Theory of Hydrogen Passivation of Shallow-Level Dopants in Crystalline Silicon

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The stable structures, vibrational modes, and passivation mechanisms of an interstitial hydrogen atom in boron- and phosphorus-doped crystalline silicon are determined by an *ab initio* pseudopotential method. Our calculated formation energies for passivated H-B and H-P complexes are 2.5 and 2.0 eV, respectively, as compared to a binding energy per H of 1.9 eV in an interstitial H_2 molecule. The higher dissociation energy of H-B relative to H-P is consistent with recent experimental observations that show a more pronounced hydrogen passivation for shallow acceptors.

The observation of atomic hydrogen (or deuterium) induced passivation of shallow[1-3] and deep[4,5] impurities in crystalline Si has led to intense interest in this area. Hydrogen passivation of neutralization, as opposed to compensation, is generally accompanied by distinctive changes in the transport properties of a doped sample: The carrier concentration decreases but the Hall mobility *increases*. A suggestive model for hydrogen passivation is that a hydrogen-defect complex is created making the defects electronically inactive. For the boron-hydrogen pair, two models have been proposed: the bond-center–site model by Pankove *et al.*[2] and DeLeo and Fowler[6] and the antibonding-site geometry by Assali and Leite.[7] For the phosphorus-hydrogen pair, a previous semiempirical calculation[3] suggest that the H atom is located at the antibonding site of a Si atom bonded to the substitutional P.

In this Letter the microscopic structure of hydrogen bonding with defects and the mechanisms for hydrogen passivation of B and P dopants in crystalline Si are examined in detail with a first-principles total-energy pseudopotential method and compared with previously proposed models. The stable structure of and interstitial hydrogen atom is found to depend on the dopant. For the various stable structures, the calculated H-associated vibrational frequencies are shown to be in good agreement with available experimental data. We also provide an explanation for the greater effectiveness of hydrogen passivation observed[3,8-10] in *p*- vs *n*-type samples.

To find the stable configurations of an interstitial H atom in the vicinity of substitutional dopants in Si, we use the *ab initio* total-energy pseudopotential method.[11] A plane-wave basis set with a kinetic-energy cutoff of 11.5 Ry is used for a supercell geometry chosen to mimic a system with isolated defects. In supercells with eight Si atoms per unit cell, the defects are well separated and all the essential information can be extracted. We estimate the errors caused by the use of a finite-sized supercell to be less than 0.2 eV.[12] For each geometry the total energy is calculated in momentum space[13] and is minimized by the calculation of the Hellmann-Feynman

forces.[14] Relaxations are included only for atoms which are nearest neighbors of the interstitial H atom. The relaxations for the next-nearest neighbors are found to be much smaller and are neglected. The hydrogen pseudopotential was tested by examination of H_2 and silane (SiH_4) molecules. The calculated H−H and H−Si bond distances of 0.80 and 1.54 Å for H_2 and SiH_4, respectively, are comparable to the experimentally measured values of 0.746 and 1.48 Å.[15]

In B-doped Si, we find that the total energy for an interstitial H atom is lowest near the bond-center (BC) site between the substitutional B and the neighboring Si atoms (see Fig. 1). This microscopic structure for a H-B pair is in good agreement with the recently reported ion-channeling data[16] and also agrees with the models suggested by Pankove *et al.*[2] and DeLeo and Fowler.[6] We have examined the bending of the linear Si-H-B chain by moving the H atom off axis along $[1\bar{1}0]$ and $[11\bar{2}]$ direc-
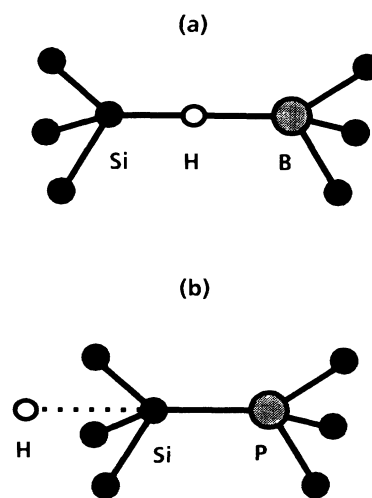

FIG. 1. The stable atomic positions of an interstitial H atom interacting with substitutional (a) B and (b) P atoms in Si. Solid and dashed lines denote strong and weak covalent bonds, respectively.

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tions normal to the [111] Si—B bond axis. The total energy is found to be lowered by smaller than 0.01 eV for displacements as large as 0.3 Å. Recent experiments by Stavola et al.[17] give some indication that the H atom may be stable off the Si-B axis. We have also tested other models[7,18] which put the H atom either at an antibonding site between the B and the interstitial tetrahedral (T_d) site or at an antibonding site of a Si atom nearest neighbor to the B. When H is placed in the antibonding site of the B atom, the minimum-energy position occurs at a H—B bond length of 1.47 Å; the total energy is higher, however, by 0.31 eV than for the BC site. In the antibonding position of a Si atom, the H atom forms a weak H—Si bond with a Si—H separation of 3.77 Å and its total energy is 0.86 eV higher than the BC site. This antibonding site for H is nearly equivalent to an interstitial hexagonal site adjacent to a Si atom.

At the stable BC site for the H atom, the substitutional B atom is found to be relaxed by 0.47 Å from its ideal fourfold-coordinated position to the nearest interstitial T_d site. This value for the relaxation is close to DeLeo and Fowler's result[6] of 0.5 Å; both values are larger than the ion-channeling results of 0.22 ± 0.04 Å.[16] The Si—H bond distance is calculated to be 1.63 Å as compared to 1.6 Å for a neutral H on the BC position in pure Si.

Microscopic models for H-B complexes are often tested by comparison of the hydrogen-related vibrational frequency with experiment. Recent Raman studies[19] and infrared absorption spectra[17,20,21] show a characteristic mode at about 1880 cm^{-1}, which has been assigned to hydrogen. Because this frequency is smaller than the normal Si-H vibrational frequency of 2162 cm^{-1} in H-implanted Si,[22] it is likely that the Si—H bond is weakened by the adjacent B atom. For the Si-H-B complex shown in Fig. 1, our calculated frequency for the H vibrational mode of 1820 cm^{-1} is in good agreement with the experimentally measured values and with previous theoretical results.[6] When H is in the antibonding position of the substitutional B atom, the frequency for the H stretch mode is calculated to be about 1000 cm^{-1}. Since this frequency is appreciably smaller than the experimental one, the antibonding-site model[7] for H is not supported by the vibrational data either. In the absence of any hydrogen, the local B vibrational mode is calculated to be 620 cm^{-1}, which is in excellent agreement with the measured value of 640 cm^{-1} (Ref. 19).

At the BC site, an interstitial H atom causes a large dilation of the Si—B bond length and forms a strong three-center bond as shown in Fig. 2. In this case, the filled bonding state lies deep in the valence band as a result of the strong overlap between H-s and Si-sp^3 orbitals and the empty antibonding state energy is in the gap and is close to the conduction-band minimum. The H-Si hybridization is found to remove the electronic state associated with the acceptor, and thus the H atom pas-
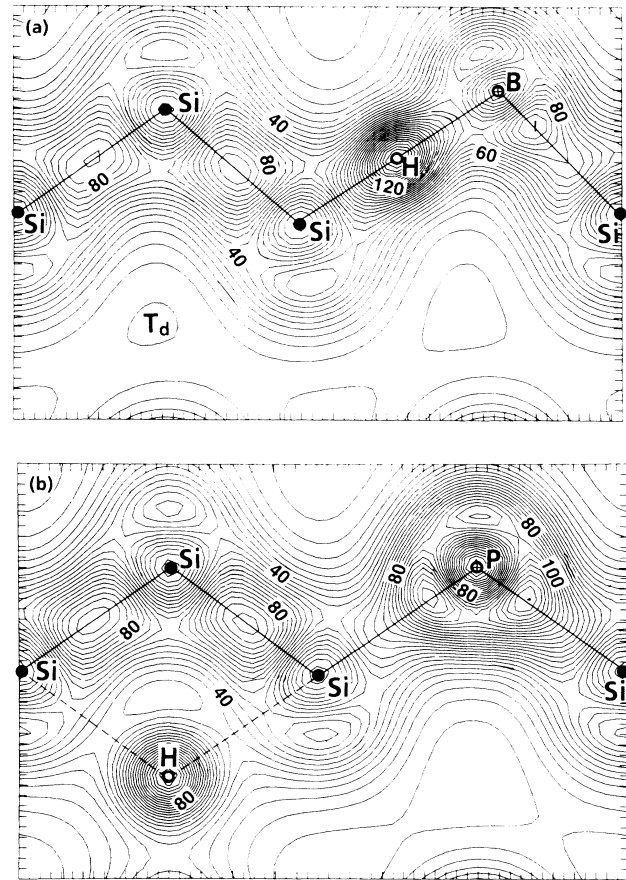

FIG. 2. Contour plots of the valence charge densities in the $(1\bar{1}0)$ planes for (a) the H-B and (b) H-P complexes of Fig. 1. Charge densities are in units of electron per cell volume of 160.365 Å^3. Solid and dashed lines represent strong and weak bonds, respectively.

sivates the acceptor B atom. From Fig. 2, we find that the electronic charge density for the H—Si bond is similar to that found in SiH$_4$; thus in the interstitial BC position the H atom is neutral. Our result for the hydrogen passivation of B is in contrast to the compensation mechanism which is the major effect of Li on B in Si.[23] An interstitial Li atom in B-doped Si behaves as a donor when it occupies an empty interstitial site and gives rise to an energy level in the gap. Our results do not support, however, a similar compensation mechanism[24] for H in p-type Si.

In P-doped Si, the minimum-energy configuration for the interstitial H atom is found near a T_d site of a Si atom adjacent to the substitutional P. The energy is lower by 1.13 and 0.57 eV as compared to the interstitial BC and the T_d sites of the substitutional P, respectively. For H on the BC position, the Si—H bond length is calculated to be 1.75 Å and this value is similar to that obtained in B-doped Si. Our result for the stable structure

of the H atom is qualitatively similar to the results of a previous tight-bonding calculation.[3] In the stable configuration of the H-P pair (see Fig. 1), the Si and P atoms are relaxed from fourfold-coordinated positions to their neighboring T_d sites by 0.09 and 0.05 Å, respectively, and the calculated H-Si separation is 2.33 Å. Since H favors a T_d position in P-doped Si, the Si—H bond is much weaker than the one formed by H in the BC site of B-doped Si and the bond distance is much larger. Furthermore, for H near the stable T_d position of the Si atom, the calculated H-stretch vibrational frequency along the cubic diagonal of about 400 cm^{-1} is 4 to 5 times smaller than in B-doped Si and a previously calculated result.[3] Since no experimental data in this frequency range are yet available, a direct comparison cannot be made.

In Fig. 2, the electronic charge density is plotted for an interstitial H atom near the T_d position of a Si atom nearest neighbor to a substitutional P. The charge density around the H atom resembles that of atomic H. Since the H-related energy level at the T_d site is lower than the donor shallow level, the H atom behaves as an acceptor. In fact, our calculations show that the donor level disappears after hydrogenation. The H atom electronically passivates the P impurity and the H-P pair is neutral. Unlike the case of acceptor passivation, donor passivation is accompanied by an effective charge transfer from P to H. In this case, it might be expected that the interstitial H should favor the T_d site adjacent to the substitutional P atom because the shorter H—P bond distance would enhance the attractive electrostatic energy between an electron and a hole. However, the large electronic charge density around the P atom results in a repulsive electrostatic interaction with the H atom which increases the Coulomb energy and makes the T_d site unfavorable energetically.

Our calculations indicate that the formation of neutral H-B and H-P complexes is the major mechanism for hydrogen passivation of these dopants. Experimentally, donor passivation is found to be less effective than for acceptors[3,8] and is not detected in some resistance measurements.[9,10] In the following we show that the dissociation energies of the H-impurity complexes provide an explanation for this behavior.

The calculated H-dopant formation (or binding) energies are shown in Fig. 3. These are obtained by comparison of the energies of the interacting pairs with those for the isolated and noninteracting H and dopant atoms in Si. The binding energy is calculated to be 2.5 and 2.0 eV for the stable H-B and H-P pairs, respectively. Because of a lack of information on the final form of hydrogen after pair dissociation, we test two possible situations. For atomic H, the binding energy away from impurities (or in pure Si) is estimated to be 0.6 eV at an interstitial BC site and 1.0 eV at a T_d site. These values are in good agreement with the measured value of 1.0
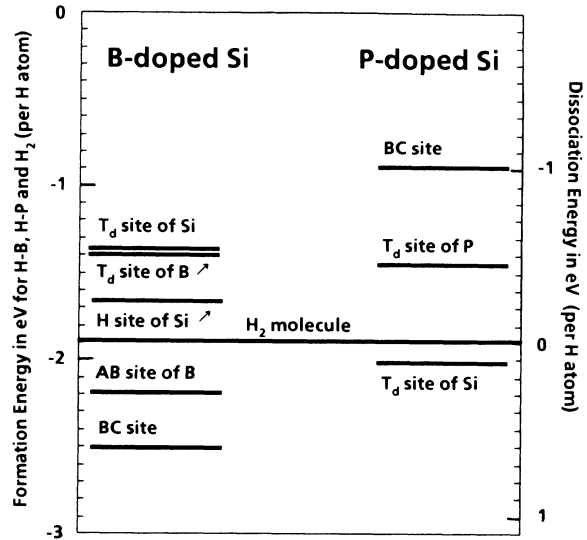

FIG. 3. Calculated formation energies (left ordinate) and dissociation energies (right ordinate) for hydrogen-impurity pairs and H_2. The dissociation energies are relative to the formation energy of H_2 at the T_d site. Bond-center, antibonding, interstitial hexagonal, and tetrahedral sites are denoted by BC, AB, H, and T_d, respectively.

eV.[3] In the case of an H_2 molecule, the calculated binding energy is 3.8 eV per molecule and the H—H bond distance is found to be 0.88 Å when the molecule occupies an interstitial T_d position oriented along the diagonal [111] axis. We have also tested the configuration where the H_2 molecular axis is perpendicular to the Si—Si bond. However, this type of molecular orientation near the BC site is unlikely because its binding energy is higher by approximately 1.8 eV per molecule than for the T_d site and the optimized bond length of 2.1 Å is too large. In pure Si, an H_2 molecule is more probably formed at the interstitial T_d site than monoatomic H. This formation of the paired electrons also agrees well with experiment since no electron-spin resonance signal is observed for H in Si.

Assuming that hydrogen atoms dissociated from dopants form H_2 molecules, we estimate the dissociation energies to be 0.6 and 0.1 eV for the H-B and H-P pairs, respectively, in Fig. 3. These results suggest that H binds more tightly to the substitutional B atom than to the P atom. Here, the calculated dissociation energies should be considered as an upper limit because other possible formations have not been yet fully investigated. From Fig. 3, we find that the H-B pair is more stable than H_2 for H in either a BC site or an antibonding site of B while only the T_d site of a Si atom stabilizes the H-P pair against the molecular formation. Although there may be an energy barrier for molecular formation, our finding of a small dissociation energy for a passivated H-P pair provides an explanation for why donor passiva-

tion is either not observed or is less effective than acceptor passivation.

In conclusion, we have found that the bond-centered structure[2,6] for the interstitial H atom in B-doped Si is the most stable. For P-doped Si, the energy is minimized for H in the antibonding position of a nearest-neighbor Si atom of the dopant. In both cases hydrogen passivates the dopants.

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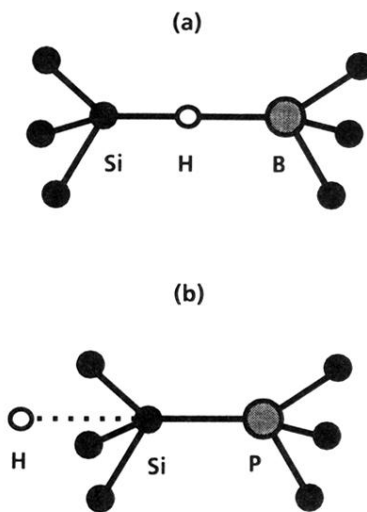
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