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Mechanism for hydrogen diffusion in amorphous silicon

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Tight-binding molecular-dynamics calculations reveal a mechanism for hydrogen diffusion in hydrogenated amorphous silicon. Hydrogen diffuses through the network by successively bonding with nearby silicons and breaking their Si—Si bonds. The diffusing hydrogen carries with it a newly created dangling bond. These intermediate transporting states are densely populated in the network, have lower energies than H at the center of stretched Si—Si bonds, and can play a crucial role in hydrogen diffusion. [S0163-1829(98)05404-6]

INTRODUCTION

Diffusion of hydrogen is a fundamental phenomena in amorphous and crystalline silicon that underlies much basic physics and device development. Although intensely studied, the mechanism of H diffusion in amorphous semiconductors is not well understood, in part because of the lack of knowledge of the bonding energies of H in the amorphous network. In contrast, crystalline silicon is better understood, with the H diffusion having an activation energy of 0.48 eV at high temperature.[1] In *c*-Si, H has the lowest energy in the bond-centered configuration for positive and neutral charge states. H diffusion is believed to occur from H passing from one bond center (BC) to another BC, thus sampling a region of high electron density.[2,3] However there is a large outward movement (0.4 Å) of the Si atoms when H is at the BC site, so that substantial Si motion is involved in the BC diffusion path.

However, in the negative charge state (e.g., in *n*-type *c*-Si) the lowest energy of H is the tetrahedral-interstitial (T) site, where the H interacts only weakly with the host crystal. Since the H-bonding level is within the valence band of the host, H attracts an extra electron to be negatively charged. Diffusion is believed to occur from one T site to another, with the H occupying regions of low-electron density.

The situation in amorphous silicon differs from *c*-Si in that H is not an interstitial, but is strongly bonded to the silicon network as an Si—H bond. H diffusion in *a*-Si:H is initiated by breaking a Si—H bond and promoting the H to a mobile transport state. This is the rate-limiting step in the diffusion process whose activation energy is commonly measured to be 1.4–1.5 eV. Once in the transport state, H is believed to diffuse rapidly through interstitial states due to the relatively lower-energy barriers.

A puzzling problem is how to reconcile such diffusion activation energies in *a*-Si:H with *ab initio* calculations. If H transports through bond-center states (analogous to *c*-Si), the energy to break a Si—H bond and create a BC is 2.5 eV for a normal Si—Si bond.[4] This would imply an activation energy close to 3.0 eV, if an additional barrier of a few tenths of an eV to escape out of the bond center is added in. Traditionally, a way to resolve this inconsistency is by assuming the chemical potential of the H is actually located much higher in energy than the Si—H state.[5] However, it is difficult to account for the small formation energy (0.2–0.5 eV) of the dangling bonds in this picture.[5] An alternative explanation[6] is that the H diffusion involves BC states with stretched bonds, which can have substantially lower formation energy than 2.5 eV.[7] However, these stretched bonds with low enough energies are typically 5–7 Å apart, making them unlikely to be the sole transporting states. Clustered H is found experimentally to have a substantially higher energy than the deeply bound dilute H,[8] but calculations cannot easily model the atomic environments of the clustered H.

It has been commonly proposed that H diffusion involves some type of H-interstitial state—the exact nature of the diffusion mechanism in *a*-Si:H is not well identified. The reactive nature of H transport proposed here has been among one of the interstitial states proposed for H-diffusion motion.[3,9]

RESULTS

In this paper we propose a picture of the diffusion mechanism of hydrogen in *a*-Si:H, that is more favorable than the bond-centered process, and has important consequences. Our simulations utilize the tight-binding (TB) molecular-dynamics model of Si—H systems[10] that has successfully modeled the energy surface of H in *c*-Si in different charge states, Si—H vibrational frequencies, and electronic and structural properties of *a*-Si:H.[6,7] Applicability and reliability of this approach has been discussed in previous publications.[6,7] We utilize *a*-Si:H networks[8] containing 10% H and 22% H with no coordination defects, that have provided a realistic description of *a*-Si:H. Models with 60–240 atoms are used.

The motion of the H involves much quantum-mechanical complexity including tunneling. Hence we focus on the static energy surface of hydrogen. By exploration of the energy surface for H in the network, we find a host of low-energy states. Using the TB model we calculate the energy to break a Si—H bond and place the H at nearby or distant silicon sites. The H is placed in antibonding sites directly opposite Si—Si (or Si—H) bonds. Remarkably, we find the H is very reactive, and can form a new Si—H bond by breaking the Si—Si bond. This is represented by

$$\mathrm{Si{-}H} + \mathrm{Si}_x\mathrm{{-}Si}_y \rightarrow \mathrm{Si}^* + \mathrm{Si}_x\mathrm{{-}H} + \mathrm{Si}_y^* . \tag{1}$$

These configurations typically consist of two dangling bonds: one left behind (Si^*) when the H is taken away, and one newly created (Si_y^*) because in the process of forming a new Si—H bond, an existing nearby Si—Si bond is broken.

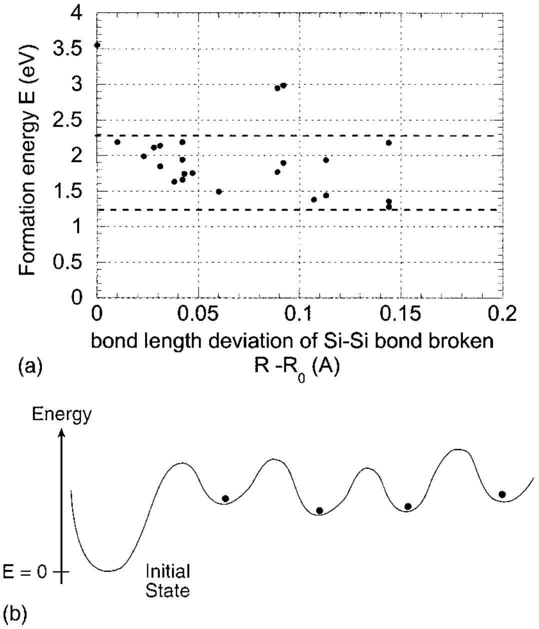

FIG. 1. (a) Formation energy of configurations where H bonds to Si atoms in the network, and creates a dangling bond on a nearby site. Energies shown as a function of the Si—Si bond length that is broken in the process [Si_b—Si_c in reaction (1)]. (b) Schematic energy surface of diffusing H in *a*-Si:H. The potential energy minima (circles) are identified with the low-energy configurations of (a). The first deep energy well represents the initial configuration before H is released from an SiH bond, which is taken as the reference energy.

The new dangling bond (Si_x^*) is in the vicinity of the H. A five-coordinated silicon, i.e., floating bond (at sites x or y) would cost more energy. Remarkably, the energy of reaction (1) is low even when the Si—H bond being broken is not a weak bond [Fig. 1(a)]. These configurations are densely populated throughout the network, and are often separated by $\leqslant 3-4$ Å. The range of formation energies 1.3–2.3 eV is reasonable because the net result of Eq. (1) is a broken Si—Si bond (with additional lattice relaxation) which may cost less than 2.3 eV needed in *c*-Si since *a*-Si:H can accommodate lattice distortion more easily. The large energy cost of breaking a SiH bond is not involved here.

The formation energies of these configurations [1.3–2.3 eV; Fig. 1(a)] does not depend much on the bond length of the Si—Si backbond that is broken. However, it is generally unfavorable to bond H to a Si atom with near-normal or compressed bond lengths. At such sites the H instead moves off into a unbonded high-energy H^--ion interstitial, with a formation energy exceeding 3.0 eV. Such weakly interacting interstitials are similar to the T in *c*-Si. The energy of some Si—H configurations on the same Si site is very high (2.5–4 eV in Fig. 1), since large bond-angle distortions are generated after formation of the new SiH bond. Hence the local bonding geometry is very important in determining the low energy of these sites. The energies of these H-bonded configurations are considerably lower than H in stretched Si—Si bonds at these sites, whose formation energy decreases almost linearly with the bond-length deviation.[7]

We identify this family of configurations with a manifold of transport states where the H can diffuse through the *a*-Si:H network. The family of lower-energy configurations in Fig. 1(a) is dense with nearest- or next-nearest-neighbor separations, and can be represented by the potential-energy minima in the schematic energy surface of Fig. 1(b). We propose that diffusion of H proceeds by the H breaking and reforming Si—Si bonds in the network, with the diffusing H carrying a transporting dangling bond along.

We illustrate this proposal of H transport by a spatial sequence of such low-energy configurations (Fig. 2) that span across the simulation cell through ≈ 8 Å. We start with the original cell with no dangling bonds [Fig. 2(a)], that defines the zero of energy. H may be released from a Si—H bond to a backbond, creating two dangling bonds [Fig. 2(b)]. This is represented by

$$\mathrm{H—Si}_a\mathrm{—Si}_b \rightarrow \mathrm{Si}_a^{**} + \mathrm{Si}_b\mathrm{—H}, \tag{2}$$

where two dangling bonds are created on the same site (Si_a). The H release from other SiH sites, however, may also be represented by Eq. (1), which leads to one dangling bond on the original site. The next configuration [Fig. 2(c)] has the H bonded to a next-nearest-neighbor Si. The transition between the configurations in Figs. 2(b) and 2(c) can be represented as

$$\mathrm{Si}_b\mathrm{—H} + \mathrm{Si}_a^* + \mathrm{Si}_c\mathrm{—Si}_d \rightarrow \mathrm{Si}_a\mathrm{—Si}_b + \mathrm{Si}_c\mathrm{—H} + \mathrm{Si}_d^* , \tag{3}$$

involving the movement of the H to a next-neighbor site (Si_c). One of the original dangling bonds (Si_a^*) rebonds and a new dangling bond Si_d^* forms in the vicinity of the H [Fig. 2(c)]. When two dangling bonds exist on the same site [Fig. 2(b)], one of them is rebonded. Finally the H can move to a neighboring configuration [Fig. 2(d)] that can also be reached from Fig. 2(c) by reaction (3). As the bound pair of mobile H and the dangling bond diffuses, it may encounter another dangling bond Si* and the two dangling bonds can annihilate, leaving the H in a trap, i.e.,

$$\mathrm{Si}_a\mathrm{—H} + \mathrm{Si}_b^* + \mathrm{Si}^* \rightarrow \mathrm{Si}_a\mathrm{—H} + \mathrm{Si}_b\mathrm{—Si}. \tag{4}$$

Our basic conclusion is that H motion is very reactive involving the breaking and reforming of Si—Si bonds in the network, with a transporting dangling bond accompanying the H. The present H-diffusion mechanism does not rely on the existing dangling bonds in the network. This mechanism of diffusion is significantly different from H motion in *c*-Si, since the amorphous network has the ability to distort and form new bonds—a feature not possible in the crystalline system. It should be contrasted with the H motion through bond-centered sites in *c*-Si, which is a somewhat less reactive process where Si-Si bonds are stretched outwards by $\cong 0.4$ Å to accommodate the H.

The calculation of energy barriers between the transporting H configurations in *a*-Si:H is very challenging due to the complexity of motions possible in the amorphous network, and may be suitable for general optimization methods. Our simulations suggest low-energy barriers occurring through SiH bond-bending distortions, where H bends in an arc toward the next transporting configuration. Paths involving SiH bond stretching have higher energy. We examined simple paths when H moves between nearest-neighbor configurations with energies in Fig. 1, and find energy barriers <0.8 eV that are at best an upper bound to the true barrier. Such barriers (E_b^{tr}) would enable H to diffuse among this

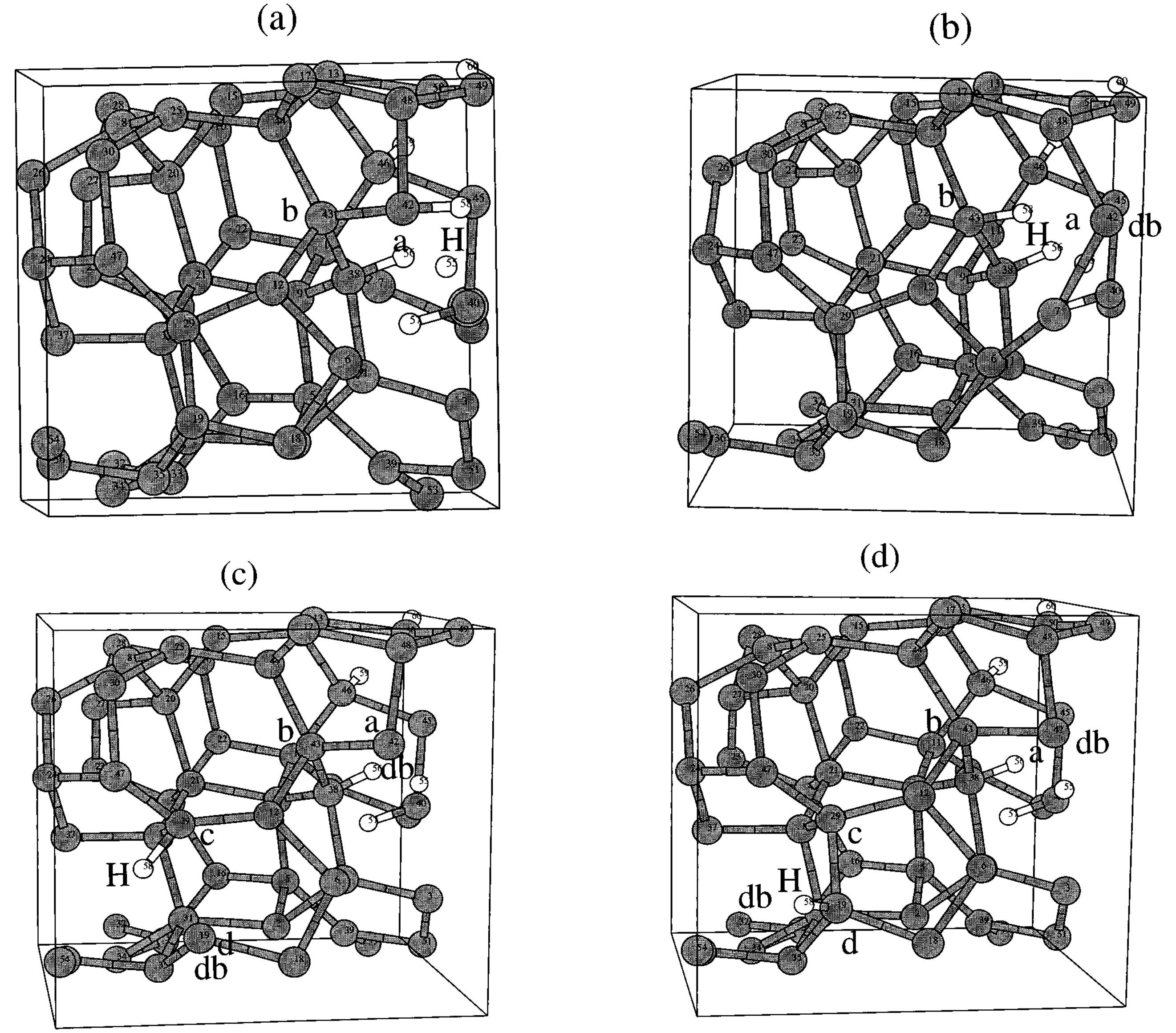

FIG. 2. Atomic configuration of the 60-atom a-Si:H cell. Atoms labeled $a-d$ follow conventions of Eqs. (2) and (3). (a) The initial state with no dangling bonds. (b) One H atom is released from a SiH bond, and bonds to a neighboring Si atom b (43) creating two dangling bonds (db) on the original site a. (c) The H (58) transports through the crystal by bonding to another Si atom c (29) creating a dangling bond on a neighbor atom d (19). The bond between a and b (43-42) is now reformed. (d) The H has moved to the neighboring site d (19)—creating a dangling bond on another silicon site (32). Atoms c (19) and d (29) are rebonded.

manifold of low-energy configurations. The magnitude of the energy barrier (E_b^{tr}) must be ≈ 0.5 eV, a number also found for c-Si. Otherwise diffusion from one broken bond site to another would not occur at typical experimental temperatures (200 °C). Experimentally the activation energy of high concentration H diffusion from an external plasma source is somewhat similar for a-Si:H [0.77 eV (Ref. 11)], polycrystalline Si [0.63 eV (Ref. 12)], and c-Si [0.72 eV (Ref. 12)], leading to similar diffusion constants in these materials.

Traditionally more relaxed states, such as the family of low-energy configurations here, would have larger energy barriers between them. Such a picture would be true for crystalline silicon where H diffuses as an interstitial, and barriers between interstitial configurations control diffusion. However this reasoning does not apply to a-Si:H. In a-Si:H the rate-limiting step in diffusion is the breaking of a SiH bond and release of H to a transport state. The large activation energy of SiH bond breaking ($E_{\mathrm{act}} \approx 1.5$ eV) controls diffusion rather than the much smaller energy barriers (E_b^{tr}) between transporting configurations [schematically, dots in Fig. 1(b)] which are far less than 1.5 eV. A change of a few tenths of an eV in the barrier E_b^{tr} would not be significant at typical H-diffusion temperatures.

DISCUSSION

The low-energy configurations found in Fig. 1 also include cases where the mobile H can break a Si—Si bond on an Si—H site, creating an SiH_2 configuration. This creates the possibility of the two H on the same site to exchange with each other. We should point out that our calculations are for the H diffusion from an isolated Si—H site. H—H repulsion, which is not included in our calculation, will further decrease the activation energy for H diffusion, if the diffusing H is initially from a region with clustered H.

The number of hydrogen in the transporting state $[\approx N_H \exp(-E_{\mathrm{act}}/kT)]$ and the number of accompanying dangling bonds is very small ($\ll 10^{14}$ cm^{-3}) since the activation energy E_{act} is 1.5 eV. Hence the ESR signal of the transporting dangling bond and its interaction with the diffusing H is below the detection threshold.

In our mechanism the diffusing H is bonded to a silicon and hence is in the neutral charge state, when the H is in the manifold of low-energy bonding configurations. The Fermi-level position will instead control the charge state of the transporting dangling bond—which will be positively charged for p-type and negatively charged for n-type material. Such charged dangling bonds will be affected by electric fields. However the H need not be neutral throughout the diffusion process. When H moves to the migration saddle point [Fig. 1(b)] between such two Si-H configurations, it too may be charged. Recent observations[13] find that strong electric fields induce H motion near p-i or n-i interfaces in a-Si:H solar cells.

Our mechanism has several important consequences. The two dangling bonds created when H is released to a transport state can be charged if the Fermi level (E_F) is away from midgap. The energy gain of creating a charged dangling bond is $|E_F - E_d| - U$. Here E_d is the relaxed energy of the dangling-bond level, and U is a bare correlation energy. During light soaking H may be released from SiH bonds. The photoexcited electrons and holes can be captured by the gap state levels created during the release of the H from the SiH bond. This results in a decrease of the energy barrier or a lower activation energy in the presence of light as is experimentally found.[14,15] The increased local H motion observed from NMR measurements of dipolar spin-lattice relaxation[16] may be caused by the H released from SiH bonds and the subsequent motion of H through the network by the present mechanism.

The time-dependent slowing of H diffusion is commonly observed. An origin of this could be that our mechanism requires the amorphous network to break and reform Si—Si bonds as a H transports through it. Entropically, not all the silicon bonds in the path of a H can rebond perfectly, leading to structural distortions in the network as H diffusion proceeds. In fact, when the transporting dangling bonds rebond as in Eq. (3), they may not rebond to the same silicon atom, causing changes in the network topology. Process (3) can then be rewritten as

$$\mathrm{Si}_b\text{—H} + \mathrm{Si}_a^* + \mathrm{Si}_c\text{—Si}_d \rightarrow \mathrm{Si}_b^* + \mathrm{Si}_a\text{—Si}_d + \mathrm{Si}_c\text{—H}. \quad (5)$$

This will increase the strain buildup in the network as H diffusion proceeds. As more H diffuses, such structural changes can generate deeper traps for the H, and the diffusion can decrease with time. Experimental observations[17] suggest structural relaxation processes occurring during H diffusion.

CONCLUSIONS

In summary, tight-binding molecular-dynamics calculations have identified a family of low-energy configurations where H atoms can bond to silicon atoms. H moves through the amorphous network by successively breaking existing nearby Si—Si bonds and simultaneously forming an intermediate Si—H bond with one of the Si, thereby creating a new dangling bond in the vicinity. The broken bonds may reform once the hydrogen moves away. Thus a diffusing H always carries with it a newly created dangling bond and the motion of hydrogen is closely correlated with the motion of transient dangling bonds in a-Si:H. Tight-binding calculations show that formation energies of these processes generally lies in the range of 1.3–2.3 eV.

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