

Theory of Hydrogen Diffusion and Reactions in Crystalline Silicon

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In recent years, the behavior of hydrogen in crystalline silicon has been the object of intense experimental interest, but understanding has been limited by the absence of reliable theoretical calculations. Here we use state-of-the-art techniques to investigate systematically the properties of H in Si: stable configurations, migration paths, charge-state effects, cooperative interactions, etc. The calculations are based on local-density-functional theory, using *ab initio* pseudopotentials, in a supercell geometry. The results are used to scrutinize and supplement existing understanding of the observed phenomena. A novel mechanism for H-induced damage is proposed.

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For many years, hydrogen was believed to play a simple role in crystalline Si, namely to saturate “dangling bonds” at defects by forming Si–H bonds. In the last few years, however, a variety of experimental data have revealed a wealth of fascinating phenomena associated with H. It has been found that H causes a dramatic increase in the resistivity of *p*-type material.^{1,2} In *n*-type material, passivation of shallow donor impurities occurs but is less pronounced than in *p*-type silicon.^{3,4} Correspondingly, the data show pairing between H and shallow acceptors,^{2,5} but indicate a different type of bonding between H and shallow donors.⁴ Recently, it was also found that H, in addition to passivating existing defects, actually induces defects as well.⁶ Understanding of these phenomena has been rather limited⁷ largely because reliable theoretical results for the properties of H in crystalline Si have been lacking. Most of the previous studies, based on semiempirical Hamiltonians and/or small clusters, were rather limited in scope, and did not produce a consistent picture. An excellent review of the existing literature was published by Pearton, Corbett, and Shi⁸ so that no further review will be undertaken here.

In this Letter we report the application of state-of-the-art solid-state techniques to describe the properties of H in Si. These techniques—density-functional theory combined with the local-density approximation (LDA) for exchange and correlation, norm-conserving pseudopotentials, and large supercells for the solution of the relevant Schrödinger equation—have established their reliability in numerous studies of point defects and impurities in Si and III-V compound semiconductors. Our studies of H in Si cover two major topics. First, we examine the behavior of a single H atom in the Si lattice. We establish the stable configurations and migration paths for a H atom in its various charge states, including sites and paths that involve strong reactions with the Si network, and determine the relative stability of the different charge states in intrinsic, *p*-type, and *n*-type material. Our results will be displayed in a novel way

that significantly enhances our ability to capture the essence of how a foreign atom diffuses in and reacts with a crystalline network. Second, we explore the phenomena that may arise from precipitation of two or more H atoms. This includes the interaction of the H atoms with each other, leading to molecule formation, as well as the cooperative reactions of several H atoms with the Si network. We will use our theoretical results to scrutinize and supplement existing understanding of the observed phenomena.

Our calculations⁹ are based on local-density-functional theory¹⁰ in the LDA, using *ab initio* norm-conserving pseudopotentials¹¹ for Si, and the Coulomb potential for H. We used supercells containing 32 Si atoms, such that the distance between neighboring defects is 9.4 Å. By comparison with calculations performed on smaller cells, this size was found to be sufficient to derive reliable results for total energies and band positions for an isolated defect. In particular, the dispersion of the H-related energy level in the gap region is larger than 1.2 eV in the 16-atom cell, but is reduced to less than 0.5 eV in the larger cell. The position of this level was determined by our taking a weighted average over the values at the special points, and changed by less than 0.1 eV when the cell size was increased from 16 to 32 atoms. Two special points (or equivalent larger sets for less symmetric configurations) were used in the integrations over the first Brillouin zone. Plane waves up to a kinetic energy of 12 Ry were included in the expansions of wave functions and potentials (those above 6 Ry in second-order Löwdin perturbation theory); tests have shown that at this cutoff, total-energy differences have converged to within 0.1 eV. Relaxation of two shells of Si atoms surrounding H atoms was included in the full calculations. Long-range relaxation was included via the Keating model.¹²

The main sources of uncertainty in the calculations are the well-known intrinsic deficiencies of the LDA—in particular, the fact that LDA predicts conduction bands and hence conduction-band-derived energy levels to be

too low. This uncertainty, combined with residual interactions between supercells, puts an error bar of ~ 0.6 eV on the position of any defect level. However, a qualitative distinction between deep and shallow levels can still be made. We also note that, while the absolute position of the defect level is uncertain, its relative motion induced by displacements of the impurity or by changes in the charge state is quite reliable. These observations will allow us to derive conclusions about the deep levels induced by hydrogen, as described later in the paper. Only in the section where we discuss the relative stability of various charge states as a function of the Fermi-level position will we be confronted with the limitations of the LDA.

In this work, we will report local-density-functional results for total energies and defect levels; spin polarization,¹³ which affects only the neutral charge state, was not included. Self-consistent spin-density-functional calculations, which are much more time consuming, were carried out at selected sites where the deviation from the spin-averaged result is expected to be largest. We found the corrections to the total energy to be smaller than 0.2 eV. The exchange splitting for H-related levels in the gap region was less than 0.5 eV. These results are consistent with spin-polarized linear muffin-tin-orbital-Green's-function calculations for H in Si.¹⁴ The effect of level splittings has been taken into consideration in the following analysis.

In order to present our results for a single H atom in a Si lattice, we introduce a novel technique to generate energy surfaces. The central point is the realization that the energy surface has the full symmetry of the perfect crystal, and can therefore be expanded in a set of basis functions which exhibit this symmetry. A small set of energy values at representative points is then sufficient to determine the expansion coefficients. At each of these points, the total energy of the impurity (in a particular charge state) is calculated for a configuration in which the surrounding Si atoms are completely relaxed. This data base is then used to determine the expansion coefficients for the entire energy surface. We used symmetrized plane waves as basis functions and found that fewer than ten stars of reciprocal lattice vectors provide sufficient accuracy. An example of the resulting energy surfaces for H^+ is shown in Fig. 1. Note that the Si relaxations for each position of the H atom are different but are not displayed in the figure.

The energy surfaces for H in the positive, neutral, and negative charge states exhibit a number of common features. In all three charge states, there are two distinct regions in which the H atoms exhibit significantly different behavior. First we consider the region of high electron density, including the bond-center site (*B* in Fig. 1), the sites *C*, *M*, etc. In this region, the nearby Si atoms relax strongly. For example, when the H atom is placed at the *B* site, the adjacent Si atoms relax out by

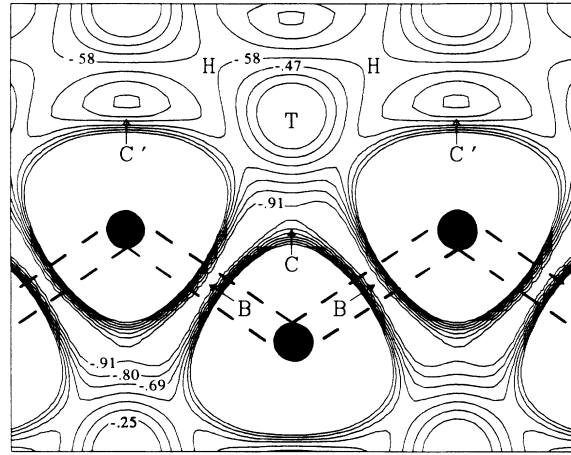


FIG. 1. Contour plot in the (110) plane of the total-energy surface for H^+ in Si. The atomic positions are indicated by solid dots, as well as the points *T* (tetrahedral interstitial site, chosen as reference, $E=0$), *H* (hexagonal interstitial site, $E=-0.61$ eV), *B* (bond center, $E=-1.04$ eV), and *C* (at the center of a rhombus formed by three adjacent Si and the nearest *T*, $E=-0.93$ eV). The energy difference between adjacent contours is 0.11 eV.

0.4 Å for a net gain in energy of more than 4 eV. Furthermore, in this high-density region, a defect level is introduced in the upper part of the energy gap; it is identified as a state formed out of an antibonding combination of the broken bonds on the neighboring Si atoms. The second region consists of the low-electron-density "channels" and includes the high-symmetry tetrahedral (*T*) and hexagonal (*H*) interstitial sites. Here, the Si atoms in the vicinity of H relax very little if at all. Furthermore, a H-related level now occurs as a resonance just below the top of the valence bands. The precise position of the defect levels changes only by ~ 0.1 eV as a function of charge state.

Figure 1 shows a contour plot of the energy surface in the (110) plane for a positively charged H (H^+). The lowest-energy positions for the H^+ occur in the high-density regions of the crystal, with the global minimum at the bond-center site. In contrast, the energy of H^+ in the low-density region is more than 0.5 eV higher.¹⁵ Note that the positive charge state does not imply that the H occurs as a bare proton; at the bond center, the missing charge is actually taken from the region near the Si atoms, corresponding to the antibonding state occurring in the band gap. A migration path in the (110) plane can be traced between the bond-center positions; the barrier along this path is less than 0.2 eV high. The saddle point occurs very close to the point indicated with *C* in the figure; the points *C'* are actually symmetry-related points along equivalent paths perpendicular to the plane of the figure. It is of course impossible to represent the energy surface (a four-dimensional object)

pictorially as a function of all three dimensions (although our choice of data points and our fitting procedure assure that we take the full three-dimensional character into account). The (110) plane and the indicated migration path should therefore only be considered as representative examples. In particular, we have also studied the behavior around the M site, which is midway between two C sites [only one of which lies in the (110) plane]. Corbett *et al.*¹⁶ proposed this site as the minimum-energy location for neutral H in Si. We find it to be at approximately the same energy as the bond center B , with no barrier between the two. The point M also lies on a line perpendicular to the Si–Si bond, connecting the bond center with the neighboring hexagonal interstitial site; all points between B and M on this line have approximately the same energy. For these “buckled” configurations, the Si–H distance remains almost constant (equal to 1.6 Å), because of appropriate relaxation of the Si atoms. The proton prefers to be symmetrically located with respect to two Si atoms.

We have also generated the energy surfaces for H in the neutral and negative charge states. For neutral H, the same features and relative positions of local minima can be recognized as in the case of H^+ , including a local minimum at the bond center. The high-density path is again favored, but the low-density path is less than 0.2 eV higher. Thus, neutral H seems to be able to move rather freely through the network with very small energy barriers. For the case of negative H (H^-), the tetrahedral interstitial site is the lowest in energy, with the energy rising sharply outside the low-density regions. In particular, the bond-center position is now more than 0.5 eV higher in energy than the interstitial site. The barrier to migration along a path through the low-density region and going through the hexagonal interstitial site is 0.3 eV.

Our results for the behavior of single H in Si are strongly supported by experimental data on muonium, a pseudoisotope of hydrogen. Muonium has been found to diffuse very rapidly in Si,¹⁷ in agreement with the low barriers found in our total-energy surface. The so-called “normal muonium” is associated with the tetrahedral interstitial site,¹⁷ whereas the “anomalous muonium” has recently been identified as occupying a bond center.¹⁸ These assignments are in agreement with the local minima that emerge from our calculations for neutral hydrogen.

We now examine the *relative* energies of the different charge states of the H, in order to determine the lowest-energy state. These relative energies depend on the position of the Fermi level, with which electrons are traded in order to alter the charge state of the defect. We will separately explore the cases of p type (Fermi level at the top of the valence band) and n type (Fermi level at the bottom of the conduction band). In p -type material, we find that the lowest-energy state is H^+ in the high-

density region; thus, H^+ diffuses via the high-density path and exhibits donorlike behavior. These conclusions are unambiguous and independent of any error bars in our LDA calculations. This result confirms the suggestion that the passivation of p -type material is a direct result of compensation, i.e., electrons from neutral H atoms annihilate the free holes in the valence band.⁷ Pairing between H^+ and negative acceptors follows compensation.¹⁹

For n -type material, our results are more sensitive to the intrinsic uncertainties of the methods. In the LDA, H is a negative- U impurity, very much like the Si self-interstitial²⁰: In p -type material, the stable state is H^+ in the high-density region; as the Fermi level is raised, however, the stable state becomes H^- in the low-density region. H^0 is not the stable state for any Fermi level. However, the uncertainty in the LDA energy levels makes the error bar too large to distinguish between H^- and H^0 as the stable state in n -type material, allowing the distinct possibility that H^0 is the more stable charge state. Thus, it is not possible at this point to confirm or rule out the suggestion⁷ that H^- does not form and that passivation of n -type Si occurs only via pairing. The latter must, however, compete with the formation of H_2 molecules and other reactions, as we discuss below.

So far, we have only discussed the properties of a single H atom in crystalline Si. Important effects can also occur as a result of the precipitation of several H atoms in a small region. First, we examine how two neutral H atoms may combine and form an H_2 molecule. We have found the minimum-energy position for the molecule straddling the tetrahedral interstitial site, oriented in the $\langle 100 \rangle$ direction, with the atoms separated by 0.86 Å (to be compared with 0.75 Å in vacuum). At the hexagonal interstitial site, which would lie on a migration path, the energy of the molecule is 1.1 eV higher. The binding energy of H_2 is 2 ± 0.5 eV per molecule, or ~ 1 eV per atom.

Another phenomenon involves the cooperative interaction of several H atoms with the Si lattice and is related to the recent observation⁶ that the hydrogenation can induce microdefects in a region within 1000 Å from the surface. These defects were characterized as “hydrogen-stabilized platelets” oriented in $\{111\}$ planes. Raman spectroscopy indicated that essentially all of the H in the region was incorporated in Si–H bonds. We have first explored the following mechanisms for the creation of damage: insertion of one H atom in each of the Si–Si bonds of a $\{111\}$ plane, accompanied by a lattice dilation, or replacement of each Si–Si bond with two Si–H bonds. To examine these processes we have performed total-energy calculations in a superlattice geometry; edge effects at the platelet boundary are thus neglected. We find that, compared with the energy of an isolated H atom, some energy can indeed be gained by the introduction of the H atoms in the Si–Si bonds of a $\{111\}$ plane,

but this gain is significantly less than the H_2 binding energy. These proposed structures would thus be unstable to H_2 molecule formation.

We have therefore examined a different type of mechanism, based on the removal of Si atoms from the defect region, with the resulting dangling bonds tied off by H atoms. This is based on our calculated result that H atoms can assist Frenkel-pair creation. In a perfect crystal, the creation of a Frenkel pair (vacancy-interstitial pair) normally costs about 8 eV.²¹ If, however, a sufficient number of H atoms are available in the immediate neighborhood of a particular Si atom, Frenkel-pair formation can actually be exothermic with a slight gain of energy. In the final configuration, a self-interstitial is emitted while four H atoms tie off the dangling bonds of the vacancy. The calculated energy gain for the process in which a neutral interstitial H atom passivates a dangling bond is ~ 2.2 eV per Si-H bond.²² This energy value was confirmed in a superlattice calculation modeling an extended defect in which a double row of Si atoms was removed in a $\{111\}$ plane, with all dangling bonds tied off by H.

These theoretical results for the interaction of several H atoms leads us to the following conclusions. On the basis of energetic considerations, H_2 molecules are the preferred state for several neutral H atoms in pure crystalline Si. Kinetic considerations also suggest that H-assisted Frenkel-pair creation would be a rare event. However, H-assisted ejection of threefold- or twofold-coordinated Si atoms is kinetically more favorable, such that enlargement of a preexisting defect is likely. The particular atomistic processes that lead to defect nucleation and enlargement cannot be described in more detail at this point; however, the energetic arguments given above for defect formation and extension suggest that the vacancy-formation mechanism is likely to be involved in the observed hydrogen-induced damage.

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