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# Hydrogen interactions with self-interstitials in silicon

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We present a first-principles investigation of complexes between one or two hydrogen atoms and a Si self-interstitial ($Si_i$). The atomic structure of these complexes is a distortion of the $\langle 110 \rangle$ split-interstitial configuration. The ($H,Si_i$) complex has donor and acceptor levels in the band gap, both about 0.4 eV above the valence band. The ($2H,Si_i$) complex is electrically inactive, with all Si atoms bonded to four neighbors. The binding energy of H to the self-interstitial is about 2.4 eV (referenced to free atomic H). Consequences of these results for observation of self-interstitials and for processes such as point-defect condensation and dislocation nucleation are discussed.

It is well established by now that hydrogen interacts with silicon in a wide variety of ways, including passivation of the surface, passivation of shallow as well as deep levels, generation of extended defects, etc.[1] The simplest among these interactions may be the binding of H to a dangling bond or to a vacancy, resulting in the formation of a Si-H bond; this type of interaction, which plays an important role in amorphous silicon, has therefore extensively been studied. It has been accepted for some time, however, that vacancies are not the only type of intrinsic defect to play a role in silicon. The early first-principles calculations of Bar-Yam and Joannopoulos[2] and Car *et al.*[3] already indicated that self-interstitials have formation energies comparable to those of vacancies; this result has been confirmed by more recent, state-of-the-art investigations by Blöchl *et al.*[4] In amorphous silicon, too, overcoordination defects (interstitials) are as likely to occur as undercoordinated atoms, as pointed out by Pantelides.[5] In addition, silicon self-interstitials are known to play a role in self-diffusion,[4] impurity diffusion,[6,7] surface reconstructions,[8] planar interstitial defects,[9] and dislocation nucleation.[10] However, because of their high mobility isolated silicon self-interstitials have never directly been observed.[11] In spite of the accepted importance of silicon self-interstitials, and of hydrogen interactions with defects in silicon, the interaction between self-interstitials and hydrogen has, to our knowledge, not previously been addressed.[12]

In this paper we describe state-of-the-art first-principles calculations for complexes consisting of one or two H atoms and a Si self-interstitial, addressing atomic structure, electronic structure, and vibrational frequencies. We find that hydrogen interacts strongly with self-interstitials; while the calculated binding energy is smaller than for H interacting with a vacancy, it is large enough for the complexes to be stable at room temperature. The work reported in this paper is relevant to the study of self-interstitials from two points of view: One, our results show that attachment of one or two H atoms to the self-interstitial produces a complex that is more stable and less mobile than the isolated self-interstitial, and thus may be amenable to direct observation. Since the complex retains some of the characteristics of the isolated interstitial, valuable information about the latter may thus be obtained. Two, since H is shown to interact strongly with interstitials, processes such as self-diffusion or impurity diffusion, defect condensation, and dislocation nucleation are bound to be affected by the presence of hydrogen, potentially in a beneficial manner that could be technologically exploited.

Our calculations are based on density-functional theory in the local-density approximation[13] and *ab initio* pseudopotentials,[14] using an 18-Ry plane-wave cutoff, a 32-atom supercell, and a highly optimized code.[15] All of our calculations include relaxation of two shells of host atoms around the defect. The numerical error bar on our calculated energies is $\sim 0.1$ eV. Vibrational frequencies for Si-H stretch modes are calculated in a frozen-phonon approach; given the mass difference between H and Si, we take the vibrating object to be the H atom and assume the Si atoms to be fixed. We place a conservative error bar of 100 $cm^{-1}$ on the calculated frequencies.

We have first investigated the structure and energetics of the isolated Si self-interstitial ($Si_i$). We find that the minimum-energy structure in the neutral charge state consists of a pair of Si atoms, oriented in the $\langle 110 \rangle$ direction, sharing a substitutional lattice site (a split-interstitial configuration); this result agrees with previous theoretical work.[2–4,16] Our calculated geometry for the self-interstitial is illustrated in Fig. 1, showing a small cluster of atoms near the core of the defect. In the perfect crystal, this cluster would contain seven atoms, five of which lie in a $(\bar{1}10)$ plane (forming the characteristic zigzag chain), and two of which lie in a perpendicular (110) plane. We can also think of the cluster as consisting of a central atom, surrounded by four nearest neighbors and two additional second-nearest neighbors. In the case of the self-interstitial, the lattice location at the center of the cluster is now shared by two atoms. Figure 1 shows the cluster viewed along the $[\bar{1}10]$ direction. We emphasize that the cluster of atoms displayed in the figure is much smaller than the supercell used in the calculations, and does not include all the atoms that have been relaxed. The coordinates of the two central atoms, as well as their first-nearest neighbors, are listed in Table I. Atoms farther away from the core of the defect are perturbed from their ideal lattice positions by less than 0.1 Å.

The two atoms at the core of the self-interstitial are essentially fourfold coordinated. Inspection of the charge density

 

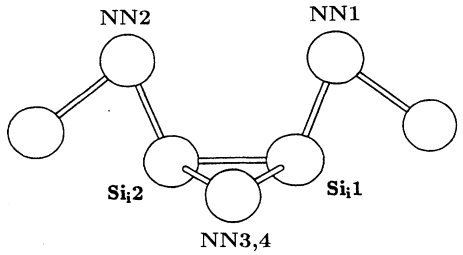


FIG. 1. Schematic representation of a cluster of Si atoms containing a Si self-interstitial in the split-interstitial configuration, oriented in the [110] direction. In the perfect crystal, the cluster consists of a central Si atom, surrounded by its four nearest neighbors, as well as two additional second-nearest neighbors. Now the central lattice site is shared by two Si atoms, labeled $Si_i1$ and $Si_i2$. The nearest neighbors NN1 and NN2, as well as the atoms to which they are bound, also lie in the plane of the figure. Nearest neighbors NN3 and NN4 lie in a plane perpendicular to the plane of the figure. The coordinates of the atoms are listed in Table I.

reveals some interaction between these atoms and the second-nearest neighbor Si atoms included in Fig. 1. Even though the distance between the "split-interstitial" atoms and those second-nearest neighbors is fairly large (2.76 Å),

TABLE I. Coordinates of the atoms at the core of the self-interstitial defect ($Si_i$) and defect complexes [(H,$Si_i$) and (2H, $Si_i$)]. The coordinates are given in units of the lattice constant (5.43 Å), in a Cartesian coordinate system with the origin chosen at the substitutional lattice site that is shared by the two Si atoms in the split-interstitial configuration. Coordinates are given for the Si atoms at the core of the defect (labeled $Si_i1$ and $Si_i2$), the H atom, and the four Si nearest neighbors (labeled NN1 through NN4). Additional atoms are displaced by less than 0.1 Å.

| | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|
| $Si_i$ | $Si_i1$ | 0.157 | 0.157 | -0.124 |
| | $Si_i2$ | -0.157 | -0.157 | -0.124 |
| | NN1 | 0.267 | 0.267 | 0.271 |
| | NN2 | -0.267 | -0.267 | 0.271 |
| | NN3 | -0.262 | 0.262 | -0.262 |
| | NN4 | 0.262 | -0.262 | -0.262 |
| (H,$Si_i$) | H | 0.269 | 0.269 | -0.269 |
| | $Si_i1$ | 0.118 | 0.118 | -0.073 |
| | $Si_i2$ | -0.186 | -0.186 | -0.156 |
| | NN1 | 0.274 | 0.274 | 0.282 |
| | NN2 | -0.256 | -0.256 | 0.260 |
| | NN3 | -0.260 | 0.265 | -0.258 |
| | NN4 | 0.265 | -0.260 | -0.258 |
| (2H,$Si_i$) | H | 0.262 | 0.225 | -0.263 |
| | H | -0.262 | -0.225 | -0.263 |
| | $Si_i1$ | 0.059 | 0.195 | -0.063 |
| | $Si_i2$ | -0.059 | -0.198 | -0.063 |
| | NN1 | 0.270 | 0.284 | 0.282 |
| | NN2 | -0.272 | -0.284 | 0.282 |
| | NN3 | -0.285 | 0.300 | -0.276 |
| | NN4 | 0.285 | -0.300 | -0.276 |

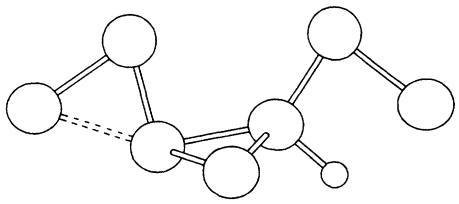

FIG. 2. Schematic representation of a cluster of Si atoms containing a complex between a Si self-interstitial and a single H atom. The Si atoms at the core of the defect are in positions that are distorted from the self-interstitial configuration illustrated in Fig. 1. The coordinates of the atoms are given in Table I.

this interaction plays a role in the structure of the complex between H and the self-interstitial, as we will see below. Our calculated formation energy for the self-interstitial is 3.33 eV, essentially the same as found by Blöchl *et al.*[4]

We now investigate complex formation between a self-interstitial and one H atom; we denote this complex as (H, $Si_i$). We have explored many potential configurations by adding the H atom (in various positions) to some of the basic configurations of the self-interstitial, including the ⟨110⟩ and ⟨100⟩ split interstitials, and the tetrahedral interstitial site. The most stable (H,$Si_i$) configuration emerging from our calculations has all atoms at the core of the defect lying in the $(\bar{1}10)$ plane, with the Si atoms distorted from their positions in the ⟨110⟩ split interstitial. The atomic positions are illustrated in Fig. 2. The H atom is bonded directly to one of the Si atoms at the core of the defect. The distance between the split-interstitial Si atom on the left and the atom in the second-nearest-neighbor position has now been reduced to 2.59 Å (only 10% larger than the Si-Si bulk bond length), indicating a stronger interaction between those two Si atoms. This interaction is represented in Fig. 2 by the dashed line, indicating a weak bond. The other Si atom at the core of the self-interstitial has moved toward the origin, and bonds more strongly to the H atom. The calculated Si-H distance is 1.57 Å, slightly larger than the value in an $SiH_4$ molecule (1.48 Å). The calculated vibrational frequency for the stretch mode of this Si-H bond is 1870 $cm^{-1}$, slightly smaller than the values in $SiH_4$, or for Si-H bonds on a Si surface.[17]

We define the *binding energy* as the energy needed to remove the H atom from the (H,$Si_i$) complex, leaving an isolated self-interstitial behind. Thus,

$$-E_{\text{bind}}=E_{\text{tot}}(\text{H,Si}_i)-E_{\text{tot}}(\text{Si}_i)-E_{\text{H}}, \qquad (1)$$

where the sign is chosen such that a positive value of the binding energy indicates a bound configuration. $E_{\text{tot}}$ is the calculated supercell energy. $E_{\text{H}}$ represents the energy of a H atom in a reference state; this could be a neutral H atom in free space, or H at an interstitial position (i.e., the bond-center site[17]) in bulk Si. For calculations of H in free space spin polarization is included, and the same convergence parameters are used as for H in the solid.[17] Consistent with our approach in Ref. 17, we have added the zero-point energy of the Si-H bond to the energies. For the (H,$Si_i$) complex in the configuration illustrated in Fig. 2 we find a binding energy of

2.39 eV, referenced to a free H atom; with respect to an isolated H interstitial (at the bond-center site), the binding energy is 1.34 eV.

Regarding the *electronic structure* of the ($H,Si_i$) complex, we have found that it has an electronic level in the band gap, about 0.4 eV above the top of the valence band. This level is occupied with one electron in the neutral charge state. We have also carried out calculations for the complex in a positive and in a negative charge state. The atomic structure of the complex turns out to be largely insensitive to the charge state. We also find that the defect is amphoteric in nature, with the acceptor level (transition level for the 0/− transition) located less than 0.1 eV above the donor level (the transition level for the +/0 transition); the difference between these levels corresponds to the value of the parameter $U$.

It is interesting to compare the energy of the ($H,Si_i$) complex with energies of other H-containing complexes in Si; results for a large number of structures were published in Ref. 17. For a H atom at a dangling bond in a vacancy-type defect, a binding energy (referenced to free H) between 3.15 and 3.55 eV was found (depending on how close the H atom is to other H atoms). The binding energy for H at a self-interstitial derived here is noticeably smaller, but still large enough to account for a very strong interaction between the H atom and the defect. The binding energy is larger, e.g., than for H bound to shallow impurities such as boron or phosphorous.[17]

We have also investigated complex formation between *two* H atoms and a Si self-interstitial. The structure of the complex is illustrated in Fig. 3; to better illustrate the distortion out of the $(\bar{1}10)$ plane, the figure displays the cluster not only viewed along the $[\bar{1}10]$ direction, but also along the $[\bar{1}\bar{1}0]$ direction (looking sideways on the zigzag chain), as well as along the [001] direction (looking up towards the underside of the atoms in the zigzag chain). The latter views clearly show that the two Si atoms at the core of the interstitial have twisted out of the $(\bar{1}10)$ plane. This distortion allows these atoms to assume nominally fourfold coordination, i.e., they are bonded to four other atoms (three Si and one H), although the bond angles are significantly distorted (by as much as 35°) from the tetrahedral bond angle of 109°. The Si-H bond length is 1.56 Å, with a calculated vibrational frequency for the Si-H stretch mode of 1915 $cm^{-1}$.

The calculated binding energy of the ($2H,Si_i$) complex is 2.40 eV per H atom (with respect to the free H atom), essentially the same as for the ($H,Si_i$) complex. The ($2H,Si_i$) complex has no levels in the band gap, consistent with all the bonds being satisfied. These results for the atomic and electronic structure indicate that a single self-interstitial is unlikely to bind more than two H atoms.

We now discuss potential consequences of the formation of these complexes. The binding energy (~1.3 eV, with respect to isolated interstitial H) is large enough to allow the complexes to be stable at room temperature. While we have not explicitly studied the migration of the ($H,Si_i$) complex, its migration barrier is likely to be substantially higher than that of the isolated self-interstitial; if migration requires dissociation of the complex, the barrier would be at least 1.3 eV.

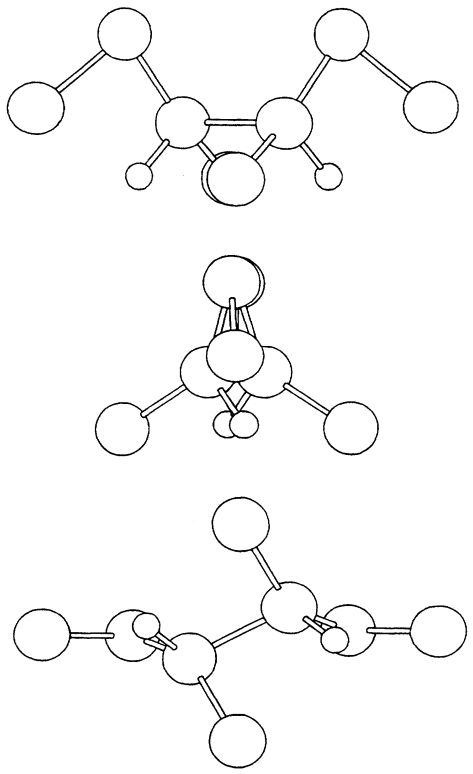

FIG. 3. Schematic representation of a cluster of Si atoms containing a complex between a Si self-interstitial and two H atoms. The Si atoms at the core of the defect are in positions that are distorted from the self-interstitial configuration illustrated in Fig. 1. In order to show the distortion out of the $(\bar{1}10)$ plane, the cluster is viewed from three different directions: along the $[\bar{1}10]$ direction (top), along the $[\bar{1}\bar{1}0]$ direction (center), and along the [001] direction (bottom). The coordinates of the atoms are given in Table I.

The introduction of H atoms into a system in which self-interstitials are present may thus "freeze in" the interstitials, rendering them accessible to experimental observation. The structures described here may also play a role in hydrogenated amorphous Si; in fact, our calculated vibrational frequencies for the Si-H stretch modes, which are somewhat lower than for Si-H bonds at dangling bonds, could help explain why the absorption band corresponding to Si-H stretch modes extends to lower frequencies.

The problem of defect condensation and dislocation nucleation, which was mentioned in the Introduction, has become increasingly important in light of attempts to suppress point defect formation and clustering, and to control formation of extended defects during silicon crystal growth.[18] A better understanding of the role of self-interstitials is therefore important, and direct experimental observations would be very useful. Our results indicate that the perturbation of the atomic structure induced by the attachment of H is modest, so that observations of ($H,Si_i$) and ($2H,Si_i$) complexes would also shed light on the structure of the self-interstitial. Because of its interaction with self-interstitials, hydrogen will also affect any processes involving self-interstitials. Observation of the effect of H on these processes may thus provide information about the underlying

mechanisms. Potentially, the hydrogen could also be used to intentionally influence processes such as impurity diffusion, defect condensation, or dislocation nucleation.

These cases involve hydrogen interacting with a system in which self-interstitials are already present, possibly in non-equilibrium concentrations. Our results also indicate that H may affect the *formation* of self-interstitials. The formation energy of a self-interstitial (in the neutral charge state) is normally 3.3 eV. Since the binding energy of an isolated interstitial H to the self-interstitial is 1.34 eV, the formation energy of the self-interstitial can potentially be reduced by this amount, if a large concentration of interstitial H is present—e.g., during plasma hydrogenation. The presence of H may therefore enhance the formation of self-interstitials. These results could be relevant in the context of recent experiments by Nickel *et al.*,[19] which revealed that prolonged exposure of polycrystalline silicon to monatomic H at elevated temperatures causes the generation of acceptor defects. Similar effects were observed in thin single-crystal silicon-on-insulator films. The electrically active ($H,Si_i$) complex described above may be a candidate for the H-induced acceptors observed in Ref. 19.

In summary, we have investigated the interaction between hydrogen and self-interstitials in silicon, using first-principles calculations. Our results for atomic and electronic structure show that complexes between hydrogen and self-interstitials can play an important role in various experimental observations and technologically important processes.

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