. The sum of these two displacement equals the increase in the Si–Al bond length found by DeLeo and Fowler [8] for H at the same BC site. The total energy for the H at this BC site is lower than the local minima found along all the three major axes. For example, it is 3.37, 0.54 and 1.86 eV lower than the local minima along ⟨111⟩, ⟨110⟩ and ⟨100⟩ axes respectively—all after relaxation. The BC site is also lower in energy than the local minima on the (110) plane, being about 1.86 eV lower than that at A or Q, and 1.18 eV lower than that at I (see figure 2(b)). Similar calculations along a circular path on the (100) plane are also performed. A minimum is obtained when the H atom
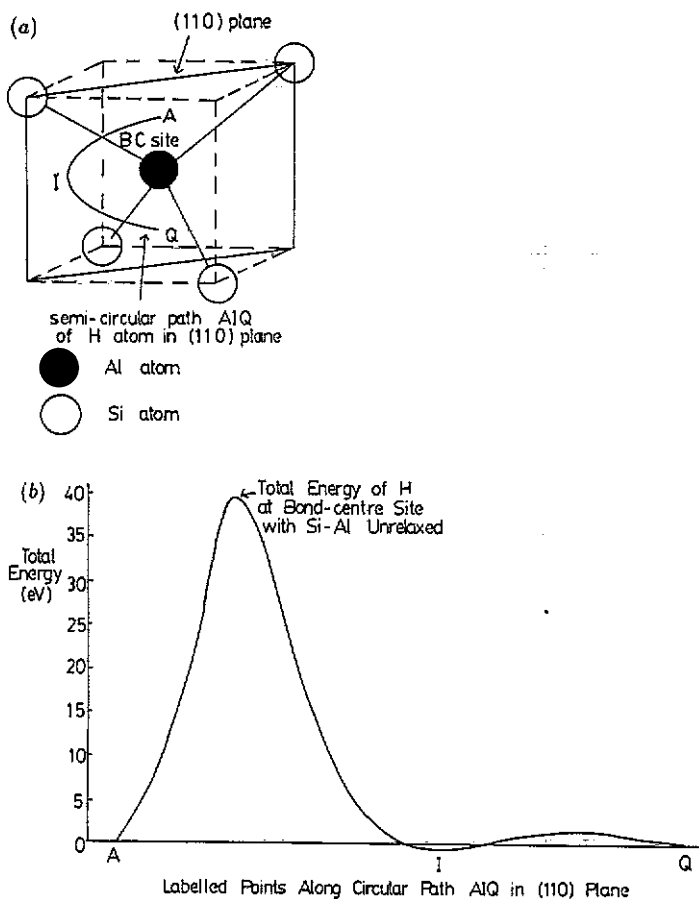

Figure 2. (a) The semicircular path of the H atom as it is moved in the (110) plane. (b) The energy profiles as the H atom is moved along the path in 2(a).

is 1.90 Å from the Al atom and 1.57 Å from the nearest Si atom. However, after relaxation, this minimum is still about 0.91 eV higher than that at the BC site. Thus, the minimum at the BC site is probably the global one.

Our observations in this aspect are similar to those for the behaviour of H found in the B–H complex in Si [7]. To have a better understanding of this aspect, further calculations are made for the movement of the H atom in the environment of four Si atoms, where one of the Si atoms is bonded to an Al atom at a substitutional site (see figure 3(a)). The results for these calculations for the H atom moving along the major axes from the Si atom bonded to the Al atom are illustrated in figure 3(b). The
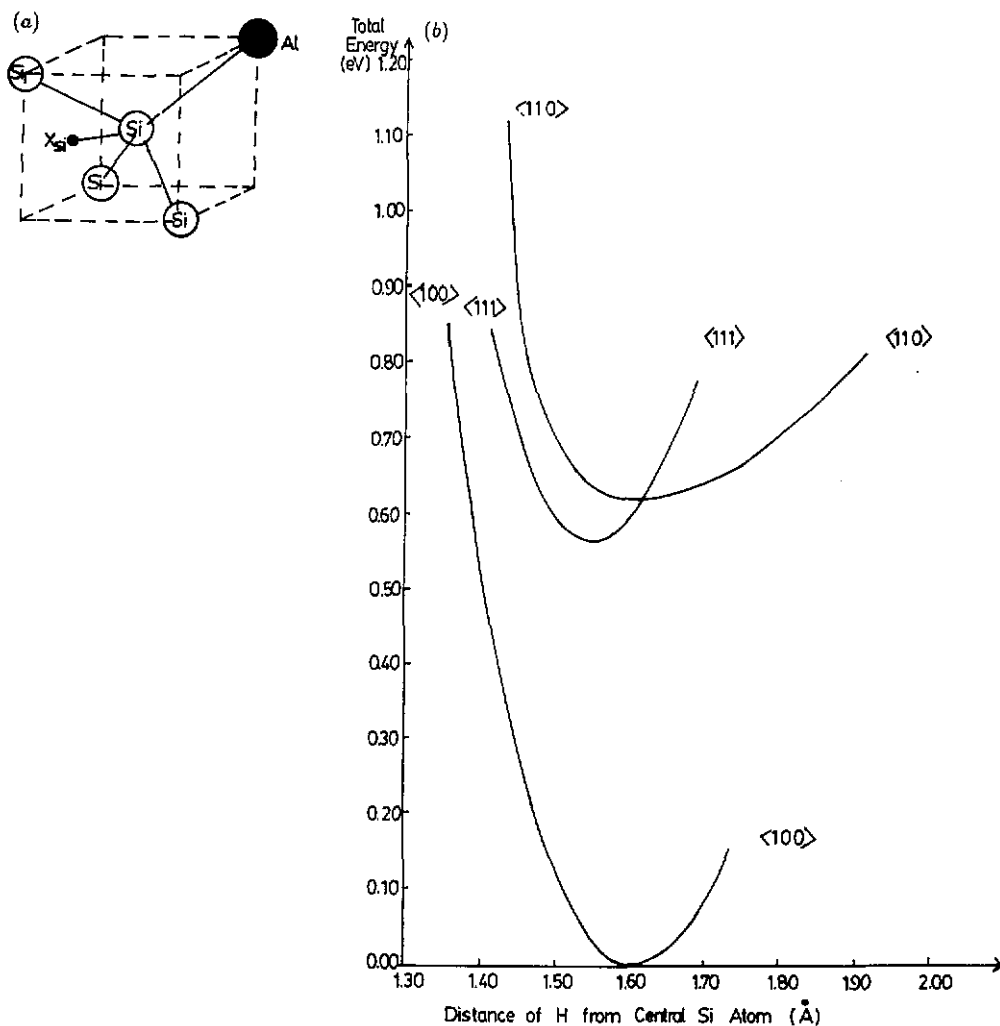

Figure 3. (a) Diagram showing the location of the H atom (X_{Si}) in the environment of four silicon atoms, where one of the silicon atoms is bonded to an Al atom at a substitutional site, on the (110) plane. (b) The variation in the total energy of the Al–H complex in the silicon crystal lattice shown in figure 3(a) along the three major axes.

equilibrium distances for the H atom from this Si atom along the $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ axes are 1.55 Å, 1.60 Å and 1.61 Å respectively.

These distances are generally in good agreement with the equilibrium distance of 1.53 Å for Si–H found for the B–H complex in Si [7], and are also compatible with the experimental value of 1.48 Å for Si–H in SiH_4. Nevertheless, the profiles of these energy curves are similar and trough-like. The similarity in the equilibrium distances strongly suggests the possibility that the H atom is able to move in a spherical shell with a radius ranging from 1.55–1.61 Å around the Si atom. However, after relaxation, none of the local minima along these three axes have a total energy lower than that at the BC site. For example, the total energies of the H atom at the local minima along the $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 100 \rangle$ axes are 1.88, 0.71 and 0.73 eV, respectively, higher than that at the BC site. Thus, the proposed global minimum at the BC site is confirmed.

At the global minimum, the Al–H distance is 1.72 Å. Though this is slightly higher than the corresponding bond length in Al_xH_y (1.55 Å) [25], it is in good agreement with the value for the Al–H bond of 1.65 Å in AlH [18]. This value is also comparable to the Al–H separation of the Al–H pair defect (1.78 Å) found by DeLeo and Fowler [8]. The corresponding Si–H distance is 1.50 Å, which is comparable to the Si–H in SiH_4 molecule (1.48 Å). This type of AlH complex may give rise to a peak at 2201 cm^{-1} observed in the infrared spectrum at He temperature. This peak can be attributed to the stretching mode of the Si–H–Al complex. According to Stavola [21], this peak is unlikely to be due to isolated Si–H, because

(i) this feature does not appear in material which is not doped with Al;

(ii) the strength of the 2201 cm^{-1} band is proportional to the Al concentration; and

(iii) the H-stretching vibrations of the acceptor–H complexes have different frequencies but share common characteristics such as the pronounced dependence of the linewidth on temperature.

Hence, the structure of the Al–H complex in Si probably involves a three-centre bond system as shown in figure 4. This structure was proposed by Pankove *et al* [1] and DeLeo and Fowler [23].
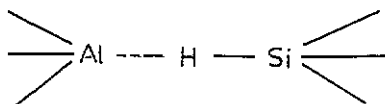

Figure 4. Proposed three-centre bond structure of the Al–H complex in silicon crystal lattice at the global minimum. (Solid lines represent stronger bonds while dotted line represents weaker bond.)

4. Comparison with B–H complexes in Si

In the present study, we have found that the global minimum for the H atom in our system, (H, Al) in Si, is also at the BC site, as in the case of B–H complexes in Si. The possible structure of the Al–H complex in Si probably also involves a three-centre bond system with bridging (figure 4). This is expected because both B and Al belong to Group III in the periodic table.

Table 2 compares the global minima in the two systems, namely (B, H) in Si and (Al, H) in Si. From table 2 it can be seen that the bond length of Al–H (1.72 Å) is longer than that of B–H (1.33 Å). Hence, it may be deduced that the B–H complexes in Si are more stable than the Al–H complexes in Si. This is probably because

(i) Al (about 1.25 Å in atomic radius) is a bigger atom than B (about 0.90 Å in atomic radius) [19];
(ii) B has a higher electronegativity than Al.

Table 2. Comparison of the global minima in (B, H) in Si and (Al, H) in Si.

	(B, H) in Si [7]	(Al, H) in Si[a]
Bond lengths:		
Si–H	1.53 Å	1.50 Å
B–H	1.33 Å	—
Al–H	—	1. 72 Å
Displacements:		
▲Si	0.23 Å	0.33 Å
▲B	0.28 Å	—
▲Al	—	0.54 Å

[a]Results from this study.

In fact, the B–H compounds are usually more stable than the Al–H compounds. For example, boron hydrides are quite stable, while the complex AlH_4^- is only stable under the presence of very strong electropositive element, e.g. Na, in the compound $Na^+AlH_4^-$.

It is also interesting to compare the extent of relaxation as the H atom is placed in between the Si–Al bond and Si–B bond. The displacements of Si and Al with respect to their perfect substitutional positions are about 0.33 Å and 0.54 Å which agree quite well with the values of 0.31 Å and 0.45 Å, respectively, obtained by Estreicher *et al* [9]. However, these values are significantly higher than the corresponding ▲Si and ▲B in (B, H) in Si, which are 0.23 Å and 0.28 Å, respectively. Here, the size of Al may bear part of the responsibility.

The Si–H bond lengths of both (B, H) in Si and (Al, H) in Si are comparable. This implies that the interaction of H with Si is similar in both cases. The B–H bond length (1.33 Å) in (B, H) in Si is the same as that in B_2H_6 (1.34 Å) [24], while the Al–H bond length (1.72 Å) in (Al, H) in Si is quite different from that in Al_xH_y (1.55 Å) [25]. This discrepancy may provide further evidence that H atom prefers to bond with Si and B, rather than Al. The Al–H complex in Si can adopt the similar structure as the B–H complex in Si, probably because the compensation effect of H will take place at maximum, when H is placed between Si and Al at the BC site.

5. Conclusion

The results of this study reveal that the H atom is probably bonded to the Si atom as well as the Al atom to form a three-centre bond structure. This is in agreement with the MNDO calculations of DeLeo and Fowler [8] and PRDDO calculations of Estreicher *et al* [9]. Stavola *et al* [10], based on their observed frequencies, have assigned their

infrared data to Al–H pairing which agrees with our results. They also suggested the possibility of forming Si–H–Al complexes in the system. Our results are also consistent with their suggestion.

Since the structure of (Al, H) in Si is similar to that of (B, H) in Si, the mechanism of the H-induced passivation may follow the following equation, as proposed by Pantelides [22]: $A^- + H^+ \rightarrow (AH)^0$ where A denotes the acceptor. But, in terms of the Al–H bond length in (Al, H) in Si, the formation of $(AH)^0$ complex seems not to be favourable. Moreover, our CNDO data show that the total Mulliken charge density of Al (2.67) is less than 3, whereas that of B (3.17) is greater than 3. Hence, it is likely that the passivation by the H atom in these two systems may be different.

Acknowledgments

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