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Microscopic structure of hydrogen–shallow-donor complexes in crystalline silicon

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A new low-energy structural model for interstitial hydrogen in P- and As-doped crystalline Si is proposed. The calculated H-vibrational frequencies of 1290 cm^{-1} for the stretching mode and 715 cm^{-1} for the wagging mode are in much closer agreement with infrared data of 1555 and 809 cm^{-1}, respectively, than for any previously suggested model.

Hydrogen in crystalline Si and GaAs has attracted considerable attention recently because of its role in the passivation of acceptor as well as donor impurities.[1-3] Such a passivation effect is of fundamental importance in technological applications because the properties of many electronic devices depend critically on the activity of shallow impurity levels. The presence of hydrogen cannot be avoided in many cases. It is generally believed that the passivation mechanism, at least in Si, is different for donors than for acceptors.[4] For hydrogen-donor-Si complexes, there is evidence that the hydrogen atom is located at the Si antibonding (Si-AB) site along a [111] direction. This position accounts for several important experimental observations including shallow-donor neutralization,[3] secondary-ion mass spectrometry profiles,[3] and infrared studies,[5] all of which suggest that hydrogen is not adjacent to the donor within the trigonally symmetric complex.[6,7] Despite such good agreement, the nearly donor-independent hydrogen-stretching frequency of about 1555 cm^{-1} determined from infrared studies[5] has not been explained satisfactorily by any of the existing theoretical models.[3,8-10] The H-stretching frequencies obtained from these models are either too large ($\simeq 2150\ \mathrm{cm}^{-1}$) or too small ($\simeq 400\ \mathrm{cm}^{-1}$) casting serious doubt on the validity of the respective structural models. Here, following a brief description of the current models, we propose a new hydrogen-bonding geometry and show that it leads to the lowest total energy of any of these models. As importantly, we show that the new structure leads to significantly improved results for the hydrogen-associated vibrational frequencies.

A recent total-energy calculation[11] for hydrogenated Si doped with P has shown that the antibonding T_d site of Si, shown in Fig. 1(a), is energetically favored by interstitial hydrogen over either the T_d site of P or the Si-P bond-centered (BC) site. This model suggests that no significant bonding between Si and H atoms takes place. As a result, its H-stretching frequency of 400 cm^{-1} is far too small in comparison with the experimental value of 1555 cm^{-1} even though the model is consistent with the donor independence of the hydrogen vibrational frequencies. In the other extreme, the normal Si-H vibrational frequency[12] in H-implanted Si of 2162 cm^{-1} corresponding to hydrogen passivation of a nearly sp^3-like Si dangling bond is substantially larger than the 1555 cm^{-1} measured for the H-P complex. On the basis of these observations, one might expect that the bonding between Si and H is intermediate between the two models. Such a possibility, in which the Si—H bonding involves a Si p_z instead of an sp^3-orbital, has been explored in several recent papers,[8-10] but no significant improvement in the vibrational frequencies has been achieved.

In this Rapid Communication, we examine more closely this type[8-10] of Si—H bonding and propose a new T_d-site model for H-donor-Si complexes. In this model, shown in Fig. 1(b), the hydrogen atom resides near the Si antibonding T_d site as before but the Si-donor bond is broken and a Si—H bond is formed in its place. To achieve this configuration, the Si atom moves substantially ($\simeq 0.66$ Å) towards the interstitial H atom and ends up in a nearly planar position relative to its three nearest-neighbor Si atoms. The trigonally symmetric bond-angle distribution

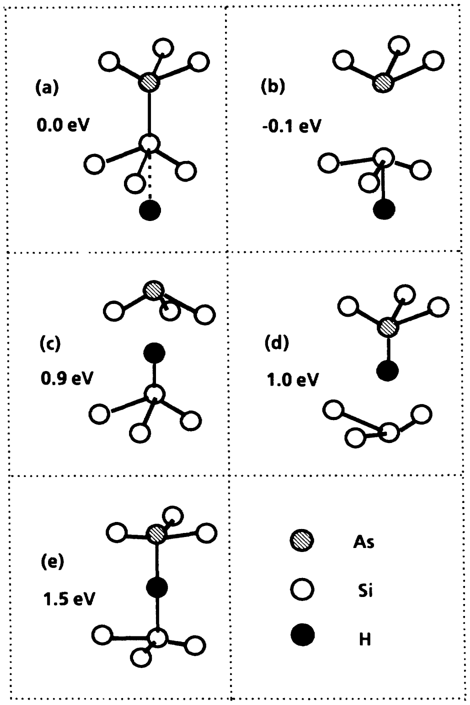

FIG. 1. Five structural models for H-donor complexes in Si as shown. (a) is a T_d site model from Ref. 11, (b) is a broken-bond T_d-site model, and (c)–(e) are three bond-center sites with different chemical environments for hydrogen atoms. Their energies, relative to model (a), are also shown.

around the displaced Si is 119.7°, indicative of sp^2 bond formation. This atomic arrangement exhibits some of the same features as a recent model[13] for an H_2 complex in Si where one hydrogen atom in a BC site saturates a Si dangling bond and a second hydrogen atom in the adjacent T_d site forms similar sp^2-type bonds with its nearest-neighbor Si atoms (Fig. 1 of Ref. 13). If the hydrogen atom in the BC site and the Si atom associated with it in this model are replaced by a donor, such as P or As, one would obtain our present model for H-donor complexes. The local chemical environment for the T_d-site hydrogen atom is nearly the same in both cases.

Our calculations show that the donor atom which breaks its bond with the displaced Si atom does *not* relax backward towards its AB site as suggested by some models.[8-10] The relaxation is, in fact, in the opposite direction towards the H atom and is driven by the tendency of group-V elements to change their hybridization from sp^3 to s^2p^3 when undergoing a coordination change from fourfold to threefold. In this relaxed position, the Si-donor interaction, although weak, plays an important role in weakening the Si—H bond and gives rise to the desired reduction in the frequency of the hydrogen local vibrational mode. We find that the Si—H bond length would shrink by more than 0.1 Å if the donor atom were removed. Hence, the force constant, which determines the H-vibrational frequency, is more sensitive to the presence of donor atoms than to their chemical difference. At the hydrogen-donor separation of 3.53 Å, only the Coulombic tail of the donor potential affects the hydrogen motion.

The H-stretching and wagging frequencies calculated from this model for P-doped Si are 1290 and 715 cm^{-1}, respectively. These numbers are in much closer agreement with the experimental values[5] of 1555 and 809 cm^{-1} than for any previously suggested model. For the doubly degenerate H-wagging mode, our result also appears to be in good agreement with that of DeLeo and Fowler[9] (660 cm^{-1}). Furthermore, total-energy calculations show that this model is the most stable one among the existing models for this system. In particular, it is 0.1 eV lower in energy than the Chang-Chadi T_d-site model[11] for both P- and As-doped Si. The latter model,[11] therefore, corresponds to a *local minimum* of the total energy for the donor-Si-H complex. There is a repulsive barrier for the transformation of this structure [Fig. 1(a)] to the more stable one shown in Fig. 1(b), explaining why this structure was not found in the previous calculations. The energy difference between the two models is expected to become larger as the size of the supercells used in the calculations is increased. This would allow more freedom for the relaxations of the neighboring atoms which is more critical for the new model.

The possibility of metastable configurations derived from the Si-P BC site [shown in Figs. 1(c)-1(e)] were also examined. We find that these geometries are generally about 1 eV higher in energy than the T_d-site model in Fig. 1(b). In addition, these models cannot explain the infrared data. For example, the H-stretching frequency for the most stable BC-site model [Fig. 1(c)] with As dopants was calculated to be 2040 cm^{-1} and is substantially higher than the experimental value. Hence, the BC-derived sites must be ruled out for H-donor-Si complexes.

We have used an *ab initio* pseudopotential total-energy method[14] in the calculations. For hydrogen the exact $1/r$ form of the potential was employed. A plane-wave basis set with a kinetic-energy cutoff of 11.5 Ry was used in the plane-wave expansion for wave functions.[15] The search for stable configurations was carried out with the help of a Hellmann-Feynman energy-minimization scheme.[16] A supercell of eight Si atoms used in previous studies on hydrogen passivation of impurity levels[11] was chosen to study the various defect structures. Kinetic-energy cutoffs up to 18 Ry were used to test the relative convergence of the hydrogen potentials for the BC and the T_d sites and we estimate our results to be accurate to within 0.1 eV.

As mentioned earlier, in the most stable configuration of Fig. 1(b) both Si and P relax from their ideal positions towards the hydrogen atom in the T_d site. These relaxations are 0.66 and 0.18 Å, respectively. The relaxation of the Si atom is consistent with several recent broken-bond models, e.g., Estreicher, Throckmorton, and Marynick[8] (0.74 Å), DeLeo and Fowler[9] (0.67 Å), and Amore-Bonapasta *et al.*[10] (0.63 Å); but the phosphorus atom in our model is relaxed in a direction opposite to these calculations, which give displacements of 0.19,[8] 0.54,[9] and 0.09 Å,[10] respectively. Hence, the Si and P separation in our model is substantially smaller than for any of these models. The Si—Si bond lengths around the relaxed Si atom are determined to be 2.31 or 0.04 Å shorter than the ideal tetrahedral Si—Si bond length, consistent with the sp^2 instead of the sp^3-like bonding of the displaced Si atom. The calculated P—Si bond length is 2.33 Å and the angles between these bonds are 103.9°. It should be noted that P in its natural form, black phosphorus, prefers threefold coordination with two slightly different bond lengths of 2.17 and 2.20 Å. The angles at the two inequivalent threefold-coordinated P atoms are 99.5° and 103.4°, respectively.[17] The calculated separation between the P-donor atom to the displaced Si atom is 2.84 Å which is about 20% larger than the ideal Si—Si bond length. The calculated Si-H bond length is, on the other hand, 1.69 Å compared with the Si—H bond length of about 1.48 Å in SiH_4.[18] Our calculations tend to slightly overestimate the Si-H distance in Si resulting in a smaller hydrogen vibrational frequency. For comparison, in the Chang-Chadi model[11] [see Fig. 1(a)], the Si—P bond length is 2.49 Å and the Si-H separation is 2.33 Å.

The total charge density for P-doped Si from our model is shown in Fig. 2. The charge-density contours are characteristic, in fact, of a broken Si—P bond and the hydrogen forms an ionic bond with the adjacent Si p_z orbital. Unlike the previous model[11] which involved charge transfer from P to H, the P atom in Fig. 2 is not ionized but is in a neutral closed-shell configuration where it forms three p_σ bonds and has its two remaining electrons in a nonbonding s orbital. In either case, the calculations show no defect states in the gap.

The vibrational frequencies of the hydrogen atom were evaluated as zone-center optical phonons of an eight-atom superlattice. Since these vibrations are very localized, the coupling between cells could be neglected. Briefly, we determined the force-constant matrix K_{ij} from the force

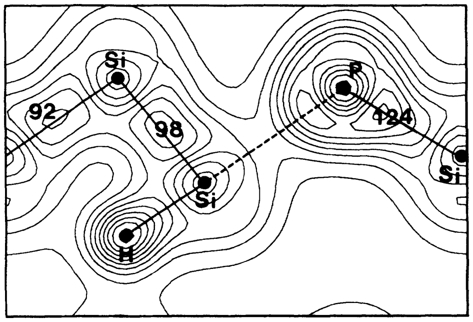

FIG. 2. Total charge density for the broken-bond T_d-site model in a (110) plane. Contour spacings are 15 in units of electrons/(160 Å^3).

induced on the ith atom by the displacement of the jth atom typically of 0.1 Å, from which the dynamical matrix D_{ij} was obtained and diagonalized to obtain the normal vibrational modes and the corresponding eigenvectors.[19] Four degrees of freedom, defined in Figs. 3(a) and 3(b), were included in the calculations for the H-stretching (H-wagging) mode. In the latter case, however, the four degrees of freedom were reduced to two because of double degeneracy of the modes. The ratio of the atomic displacements of hydrogen and Si for the stretching mode, $u_2/u_1 = -0.13$, is found to be quite small [see Fig. 3(a)]. All other displacements are negligible.

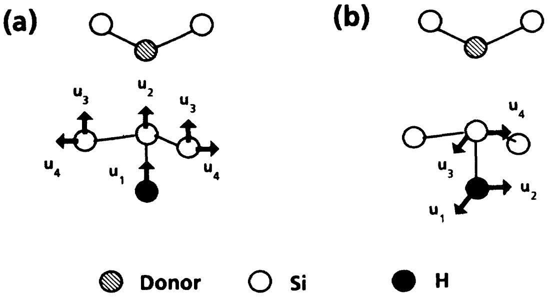

FIG. 3. Atomic displacements used in the calculation of hydrogen local vibrational frequencies are shown.

The calculated H-stretching frequency for As-doped (P-doped) Si is 1260 cm^{-1} (1290 cm^{-1}). Experimentally, this frequency is 1561 cm^{-1} and is about 6 cm^{-1} higher than that for P-doped Si.[5] This difference is too small to calculate within the uncertainty of our calculations, which is estimated to be a few percent for vibrational frequencies. Nevertheless, our results demonstrate that the hydrogen-stretching mode is nearly donor independent in agreement with the experimental data. Since the calculations were carried out at an 11.5-Ry energy cutoff and the Si—H bond length is expected to decrease by about 0.1 Å as the cutoff is further increased, our values for H-stretching frequencies in both cases should be *lower* than the true theoretical values.

In conclusion, we propose a new structural model for hydrogen-donor complexes in Si which is energetically more favorable than previously suggested models. The new bonding geometry explains satisfactorily the infrared data in addition to all other experimental observations.

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