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Hydrogen-acceptor pairs in silicon: Pairing effect on the hydrogen vibrational frequency

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We calculate the electronic structures of the hydrogen-boron and hydrogen-aluminum pairs in silicon which are believed to form when the corresponding shallow acceptor activity is neutralized by hydrogen. In particular, computed infrared vibrational frequencies are reported for the first time and compared with recent experimental measurements. Both theory and experiment reveal an interesting reduction in the vibrational frequency for hydrogen in the H-B pair with respect to the isolated monohydride. This we analyze in terms of two- and three-body interactions involving the hydrogen, the acceptor impurity, and the nearby silicon atoms.

It has recently been established by experiment that the acceptor activity of boron, aluminum, and indium in *p*-type silicon can be neutralized by exposure to hydrogen.[1-6] The models proposed for the deactivation all require a reaction that leaves the acceptor atom properly (threefold) coordinated with its neighbors. A particular model for this complex is a substitutional hydrogen-acceptor pair with the acceptor off center in the $\langle\bar{1}\bar{1}\bar{1}\rangle$ direction and the hydrogen off center in the $\langle 111\rangle$ direction. In a recent publication, we reported computational results which support both the stability and the property of acceptor deactivation for these substitutional H-B and H-Al pair models.[7] More recent experimental studies on the hydrogen-boron system have provided two types of additional support for this model. First, it has been found that oxygen is not present in the defect complex,[4,5] although its presence had been previously suggested.[8] Second, the existence of a hydrogen-silicon bond in the complex has been established from two independent infrared studies.[4,6] The hydrogen stretching mode for the hydrogen-boron defect is found at 1870 cm^{-1} (Ref. 6; 1875 cm^{-1} from Ref. 4), which is not only near the range appropriate for a hydrogen-silicon bond, but changes properly with replacement of hydrogen by deuterium to 1360 cm^{-1} (Ref. 6).

In this paper, we explore *theoretically* a striking feature of the H-B system which has been revealed by these recent infrared studies. Although what is observed is clearly a hydrogen-silicon bond, the vibrational frequency is significantly *lower* than those appropriate to typical Si-H molecular systems, which fall in the approximate range 2100–2300 cm^{-1} (Ref. 9). Other Si-H systems have been detected in *a*-Si and *c*-Si (Refs. 10 and 11; also see Ref. 12); however, the H-B pair is particularly appropriate for theoretical study since its structure has been established and it is relatively simple.

From our calculations, we produce hydrogen vibrational frequencies for both the H-B and H-Al pairs in silicon. The H-B result is compared with the recently measured value; the H-Al result constitutes a prediction since this has not yet been observed. We consider the nature of this frequency reduction for the H-B pair in terms of a simple model which is similarly applied to the H-Al pair.

The defect-electronic-structure methods which we have applied to the H-B and H-Al systems have been described in previous publications,[13] so we discuss them here only briefly. We proceed by simulating the defect environment by small fragments of crystalline silicon, suitably terminated by hydrogen atoms; i.e., we use a cluster approach. The electronic structures appropriate to these clusters are generated by two well-tested and well-documented self-consistent electronic-structure methods: scattered-wave $X\alpha$ (SW$X\alpha$) (Ref. 14) and modified neglect of diatomic overlap (MNDO).[15] The SW$X\alpha$ method is an *ab initio* approach which employs the Slater statistical exchange and a muffin-tin approximation to the potential energy. The MNDO method is a semiempirical Hartree-Fock linear combination of atomic orbitals approach. We use the SW$X\alpha$ method to provide reliable single-particle energies, and the MNDO method primarily to provide reliable total energies with respect to atomic displacements.[13]

Both methods have been applied to the small cluster $\text{BHSi}_4\text{H}_{12}$, and the MNDO method has been applied to a larger cluster $\text{BHSi}_{16}\text{H}_{36}$ (Ref. 7). Both the SW$X\alpha$ and MNDO single-particle electronic structures predict electrically inactive defects, consistent with the observed shallow-acceptor neutralization.[7] A similar MNDO study was reported for the H-Al pair.

The MNDO method allows us to minimize the total energy with respect to the H, B (Al), and Si coordinates. The proper response of the silicon atoms was produced by using our "hybrid" cluster.[7,13] Here, we use the smaller of our two clusters, but with external springs connected to the four $\langle 111\rangle$ silicon atoms in order to simulate the restoring forces of the host outside of the cluster. The hybrid-cluster total energies with respect to combined silicon and acceptor coordinates (see figure caption) are shown in Figs. 1 and 2 for the H-B and the H-Al pairs, respectively. The stable geometries are also shown. We found in both cases that the hydrogen-acceptor pairs are oriented along the $\langle 111\rangle$ silicon direction, consistent with the proposed model.

We now consider small vibrations of the hydrogen impurity appropriate to the equilibrium positions previously established by the calculations summarized above. In the harmonic approximation, the change in energy with respect to $\langle 111\rangle$ (bond-stretching) displacements from equilibrium of the acceptor, u_x, and the hydrogen, u_H, can be written as

$$E=\tfrac{1}{2}(\phi_{XX}u_X^2+\phi_{\text{HH}}u_\text{H}^2+2\phi_{X\text{H}}u_Xu_\text{H}) \ , \qquad (1)$$

where X refers to either B or Al. Force-constant matrix ele-

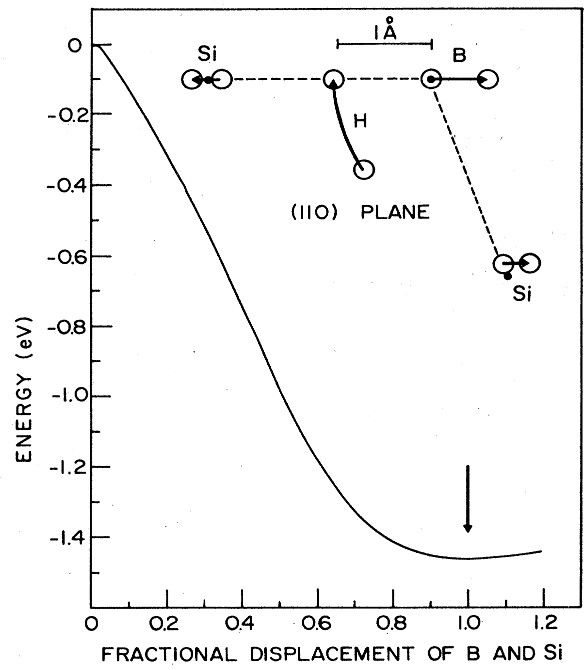

FIG. 1. Total energy and structure for the H-B pair. The total energy is for the cluster, $BHSi_4H_{12}$ (MNDO-hybrid), as a function of fractional displacement of B and Si from the "reference" configuration, with H following adiabatically. The reference configuration is established according to a two-step process. (i) Allow silicons to relax about an isolated, on-center B^- substitutional. (ii) Freeze in these silicon coordinates and allow H to locate its equilibrium position (see Ref. 7). Inset shows relaxed and reference configurations (open circles) relative to normal-lattice sites (solid circles).

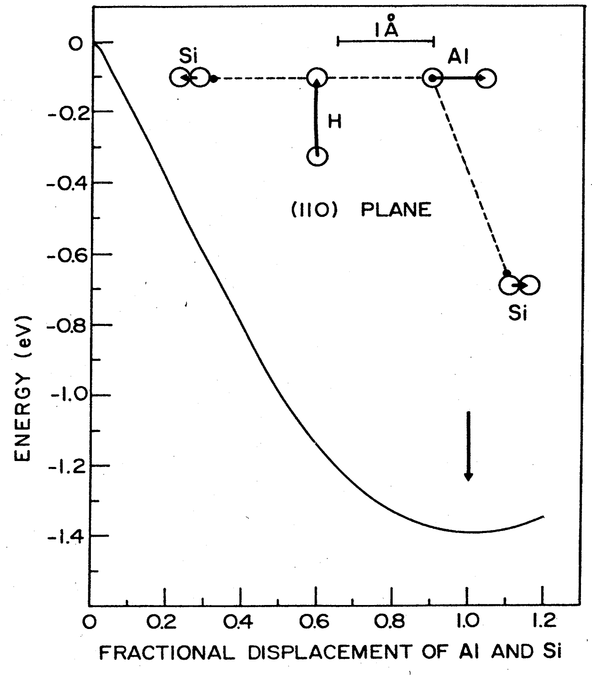

FIG. 2. Total energy and structure for the H-Al pair (see caption, Fig. 1).

ments ϕ_{XX} and ϕ_{HH} are readily computed by taking second derivatives with respect to u_X and u_H, respectively. ϕ_{XH} can be determined by taking the second derivative with respect to a uniform displacement, ξ ($\xi = u_X = u_H$); this second derivative is equal to $\phi_{XX} + \phi_{HH} + 2\phi_{XH}$, which we call Δ. Displacements of 0.01 Å are used in calculating the derivatives. The computed force-constant matrix elements are given in Table I. The corresponding hydrogen vibrational wave numbers are 1880 cm^{-1} and 2220 cm^{-1} for the H-B and H-Al pairs, respectively.[16] The H-B result compares favorably with the measured value of 1870 cm^{-1}; the H-Al result remains to be tested by experiment.

For comparison, we simulate an isolated Si-H system by this cluster, but with the XSi_3H_9 part removed (i.e., H-SiH_3). Here, the hydrogen is found to move back toward the silicon ($d_{\text{Si-H}} = 1.43$ Å, compared with 1.46 Å for the H-Al pair and 1.50 Å for the H-B pair), and the force constant increases to 19.1 eV/$Å^2$; this corresponds to a wave number of 2270 cm^{-1}, which can be compared with the Si-H stretch mode of 2190 cm^{-1} for silane. Hence, we conclude that the computed frequency of our model-isolated Si-H system (2270 cm^{-1}) is significantly reduced when a boron is nearby in this configuration (1880 cm^{-1}), but is almost unchanged by the presence of an aluminum (2220 cm^{-1}).

This reduction in the frequency when in the presence of the boron is indeed interesting. Pankove, Zanzucchi, Magee, and Lucovsky[4] have suggested that this may be due to the presence of significant three-body forces involving the B-H-Si chain of atoms. This we find to be one of the contributions, as we describe below.

We explore the nature of the interatomic forces by expressing Eq. (1) in a different form. Assume that the total energy can be expressed in terms of the usual two-body interactions between Si_3 and X, X and H, and H and Si, by the spring constants k_1, k_2, and k_3, respectively (see Fig. 3). Also add the effect of three-body interactions, characterized by k_{12}, k_{23}, and k_{13}. The total energy is then

$$E = \tfrac{1}{2}(k_1 u_1^2 + k_2 u_2^2 + k_3 u_3^2 + 2k_{12} u_1 u_2 + 2k_{23} u_2 u_3 + 2k_{13} u_1 u_3) \quad . \tag{2}$$

The u_i are the changes in the separations between the appropriate pair of atoms (e.g., u_3 represents the change in the separation between H and Si). They are related to the coordinates appearing in Eq. (1) as follows: $u_1 = u_X$, $u_2 = u_H$

TABLE I. Computed force constants appropriate to the H-B and H-Al defect pairs [see Eqs. (1) and (2), and Fig. 3]. Units are eV/$Å^2$; X refers to either B or Al.

	H-B	H-Al
ϕ_{XX}	6.8	6.3
ϕ_{HH}	13.2	18.3
ϕ_{XH}	2.4	−0.9
Δ	24.8	22.8
k_1	10.2	5.0
k_2	0.5	3.3
k_3	14.9	18
k_{12}	1.95	1.0
k_{23}	1.1	1.5
k_{13}	0.15	0.1

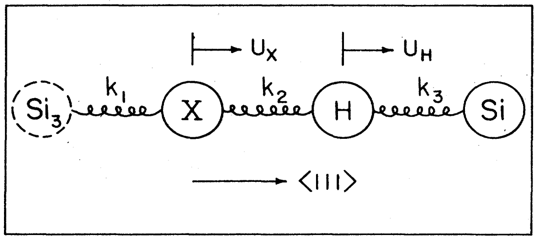

FIG. 3. Spring model for Si_3-X-H-Si system, where X is either B or Al.

$-u_X$, and $u_3 = -u_H$. Hence, these spring constants are related to the force-constant matrix elements by

$$\phi_{XX} = k_1 + k_2 - 2k_{12} \ , \tag{3a}$$

$$\phi_{HH} = k_3 + k_2 - 2k_{23} \ , \tag{3b}$$

and

$$\phi_{XH} = -k_2 - k_{13} + k_{12} + k_{23} \ . \tag{3c}$$

The spring constants k_1, k_2, and k_3 are calculated first. Spring constant k_i is calculated by taking the second derivative of the energy E with respect to interatomic separation u_i, with all other separations held fixed. The remaining three parameters k_{12}, k_{23}, and k_{13} are calculated from Eqs. (3) using the results given in Table I. In so doing, we isolate the three-body effects by comparing force constants which involve simultaneous changes in two interatomic separations (ϕ_{ij}, or Δ) with those involving only one (k_i). This is readily seen by a simple rearrangement of Eqs. (3); hence

$$k_{12} = \tfrac{1}{2}(k_1 + k_2 - \phi_{XX}) \ , \tag{4a}$$

$$k_{23} = \tfrac{1}{2}(k_3 + k_2 - \phi_{HH}) \ , \tag{4b}$$

and

$$k_{13} = \tfrac{1}{2}(k_1 + k_3 - \Delta) \ . \tag{4c}$$

The results are given in Table I.

This simple model now reveals the nature of the changes in the hydrogen vibrational frequency when in the presence of an acceptor impurity. Since this mode involves hydrogen motion almost exclusively, we consider the related quantity ϕ_{HH} for the H-acceptor pair (see Table I), and we monitor how it evolves from the isolated Si-H force constant of 19.1 eV/Å^2. We first consider the contribution to ϕ_{HH} from k_3, as it appears in Eq. (3b). For both defect pairs, k_3 is smaller than the isolated Si-H force constant. This difference can be identified with the anharmonicity of the H–Si bond, which becomes significant when the bond is sufficiently stretched. This is best demonstrated by noting that the isolated Si-H force constant of 19.1 eV/Å^2 reduces to 17.8 eV/Å^2 (close to $k_3 = 18$ eV/Å^2) when evaluated at the Si-H separation of 1.46 Å appropriate to the H-Al pair, and reduces to 15.3 eV/Å^2 (close to $k_3 = 14.9$ eV/Å^2) when evaluated at the Si-H separation of 1.50 Å appropriate to the H-B pair. Hence, this reduction is common to both pairs, but considerably smaller for the H-Al pair.

We next consider the contribution to ϕ_{HH} [Eq. (3b)] from the three-body term, k_{23}. From Table I, it is seen that this contribution is positive and significant for both defect pairs. This then further reduces the force constant (or frequency) from the isolated Si-H value. Such a positive three-body term is consistent with those inferred from other solid-state and molecular systems.[17,18] The positive sign reflects the weakening of the Si-H interaction that occurs when the H-acceptor interaction is strengthened by a reduction in the H-acceptor separation.[18]

The last contribution to ϕ_{HH} appearing in Eq. (3b), k_2, represents the direct interaction between the hydrogen and the acceptor. For the H-B pair, k_2 is positive, but small (Table I). This is again an anharmonic effect which is fully consistent with the present situation since the H-B distance is equal to 1.63 Å for this defect, whereas it is only 1.13 Å in the molecule BCl_2H (Ref. 19). For the H-Al pair, this interaction is considerably larger (k_2 from Table I), and herein lies the second significant quantitative difference between the H-B and H-Al pairs. This large value of k_2 is consistent with the *small* relative difference between the hydrogen-aluminum separations of the AlH molecule (1.65 Å) (Ref. 19) and the H-Al pair defect (1.78 Å).

One final point concerns our model for the isolated Si-H system, with which we compare our defect-pair frequencies. This H-SiH_3 fragment resembles the molecule silane which, from electronegativity considerations, may be expected to have a higher frequency than that of a true Si-H monohydride (H-$SiSi_3$ . . .).[9] In fact, a hydrogen mode in *a*-Si and *c*-Si at 1990 cm^{-1} has been identified with such an isolated monohydride, consistent with electronegativity arguments.[9-12] However, hydrogen defects in silicon have been rather elusive to microscopic detection, so their true structures are not really known. In fact, the environment of this hydrogen may produce a reduction in the frequency (to 1990 cm^{-1}, for example) by mechanisms similar to those just described for the H-B system. On the other hand, *if* this 1990 cm^{-1} defect *is* a well-isolated monohydride, then our computed wave-number reduction for the H-B pair of 390 cm^{-1} (2270 minus 1880) would significantly overestimate the experimental value of 120 cm^{-1} (1990 minus 1870), with which our theoretical number should be compared.[20]

We summarize and conclude by collecting and comparing the above contributions. The hydrogen vibrational frequency computed for the H-B pair (1880 cm^{-1}) is considerably lower than that of the corresponding isolated Si-H system (2270 cm^{-1}) primarily for two reasons: (i) the anharmonicity associated with a significant stretching of the Si-H bond, and (ii) the presence of a significant, positive three-body effect involving the B-H-Si chain of atoms. These conspire to reduce the frequency, producing a theoretical result which is in good agreement with experiment (1870 cm^{-1}). The H-Al pair also seems to exhibit a significant three-body effect involving the chain Al-H-Si. This tends to lower the frequency relative to the isolated Si-H system as well. An additional small reduction also comes from anharmonicity in the Si-H interaction. However, unlike the H-B pair, the H-Al system exhibits a *strong* two-body interaction between the hydrogen and the aluminum, i.e., a large value for k_2. In the H-Al complex, there is not enough room for *relatively isolated* H-Si and Al-Si_3 systems to coexist. This large hydrogen-aluminum interaction more than compensates for the tendencies to a reduced frequency which prevail in the H-B system. We therefore predict a vibration (2220 cm^{-1}) for the H-Al pair which is in the range appropriate to molecular Si-H systems, but larger than the monohydride tentatively identified in *a*- and *c*-Si.

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