

Hydrogen Flip Model for Light-Induced Changes of Amorphous Silicon

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We propose a new metastable defect associated with hydrogen atoms in amorphous silicon. A higher energy metastable state is formed when H is flipped to the backside of the Si-H bond at monohydride sites. The defect is described by a double-well potential energy. The dipole moment of this “H-flip” defect is larger and increases the infrared absorption. This defect accounts for large structural changes observed on light soaking including larger infrared absorption and volume dilation. [S0031-9007(99)08713-X]

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Hydrogenated amorphous silicon (*a*-Si:H), a material with many technological applications, suffers from the well-known light-induced degradation or Staebler-Wronski effect [1]. The characterization of the Staebler-Wronski (SW) effect and its microscopic origin has attracted intense scientific studies. The SW effect involves the creation of metastable silicon dangling bonds with midgap electronic states at densities of 10^{16} – 10^{17} cm⁻³. There are strong indications that hydrogen is involved in the degradation [2], since annealing of metastable defects occurs at temperatures (>180 °C) where H diffusion becomes important.

In the past few years several new experimental measurements of the SW effect have demonstrated additional changes of the amorphous network [3–8] that exceed the low density of dangling bond (D^0) defects. Infrared absorption [4] and x-ray photoemission [5] find changes involving $\approx 10^{19}$ cm⁻³ sites on light soaking. Nuclear magnetic resonance [6], $1/f$ noise statistics [7], compressive stress, and photodilation [8] all indicate metastable changes to the network that are much larger than the small fraction of sites (10^{-6} – 10^{-5}) at which the dangling bond D^0 defects are formed. The origin of these large structural changes is unclear. Recently, mobile H has been suggested [9] to cause such changes. We propose a simple “H-flip” model of rearrangements of bonded H atoms that accounts naturally for many of these new observations. These metastable H rearrangements occur *in addition* to the formation of metastable dangling bonds. Another aspect that we find closely related is the anomalous low temperature properties [10] universally found in amorphous solids that indicate the existence of a broad distribution of low energy excitations.

Our starting point is a 240-atom or 60-atom *a*-Si:H cell where all the H are in monohydride (Si-H) groups. This cell has been very successful in modeling *a*-Si:H [11,12] with the tight-binding molecular dynamics model used here.

Our basic finding is that H atoms in monohydride configurations in *a*-Si:H surprisingly have *two* bonding

configurations with differing energies. The lower energy configuration is the normal tetrahedral bonding, with a H-Si₁ bond length of 1.48 Å and a distribution of H-Si₁-Si bond angles around tetrahedral (Fig. 1). In the higher energy configuration (Fig. 1), H is bonded to the same Si₁ atom but in its backplane. Effectively, the H atom is flipped to the backside of the H-Si bond. The Si₁ also moves about 0.5 Å into the backplane, resulting in a very similar H-Si₁ bond length. The movement of the Si₁ into the backplane helps the defect to form. In the H-flip configuration the back bonds of the Si₁ atom become more planar, with the H-Si₁-Si bond angles deviating away from tetrahedral and toward 90°. The Si displacements at this defect are similar to the floppy mode eigenvectors previously found for dangling bonds [13] in *a*-Si.

All the H atoms in our model display these two locally stable energy states. The flipped configuration is a metastable local minimum calculated to be between 0.18 and 0.7 eV higher than the original configuration (Table I). The energy of the H-flip defect (Fig. 2) scales well with the average bond angle on the Si₁ site. Monohydride sites that are distorted toward planar are easier to convert to the H-flip defect and have a lower defect energy. We have checked these tight-binding results by performing *ab initio* calculations and found very good agreement. Using the *ab initio* Car-Parrinello method with plane wave cutoffs of up to 18 Ry, we also found locally stable configurations with very similar geometries as the tight-binding results for two of the H sites we examined. These *ab initio* calculations predicted defect energies that were within 0.05–0.12 eV of the tight-binding results.

A substantial energy barrier exists between the original (Fig. 1a) and metastable H-flip defect (Fig. 1b) configurations. We examined a few simple transition paths between the two configurations and found lower barriers (~ 1.8 – 2 eV) when H passes between the Si-Si₁ back bonds [analogous to a bond-centered (BC) site in *c*-Si], accompanied by relaxation of the Si atoms (Fig. 1c). Finding optimized transition paths in this complex network requires recent activated techniques [14] for exploring the global

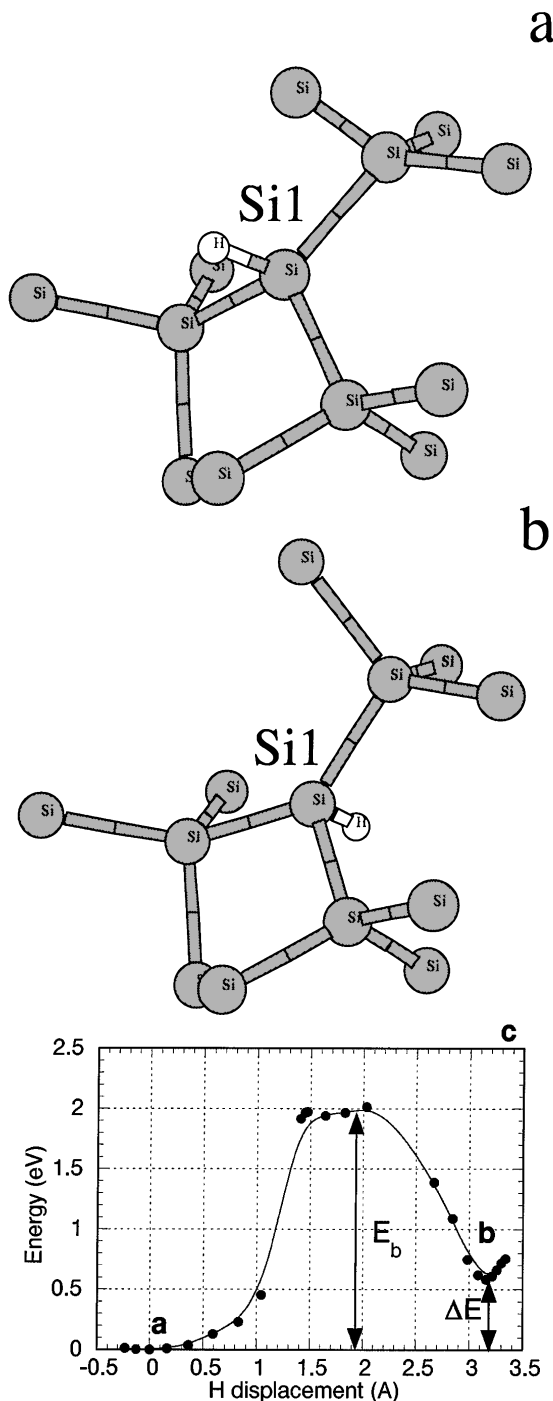


FIG. 1. (a) Normal bonding configuration for a H atom at a silicon site (Si_1) in the $a\text{-Si:H}$ network. For clarity only a portion of the network up to the second neighbor shell of Si_1 is shown. (b) The higher energy H-flip defect where the H is at the backplane of Si_1 . The Si_1 also moves ≈ 0.5 Å. (c) A calculated double-well potential energy surface connecting configurations (a) and (b). The H approximately moves in an arc through the $\text{Si}_1\text{-Si}$ back bond. The network was relaxed for each H position. The line is a smooth fit to the calculated energies (circles).

energy surface. We may adopt the experimental activation energy for H diffusion of ~ 1.5 eV for the estimated energy barrier between the Figs. 1a and 1b configurations.

This value is also supported by *ab initio* calculations of the BC state in $c\text{-Si}$ [15]. Each H atom then resides in a double-well potential energy surface (Fig. 1) with the energy wells (Figs. 1a and 1b) differing by an energy (ΔE) and separated by an energy barrier (E_b) close to 1.5 eV. We expect a uniform distribution of energies (ΔE) would emerge in calculations for large $a\text{-Si:H}$ models. The energy surface of the amorphous material then has multiple local minima connected by H motions. This is among the first identifications of a simple double-well potential configuration in amorphous semiconductors.

These defects can be connected to light soaking since the recombination energy of photoinduced carriers can promote H to the H-flip bonding defect over the energy barrier E_b . Another connection between light soaking and H motion has recently been developed by Branz [9]. Recombination of photoinduced carriers generates sufficient energy (~ 1.5 eV) to break Si-H bonds and creates mobile H [9], which diffuses through the network and was suggested to cause structural changes [9]. With molecular dynamics we found that a diffusing unbonded interstitial H (H'_i), approaching the backplane of a normal Si-H bond, can break the SiH bond and form a new distorted Si-H' bond where the H' configuration is flipped. The first H is released as an interstitial. The two H effectively exchange, through



suggesting that the H-flip defect can be created by the motion of mobile H during light soaking. When H diffusion occurs at a higher temperature, the defect can be flipped back to its original configuration by a diffusing H atom, through the reverse of (1). This process may be an important component of H-D exchange during H diffusion [16].

This new H-flip defect accounts for several recent observations of light-induced changes, including the unexplained increase of infrared (ir) absorption [4]. The integrated ir absorbance I is proportional to the H content N_H through $N_H = AI$. The absorption coefficient A is inversely proportional to the square of the dynamic effective charge e_d^* of the oscillator mode (i.e., $A \propto e_d^{*-2}$). The oscillator strength is dominated [17] by the dynamic effective charge e_d^* , rather than the static contribution.

At the H-flip defect the back bonds of the Si_1 are weakened resulting in a charge transfer or slight increase in the

TABLE I. Energy of H-flip defects ΔE , their dynamic effective charge e_d^* before (original) and after formation of defect, and the volume changes induced by the defects.

H	ΔE eV	e_d^* Original	e_d^* Defect	Volume Change %
55	0.69	0.21	0.46	0.613
56	0.56	0.21	0.40	0.088
57	0.48	0.24	0.39	0.516
58	0.60	0.30	0.48	0.074
59	0.18	0.38	0.36	0.000
60	0.28	0.25	0.30	0.306

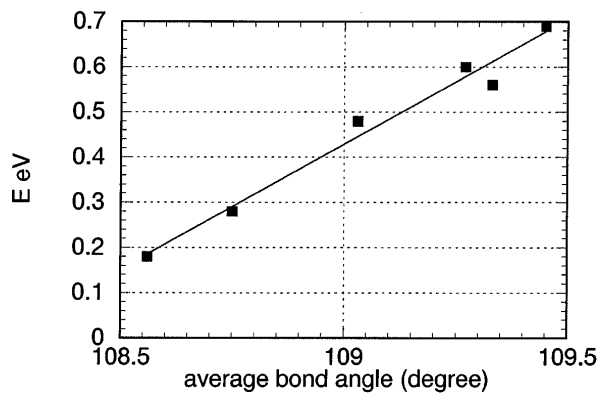


FIG. 2. The energy of the H-flip defect (Fig. 1b) plotted as a function of the average bond angle on the silicon site (Si_1 in Fig. 1a). Each point is for a different H in the $a\text{-Si:H}$ model.

static effective charge e^* of the H, from the normal bonding state. In the Si-H stretch mode, there is a much larger variation of the effective charge of the defect (Fig. 1b) than the normal configuration (Fig. 1a) (Fig. 3). We calculated the dynamic dipole moment $p(l) = e^*(l) \times l$ as a function of the Si-H bond length (l) (Fig. 3 for a typical case) and extracted the effective charge e_d^* from the slope dp/dl . At every H-flip defect, we find the dynamic effective charge e_d^* increases substantially (by a factor of 1.2–2.2) (Fig. 4) depending on the local geometry. Our interpretation of the ir measurements [4] is that the number of Si-H bonds remains constant unlike earlier suggestions [4]. Instead, a fraction of the Si-H bonds change their bonding environment when the H-flip defects are created, and these defect sites have a substantially larger dynamic charge e_d^* that increases the ir-oscillator strength. This can also explain enhanced Si-H oscillator strengths found after ion bombardment of $a\text{-Si:H}$ [18]. We do not find appreciable Si-H frequency shifts between the Figs. 1a and 1b states.

A density of H-flip defects can be created by either thermal effects or light soaking. To deconvolute these con-

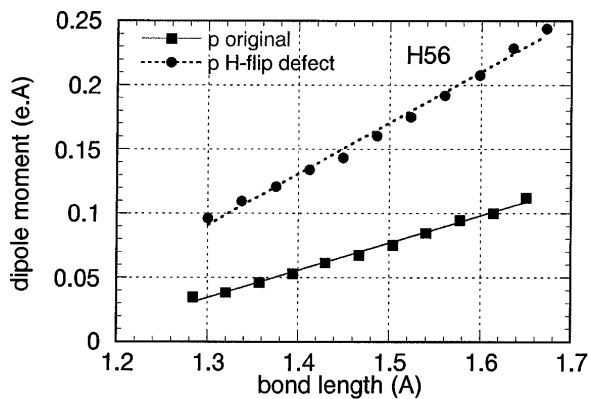


FIG. 3. The dynamic dipole moment ($p = e^*l$) for the SiH stretch mode as a function of the bond length l . Results for a representative H-flip defect are compared with the original bonding configuration. The dynamic effective charge e_d^* is the slope of either plot.

tributions, we used rate equations for thermally induced and light-induced generation and annealing in the double-well system. The strength of the light-induced terms is proportional to the light intensity [9]. Computational details will be published elsewhere. We estimate that light excitation can generate a saturated macroscopic fraction ($\sim 0.5\% - 1\%$) of H-flip defects. For a typical H content of 10% this predicts a macroscopic density of H-flip defects ($\sim 10^{19} \text{ cm}^{-3}$)—much larger than the small density of metastable dangling bonds ($10^{16} - 10^{17} \text{ cm}^{-3}$). When 0.5%–1% of bonded H increase their dynamical effective charge e_d^* by a large factor ($\sim 1.2 - 2.2$, Table I), the increase in ir absorption of the Si-H stretch is (0.75%–1.5%), very similar to the 1% increase observed experimentally [4].

There is a substantial local motion of 3–3.5 Å of the H that have converted to the H-flip defect (Fig. 1). The H-flip defect significantly distorts the local atomic structure around it, through displacements of 0.1–0.2 Å for several neighboring silicon atoms (Fig. 5). We unexpectedly find that other H atoms in the vicinity of this H-flip defect are displaced by 0.1–0.4 Å, involving a reorientation of their H-Si bonds. There is a large local motion of $\sim 1\%$ of H by 3–4 Å and additional smaller local motions of several nearby H by ≤ 0.4 Å. A similar conclusion of enhanced local motion of a macroscopic number of H was reached from NMR measurements of $a\text{-Si:H}$ [6] after light soaking. In our model, the local H-flip defects may be generated by diffusing H, hence one expects a natural correlation between the local H motion and long-range H motion as found earlier [6]. The local motion of H between the normal configuration and the H-flip

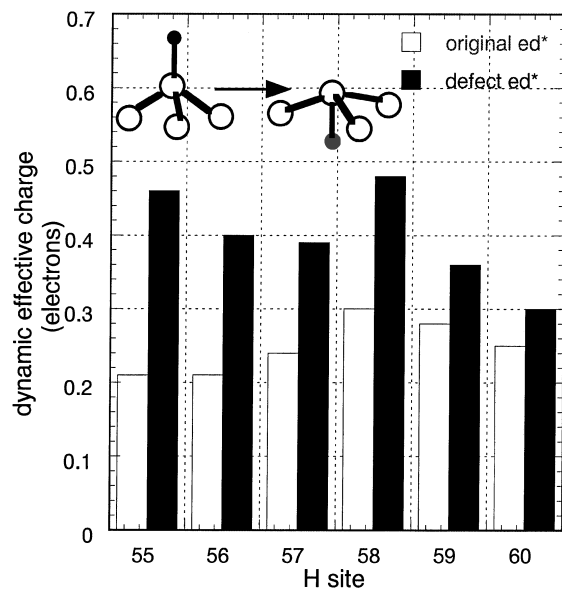


FIG. 4. The dynamic effective charge e_d^* of the SiH stretch for each of the H-flip defects in our model, compared with the initial H configuration. The ir absorption is proportional to the square of the effective charge. The inset is a schematic picture of the structural change.

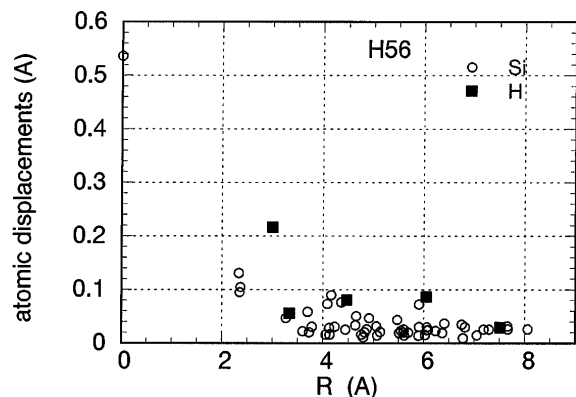


FIG. 5. Local displacements of atoms from their initial positions after formation of a H-flip defect as a function of their distance (d) from the Si_1 site that the H is bonded to. The Si_1 site has the large displacement at $d = 0$. The displacement of the flipped H is large (3.5 Å) and not shown. Results are for a representative defect at H56.

defect, together with atomic distortions in its vicinity, can also generate conductance fluctuations in current-carrying microchannels and may account for the random telegraph noise observed in conductance measurements [7] in α -Si:H. H motion has been suggested [7] to cause these fluctuations.

The H-flip defect induces a small volume expansion of the network (Table I). Since the Si-Si back bonds at this defect site are strained, the network preferentially expands to relieve the bond-angle strain. In our computational 60-atom cell with one H-flip defect, we find (Table I) volume expansions between 0%–0.6% or an average expansion of 0.26%. Scaling the density of H-flip defects to the expected experimental case of $\sim 1\%$ of the H content, we predict volume expansions less than 4×10^{-4} or averaging $(1-2) \times 10^{-4}$. This compares very favorably with the measured increase in compressive stress [8], although it is slightly larger than optical-lever based measurements [19] of the light-induced expansion of the film.

We find the H-flip defect is a high energy local minima in crystalline silicon and consequently less important in c -Si. We calculate the H-flip defect for H at a Si(111) surface to be $\Delta E \approx 0.9$ eV above the initial bonding state. At a hydrogenated vacancy we find an even higher energy of $\Delta E \approx 1.3$ eV. The much higher defect energies in c -Si are because the lattice cannot deform easily to relax the strain, as the amorphous network can. The high energies of the defect imply that the annealing barrier ($E_b - \Delta E$) is only 0.6–0.2 eV in these crystalline systems. Hence at room temperature such defects would easily self-anneal.

We find double-well potentials associated with the H atoms. The fraction of these systems with almost degenerate energy wells ($E \rightarrow 0$) may result in tunneling states that can contribute to anomalous low temperature properties. Quantitatively relating the H displacements at our defect to the observed tunneling states in α -Si:H, whose density can be controlled by varying the H content of hot-wire α -Si:H [10], requires further work.

In conclusion, we have found a new metastable defect in amorphous silicon, involving the flipping of bonded H atoms. This defect has a double-well potential energy surface involving simple atomic displacements and a close connection to two-level systems. This defect occurs in conjunction with the formation of metastable dangling bonds. The dipole moment of the Si-H bond increases accounting naturally for increased ir absorption changes and recently observed metastable changes. We expect this defect to occur in other amorphous group IV materials, α -SiGe:H alloys, or glasses containing H or low-coordinated atoms.

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