

Structure, energetics, and dissociation of Si-H bonds at dangling bonds in silicon

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We investigate the interaction of hydrogen with dangling bonds in bulk silicon, using first-principles pseudopotential-density-functional calculations. Two geometries are employed: the first is that of a hydrogenated vacancy; the second geometry allows investigation of an isolated dangling bond and minimizes any H-H interactions. The effect of H-H repulsion is quantified. We find that the energy required to remove the hydrogen from the dangling bond and place it in an interstitial position is 2.5 eV. We also investigate the effect of strain in the back bonds on the energy of the Si-H bond. Finally, we propose a low-energy path for the dissociation of the Si-H bond, and discuss the effect of carriers on the dissociation process.

The ability of hydrogen to passivate dangling bonds has been widely exploited for technological applications. Hydrogen ties off dangling bonds on the surface, at grain boundaries, and in an amorphous network; the latter application has led to a significant improvement in the electronic properties of amorphous Si (*a*-Si). The interactions of H with Si have recently been studied with various theoretical and experimental methods.¹ Nonetheless, little information is available about the energetics of the Si-H bond in bulk Si. It has mostly been assumed that the bond strength would be similar to that in a silane (SiH₄) molecule, but then effects of the crystalline environment and possible distortions of the bonding configuration are ignored. Here we present results of first-principles calculations which include such effects. Even though the present study does not explicitly deal with amorphous networks, our comprehensive investigation of the Si-H bond in the crystalline environment provides information that is also relevant for the amorphous case.

We proceed by investigating the structure and energy of the Si-H bond in a number of distinct configurations. One geometry is that of the hydrogenated vacancy; here the H atoms are close enough to significantly interact. We therefore also investigate a second geometry, which places a dangling bond in a larger void, created by the removal of four Si atoms. For this configuration we find that the energy required to move the H atom from the Si-H bond to an interstitial position is 2.5 eV. The energy found in the case of the hydrogenated vacancy is smaller by 0.4 eV; this is attributed to H-H repulsion effects, which we will quantify. We also investigate the effect of strain in the back bonds, by displacing the Si atoms which are neighbors of the Si atom that carries the dangling bond. Such strain effects could play a role in the case of *a*-Si. We find, however, that the energy of the Si-H bond is not very sensitive to these changes in the network. Finally, we study the dissociation of the Si-H bond. Since interstitial H in crystalline Si occupies a bond-center (BC) position, it is natural to envision a path where H moves from the dangling bond into a BC site in one of the neighboring Si-Si bonds. Not only do we find this to be a favorable path, but the energy levels which are introduced into the band gap in the course of the dissociation process open

the way for carrier-enhanced dissociation.

Our calculations are based on density-functional theory in the local-density approximation,² using a plane-wave basis set and a supercell geometry, with an *ab initio* pseudopotential for Si (Ref. 3) and the Coulomb potential for H. Convergence tests indicate that 32-atom supercells and plane-wave cutoffs up to 18 Ry are sufficient to obtain results converged to within ± 0.1 eV. Relaxation of host atoms is included. This calculational approach has previously been successfully applied to the study of interstitial H in Si,⁴ as well as H on Si surfaces.⁵ The calculated values correspond to zero-temperature formation energies; contributions from zero-point energy are included.^{5,6}

For reference, we have performed calculations on the SiH₄ molecule (in a supercell). We find a converged Si-H bond length of 1.50 Å, quite close to the experimental value (1.48 Å, see Ref. 7). We have also investigated the configuration of an isolated interstitial H atom, which serves as a reference level for the calculated energies. The stable site for the interstitial H is at the bond center;⁴ the energy of this configuration is 1.05 eV below the energy of a neutral H atom in free space.⁶

We study the binding energy of H at a dangling bond in two configurations. The first configuration (Fig. 1) is that of a hydrogenated vacancy, i.e., one Si atom is removed, and the resulting dangling bonds are tied off by H atoms. An investigation of breathing relaxations shows that the Si-H distance is reduced by 0.03 Å compared to its value in SiH₄. The Si atoms move away from the vacancy by 0.16 Å measured from their ideal lattice site. No evidence was found for asymmetric relaxations. The energy gained due to relaxation is significant: compared to a reference configuration in which the Si atoms occupy their ideal lattice sites and the Si-H distance is the same as in SiH₄, close to 1.0 eV is gained. In the process, the H-H distance is increased from 1.3 Å to 1.6 Å. H-H repulsion is the driving force for the relaxation; even in the relaxed configuration this interaction remains significant.

One way to assign an energy to the Si-H bond is by expressing the *formation energy* of the structure. This requires choosing appropriate reference states; for Si, the reference is bulk Si; for H, we choose the reference to be

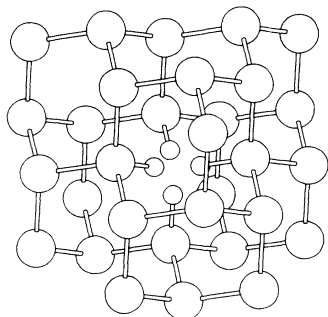


FIG. 1. Schematic representation of a hydrogenated vacancy. Si atoms are represented by large spheres, H atoms by small spheres. A Si atom has been removed from the lattice, and four H atoms tie off the dangling bonds. The cluster of host atoms shown here is purely for illustrative purposes and bears no relation to the actual supercell used in the calculations.

a neutral H interstitial at its stable site in bulk Si (i.e., the BC site⁴). Suppose we carry out a calculation for a supercell containing n_H H atoms and n_{Si} Si atoms. We then define a formation energy for this configuration:

$$E_{\text{form}} = [E_{\text{tot}} - n_{Si}E_{Si} - n_H E_{H,BC}] / n_H, \quad (1)$$

where E_{tot} is the calculated supercell energy, E_{Si} is the energy of a Si atom in the bulk, and $E_{H,BC}$ is the energy of an interstitial H at BC; the latter is obtained by taking an energy difference between a supercell containing the interstitial, and a bulk supercell. The factor $1/n_H$ yields the energy *per H atom*. The formation energy for the hydrogenated vacancy is reported in Table I.

The second way to define an energy for the Si-H bond is to address the question: how much energy is needed to remove the H atom from a Si-H bond, leaving a dangling bond behind? To our knowledge, the energy of an isolated dangling bond has not been calculated before; calculations for vacancies (which contain four dangling bonds) are quite different in nature, since the dangling bonds in that case strongly interact. We call the resulting energy a *binding energy*; it is defined as

$$-E_{\text{bind}} = [E_{\text{tot}}(\text{VH}_4) - E_{\text{tot}}(\text{VH}_3)] - E_{H,BC}. \quad (2)$$

VH_4 represents the configuration of the fully hydrogenated vacancy, and VH_3 the configuration in which one H has been removed, leaving a dangling bond behind.⁸ We have chosen the sign such that a positive value of the binding energy indicates a bound configuration. The value of this binding energy is also reported in Table I.

TABLE I. Formation energy [Eq. (1)] and binding energy [Eq. (2)] for hydrogen in different configurations, referred to H in a bond-center site. All values in eV per H atom.

Configuration	E_{form}	E_{bind}
H at BC	0	0
Hydrogenated vacancy, unrelaxed	-0.71	
Hydrogenated vacancy, relaxed	-0.96	2.10
Isolated Si-H (+ nine unrelaxed Si-H)	-0.87	2.50
Ideal Si-H (no H-H interaction)	-1.12	2.50

As pointed out above, however, in the case of the hydrogenated vacancy the interaction between H atoms may be quite significant. We have therefore devised an alternative configuration, which minimizes interactions between H atoms. It is illustrated in Fig. 2, and is generated by removing four Si atoms from the lattice. One can envision first creating one vacancy, focusing on one of its dangling bonds, and then removing three of the four Si atoms surrounding the vacancy. This process generates nine new dangling bonds, which are much farther removed from the “central” dangling bond we are focusing on. All of the dangling bonds are then hydrogenated. This geometry bears some resemblance to the one employed by Northrup⁹ to study an isolated dangling bond; however, our geometry is incorporated within the bulk crystal structure, whereas Northrup’s involves a surface. Nine of the resulting Si-H bonds still have H atoms which interact with other H atoms; however, the H atom on the “central” Si-H bond is 3 Å away from the others, virtually eliminating any undesired interactions.

In the configuration of Fig. 2, the central Si-H bond undergoes virtually no relaxation: the Si-H distance remains the same as in SiH_4 , and we find only a small inward relaxation of the Si atom, by 0.03 Å. The energy gained in this relaxation is only 0.04 eV. We do not allow any relaxation at the other nine Si-H bonds; in the calculation of the binding energy [equivalent to Eq. (2)] any contributions related to these nine Si-H bonds drop out. However, the formation energy [Eq. (1)] of this configuration does include a contribution from the additional H-H interactions at those nine Si-H bonds. Since the ten H atoms in this configuration are not equivalent, the calculated formation energy bears no direct physical meaning; however, it can be used to extract an interesting quantity, namely, a hydrogen-hydrogen interaction energy.

We denote the hydrogen-hydrogen interaction energy by U (for the relaxed case) or U' (for the unrelaxed case). Let us assume that the formation energy of a Si-H bond consists of an intrinsic part (for an “ideal” bond), plus a part (U or U') due to H-H repulsion. Considering first the unrelaxed case, the entry in Table I for the unrelaxed

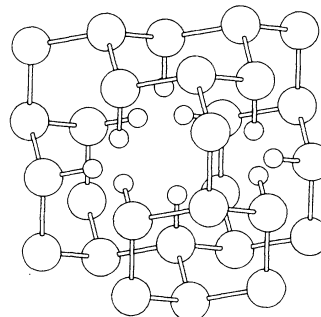


FIG. 2. Schematic representation of a structure used to study an isolated dangling bond. Si atoms are represented by large spheres, H atoms by small spheres. The orientation of the cluster is the same as in Fig. 1. Four Si atoms have been removed from the lattice, and ten H atoms tie off the dangling bonds. The “central” Si-H bond, located along a vertical direction near the bottom center of the cluster, has a H atom which is far removed from any other H atoms.

hydrogenated vacancy (-0.71 eV) contains a term $6/4 U'$ (because there are six H-H interactions possible between the four H atoms, and we want the energy *per H atom*). The entry for the "isolated Si-H bond" (-0.87 eV) contains a term $9/10 U'$ (because there are three times three H-H interactions possible, and there are a total of ten H atoms). Comparison of the two values produces a value $U'=0.27$ eV. Furthermore, we found that relaxation lowers the energy of the hydrogenated vacancy by 0.25 eV per H atom. If we assume that this lowering is entirely due to a reduction in H-H repulsion, we can define an interaction energy U appropriate for the relaxed configuration as follows: $U' - U = 4/6 \times 0.25$ eV = 0.16 eV. This leads to $U=0.11$ eV. These values for U and U' are remarkably close to those calculated by Northrup for H-H interactions on Si(100) surfaces.⁵

When the central H atom is removed in the configuration of Fig. 2, a dangling bond is left behind; the Si atom with the dangling bond relaxes toward the plane of its three neighbors by 0.15 Å. The relaxation found here is very similar to the result of Ref. 9, where a more complete study of the structure of dangling bonds was carried out. The binding energy resulting from the calculations on this configuration is 2.50 eV; the contribution from H-H repulsion to this value is probably negligible. On the other hand, the value of the binding energy we found in the case of the hydrogenated vacancy includes a term $3U$. We thus find $3U = 2.50$ eV $- 2.10$ eV, i.e., $U=0.13$ eV, consistent with the value of 0.11 eV determined above.

Using the derived value of U or U' we can actually define a formation energy which excludes the effect of H-H repulsion; e.g., starting from the value for the relaxed hydrogenated vacancy, we find for this "ideal" formation energy: $-0.96 - 6/4 \times 0.11 = -1.12$ eV, a value which is also listed in Table I. The difference between this value and the negative of the binding energy in the ideal configuration is 1.38 eV; the latter constitutes an estimate for the formation energy of a dangling bond. Note that it is somewhat larger than might be expected from dividing the formation energy of a neutral vacancy by four,¹⁰ due to the fact that the four dangling bonds in the vacancy interact to lower the energy. We also note that the formation energy of a dangling bond may be lower in an amorphous network; this would cause a corresponding reduction in the binding energy of the Si-H bond.

We can also express the formation energy on an energy scale where we choose the energy of the free neutral H atom as the origin.⁶ Since we found that the formation energy of the "ideal" Si-H bond is -1.12 eV, when expressed with respect to interstitial H, and since the energy of a H interstitial in the BC site is -1.05 eV, we find that the formation energy of the Si-H bond is -2.17 eV on this energy scale. This value is very close to our calculated value for the SiH₄ molecule, -2.22 eV, expressed with respect to bulk Si and a free H atom. It is worth noting that the values of binding energies and formation energies calculated here assume that both the dangling bond and the interstitial H atom occur in the neutral charge state; starting from the current values, the corresponding values for other charge states can be derived if the energy levels of the dangling bond and of the H

interstitial are known.

Next, we investigate whether strain in the back bonds affects the strength of the Si-H bond. Strain effects might be important in the case of an amorphous network. To simulate strain, we take the three Si atoms to which our "central" Si atom is bonded (in the configuration of Fig. 2), and move them outward. The displacement is chosen to be in the plane of these three atoms, and has a magnitude of 0.13 Å; this value was chosen by the criterion that, in order to maintain the standard Si-Si bond length (2.35 Å), the central Si atom would have to move all the way down into the plane of its neighbors. This represents a sizable strain, since it corresponds to 5% of the bond length. These three neighbors are then kept fixed, and only the central Si atom and the H bonded to it are allowed to relax. After performing the relaxations for the dangling bond and for the Si-H bond, we find a binding energy which is only 0.05 eV smaller than in the unstrained case. We conclude that strain effects have only a modest influence on the binding energy.

Finally, we investigate the dissociation of the Si-H bond. Several pathways can be considered. The H atom can move along the direction of the Si-H bond away from the Si atom (see Fig. 3); however, this is unlikely to be the most favorable path, for two reasons: (a) the barrier in that direction is probably high, as indicated by the high vibrational frequency (around 2000 cm⁻¹) for the Si-H stretch mode; (b) this path eventually leads to a position of the H atom in the interstitial channel, which is not the lowest-energy site for H in the neutral or positive charge state (in crystalline Si) (Ref. 4) (however, since H⁻ prefers the interstitial region, the path may occur in *n*-type material). Both of these arguments actually favor a path (path II in Fig. 3) in which the H atom stays at approximately constant distance from the Si atom to which it is bound: (a) the barrier in that direction is much lower, as indicated by the vibrational frequency (around 700 cm⁻¹) for the Si-H wagging mode; (b) this path leads to a H position near the BC site, which is the stable site for H⁰ (and also for H⁺) in crystalline Si.

We find that the intermediate state, with the H atom in a bond-center site next to the dangling bond, is 1.5 eV higher in energy than the Si-H bond, to be compared with the 2.5 eV it costs to remove the H to a position far away from the dangling bond. Even before the H atom

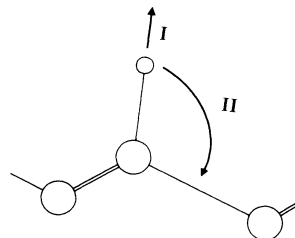


FIG. 3. Schematic representation [projected on a (110) plane] of a Si-H bond and the neighboring Si atoms. Si atoms are represented by large circles, and the H atom by a small circle. Two paths for removing the H atom from the Si-H bond (leaving a dangling bond behind) are indicated; path I moves the H atom towards a tetrahedral interstitial site, path II moves the H atom towards a neighboring bond-center site.

reaches this intermediate position, however, two energy levels are introduced into the band gap (near the valence band and near the conduction band), enabling the complex to capture carriers; after changing charge state there is virtually no barrier to further dissociation. Experimentally, the involvement of carriers in the migration of H in α -Si was established in Ref. 11: it was found that the motion of H is strongly suppressed in a depletion region under reverse bias, where no free carriers are available. We conclude that the barrier for dissociation can be significantly reduced in doped material or in the presence of light-induced carriers.

While the dissociation mechanism discussed here bears some similarity to that proposed by Zhang *et al.*¹² for dissociation of diatomic hydrogen (H_2^*) complexes in Si, the following differences should be stressed: (a) the carrier-enhanced dissociation is applied here to "standard" Si-H bonds, without invoking H_2^* , and (b) the pathway in which H moves into a neighboring BC site is lower in energy than the paths leading to interstitial positions con-

sidered in Ref. 12.

In summary, we have explored various configurations in which H is bonded to Si dangling bonds. The resulting energy values are summarized in Table I. In the absence of any H-H repulsion, the values for the "ideal" Si-H bond are very similar to those in SiH_4 , and strain in the back bonds has only small effects on the binding energy. H-H repulsion, which we have quantified, can lead to a measurable decrease in the binding energy, a fact which could play a role in α -Si:H in which there is evidence of hydrogen clustering.¹³ Repulsion between H and host atoms may also be significant in an amorphous network; realistic simulations of α -Si:H would be required to quantify such effects. Finally, we have proposed a low-energy dissociation path for the Si-H bond, and pointed out the possibility of carrier-enhanced dissociation.

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¹ *Hydrogen in Semiconductors*, Vol. 34 of *Semiconductors and Semimetals*, edited by J. I. Pankove and N. M. Johnson (Academic Press, Boston, 1991).

² P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

³ D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).

⁴ C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, *Phys. Rev. B* **39**, 10791 (1989).

⁵ J. E. Northrup, *Phys. Rev. B* **44**, 1419 (1991).

⁶ C. G. Van de Walle, *Phys. Rev. B* **49**, 4579 (1994).

⁷ *CRC Handbook of Chemistry and Physics*, 73rd ed., edited by D. R. Lide (CRC Press, Boca Raton, FL, 1992).

⁸ Spin-polarization has been taken into account in the calculations for neutral dangling bonds (which contain an unpaired electron); see also Ref. 9.

⁹ J. E. Northrup, *Phys. Rev. B* **40**, 5875 (1989).

¹⁰ P. E. Blöchl, E. Smargiassi, R. Car, D. B. Laks, W. Andreoni, and S. T. Pantelides, *Phys. Rev. Lett.* **70**, 2435 (1993).

¹¹ P. Santos and N. M. Johnson, *Appl. Phys. Lett.* **62**, 720 (1993).

¹² S. B. Zhang, W. B. Jackson, and D. J. Chadi, *Phys. Rev. Lett.* **65**, 2575 (1990).

¹³ F. Buda, G. L. Chiarotti, R. Car, and M. Parrinello, *Phys. Rev. B* **44**, 5908 (1991).