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Structure, energetics, and vibrational properties of Si-H bond dissociation in silicon

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We investigate hydrogen dissociation from an isolated Si-H bond in bulk silicon, using *ab initio* density-functional total-energy calculations. From the bonding site, we find that hydrogen needs to overcome a barrier of less than 2.0 eV in order to reach the next lowest local minimum in the energy surface. This minimum occurs at the antibonding site and is 1.2 eV higher in energy than the ground state. In addition, we consider the role of lattice relaxations and free carriers during the dissociation process. We discuss the relevance of our results for Si-H dissociation in several systems, including the Si-SiO_2 interface. [S0163-1829(99)05919-6]

I. INTRODUCTION

The introduction of hydrogen into silicon-based materials is an important step for the fabrication of many electronic devices.[1] Besides hydrogen's ability to relieve network strain and passivate shallow donor states, hydrogen can also passivate electrically active midgap states. The latter are commonly associated with silicon dangling bonds and are found at surfaces, grain boundaries, interfaces, and in bulk silicon.[1–6] Incorporation of hydrogen during the growth of amorphous silicon (a-Si) films is essential for producing devices such as solar cells. Also, device quality silicon-based transistors are annealed in a hydrogen-rich environment in order to passivate defects at the Si-SiO_2 interface. During device operation, however, electronic defects are created that limit device lifetimes, and hydrogen has been observed to be involved in this degradation process. For instance, hydrogen is known to play a role during hot-electron degradation in silicon-based transistors,[7] as well as during light-induced degradation in a-Si:H solar cells.[8] The created defects are isolated and immobile. Hydrogen desorption from silicon dangling bonds is usually considered to be the dominant mechanism by which defects are created.

A fundamental understanding of the Si-H dissociation process is essential for analyzing and controlling these phenomena. The present calculations build on earlier theoretical work[4,9–12] which found that hydrogen interacts strongly with impurities as well as with defects in bulk crystalline and amorphous silicon. The strongest of these interactions is with the dangling bond, where Si-H bonds are formed with bond strengths of up to 3.6 eV, similar to those found in silane. Although the energy to take a neutral hydrogen atom from an isolated dangling-bond site to free space is 3.6 eV, the energy to move the hydrogen into a bulk interstitial site is only about 2.5 eV.

Here we present *ab initio* density-functional calculations of the interactions of a hydrogen atom with an isolated dangling bond in bulk crystalline silicon. We have explored the adiabatic total-energy surface of this system, and explored vibrational and electronic properties. Our main results are as follows. The ground state of the system is with hydrogen passivating the dangling bond, forming a strong Si-H bond. An additional local minimum is found for hydrogen at the antibonding site (i.e., behind the Si atom, on the other side of the dangling bond). Compared to hydrogen in the bonding site, hydrogen in the antibonding site has an energy 1.2 eV higher, an Si-H bond length $\sim 3\%$ longer and an Si-H stretch-mode frequency which is 180 cm^{-1} lower. When hydrogen is trapped in the antibonding site, electronic levels are introduced into the gap allowing for carrier-enhanced Si-H dissociation. The saddle point for migration from the dangling bond to the antibonding site occurs at the bond-center site, with a migration barrier of 1.75 eV. Large lattice relaxations are required for the H atom to approach the bond-center site; the kinetics of Si-H dissociation through the bond-center site will thus be tied to *silicon-silicon* vibrational modes. An alternative pathway from the ground state to the antibonding site exists, which does not go through the bond-center site, but still requires sizable displacements of the Si atoms; this pathway has a slightly higher barrier (1.9 eV).

The rest of this paper is organized as follows. In Sec. II, we discuss details of the theoretical approach. Our results are reported in Sec. III. In Sec. IV we discuss the implications of these results for device degradation and for experiments performed on hydrogen-passivated Si-SiO_2 interfaces. Sec. V summarizes the paper.

II. CALCULATIONAL APPROACH

We carry out *ab initio* total-energy calculations using a self-consistent, spin-averaged implementation of density-functional theory (DFT).[13] We use norm-conserving, nonlocal pseudopotentials developed by Troullier and Martins,[14] with a core radius of 1.2 and 0.2 Å for silicon and hydrogen, respectively. For the exchange-correlation potential in the local density approximation (LDA), we employ the established results of Ceperley and Alder[15] as parametrized by Perdew and Zunger.[16] Integrations over the first Brillouin zone are replaced by summations using a $2\times2\times2$ sampling which reduces to 2–4 high-symmetry **k** points in the irreducible wedge.[17] For our plane-wave basis, we find a cutoff energy of $E_c = 18$ Ry to be sufficient. Test calculations at $E_c = 22$ Ry were performed for hydrogen at the dangling-bond site and the neighboring bond-center site. Although the *absolute* energies changed significantly, the energy *difference* between the two sites changed by less than 0.05 eV, suggesting the results at $E_c = 18$ Ry are adequately converged. Similar implementations of density-functional theory have been widely used to investigate H in bulk Si; Refs. 4, 10, 11, and 18 contain more details regarding the methodology.

We employ the model of an isolated dangling bond in bulk *c*-Si used in Ref. 12. The model consists of a 32-atom bcc periodic supercell. The theoretical lattice constant (5.38 Å) was used. To create an isolated Si-H, one Si and three of its four neighbors were removed from the supercell, and all dangling bonds were passivated with hydrogen atoms. This procedure creates a Si-H bond on the first Si atom that is well isolated from the other Si-H bonds; the distance between the H atom on the ''central'' Si-H and all other H atoms is more than 3 Å. For all calculations, two neighbor shells of silicon atoms are allowed to relax around the central H atom. In test calculations, relaxing more neighbor shells did not affect the relative total energies. The silicon atoms are relaxed until each component of the atomic force is less than 0.1 eV/Å. Our chosen geometry allows us to address the structural and electronic aspects of Si-H dissocation in a bulk environment. The properties of the interaction between hydrogen and the dangling bond are largely local in nature; we therefore expect our results to apply to other environments in which Si-H bonds occur.

Given the convergence of the basis set, the **k**-point sampling, the cell size, etc., we estimate a ±0.1 eV numerical uncertainty for calculated relative energies.[10] We did not explicitly include zero-point energies in our analysis. For Si-H bonds these energies are ~0.2 eV,[4] and they are expected to largely cancel in the energy differences for the configurations considered here. In general, *ab initio* DFT-LDA calculations reproduce structural properties such as bond lengths and lattice constants to within 1–3 % of experiment, and binding energies to within 5%.[11] LDA calculations are known to consistently underestimate the band gap for silicon; any reported gap levels should therefore only be considered qualitatively. At the present time theoretical methods that produce accurate band gaps are too computationally intensive and do not provide total-energy capability.

Vibrational frequencies of the Si-H stretch modes were calculated in the frozen-phonon approach; this is a reasonable approximation since hydrogen is much lighter than silicon. For these frequency calculations, we perform several total-energy calculations displacing the hydrogen by less than 5% of the equilibrium Si-H bond length. We estimate a ±100 cm^{-1} uncertainty in the reported frequencies. When comparing our frequency results with experiments, one should be aware that DFT-LDA methods tend to underestimate vibrational frequencies by 5–10 %.

III. RESULTS

The energies per H atom for various configurations are presented in Fig. 1 where we choose the reference energy to be that of hydrogen at a pre-existing isolated silicon dangling bond in bulk *c*-Si. The antibonding (AB) and bond-center (BC) sites adjacent to the dangling bond (DB) are labeled as (AB,DB) and (BC,DB), respectively. When these sites are occupied by a hydrogen we use the notation (H-AB,DB) and (H-BC,DB). This convention is used to distinguish these sites from AB and BC sites in bulk silicon. In Fig. 1, the labels H(free) and H_2(free) are for the neutral hydrogen and H_2 molecule in free space. The energies of H(free), H_2(free), and H-BC in bulk Si are DFT-LDA results (including zero-point energies) reported in Ref. 4. Compared to H_2(free), the energy of H_2 in *c*-Si is about 0.4 eV per H higher.[4] Since SiO_2 has larger cavities than c-Si, the energy of H_2(free) should be a good approximation to the energy of H_2 in SiO_2. The energy for H-BC in bulk *c*-Si is for a neutral hydrogen in bulk crystalline silicon far from any defects. The bond-center site is the minimum-energy interstitial site for hydrogen in the neutral and positive charge states, whereas for the negative charge state hydrogen prefers the tetrahedral interstitial site. Since hydrogen is a negative-*U* center in crystalline silicon, charged hydrogen is always lower in energy than neutral hydrogen.[10]

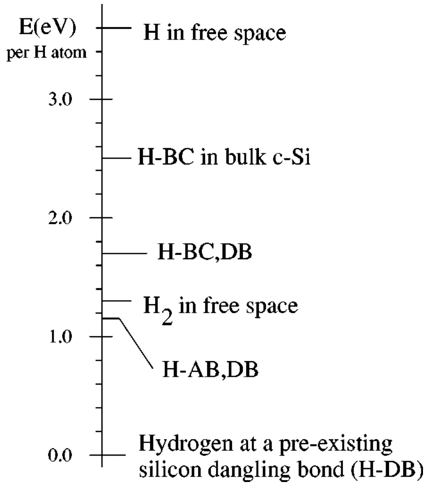

FIG. 1. *Ab initio* energies (in eV) per H atom for various configurations considered in this study.

Before examining the paths for adiabatic Si-H bond dissociation, we consider the local minima for a neutral H atom near a silicon dangling bond. In Figs. 1 and 2(a) we report the energies and the positions of the three local minima found in our investigation. The larger filled circles labeled Si1 and Si2 in Fig. 2 represent silicon atoms at their unrelaxed positions in bulk *c*-Si. Other silicon atoms are not included for the sake of clarity.

The first configuration we consider is hydrogen at the bonding site—labeled H-DB. We find the Si-H bond length is 1.54 Å and the energy gain due to silicon relaxations is less than 0.1 eV. From our calculation of electronic levels, we find that hydrogen fully passivates the dangling bond. We also find that the energy difference between hydrogen at the dangling bond and interstitial hydrogen in a bond-center site is 2.6 eV. These findings are all in agreement with Ref. 12. We have also calculated the vibrational stretch mode of the isolated bulk Si-H bond, finding a frequency of 1970 cm^{-1}. This value is close to a previous DFT-LDA result for Si-H at the Si(111)(1×1) surface.[19] The LDA result for the Si-H surface stretch mode is ~100 cm^{-1} lower than the measured

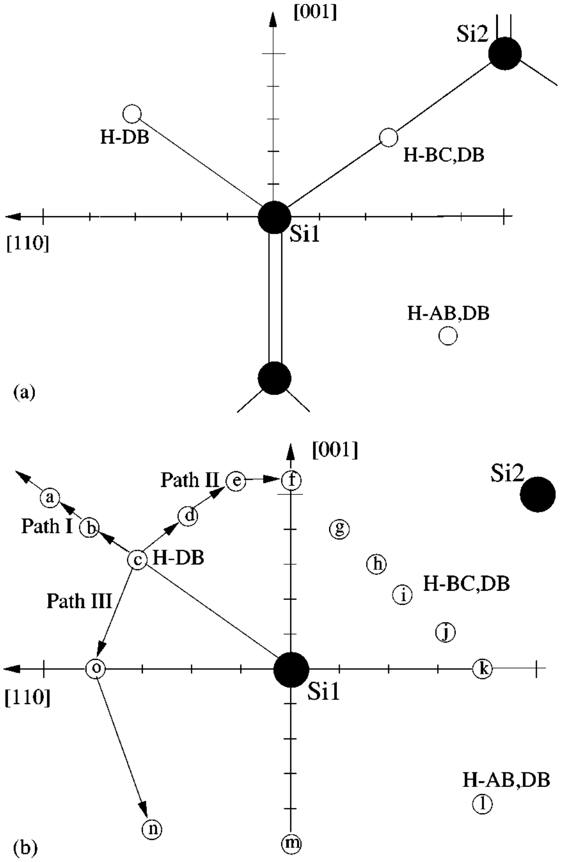

FIG. 2. Schematic illustration of (a) the local minima for hydrogen around a Si dangling bond, and (b) the minimum-energy paths between the H-DB and (H-AB,DB) configurations. The filled circles represent silicon atoms in their equilibrium *c*-Si positions. The energies corresponding to the hydrogen positions shown here are reported in Fig. 3.

value,[19] consistent with the overestimate of the Si-H bond length.

We find that the antibonding position is also a local minimum. This hydrogen configuration is labeled (H-AB,DB) in Figs. 1 and 2. As reported in Fig. 1, the (H-AB,DB) has an energy 1.20 eV higher than the H-DB. This energy difference is in good agreement with a value reported in Ref. 10, in the case of a hydrogenated vacancy. The energy gain due to silicon relaxations is again less than 0.1 eV. The energy of the (H-AB,DB) configuration is more than 1.3 eV lower than for H in bulk interstitial sites. The hydrogen atom at the (AB,DB) site can therefore not be considered to be fully dissociated from the dangling bond. For the (H-AB,DB) complex, the Si-H bond length is 1.58 Å and the vibrational stretch-mode frequency is 1790 cm^{-1}. The electronic states of the (H-AB,DB) include an unoccupied defect level in the upper part of the band gap and an occupied level near the top of the valence band. A deconvolution analysis shows that the higher-lying eigenstate is localized on Si1 (see Fig. 2), suggesting it is related to the dangling bond, while the lower-lying state is localized on the hydrogen atom.

Next, we consider the configuration with H at a bond-center site adjacent to the dangling bond which is labeled (H-BC,DB) in Figs. 1 and 2. Initially, both Si1 and Si2 (see Fig. 2) are 1.2 Å away from the bond-center position; after the cell is fully relaxed Si1 and Si2 are 1.65 and 1.58 Å away from the hydrogen atom, respectively. In addition, we find Si1 relaxes mostly along the $[\bar{1}10]$ direction whereas Si2 relaxes mostly along the $[\bar{1}\bar{1}1]$ direction. As reported in Fig. 1, we find the energy of the (H-BC,DB) configuration to be 1.75 eV higher than that of H-DB. This result is slightly higher than the value of 1.5 eV reported in Ref. 12. The energy surface near (BC,DB) is fairly flat in the direction perpendicular to the bond, making it difficult to determine whether the site is an actual local minimum. Even if it is, however, the barriers are unlikely to be large enough to effectively contain the light hydrogen atom. The near-gap electronic levels of the (H-BC,DB) complex include an unoccupied gap level near the conduction-band edge and a doubly occupied gap state near the valence-band edge. A deconvolution analysis indicates that the state near the conduction band is related to H-BC, while the state near the valence band is related to the dangling bond.

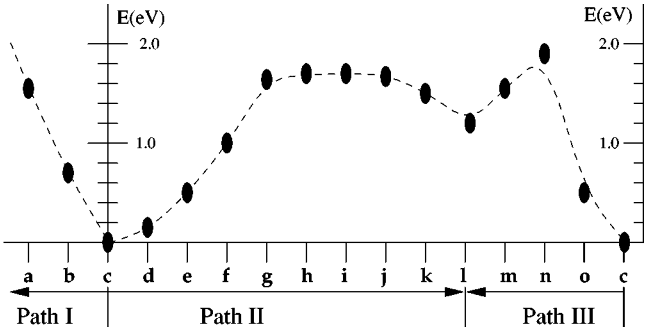

FIG. 3. Energetics along the pathways with hydrogen positions shown in Fig. 2(b). Relaxation of the silicon lattice is included. The filled ovals represent calculated *ab initio* total energies; the size of the ovals is indicative of the error bar. Note the x axis here does not represent distance; to estimate the distance between each pair of sites, see Fig. 2(b).

In order to determine the adiabatic Si-H dissociation barrier it is necessary to determine the activation barrier for each dissociation path in the complete configuration space which connects the initial Si-H configuration with the final state, which is for H at an interstitial site far from the dangling bond. The minimum barrier is the dissociation activation energy. In practice, calculations are limited to a physically reasonable portion of the configuration space, but we will argue that our calculated configurations are close to the actual saddle point along the path. We focus our investigations on hydrogen positions in the $(1\bar{1}0)$ plane as illustrated in Fig. 2(b). We fix the charge state of the system to be neutral, and consider two types of dissociation paths as suggested in Ref. 12. In addition to calculating the total energy of the hydrogen atom along each dissociation path, we also examine the electronic levels and the role of lattice relaxations.

Path I is along the direction of the Si-H bond. We place the H atom at sites **a-c** where site **c** represents the H-DB configuration discussed above. The total energies for H fixed at these sites, and allowing for relaxation of the Si atoms, are reported in Fig. 3. At site **a**, where the H atom has moved 1.0 Å from the equilibrium site, the energy has increased by 1.5 eV. At site **a**, a gap level emerges near the conduction-band edge, with a state localized on H and Si1. Lattice relaxations play a minor role, lowering the total energies by less than 0.2 eV.

Path II is initially perpendicular to the bond direction. We have performed a large number of calculations on a grid in the regions of interest. The sites shown in Fig. 2(b) correspond to the lowest-energy positions for H at given distances along the path. The corresponding energies are reported in Fig. 3. Sites **g**-**j** all have an energy of ~1.75 eV. The region near the bond-center site represents a saddle point between the DB and the (AB,DB) sites. At site **i** where H is at the (BC,DB) site, the force on H is zero within the uncertainty of our calculations. Also, we examined H at sites within 0.2 Å of the (BC,DB) site. We found the (BC,DB) site to be a maximum along Path II, and a minimum along a line perpendicular to Path II along the $[\bar{1}\bar{1}1]$ direction. These results indicate that site **i** with H at the (BC,DB) position is very near (within 0.1 eV in energy) to the saddle point between the minima at DB and (AB,DB). Along Path II, gap levels appear near the conduction-band edge when H is at site **f**. As H approaches site **i**, gap levels also emerge near the valence-band edge. We find that significant lattice relaxations are required for H to insert into sites **g**-**j**. These relaxations account for an energy gain larger than 2.0 eV. Such large lattice relaxations are well known for the bulk H-BC.[10]

Path III. We also explored the possibility that H reaches the (AB,DB) site via a minimum energy path from **c** to **o** to **n** to **m** to **l**. Again, we note that Fig. 2(b) only reports a subset of our calculations. The minimal barrier along this path is 1.9 eV, slightly higher than for Path II. By a procedure similar to the one described for the (BC,DB) site along Path II, we found the H atom at site **n** to be very near the saddle point between the minima at DB and (AB,DB). Moving H adiabatically from site **o** to site **n**, the relaxations of Si1 are primarily in the $[00\bar{1}]$ direction. In order to facilitate moving the H from site **n** to site **m**, Si1 must move more than 0.5 Å in the [112] direction. Fixing Si1 at its equilibrium *c*-Si position would increase the energy barrier by more than 0.2 eV. Silicon displacements are therefore seen to play a crucial role in facilitating the migration of hydrogen from the DB to the (AB,DB) site.

IV. DISCUSSION

Isolated Si-H bonds can be present at silicon surfaces, grain boundaries, in bulk *a*-Si, and at silicon interfaces. Clustering of Si-H bonds often complicates the picture, for instance through the interaction between H atoms in a fully hydrogenated vacancy in *c*-Si,[12] or because of clustering of Si-H bonds in *a*-Si.[20] The results presented above do not take such clustering into account. We now discuss some consequences for Si-H bond dissociation implied by our calculations.

Bond dissociation along Path I seems straightforward: the H energy would increase to the value of H(free) given in Fig. 1. With no additional local minima, the barrier to full dissociation is simply the Si-H binding energy, ~3.6 eV. Such a dissociation mechanism might seem like the simplest possible process at a Si(111) surface. In practice, of course, desorption as H_2 molecules is much more likely, since the binding energy of H_2 will reduce the desorption energy. If we restrict the dissociation process to single H atoms, our results show that the Si-H dissociation barrier may be greatly reduced by choosing a path where hydrogen can interact with the surrounding host atoms (i.e., Path II). While the energy to take a neutral hydrogen atom from a dangling-bond position and place it in free space is 3.6 eV, only 2.5 eV is needed to place the hydrogen in a BC site in bulk *c*-Si. Even less energy may be required, because both the H interstitial and the silicon dangling bond can become charged, thus lowering the energy of the final state. Once in the BC site, the H atom is mobile and has a migration barrier of less than 0.5 eV. Interstitial hydrogen will subsequently lower its energy, e.g., by binding to other defects or by forming an H_2 molecule. At surfaces or interfaces with open materials such as SiO_2, H_2 can easily escape from the material. Overall, the Si-H dissociation activation energy is expected to be less than 3.0 eV.

In our calculations, we employ the adiabatic approximation when calculating the barriers for Si-H bond breaking. As the hydrogen moves from one local minimum to another, the neighboring silicon atoms are allowed to fully relax. Given that the silicon atoms are much heavier than the hydrogen atom, one may question whether the adiabatic approximation affects our conclusions. For the dissociation energy along Path I, we can state that our conclusions are insensitive to this approximation; the total barrier is essentially determined by the Si-H binding energy (~3.6 eV). The dissociation along Path III may be somewhat more sensitive to the adiabatic approximation. As a limiting case, we could fix the silicon atoms in their initial positions; this would increase the barrier from 1.9 eV to about 2.5 eV. For Path II, finally, freezing the Si positions would lead to a prohibitively high barrier.

We note, however, that freezing the Si atoms is not a good test of the adiabatic approximation. Instead of questioning whether the Si atoms can follow the rapid motion of the hydrogen (which they cannot), a more realistic scenario is to consider the dissociation process to be essentially controlled by the motion of the Si atoms. The very light H atom can readily find the lowest-energy configuration offered by the particular position of the Si atoms. In our opinion, the adiabatic total-energy surfaces offer a meaningful approximation of this mechanism. A complete description, which would treat the motion of the silicons as well as the hydrogen fully consistently, is beyond the capabilities of current first-principles approaches. We note, however, that the intrinsic value of adiabatic total-energy surfaces for calculating barriers was demonstrated in calculations of hydrogen diffusion coefficients by Blöchl, Van de Walle, and Pantelides.[21]

Detailed experiments have been performed on hydrogen desorption at the Si(111)-SiO_2 interface.[6] Analysis of the data showed that the kinetics of Si-H dissociation were activated with an activation energy of 2.56 eV. This value is entirely consistent with a neutral hydrogen dissociating into the bulk silicon side of the interface. A dissociation activation energy of 2.56 eV would be inconsistent with a neutral hydrogen dissociating into a free-space-like environment (see Fig. 1). Whether or not an activation energy of 2.56 eV is consistent with hydrogen dissociating into the SiO_2 side of the interface depends on the energy of interstitial hydrogen in SiO_2. While it is commonly assumed that the energy of H in SiO_2 is close to the energy of H in free space,[22] a conclusive determination by experiment or *ab initio* calculation has not yet been performed.

Deuterium desorption from internal surfaces in Si was studied by Wampler, Myers, and Follstaedt,[23] who derived a thermodynamic silicon-deuterium binding energy based on their data. This value cannot be directly compared with our results, which only address the dissociation energetics along various paths. A discussion of the results of Wampler, Myers, and Follstaedt in the context of first-principles total-energy calculations has been presented in Ref. 24.

The dissociation paths examined in our study exhibit distinct characteristics. Our results show that the activation energy for Si-H bond dissociation depends greatly on the path, with Path I leading to a free-space-like final configuration, and Path II leading to a final configuration in a bulk environment. The kinetics of Si-H bond dissociation may also distinguish between these paths. For Path I, the kinetics are governed by the *silicon-hydrogen stretch-mode* frequency. For Path II, on the other hand, where hydrogen enters a (AB,DB) or a bulk BC site, significant relaxations of the silicon atoms are necessary. The kinetics are therefore governed by Si-H *bending modes*, and would also reflect *silicon-silicon* vibrations. We note that the interactions between Si-H(D) vibrational modes and lattice phonons have been proposed to be important for explaining H(D) desorption by multiple vibrational excitations.[25]

The presence of free carriers may reduce the activation barrier for Si-H bond dissociation. For instance, Si-H bond dissociation may occur by a two-step process. First, the hydrogen is excited over a 1.75 eV barrier along Path II into the (AB,DB) site. It will remain there for some time since a barrier of about 0.5 eV prevents it from jumping back into the DB site. While in the (AB,DB) site, the hydrogen is still bound to the DB, needing an additional ~1.3 eV to reach an interstitial site far from the dangling bond. However, the (H-AB,DB) complex is electrically active, with an unoccupied level in the upper part of the band gap and an occupied level near the top of the valence band; these levels can capture carriers. When the complex is charged, the binding between hydrogen and the dangling bond is significantly reduced. Dissociation will thus proceed efficiently with a much-reduced barrier. Such a mechanism may play a role in doped materials with an abundance of free carriers. Free carriers also occur during operation of devices such as solar cells and transistors. These carriers may play a role in device degradation by reducing the barrier to Si-H bond dissociation.

Finally, we discuss vibrational frequencies. The (H-AB,DB) complex has an Si-H vibrational stretch mode frequency of ~1790 cm^{-1}, which is significantly lower than typically observed for Si-H bonds. In equilibrium the (H-AB,DB) configuration is unlikely to occur in high enough concentrations to be observed, but it may be possible to populate and observe such modes in nonequilibrium situations. In fact, a recent IR study by Darwich *et al.*[8] found that, in *a*-Si:H films, an interesting H related IR mode at 1730 cm^{-1} appears when the films are light soaked. In Ref. 20, it was reported that dissociation of Si-H clusters may lead to hydrogen being weakly bound to an overcoordinated silicon, exhibiting a lower stretch-mode frequency consistent with the mode reported in Ref. 8. Our present calculations for the (H-AB,DB) configuration also produce a vibrational frequency consistent with the results of Ref. 8.

V. CONCLUSION

We have presented *ab initio* density-functional calculations of the interactions of a hydrogen atom with an isolated dangling bond in bulk crystalline silicon. We have explored the adiabatic total-energy surface of this system, finding a local minimum for H at the (AB,DB) site. Compared to hydrogen in the DB site, hydrogen in the (AB,DB) site is 1.2 eV higher in energy and the Si-H stretch mode frequency is 180 cm^{-1} lower. The (H-AB,DB) vibrational properties appear consistent with recent observations in light-soaked *a*-Si:H films.[8] When hydrogen is trapped in the (AB,DB) site, electronic levels are introduced into the gap allowing for carrier-enhanced Si-H dissociation. The saddle point for migration from the dangling bond to the antibonding site occurs near the bond-center site (see Figs. 2 and 3). We have discussed mechanisms by which the energy barrier for Si-H desorption may be less than the Si-H binding energy. Dissocation of Si-H bonds with H going into bulk Si is found to be consistent with the analysis of observations of hydrogen desorption of the Si-SiO_2 interface. Finally, our results should be useful as a basis for future studies of Si-H dissociation in more complex environments such as silicon surfaces, bulk *a*-Si:H, grain boundaries, and interfaces.

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