

Nonradiative Electron-Hole Recombination by a Low-Barrier Pathway in Hydrogenated Silicon Semiconductors

S. B. Zhang and Howard M. Branz

National Renewable Energy Laboratory, Golden, Colorado 80401

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A microscopic pathway for nonradiative electron-hole recombination by large structural reconfiguration in hydrogenated Si is found with first-principles calculations. Trapped-biexciton formation leads to a low-barrier reconfiguration of the H atom, accompanied by crossing of doubly occupied electron and hole levels in the band gap. This crossing represents the nonradiative recombination of the carriers, without multiphonon emission. The proposal provides a mechanism for carrier-induced H emission during metastable degradation of hydrogenated amorphous silicon.

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Nonradiative recombination (NRR) of electron-hole ($e-h$) pairs in semiconductors is a field of broad interest [1]. NRR is of particular interest in the technologically important silicon semiconductors, including crystalline (c -Si), nanoparticulate, porous, microcrystalline, and amorphous (a -Si) forms. Because the probability of multiphonon emission falls exponentially with the number of emitted phonons [2] band-to-band NRR by multiphonon emission is not a significant process in silicon. NRR is mediated by large structural reconfigurations in various solids [1], including alkali-halide salts [3], chalcogenide glasses [4], SiO_2 [5], and GaAs [6], but there remain many open questions, especially the details of the energy transfer mechanism from carriers to the metastable configuration. In this Letter, we propose the microscopic mechanism for a NRR process mediated by structural change in hydrogenated silicon.

Nonradiative recombination in nanocrystalline and porous Si is thought to be dominated by surface defects [7], but structural reconfiguration might also be important in these hydrogenated Si materials. This is suggested, for example, by hydrogenated a -Si (a -Si:H), which exhibits weak luminescence [8] and rapid nonradiative recombination [9] under conditions at which defect recombination is negligible. To account for NRR unrelated to defects, Yelon, Fritzsche, and Branz (YFB) [10] proposed that emission of H from Si-H bonds into a mobile configuration can be a significant recombination channel for high $e-h$ pair densities in a -Si:H. However, they identified no microscopic pathway for the H emission. Some support for the YFB proposal comes from the observation that $e-h$ pair recombination causes enhanced migration of H atoms in a -Si:H films [11,12]. A related phenomenon in a -Si:H is the light-induced creation of metastable threefold-coordinated dangling-bond (DB) defects. This "Staebler-Wronski effect" (SW) [13] is a 25-year-old scientific puzzle that is still not completely understood, but photocarrier-induced excitation of H from Si-H bonds is likely a key step in the process [14–16].

Previous theories postulating H emissions driven by a single $e-h$ recombination fail to provide a convincing mechanism for low-barrier H dissociation from the Si-H bond and they do not provide details of the NRR process. It was suggested [17,18] that Si-H dissociates via a rotation of the H atom (toward a neighboring Si-Si bond) that produces localized levels in the gap. These levels trap and localize the photocarriers which assist the dissociation. However, quantitative study [19] showed that until the H atom is displaced considerably, at a cost of about 1 eV, no such localized levels appear in the gap. We need another theory.

Recently, Mauri and Car [20] described a first-principles study which suggested that two $e-h$ pairs (a biexciton) have a stronger tendency than monoexcitons to self-trap in diamond. In this paper, we explore the formation of trapped biexcitons in a covalent semiconductor, at a Si-H bond in hydrogenated silicon. We find that, using first-principles total energy calculations, recombination of a biexciton in hydrogenated Si can stimulate low-energy-barrier H emission from a Si-H bond into a metastable configuration. There are several key features of this process: (i) Asymmetric distortion of a Si-Si bond creates localized levels that can each be doubly occupied (i.e., form a trapped biexciton). (ii) Subsequent H rotation toward a metastable bond center site (BC) on a neighboring Si-Si bond causes the trapped biexciton to recombine nonradiatively. This NRR occurs when the high-lying electron-occupied level falls and the low-lying hole-occupied level rises until they cross in the gap. (iii) A significant fraction of the biexciton energy is absorbed in promoting H to the metastable configuration. We denote the new H configuration as (H-BC, DB), to include the proximate DB that is created. (iv) From (H-BC, DB), the H may either escape to infinity as mobile H (H_m) or be retrapped to the DB. *This low-activation-barrier pathway provides an explanation for carrier-induced emission of H from Si-H bonds, as well as a mechanism for the defect-independent NRR in a -Si:H.*

The calculation is carried out using *ab initio* pseudopotentials by Troullier and Martins [21] in a plane wave basis set [22] and the local density approximation (LDA) [23]. To study H dissociation induced by the biexciton, we remove two neighboring Si atoms from a cubic, 64-atom *c*-Si unit cell and passivate the resulting six Si DBs by H atoms. We calculate the total energies of the Si and Si:H systems using a 10 Ry kinetic energy cutoff and a two special *k*-point scheme in the supercell Brillouin zone sum. The calculated band gaps are 0.7 and 0.8 eV for *c*-Si and *c*-Si:H, respectively. The LDA approximation causes this 0.4 eV underestimation of the band gaps. Because there is no periodicity in *a*-Si:H, the extended states are dispersionless. Therefore, we take the calculated gap between the *k*-point average of the extended states in the *c*-Si:H cell as a representative mobility gap for *a*-Si:H: It is ~ 1.5 eV, near the measured mobility gap of 1.7 to 1.9 eV in *a*-Si:H. The simple H-rotation dissociation pathway in *a*-Si:H was studied previously in *c*-Si [18,19]; here we examine the path using an *a*-Si:H model of 61 Si and ten H atoms [24] to evaluate the effect of amorphization. The calculated gap between the tail states in the *a*-Si:H model is 1.0 eV, underestimating the measured *a*-Si:H gap by 0.7 to 0.9 eV. All atoms not subject to explicitly stated constraints are relaxed according to the forces. The calculated H emission barrier from Si-H to (H-BC, DB) in *c*-Si:H agrees to within 0.1 eV with the previous LDA calculations [17,18] performed at an 18 Ry cutoff but with a supercell half the size of ours.

The simple H-rotation dissociation pathway.—We study this pathway in *amorphous* Si:H, and compare results to the previous *crystalline* Si:H calculations [18]. In *a*-Si:H, all of the Si-H bonds are strong, but the strength of adjacent Si-Si bonds and the H reconfiguration energies are site dependent. Our calculations indicate a slightly lower emission barrier at H sites near a weak Si-Si bond. We remove a charge-neutral H atom from the Si-H bond, leaving behind a Si dangling bond. We then place the neutral H atom into a separate *a*-Si:H supercell at a BC site, and separately at the analog of the *c*-Si's tetrahedral T_d -symmetry (TD) interstitial site. In *c*-Si:H, the BC site is a local energy minimum 2.5 eV above the ground-state Si-H configuration [17], while near the TD site is a saddle point, 0.2 to 0.3 eV higher in energy [25]. We obtain 2.2 eV for H on the BC site and 2.4 eV for the TD site in *a*-Si:H. The 0.3 eV reductions of the BC and TD site energies in *a*-Si:H, relative to *c*-Si:H, are primarily the effect of strain relaxation at the weak (10%-stretched) Si-Si back-bonds in the initial *a*-Si:H configuration.

In the actual mobile H emission process, the H atom must move in steps. It hops from one BC site to another, passing through the saddle TD points. The initial H emission step to the nearby BC site, (H-BC, DB), requires a large energy because the H displacement breaks the Si-H bond. In (H-BC, DB), the H atom is (+1) charged and the DB is (-1) charged (in electron units). This is because the DB energy is near the valence band maximum (VBM)

while the H-BC orbital energy is near the conduction band minimum (CBM).

Figure 1(a) shows the total energy curve (solid line) for such an initial hop, where the H atom is simply rotated from $\Theta \approx 110^\circ$ to $\Theta \approx 0^\circ$ to form (H-BC, DB). The Fig. 1 inset defines Θ . The energy barrier to this rotation, ΔE_b , is 1.4 eV. The energy barrier for the reverse process is 0.3 eV; thus (H-BC, DB) is metastable. The final energy difference between (H-BC, DB) and the ground-state Si-H configuration is 1.1 eV, compared to 1.5 eV in *c*-Si [17]. Thus, hopping farther away to distant BC sites in *a*-Si:H requires $2.2 - 1.1 = 1.1$ eV, to overcome the Coulomb attraction between the mobile H atom (H_m^+) and the DB^- . The Coulomb interaction is long range and decays slowly with the displacement of H_m^+ from DB^- ; it disappears once either is neutralized.

Figure 1(b) depicts the highest-occupied and the lowest-unoccupied molecular orbitals (HOMO and LUMO) through the H rotation to (H-BC, DB). The LUMO state never drops significantly below the CBM, while the HOMO state remains below the VBM until the H atom is rotated from $\Theta \approx 110^\circ$ to 60° . Hence, photogenerated *e-h* pairs can have *no* effect on the H dissociation through exciton localization until the H is displaced significantly—over an energy barrier greater than 0.8 eV. Indeed, our calculations with one or two *e-h* pairs in the HOMO and LUMO states (i.e., exciton or biexciton)

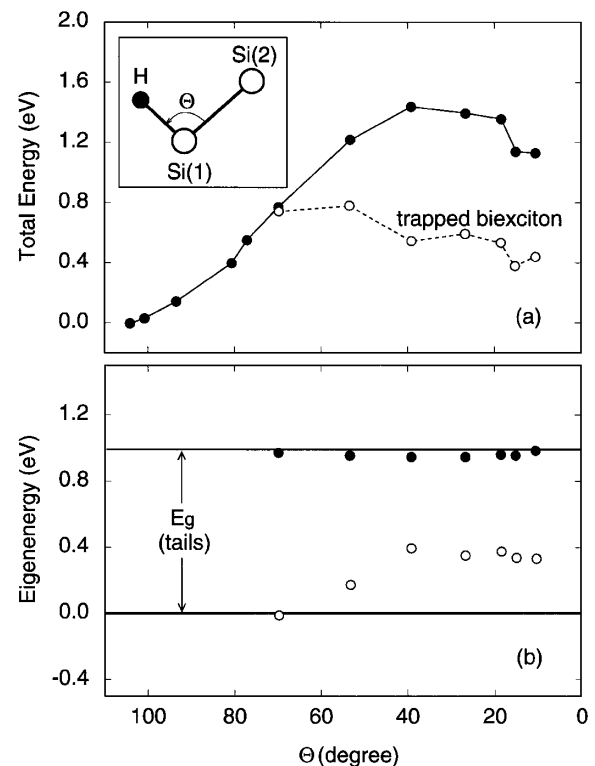


FIG. 1. (a) Total energies and (b) corresponding HOMO (\circ) and LUMO (\bullet) eigenenergies as functions of the angle of H rotation, Θ , defined in the inset. Horizontal lines in (b) indicate the energy gap, E_g . The dashed line in (a) shows the total energy (shifted by $2E_g$) with a trapped biexciton on the levels in (b).

show no sign of barrier reduction down to this value of $\Theta \approx 70^\circ$. The dashed curve in Fig. 1(a) shows the total energy with a biexciton in the HOMO and LUMO states, shifted in energy by $2E_g$. The biexciton becomes trapped when either of the states moves into the gap and the wave function becomes localized. Because of the large energy barrier with and without excitons, this simple H-rotation dissociation pathway can explain neither the observed nonradiative exciton recombination nor the H emission step in the SW effect at room temperature and below. More important, the minimum HOMO-LUMO gap in Fig. 1(b) is 0.55 eV, too high for NRR by multiphonon emission.

The low-energy bixceton H-dissociation pathway.—We study this pathway in the *c*-Si:H supercell, because it is easy to quantify the atomic displacements. We find the following low-energy-barrier (<0.4 eV) pathway that leads from the Si-H ground state configuration to the metastable (H-BC, DB) configuration in the presence of biexciton. The Fig. 2 inset illustrates three coordinates that describe the configuration, d_{Si} , d_{H} , and Θ ; $D_{\text{Si}(1)}$ is the position of Si(1) in the lattice. Along the entire path illustrated in Fig. 2, the Si-H bond length, d_{H} , is nearly a constant. We describe the changes in $(d_{\text{Si}}, \Theta, D_{\text{Si}(1)})$ by $(\delta d_{\text{Si}}, \Theta, \delta D)$, where δd_{Si} is the change in d_{Si} and δD is the change in $D_{\text{Si}(1)}$. Figure 2(a) shows the total energy of the new low-energy path for biexciton occupation. There are three steps in the process: (i) We displace Si(2) away from the stationary Si(1) by δd_{Si} , while Θ remains roughly constant.

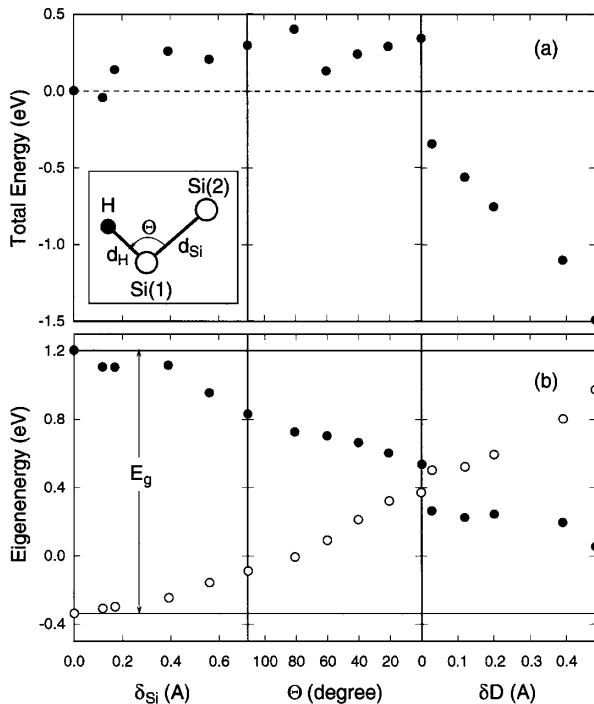


FIG. 2. Same as Fig. 1 but for the asymmetric dilation H rotation pathway described in the text. Total energy (a) is for biexciton occupation. Coordinates δd_{Si} , Θ , ΔD are defined in the text. Indicated total energies are an upper bound to the actual path.

This asymmetric bond stretching increases the total energy by only 0.26 eV at $\delta d_{\text{Si}} \sim 0.4$ Å but immediately brings levels into the gap that enable trapped biexciton formation. (ii) We rotate the H into the BC site (from $\Theta \sim 110^\circ$ to $\Theta \sim 0^\circ$), while δd_{Si} remains roughly constant, and find a maximum additional barrier of 0.15 eV. (iii) We relax Si(1) and Si(2) through (δD) without significant change of either δd_{Si} or Θ , which reduces the total energy by an additional 1.5 eV. We have not made an exhaustive search of the energy surface in the $3D$ - $(\delta d_{\text{Si}}, \Theta, \delta D)$ configuration space; an optimal path with a much lower energy barrier could undoubtedly be found. However, there are several key features illustrated by the pathway shown in Fig. 2.

(a) An asymmetric dilation brings localized states into the mobility gap of *a*-Si:H with negligible barrier: This permits trapped biexciton formation which leads to the recombination.

(b) An asymmetric dilation creates two Si dangling bonds with different characters: The asymmetric bond-breaking mechanism here parallels the DX [26] distortion in crystalline III-V compounds. In *c*-Si:H, we find two Si-derived DBs; the one associated with the displaced Si(2) is DX-like and *near* the VBM, while the DB* on Si(1) is the usual sp^3 -like state. In contrast, a symmetric dilation would result in two nearly identical dangling bonds.

(c) The HOMO-LUMO gap closes to zero upon H rotation: This is the key to reaching the low-energy final state over a low barrier but with neither photon nor phonon emission; the biexciton-occupied levels actually cross in the gap. The behavior of the gap states along the NRR path in Fig. 2(b) is illustrated schematically in Fig. 3(a), which also identifies the associated orbitals. As the H atom then rotates towards Si-H-Si, the DB* on Si(1) rotates in the opposite direction and becomes the DB in (H-BC, DB). In contrast, Fig. 3(b) shows a schematic diagram of the gap states for the simple H-rotation path

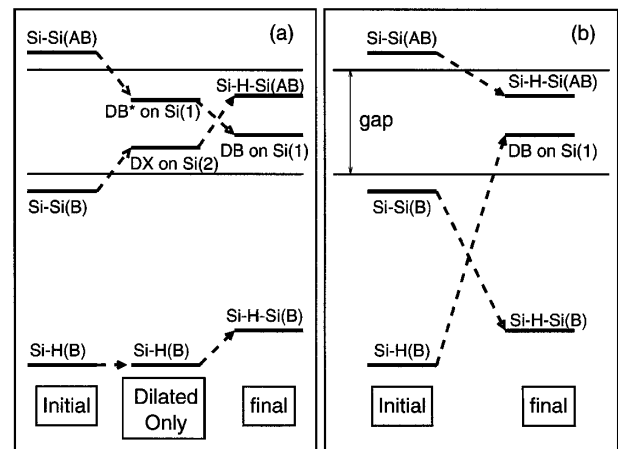


FIG. 3. Schematic diagrams of the evolution of HOMO and LUMO eigenenergies during H rotation from $\Theta \sim 110^\circ$ to near 0° for (a) asymmetric dilation and H rotation, and (b) for simple H rotation. Antibonding (AB) and bonding (B) states are indicated.

of Fig. 1(b). In this case, the Si-H bond breaks, leaving behind a DB when the H rotates into the neighboring Si-Si bond. The Si-Si bonding and antibonding states evolve to the Si-H-Si bonding and antibonding states, respectively, and there is no level crossing. The minimum HOMO-LUMO gap in Fig. 2(b) is 0.16 eV. A gap this small facilitates NRR even if the levels repel each other rather than cross, because recombination requires the emission of only a few phonons. Nonetheless, we confirm the level crossing by tracking the characters of the evolving states. Spatial separation of the HOMO and LUMO wave functions prevents radiative recombination during the level crossing.

(d) The level crossing is the nonradiative recombination of the biexciton: Figure 2(b) shows how the two photo-generated electrons (initially in the LUMO state near the CBM) evolve to near the VBM, while the two photogenerated holes (initially in the HOMO state near the VBM) evolve to near the CBM. The biexciton is thus annihilated and a portion of the photoexcitation energy is absorbed into the H reconfiguration.

We also studied the asymmetric [111] displacement of a Si (δ_{Si}) in *c*-Si, without H. A trapped biexciton greatly “weakens” the Si-Si bond and the total energy decreases slightly with Si displacement up to $\delta_{\text{Si}} \approx 0.8 \text{ \AA}$. However, the HOMO-LUMO gap does not close to zero. The minimum Γ gap is 0.34 eV at $\delta_{\text{Si}} = 1.0 \text{ \AA}$ and the minimum *k*-averaged gap is 0.46 eV at $\delta_{\text{Si}} = 1.4 \text{ \AA}$. Thus, nonradiative recombination in *c*-Si must be a slow-multiphonon emission process. Also, there is no barrier in *c*-Si that prevents reemission of the trapped biexciton and a return to $\delta_{\text{Si}} = 0$. Thus, excess carriers do not cause metastable structural change in *c*-Si as they do in *a*-Si:H.

In light of our newly discovered NRR pathway (Fig. 2), we propose a representative mechanism for light-enhanced H diffusion [27] in *a*-Si:H. A photogenerated hole can trap at the localized HOMO level when a low-energy asymmetric distortion occurs. This positively charged center attracts an electron to the localized LUMO level, neutralizing the site. Then, either a second hole-trapping or direct photoexcitation of a HOMO electron into the CBM charges the center positively. Finally, a second electron capture forms the biexciton and drives the defect downhill into NRR by metastable reconfiguration to (H-BC⁺, DB⁻). After the NRR, further electron and hole trapping on localized levels neutralizes the Coulomb binding and permits the H to hop to a neighboring BC site where it is fully mobile. Based upon this mechanism, light-induced diffusion in *a*-Si:H could be enhanced by infrared excitation of both Si-Si stretching and Si-H bending modes.

In summary, our first-principles total energy study of the mechanism of H emission from Si-H bonds in hydrogenated silicon identifies a low-barrier H emission pathway that involves the trapping of not one but two electron-hole pairs. Thus, one model resolves two long-standing

experimental puzzles in *a*-Si:H (1) the nonradiative decay of light-induced carriers and (2) the mechanism of carrier-induced H emission from Si:H bonds.

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