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The nature of the hydrogen-phosphorus system in crystalline Si

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Abstract. We have used a semi-empirical self-consistent method to investigate the motion of the H atom in the Si lattice in the presence of a P impurity. Our findings indicate that the P atom localizes the H atom, impeding its diffusion through the lattice. However, our most stable configuration has the H atom sandwiched in the interstitial space between the P and Si atoms compared with the model suggested by Johnson, Herring and Chadi in 1986 with the H atom at the AB site of a Si nearest neighbour of a substitutional P. Our results also agree qualitatively with the general observations regarding the H-P system from experimental data.

1. Introduction

The past few years have seen advances in the sophistication of the techniques for studying defect structures in semiconductors. One result of such advances is the observation that atomic hydrogen is able to induce the passivation of shallow [1-3] and deep [4, 5] impurities in crystalline Si. This has led to intense interest in this area because H passivation of these impurities leads to changes in the electronic properties of Si. Most studies on shallow acceptors like B, Ga, Al, In and Tl demonstrate a H-induced passivation [6-9] while for shallow donors, H produces no detectable passivation [1, 8, 10]. However, there has been one report of experimental observation of partial passivation of phosphorus (P) [11]. The corresponding total energy calculations based on an empirical tight-binding method carried out on the H-P system predicted an energy minimum for H at the antibonding (AB) site of a Si nearest neighbour of a substitutional P [11]. Further calculations by Chang and Chadi [12] using an *ab initio* pseudopotential method yielded a minimum energy configuration for interstitial H near a tetrahedral (T) site of a Si atom adjacent to a substitutional P. Dentener *et al* [13] have also recently calculated a global minimum for interstitial H at the AB site of a Si nearest neighbour of a substitutional P.

The discrepancy in the minimum energy configuration for the H-P system in Si as well as the lack of experimental data on an H-induced passivation mechanism for shallow donors suggest a great need for more theoretical and experimental work to establish a consolidated model for the H-P system in Si. It is with this aim in mind that we report the results of our investigation on the nature of the H-P system in crystalline Si.

2. Theoretical tool (the CNDO method)

In our calculations, we systematically approximate the matrix elements of the Hartree-Fock-Roothaan equations by introducing three semi-empirical parameters: an orbital exponent (ξ), the electronegativities (ϵ) and a bonding parameter (β). From these approximations, the complete neglect of differential overlap (CNDO) method [14] then gives self-consistent solutions similar to Hartree-Fock solutions. In our work, we implement the Harwell MOSES code [15] and the H and P parameters we have used here are from Pople and Beveridge [14] while the Si parameters are from Harker and Larkins [16] who fitted the bulk properties of Si to their theoretical predictions by using a 16-atom periodic large unit cell. The parameters we have used here are listed in table 1. This method has been used successfully on hydrogen in diamond and silicon [17], hydrogen in germanium [18], self-interstitials in Si and Ge [19, 20] and hydrogen complexes in Si [21, 22].

Table 1. The CNDO parameters used.

Element	Orbital exponent ξ_{sp} (Bohr ⁻¹)	Electronegativity		Bonding parameter
		ϵ_s (eV)	ϵ_p (eV)	β (eV)
H	1.2	7.8	—	-9.0
P	1.65	11.20	5.20	-10.5
Si	1.54	6.30	4.50	-6.4
Si*	1.54	6.30	4.50	0

3. Cluster description and calculations

In our calculations, we use a 59-atom (29 Si 30 Si*) cluster centred at a substitutional site (see figure 1). The edges of this cluster are saturated by Si hybrid pseudoatoms (Si*).

For our first set of calculations, we place the P atom at the centre of the cluster, normally occupied by a Si atom so that it is tetrahedrally bonded to four nearest-neighbour Si atoms. The H atom is then moved in the interstitial space in the vicinity of this substitutional P atom.

In our next set of calculations, the H atom is then moved in the vicinity of a Si atom, located at the centre of the cluster. This central Si atom is bonded to a neighbouring substitutional P atom as well as three other Si nearest neighbours. These two configurations are illustrated in figure 2. In both cases, as the interstitial H atom is moved around the P or Si atom, the total energy of the system is calculated and the profile of the total energy variation can be plotted.

4. Results and discussion

Figure 3 shows the variation of the total energy of the H atom as it is moved away from the substitutional P atom along the (111) axis in the backbond direction. This set of calculations is for the case of no lattice relaxation. From figure 3, we can deduce

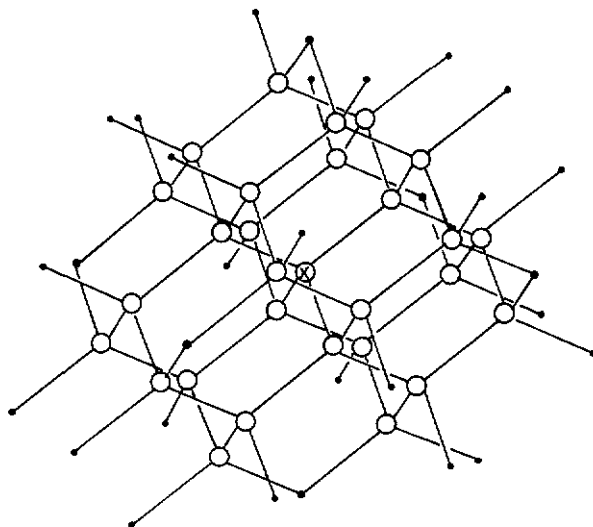


Figure 1. The 59-atom (29 Si 30 Si*) substitutional centred cluster. The centre is marked with a cross (x) and the dangling bonds of the cluster are saturated by Si hybrid atoms (Si*).

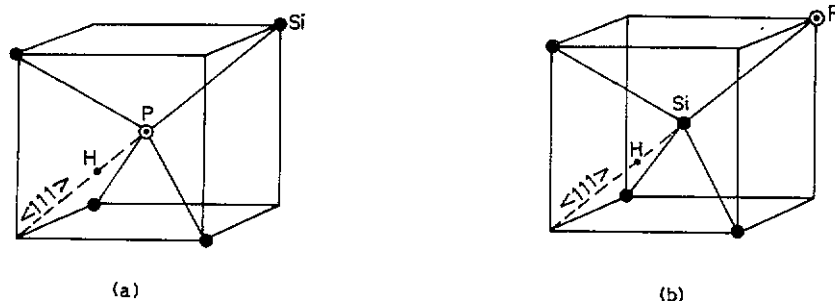


Figure 2. (a) The configuration representing the H atom in the immediate vicinity of a substitutional P atom. (b) This configuration depicts the H atom in the immediate vicinity of a Si with a P atom as a nearest neighbour.

that the H atom appears to be weakly attracted to the P atom when it is at the AB site. However, this site is a saddle point and another location further away along the backbond direction has an energy 0.78 eV less than that at the AB site close to the P atom. This location (L_P) is very close to the second tetrahedral site (labelled T_2) which is nearer to the Si atom labelled 1 in figure 4.

Total energy calculations for the movement of the H atom along the other two major axes, $\langle 001 \rangle$ and $\langle 110 \rangle$ indicate higher energy levels with the local minima higher as well compared to location L_P in figure 4. Hence, we will not consider them further in our discussion.

Additional calculations for the H atom in the vicinity of the Si atom bonded to a nearest-neighbour P atom yield the results illustrated in figure 5 (an unrelaxed

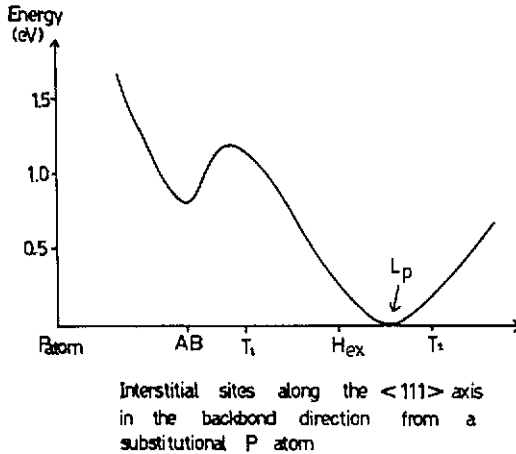


Figure 3. The total energy variation for the H atom as it is moved away from the substitutional P atom in the backbond direction. The global minimum is at L_p , close to the tetrahedral site (T_2). T_1 is closer to P while T_2 is closer to atom 1 (Si) in figure 4.

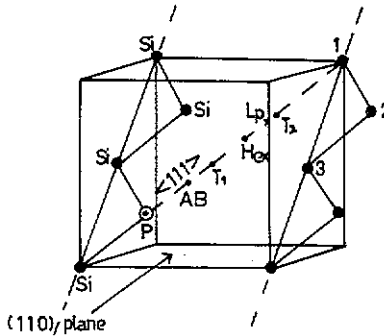


Figure 4. The (110) plane where the global minimum position for the H atom is located.

lattice). Figure 5 shows the total energy profile of the interstitial H atom as it is moved in the backbond direction along the $\langle 111 \rangle$ axis away from the Si atom. The results suggest that the presence of the P atom in the crystal lattice has somehow impeded the diffusion of the H atom, localizing it at the AB site along the $\langle 111 \rangle$ direction in the Si lattice. This result agrees with the experimental findings of Johnson *et al* [11] using secondary-ion mass spectrometry (SIMS). Moreover, the results of Mainwood and Stoneham [17] suggest that the motion of atomic hydrogen in crystalline Si is relatively athermal in the absence of impurities, with hardly any barrier to motion for the interstitial H atom along the $\langle 111 \rangle$ direction. In addition, the Si-H distance for the H atom at the AB site near to the Si atom is calculated to be 1.61 \AA , in excellent agreement with the 1.6 \AA separation determined experimentally by Picraux and Vook

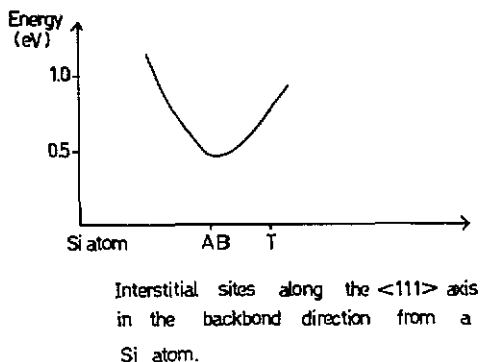


Figure 5. The total energy variation for the H atom as it is moved away along the backbond direction from a Si atom with a P atom as a nearest neighbour.

[23] for D centre in H-implanted Si, which they assigned to the H atom in the AB position. This unrelaxed AB configuration is about 0.46 eV higher than the minimum position (L_P) near the tetrahedral site discussed earlier in figure 4. However, if both the Si atom and its P nearest neighbour are relaxed with the H atom still at the AB site, then the total energy decreases until it reaches a value just 0.01 eV higher than that of L_P in figure 4. In this relaxed AB configuration with the H, Si and P atoms all aligned along the $\langle 111 \rangle$ direction, the Si-H distance is calculated to be 1.485 Å, in excellent agreement with the experimental value of 1.48 Å for Si-H in SiH_4 [24].

Alternatively, keeping the lattice unrelaxed and with the Si-H distance kept at 1.61 Å, the H atom is moved in a circular arc RS around the Si atom in the (110) plane as shown in figure 6(a). From figure 6(b), the total energy calculations show that as the H atom squeezes into the Si-P bond, the total energy rises. With the H atom inserted into the Si-P bond (BM site), it is about 10 eV higher than the total energy at the unrelaxed AB site. However, with the H atom at the BM site, when the Si-P bond is allowed to relax, the total energy drops until it reaches a value 0.03 eV above that at L_P (see figure 4). In this relaxed BM configuration, the H-P and H-Si distances are calculated to be 2.61 and 1.476 Å respectively. This implies that the distortion, especially the displacement of the P atom from its substitutional site, must be very great before the H atom can lodge itself within the Si-P bond via migration from the AB site close to the Si atom. Hence, the path RS represented in figure 6(a) is highly unlikely in addition to the initial high energy barrier of more than 10 eV.

Therefore, the position labelled L_P , close to the tetrahedral site along the backbond direction of a Si atom with a P atom close by as depicted in figure 4 is the global minimum position for the H atom for the H-P system in crystalline Si. Since this site is closer to the Si atom, and the H atom is much more than 3.5 Å away from the P atom (the H-P distance in phosphene, PH_3 , is 1.4 Å), it is unlikely for the H atom to be bonded to the P atom although the presence of the P atom leads to localization of the interstitial H atom in the vicinity of the Si atom. This is compatible with the suggestion that the H atom is not bonded to the donor [13], based on experiments [25] showing that all H-donor pairs in Si have similar infrared absorption spectra. Our calculated results also give strong support to L_P as the global minimum position for interstitial H, instead of the model suggested by Johnson *et al* [11] where their global

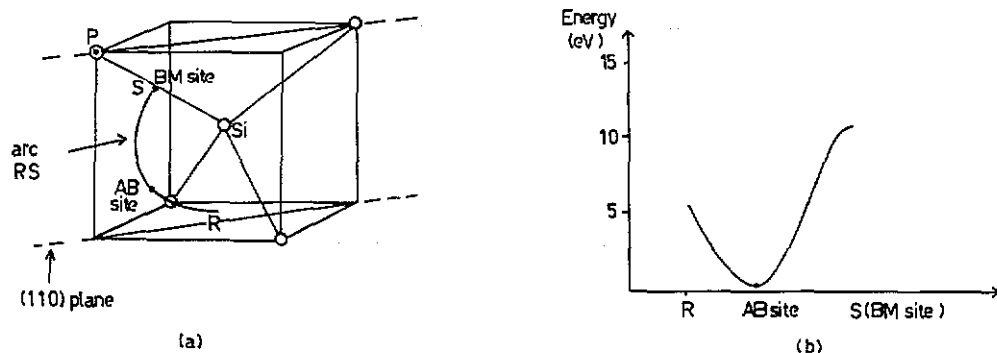


Figure 6. (a) The path of the H atom along the arc RS. (b) The corresponding total energy variation for the H atom along the path RS as it moves towards the Si-P bond.

location for H atom is at the AB site of a Si atom bonded to a P nearest-neighbour atom. Our proposed model can be explained with the aid of figure 4.

When a H atom is moving in the interstitial space in the Si crystal lattice where a P atom is nearby, its diffusion is greatly slowed down, causing it to localize at site L_P near three Si atoms, labelled 1, 2 and 3 in figure 4. If the lattice then undergoes relaxation, the H atom can easily slip into the AB site, near one of the Si atoms preferably atom 1, because the relaxed AB site is merely 0.01 eV higher than L_P . This implies that the H and P atoms are always in a $\langle 111 \rangle$ orientation with a possible model for this configuration being $Si_4P \dots H \dots SiSi_4$ instead of the $Si_3PSi \dots H$ chain suggested by Johnson *et al* [11]. The interstitial H atom is therefore easily mobile between the T site and the AB site if lattice relaxation close to the Si atom occurs.

5. Conclusion

Our calculations for the motion of the H atom in the vicinity of a Si atom with a P atom as a nearest neighbour yield the same results as those of Johnson *et al* (11). In this configuration, the H atom localizes itself at the AB site close to the Si atom. Later calculations by Chang and Chadi [12] placed the global minimum position for H closer to the tetrahedral site. Qualitatively, therefore, our results described in this article have the P, Si and H atoms aligned in a $\langle 111 \rangle$ direction and the H atom not bonded to the P atom. This model appears to suggest that the Si atom has an immediate localizing effect on interstitial H. However, one set of our calculations with the H atom in the interstitial space between the P and Si atoms suggests that the H atom has an even lower energy at a location called L_P (see figure 4). L_P is located close to the tetrahedral site along the backbond direction of the Si atom. This model allows for the direct influence of both the P and Si atoms because the H atom is between them. We feel this model is a more appropriate representation of the H-P system in crystalline Si because firstly, the H-induced passivation is caused by the impurity, in this case P. Our model has the H atom close to the P atom whereas in the earlier model, the effects of the P atom could be minimized by the Si atom which is the immediate neighbour of the H atom at the AB site. Secondly, Chang and Chadi [12] have found a global minimum for the H atom close to the tetrahedral site. In our

model, the H atom is located at L_p , very close to the tetrahedral site of the Si atom. Thirdly, the {111} orientation of the H-P-Si system is retained.

We hope that future experimental and theoretical work can shed more light on the H-P complex in Si.

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