Diffusion Mechanism of Hydrogen in Amorphous Silicon: *Ab Initio* Molecular Dynamics Simulation

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The mechanism of H migration in amorphous Si has remained an unresolved problem. The main issue is the small activation energy (1.5 eV) relative to the known strength of Si-H bonds (2–3.5 eV). We report first-principles finite-temperature simulations which demonstrate vividly that H is *not* released spontaneously, as proposed by most models, but awaits the arrival of a floating bond (FB). The "migrating species" is an FB-H complex, with H jumping from Si to Si and the FB literally floating around it. Migration stops when the FB veers away.

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Hydrogenated amorphous silicon (*a*-Si:H) is a prototype amorphous semiconductor that has attracted considerable attention for both scientific study and technological applications, e.g., photovoltaics and thin-film transistors for displays. Its properties have been under active investigation both theoretically and experimentally for several decades [1,2]. One of the major unresolved issues is the diffusion mechanism of hydrogen and the role of the Si coordination defects in the diffusion process. In the 1970s, vibrational spectroscopy established that H exists primarily in Si-H bonds [3,4], effectively passivating dangling bonds (DB), namely Si atoms with only three Si neighbors. H diffusion was measured in the early 1980s using several methods. The activation energy was found to be ~1.5 eV [5–8], which posed an immediate problem as Si-H bonds were known to be very strong. For example, at hydrogenated Si surfaces, Si-H bonds break with an activation energy of ~3.5 eV [6]. The mechanism for the release of H from Si-H bonds in *a*-Si could not be explained.

In 1986, Pantelides introduced the notion of floating bonds (FBs) [9], namely fivefold-coordinated Si atoms, as an additional defect, conjugate to dangling bonds. It was further proposed [10] that FBs migrate by bond interconversion and can easily release an H from an Si-H defect without leaving behind a dangling bond. Numerical simulations have since found that both FBs and DBs are present [11–13], but subsequent work on H diffusion focused attention on spontaneous H release. Jackson and Tsai [14] and later Van de Walle and Street [15] suggested that the determining factor for spontaneous H release is the chemical potential μ_H. It was further suggested [15] that the energies of H-related defects form two overlapping "bands" corresponding to Si-H and Si-H-Si defects and that μ_H lies at the dip between the two bands, accounting for its small value. These arguments, however, are equivalent to postulating that only those Si-H defects in which H is weakly bound contribute to diffusion (analogous to only electrons near the Fermi energy contribute to transport in metals). Such an assertion has no independent corroboration. In addition, subsequent calculations by Biswas *et al.* [16] found that the relevant energy distribution still yields an energy of ~2 eV for the spontaneous release of H.

In this Letter, we report first-principles, finite-temperature molecular dynamics (MD) simulations through which we investigate in detail the atomic processes that spontaneously occur at finite temperatures in a cell of *a*-Si containing H and coordination defects. We find that Si-H bonds *do not* spontaneously release H. In contrast, migration of a bonded H atom is initiated by the arrival of a FB, which causes the Si atom of the Si-H bond to become overcoordinated. However, the Si-H bond weakens only slightly and the H atom is *not* released as proposed in Ref. [10]. The local overcoordination enables other nearby Si atoms to compete for "ownership" of the H atom through bond interconversion processes. Transfers of the H atom from one Si atom to another occur with rather complex but small local motions of the surrounding Si atoms. The FB is truly "floating around" as the H atom migrates, with several Si atoms in the immediate vicinity undergoing variations in their bond lengths from 2.3 to 3.0 Å. It is virtually impossible to assign the extra bond definitely to a particular Si atom for more than a few time steps. There is no doubt, however, that the "migrating species" is a FB-H complex, with the H atom jumping from Si to Si and the FB floating in the vicinity. If the FB veers away, the H atom gets stuck in a strong Si-H bond and awaits the arrival of a new FB for the migration process to start over. The entire pool of Si-H bonds participates in the process.

In the simulations, the ionic motions are treated classically with discrete time steps of about 1 fs. The positions of the ions at each time step are obtained from the previous time step by Newton's law of motion with the force on each ion determined by the instantaneous electronic ground state using the Hellmann-Feynman theorem. The electronic ground state at each time step is calculated using density functional theory and the local density approximation for the exchange-correlation potentials [17,18]. We used ultrasoft Vanderbilt pseudopotentials to represent the ion cores and a plane wave basis set to expand the electron wave functions. The cutoff energy for the plane waves is set to 240 eV. The Brillouin zone of the supercell lattice is sampled at the Γ point alone. More accurate setups like higher cutoff energy and more sampled *k* points seem to slightly affect the detailed atomic motions, but the general picture remains the same.

We adopted the canonical ensemble scheme: the average kinetic energy of the ionic motions is constantly rescaled to the simulation temperature. Although experiments on H diffusion in *a*-Si:H were performed in the region below 500 °C, our simulations were done in the range of 600–900 °C, chosen to increase the number of H migration events and yet remain below the melting point [11]. Multiple migration events were observed in simulations above 700 °C, with accumulated simulation times up to 40 ps.

We used an amorphous supercell containing 64 Si atoms and 2 H atoms, obtained using the method of Barone and Maroudas [19]: we started with a crystalline Si supercell and introduced ~25% Frenkel pairs, then annealed the system for 5–10 ps. Several attempts produced similar final structures. Radial distribution functions, calculated using finite-temperature simulations, were in very good agreement with experimental data [20]. The cells typically had two DBs and about four FBs. Such defect concentrations are of course unrealistic (even a single point defect in a 64-atom cell means a defect density of 8×10^{20} cm^{-3}), but our purpose here is to have one or two DBs and one or two FBs in order to examine their role in the diffusion of H. We then added two H atoms at random but well-separated locations in the pure Si supercell and annealed the system again (using two H atoms results in an even number of electrons in the supercell, which facilitates the calculations). In the resulting stable structure, each H is bonded to a single Si (Si-H bond) that has three other Si-Si bonds, consistent with experimental observations [3,4]. After hydrogenation, the number of DBs decreased or went to zero, but the number of FBs remained the same, suggesting that H passivates DBs with a larger energy gain.

Extensive simulations and detailed examinations of H atomic jumps reveal that initiation of diffusion is always mediated by a FB. As first described by Pantelides [9], a FB is an extra Si-Si bond that can be passed from one Si atom to another by minor atomic motions (bond interconversion). When the extra bond is handed over to a Si atom which has three Si-Si bonds and one Si-H bond, the Si-H bond becomes one of five bonds of a now overcoordinated Si. A plot of the electron density around such an overcoordinated Si atom shows that the electron density associated with the Si-H bond remains virtually unaltered. Figure 1(a) shows the newly arriving "fifth" bond, the FB, with bond length 2.9 Å and Fig. 1(b) shows the electron density when the new bond has a normal bond length of 2.35 Å. Note that the central Si atom has *three* other normal Si-Si bonds, only one of which is visible in the plotting plane. They are weakened slightly. For comparison, we show in Fig. 1(c) the electron density for an H atom at an antibonding site in *crystalline* Si. The effect is very similar. The H atom robs virtually all the electron density from the Si-Si bond on the backside of the central Si atom. We know from calculations in the crystal, however, that such a configuration is not as strong an Si-H bond as when an H atom bonds to a Si with only three Si neighbors, as in a vacancy or free surface [21]. Thus, we infer that the configurations of Figs. 1(a) and 1(b) are weaker than normal Si-H bonds. This inference is supported by the fact that, once an FB arrives, migration of H ensues, as described below.

In Fig. 2, we show a typical evolution of the Si-H distance in the vicinity of a migration event from Si atom *A* to Si atom *B*. The red curve is the *A*-*H* distance and the blue curve is the *B*-*H* distance. At any given time, only the smaller of the two represents a bond and the plot shows clearly its harmonic vibration. Prior to the initiation of migration the period is 16 fs, in excellent agreement with infrared absorption data [3,4] that find sharp lines at 2000 and 2100 cm^{-1} (17 and 16 fs). The Si-H bond length is ~1.55 Å and the vibration amplitude is ±0.1 Å at $T = 800$ °C. After migration is initiated, the vibrational period increases by only 1–2 fs, suggesting that, even when H is one of five bonds, it "asserts itself" as is evident in Fig. 1.

Figure 2 shows a jump of the H atom from Si atom *A* to Si atom *B* at about 8 ps, back to *A* at about 8.4 ps, and then back to *B* at about 8.55 ps, which is the end of the jump event. Throughout the simulation the Si-H bond

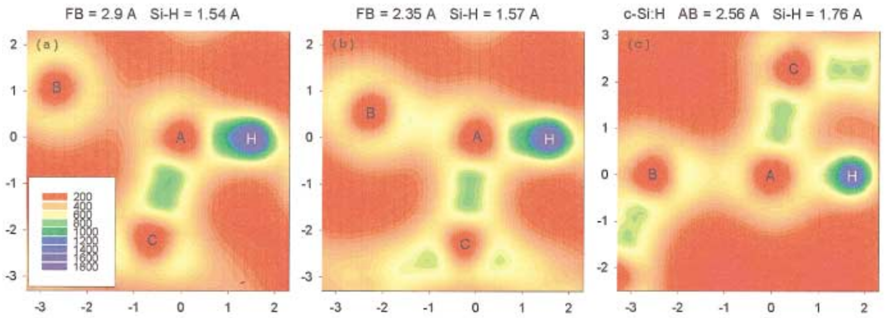

FIG. 1 (color). Electron density plots illustrating (a) in *a*-Si, an extra Si-Si bond (*A*-*B*) starting to form with Si atom *A* which has three Si-Si and one Si-H bonds (only one of the three Si-Si bonds, namely *A*-*C*, is shown). (b) Same as in (a), with the new bond acquiring normal length. (c) An H atom at an antibonding site in crystalline Si. Without the H atom, the bond *A*-*B* is a full "green" bond.

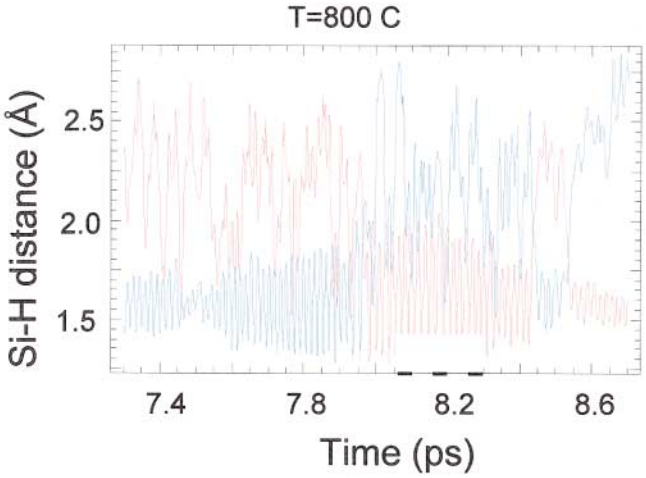

FIG. 2 (color). Time evolution of the *A-H* and *B-H* distances, where *A* and *B* are Si atoms, during a migration event.

length does not exceed the value 2 Å and is not near that value very often, suggesting that *H is not released in the interstitial regions* defined by the middle of the Si rings.

Figure 3 shows a schematic diagram of the essential features of a migration event. When a FB migrates to the Si atom that has an Si-H bond, the Si becomes overcoordinated. At this moment, if another nearby Si happens to move close to the H, a three-center Si-H-Si bond begins to form and the two Si atoms compete for ownership of the H atom. The *H atom actually slips back and forth several times* until finally it may switch over to the new Si. *No bonds ever break in the process.* Now, the intruding Si becomes overcoordinated, and the process repeats until, at some point, the FB migrates away. When that happens, the H is stuck again and waits until another FB arrives to introduce another migration opportunity.

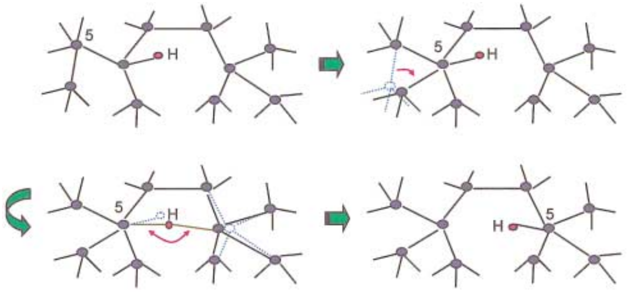

FIG. 3 (color). Schematic diagrams capturing the essence of a migration event of an H atom, mediated by a floating bond.

Figure 4 shows the electron densities during an actual migration event. The five panels correspond to five points on the time axis as indicated in the sixth panel. The H atom, initially bonded to Si atom *A* jumps to Si atom *B*. At the top of each panel we show the two Si-H distances and the bond lengths of all the neighbors of atoms *A* and *B*. The figure is consistent with the schematic of Fig. 3, but we emphasize that, as indicated in the last panel in Fig. 4, there are many intermediate steps for a migration event. Examination of these configurations suggests that the process can be best described by saying that the FB is literally floating around the migrating H. Several Si atoms around the H atom have two or three bond lengths that vary from 2.3 to 3.0 Å during the complex migration event that lasts 50 fs or more. Often, the H atom jumps back and forth between the same atoms before it moves

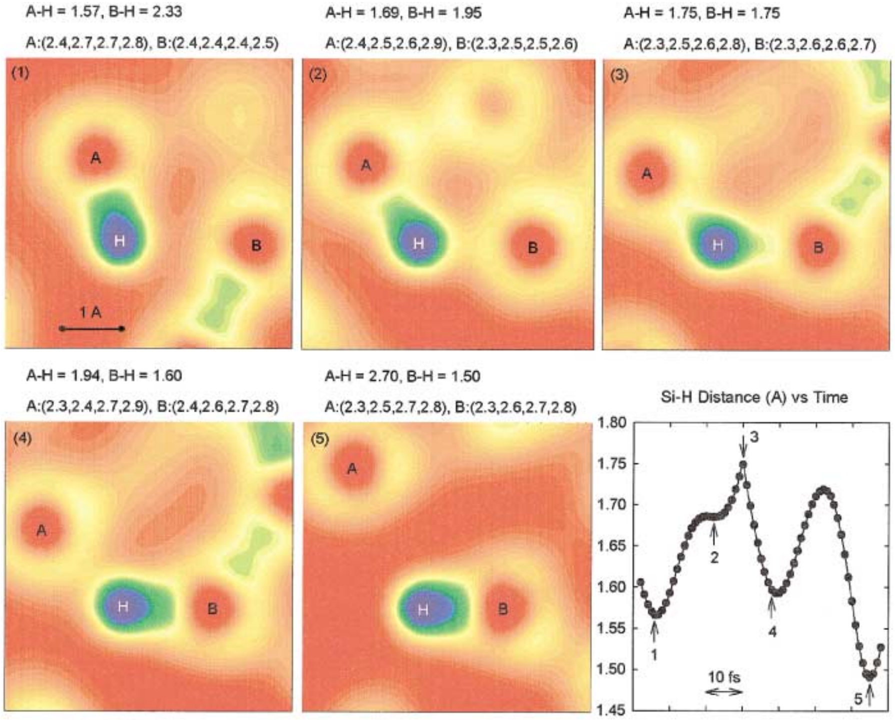

FIG. 4 (color). Five snapshots of the electron density showing a migrating H atom assisted by a floating bond. The times correspond to those indicated in the sixth panel, where the distance of H from the nearest Si atom is plotted versus time.

on. It is virtually impossible to assign the "extra bond" to the same Si atom for more than a few time steps. Overall, we have a relatively diffuse FB-H complex that migrates. If, however, the FB veers away from the H atom, the H atom gets stuck in a strong Si-H bond.

It is noteworthy that we *do not observe H migration through bond centers*. The bond center is the low-energy configuration for H in crystalline Si [22]. Such a configuration in *a*-Si would be asymmetric because of the lack of symmetry in the amorphous network. Biswas *et al.* [16] in fact found that H in *a*-Si migrates through bond centers with asymmetric configurations, i.e., a stronger Si-H bond on one side with effectively a dangling Si bond on the other side. Those simulations, however, used cells that contained *no* FBs. The present simulations demonstrate that, in the presence of FBs, the preferred migration mode is the one described in this Letter. We found no evidence for the mode described by Biswas *et al.* Tuttle and Adams [23] recently reported first-principles calculations of static configurations of H in *a*-Si, classifying them as "transport traps," "shallow traps," and deep traps. In the present dynamical simulations, no such classification is possible. We find only one stable configuration, the Si-H bond, and never observe an interstitial H. During diffusion, a loose H-FB complex is formed and H jumps from Si to Si as a fifth neighbor that asserts itself as shown in Fig. 1.

It is not possible to extract a diffusion activation energy from the simulations. Calculation of the migration barrier for a single H jump is thwarted by the fact that several atoms are involved and "a jump" consists of several failed attempts and back-and-forth jumps. In principle one can determine an activation energy by simulating long enough to obtain a plot of diffusion distance versus time, but such calculations are not practical because they would require very long simulations and larger cells. Nevertheless, the frequency of migration events that occur at 700–800 °C suggest an activation energy that is less than 2 eV. Furthermore, since one must simulate for a long time awaiting an FB to arrive at an Si-H bond and initiate diffusion, whereas an H-FB complex migrates readily until the FB veers away, we infer that the rate-limiting step corresponding to the observed activation energy must be the diffusion of FBs. It should also be noted that the density of FBs needed to account for the observed diffusion is quite small, as evinced from the fact that diffusion of dopants in crystalline Si is mediated by vacancies and interstitials whose concentrations are typically of order 10^{10} cm^{-3} (because their formation energies are 3–4 eV) [24]. Thus, even if one rules in favor of DBs as the dominant EPR-active defect in *a*-Si, the concentration of FBs needed for H diffusion is below the limit of detection by any known techniques.

During the course of the simulations, there was one time that the two H atoms in the supercell met each other and formed a very stable complex. The lifetime of the two-H complex was so long that we had to restart the simulation with a new initial configuration to get the H diffusion going again. The structure looks like the doubly hydrogenated Si-Si bond (Si-H H-Si) proposed as a negative correlation energy two-H center by Zafar and Schiff [25], which is taken as one possible candidate for the metastable $M(\text{Si-H})_2$ complex in Branz's hydrogen collision model [26]. This stable structure also seems to reflect the H clustering effect reported in the literature [11,27].

In summary, the finite-temperature simulations suggest that H does not migrate as a free interstitial in a well-equilibrated *a*-Si:H system. Furthermore, unlike the case of hydrogenated crystalline Si, the H diffusion path does not proceed via cutting through Si-Si bond centers. H migration is achieved through the mediation of a floating bond. The migrating species is essentially an FB-H complex.

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