# Impurity-Defect Complexes and Doping Mechanism in *a*-Si:H

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The most outstanding feature observed for dopants in hydrogenated amorphous silicon—a shift in the Fermi level accompanied by an increase in the charged-defect density—has previously been postulated to stem from the formation of substitutional-dopant–dangling-bond complexes. Using first-principles self-consistent pseudopotential calculations in conjunction with a supercell model for the amorphous network and the ability of network relaxation from the first-principles results, we have studied the electronic and structural properties of substitutional fourfold-coordinated phosphorus and boron at the second-neighbor position to a dangling-bond defect. We demonstrate that such impurity-defect complexes can account for the general features observed experimentally.

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There exist a number of proposals[1-3] attempting to explain doping of hydrogenated amorphous silicon (*a*-Si:H). Among them are the modified $8-N$ rule suggested by Street[1] which requires a coupled relation between the dopant atom and an unspecified point defect and is now called the pairing model. Robertson[4] showed qualitatively that an ionized fourfold-coordinated (⟨4⟩) P ($P_4^+$) atom paired with a threefold-coordinated (⟨3⟩) silicon atom ($D^-$) can account consistently for the following experimental data: (i) The dangling-bond density increases with the doping level;[5,6] and (ii) no electron-spin-resonance signal can be associated with dopants.[5] More recently, Kocka[7] and Kocka, Vanacek, and Schauer[8] have found from constant-photocurrent measurements that the neutral Si dangling bond ($D^0$) in undoped samples has the same position in the energy gap as the $D^-$ level in P-doped samples. In B-doped samples, however, they found that the energy of the positively charged dangling bond ($D^+$) is 0.4 eV closer to the conduction band edge than is the $D^0$ level. These authors pointed out that their data were consistent with the pairing model between dangling bonds and dopants, but noted that because of the long-range nature of the Coulomb interaction, the defect and dopant need not be nearest neighbors. In this paper, we present theoretical results for the electronic structure of a ⟨4⟩ substitutional impurity atom paired at the second-neighbor position to a dangling-bond defect in an *a*-Si:H model as schematically shown in Fig. 1. An *a*-Si:H supercell model containing 60 atoms was used in our studies to provide a basis in forming the ⟨4⟩-impurity–defect complex. Because of the limitation of the supercell size, our results will focus on this particular arrangement only. Although Kocka, Vanacek, and Schauer[8] have noted that the dangling-bond and P (or B) can be farther away than the second-nearest-neighbor configuration, our model could be more important if the screening effect is taken into account. We choose three different configurations in the supercell model which have varying degrees of local bond-angle and bond-length distortions to examine the effects of local geometry on the electronic structures of the defect states. The results are relevant to the understanding of the doping mechanism in *a*-Si:H.

In any type of solid-state system, the proposal of a defect complex must necessarily be accompanied by a plausible mechanism for creating the complex, even though such mechanisms are difficult to study both theoretically and experimentally. Street[1] proposed that dopant–dangling-bond pairs may be created from ⟨3⟩ neutral impurities via the schematic reaction

$$P_3^0 \leftrightarrow P_4^+ + D^- . \tag{1}$$

This proposal has some support from conclusions based on H diffusion data in *a*-Si:H (Ref. 9) and there is some indication that this mechanism may be applicable in the high-doping regime.[10] We show from our calculations below that such an impurity-defect complex can indeed

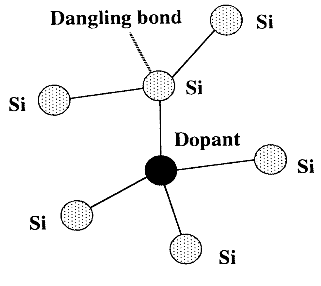

FIG. 1. The second-nearest-neighbor configuration of an impurity-defect complex in *a*-Si:H model, where the dangling bond and the dopant share a common Si atom. The dopant can be either P or B. The dashed line is a dangling bond.

effectively dope *a*-Si:H and that such complexes also can account for the low doping efficiency, but we cannot obtain information on the formation mechanism of these complexes.

A computer-generated model of *a*-Si:H with periodic boundary conditions[11] has been used as the basis of our calculations. The model contains 54 Si and 6 H atoms, in which no more than one H atom is bonded to any Si atom and all Si atoms are fourfold coordinated. The lattice constant is 10.257 Å. The dangling bond was modeled by removing one H atom from the network. Several earlier calculations[12] with similar models show that the essential physical results can be extracted from such models. The electronic parts of the calculations are based on the self-consistent pseudopotential method in conjunction with the density-functional theory, within the local-density approximation (LDA).[13] The generalized norm-conserving pseudopotentials of Hamann[14] and the Kleinman-Bylander form[15] for P, B, H, and Si atoms were used. A plane-wave basis set for the potentials and wave functions was utilized with a kinetic-energy cutoff of 15 Ry, resulting in 7123 plane waves at the sampling $\mathbf{k}=0$ point. Indeed, we have tested this approximation by examining the total density of states at $\mathbf{k}=(2\pi/a)(\frac{1}{4},\frac{1}{4},\frac{1}{4})$, where $a$ is the lattice constant, and find no difference in the total density of states as compared to the $\mathbf{k}=0$ case.

The treatment of the lattice relaxation in the study of the electronic structure has been known as one of the difficult problems in condensed-matter theory. In amorphous materials, the ions are in metastable states and, therefore, the effect of lattice relaxation has been considered essential in determining the energy of the donor or the acceptor state. We have employed local optimization techniques for the electronic and the ionic degrees of freedom toward the total-energy minimum of the system throughout our calculations. A preconditioned conjugate gradient method[16] is used to obtain solutions of the Schrödinger-like equation and the Hellmann-Feynman forces are then calculated in conjunction with the conjugate gradient method for the relaxation of the ions. Relaxation of the network was performed from the self-consistent results until the force acting on each atom is less than $10^{-4}$ Ry/a.u. By calculating the participation ratio

$$p=\frac{\int|\phi_i(\mathbf{r})|^2 d\mathbf{r}}{\Omega\int|\phi_i(\mathbf{r})|^4 d\mathbf{r}}\,, \tag{2}$$

where $\phi_i(\mathbf{r})$ is the $i$th electron wave function and $\Omega$ is the volume of the supercell, the $p$ value ranges from 0 to 1, indicating the degree of localization for $\phi_i(\mathbf{r})$.

Because we are also interested in the defect energy levels of various models, a proper reference is necessary to determine the relative energy position for each case. We have carefully checked the valence-band maximum (VBM) and find that the electronic structure of the VBM persists for every case that we have studied, implying that the VBMs can serve as a reference for other energy levels.

To have a reference for the rest of our calculations, we first calculated the electronic properties of undoped *a*-Si:H. The energy gap is 1.0 eV which is about 0.8 eV smaller than the commonly accepted value.[17] This is a consequence of the LDA used in treating the electron-electron interactions. The properties of the isolated dangling bond have been studied by examining four dangling-bond sites chosen in the model. The average energy of the dangling-bond state is $0.55\pm0.15$ eV above the top of the valence band ($E_v+0.55\pm0.15$ eV) where the variation indicates the energy-level variation due to the local geometry. This result is in reasonable agreement with the experimental data[7,18] ($E_v+0.9\pm0.1$ eV). Especially, the position of the $D^0$ state, which is sitting near the *middle* of the energy gap, is consistent between theory and experiment. The corresponding charge distribution of one of the dangling-bond states is shown in Fig. 2. The $D^0$ is a nonbonding state and it is *p*-like in character. The $p$ value is found to be 8.85% of the cell volume, which gives the extent of the $D^0$ state to be about 96 Å$^3$. As compared to the unit-cell volume of 1080 Å$^3$ the $D^0$ state is well localized.

When the dangling bond is paired with a $\langle 4\rangle$ P atom at the second-neighbor site, the average energy of the resulting $D^-$ states is 0.05 eV *lower* than the $D^0$ state, in good agreement with the constant-photocurrent results.[7,8] More importantly, however, the average energy of the P states moves well up into the conduction bands. The charge density associated with one of the $D^-$ states is shown in Fig. 3. As compared to the charge density of the $D^0$ state (Fig. 2), the center of mass of the $D^-$ charge density is moved toward the P atom by 0.06 a.u. The significant difference between the $D^0$ and $D^-$ state is the relative intensity of the two lobes around the Si atom. The decrease of the charge density of the lower lobe in the $D^-$ state indicates that this state is essentially an *s*-*p* hybrid in character. By examining the difference between the charge densities in Figs. 2 and 3, there is a 26% increase in the charge for the latter figure.[19] The $p$ value of the $D^-$ state also increases to a value of 9.2% of the cell volume, i.e., about 99.3 Å$^3$. The results suggest that there is an intimate relation between the $D^-$ state and the $P_4^+$ ion such that the charge density of the $D^-$ state spreads more than that of the $D^0$ state. As a result, the donor electron is trapped by the neutral dangling-bond defect state and thus the formation of a shallow donor state is not available under the present doping scheme.

Whereas the Fermi level for the $P_3^0$ configuration lies somewhere near midgap (pinned by the dangling-bond states), the Fermi level shifts upward upon conversion to the $P_4^+$-$D^-$ configuration. The reaction as written in Eq. (1) thus provides an explanation for doping in *a*-Si:H by induced changes in the Fermi level. Furthermore, the low doping efficiency of *a*-Si:H can be en-

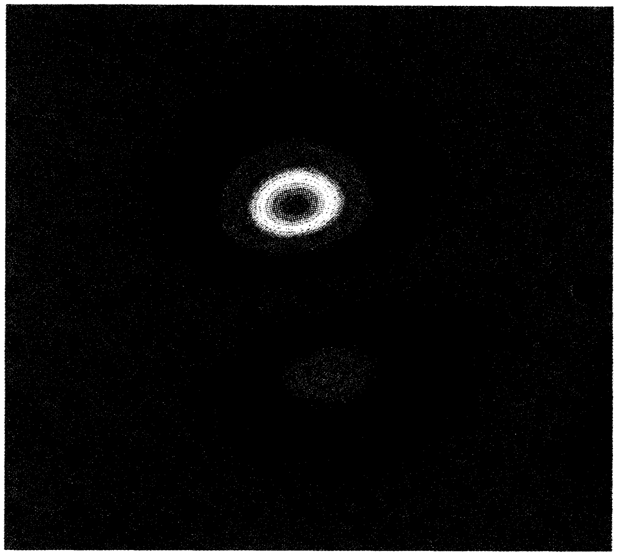

FIG. 2. Charge-density contour plots of the $D^0$ state. This state has a $p$-like nonbonding character. The Si atoms are shown by green circles.

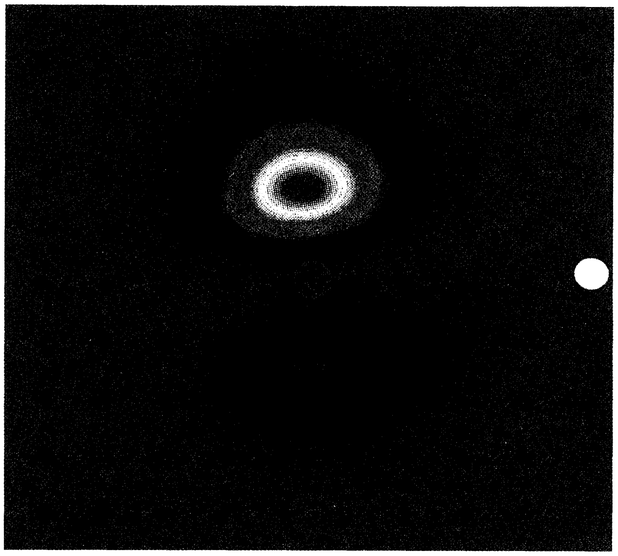

FIG. 3. Charge-density contour plots showing the $D^-$ state. Positions of the Si and P atoms are shown by solid circles (green and yellow, respectively). This state has an $s$-$p$ hybridization character.

visioned to occur because the creation of a dangling-bond defect coincident with the creation of the doping state prohibits Fermi level shifts above the band of dopant states, i.e., to the conduction-band edge. In Fig. 4, we illustrate schematically the electron density-of-states diagrams and Fermi levels of undoped $a$-Si:H containing one neutral dangling bond and P-doped $a$-Si:H with charged dangling bond.

To study the B-dangling-bond pair, we replaced the P atom by a B atom for each of the three chosen sites. Because of the transfer of charge from the dangling-bond state to the B atom, the energy level of the $B_4^-$ atom merges well into the valence band. Shallow acceptor states do not appear for the dopant–dangling-bond complex. The average energy of the $D^+$ states moves upward by $0.30 \pm 0.05$ eV with respect to that of the $D^0$ states. Kocka, Vanacek, and Schauer[7,8] also found in constant-photocurrent measurements that the $D^+$ states shifted upward by 0.4 eV relative to the $D^0$ levels. The small difference between theory and experiment could be attributed to the LDA which underestimates the energy level of the unoccupied state. However, our calculations indicate the qualitative feature that the $D^+$ energy level is higher than that of the $D^0$ state. Compared to the $D^0$ state shown in Fig. 2, the $D^+$ state (the charge-density contours are not shown here) has a more extended charge distribution—the $p$ value increases up to 15.3% of the cell volume—and an increased $s$-$p$ hybridization character. The center of mass of the $D^+$ state is moved away from the B atom by 0.83 a.u. as compared to the $D^0$ state to the corresponding Si atom. The increased $s$-$p$ hybridization character of the positively charged defect state ($D^+$) is manifested clearly by the shift in the charge density toward the dopant atom.

Finally, we report the effects of local geometry and structural relaxation. We find that there is only a small energy shift (by ~0.05 eV) for the relaxed states. However, the total energies are lowered by about 1.0 Ry per unit cell as compared to the unrelaxed one. The bond-length and bond-angle relaxations of the host network surrounding the P impurities are less than 1%. Such small relaxation around P impurities can be understood because the covalent radius of the P atom is similar to

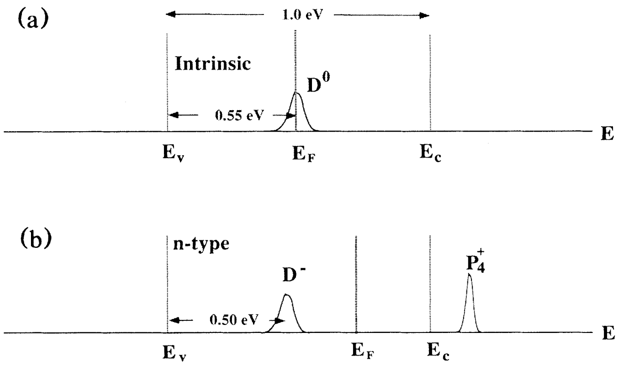

FIG. 4. Schematic density-of-states diagram showing the energy level and Fermi energy ($E_F$) of (a) undoped $a$-Si:H containing a neutral dangling-bond state, where $E_F$ is near the middle of the gap (pinned by the $D^0$ states), and (b) the $P_4^+$-$D^-$ complex in $a$-Si:H, where $E_F$ shifts upward but is still below the donor level ($P_4^+$). The data shown here are the theoretical results.

TABLE I. The average energies and participation ratios of the dangling-bond defect states. $E_{D^0}$ is the $D^0$ state energy level and $E_v$ is the energy of the top of the valence band. The unit-cell volume is 1079.10 Å$^3$.

| Species | Energy level (eV) | Experiment | Participation ratio (%) |
|---|---|---|---|
| $D^0$ | $E_v+0.55\pm0.15$ | $E_v+0.9\pm0.1$ eV [a] | 8.85 |
| $D^-$ | $E_{D^0}-0.05\pm0.10$ | $E_{D^0}$ [b] | 9.20 |
| $D^+$ | $E_{D^0}+0.30\pm0.05$ | $E_{D^0}+0.4$ eV [b] | 15.30 |

[a] References 7 and 18.

[b] References 7 and 8.

that of Si. However, the bond-length relaxation is ~3% and the bond-angle relaxation is ~9% in the B-doped cases. The $D^+$ levels associated with $B^-$ impurities are relatively insensitive to the local geometry, as evidenced by a 0.1-eV total variation in the position of the calculated levels. The $D^0$ levels and the $D^-$ levels associated with $P^+$ impurities show greater sensitivity (with a 0.3-eV and a 0.2-eV total variation, respectively) to the local environment. In short, the occupied states are more sensitive to the local environment in our calculations. The results of all the calculations and experiments are summarized in Table I.

In summary, the electronic and structural properties of $P_4^+$-$D^-$ and $B_4^-$-$D^+$ pairs in *a*-Si:H were calculated by local optimization techniques for the electrons and the ions and compared with those of the $D^0$ state. For each case, three pairs at different sites (and hence with different local distortions) in *a*-Si:H were examined. The average energies of $D^-$ and $D^+$ with respect to the $D^0$ states agree well with experimental measurements, especially the occupied states. The small shift in energy of the $D^-$ state with respect to the $D^0$ state suggests that the reaction shown in Eq. (1) may indeed reflect the microscopic mechanism of doping in *a*-Si:H. The absence of shallow donor and acceptor states suggests that the doping efficiency is low in *a*-Si:H. Further, the good agreement between the theory and the experiment on the energy shift of the $D^-$ state relative to the $D^0$ state demonstrates that our techniques can be applied to the study of the electronic structures of the occupied defect states in a very efficient fashion.

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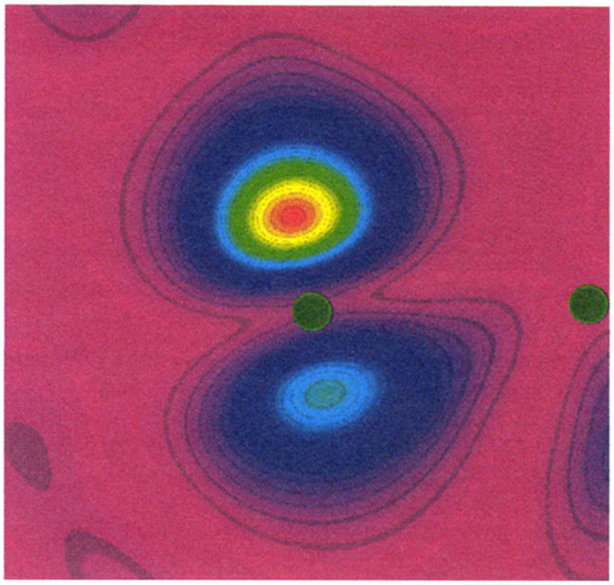
[19] In order to compare the charge difference between $D^0$ and $D^-$ states, we integrated the charge density inside a cube centered at the Si atom for each case, where the size of the cube is determined by the *p* value of the defect state.



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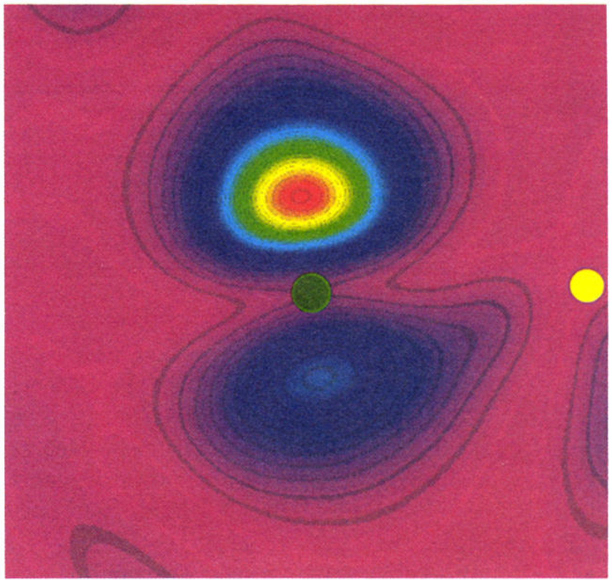

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