Hydrogen rebonding and defect formation in *a*-Si:H

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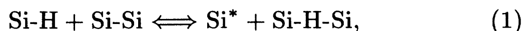
(Received 25 May 1995)

The effect of short-range hydrogen rebonding in creating metastable defects in *a*-Si:H is studied with a tight-binding molecular-dynamics model that takes into account both electronic and structural energies. The formation energy of defects created by transferring hydrogen from Si-H sites to weak Si-Si bond sites is found to scale linearly with the Si-Si bond length. This H rebonding mechanism can account for several features of thermally generated and light-induced defects. This suggests that the bond-length disorder may be the dominant factor in controlling the defect density in *a*-Si:H.

Defect formation in amorphous semiconductors, and in hydrogenated amorphous silicon (*a*-Si:H) in particular, has been of intense interest for fundamental studies and for consequences for device performance.[1] It is now well recognized that both the thermally generated (equilibrium) and light-induced defects in *a*-Si:H are silicon dangling bonds that reduce the efficiency of solar cells. Hydrogen does passivate dangling bonds, but it may play a complex role in also creating metastable defects. Among all the microscopic mechanisms proposed for defect creation, the idea of bond breaking and weak-bond to dangling-bond conversion[1–5] provides the basis for much of our current understanding of the defect creation and metastability in *a*-Si:H. However, further progress in understanding what controls the defect density or the quality of the material requires reliable information on the energetics of the defect creation processes.

In this paper, we present tight-binding molecular-dynamics simulations of dangling-bond formation energy over several defect sites in a computer-generated *a*-Si:H model and demonstrate the importance of the bond-length disorder in controlling the total defect density of the material. We find the H-induced process can account for both thermal and light-induced defect creation. However, this H-induced process does not preclude the occurrence of other defect creation mechanisms that may be operating simultaneously.

The fundamental H-induced defect creation process we study involves transferring the hydrogen from a Si-H bond site to a weak Si-Si bond, leaving behind a dangling bond (Si*) and producing a H defect complex at the weak Si-Si bond. This process, represented by



$$\text{Si-H} + \text{Si-Si} \Longleftrightarrow \text{Si}^* + \text{Si-H-Si}, \qquad (1)$$

has been proposed by Smith and Wagner[3] and Street and Winer[4] as the underlying mechanism of defect equilibration in *a*-Si:H networks. This process has also been invoked as a possible microscopic model for the light-induced degradation (i.e., Staebler-Wronski effect[6]) in *a*-Si:H. The hydrogen insertion reaction occurs during film growth where excess H from the growth flux anneals weaker Si-Si bonds at the growth surface. H diffusion in *a*-Si:H involves the motion of H in a transport state, from where it may be trapped in a weak Si-Si bond such as in reaction (1). Hence a quantitative knowledge of the energetics of this H-rebonding process is fundamental to an understanding of hydrogen in the amorphous network, and applicable to several diverse processes in *a*-Si:H.

Our calculations are based on the tight-binding molecular-dynamics approach,[7] which has emerged as a versatile tool for the study of complicated processes and simulates cells of several hundreds of atoms for which first principles calculations may not be feasible. The reliability of this approach has been demonstrated through extensive simulations of the structural and dynamical properties for silicon and carbon, including bulk crystalline structures, point defects, amorphous and liquid states, and C clusters. In this approach, the electronic states are approximated by a superposition of atomic orbitals. By fitting the parameters of the Si-Si and Si-H model to both *ab initio* calculations and experimental data, we have been able to successfully model[8,9] a wide range of properties of crystalline silicon, Si-H vibrational properties in good agreement with experiment, and the energy surface of H in *c*-Si, including the stability of bond-centered H for positive and neutral charge states and tetrahedral-interstitial H for the negative charge state. Most importantly, the tight-binding model describes well the electronic and structural properties of *a*-Si:H models. H diffusion in *c*-Si has also recently been successfully modeled with tight-binding molecular dynamics.[10]

The defect formation energy of (1) is the difference in total energy before and after the reaction, calculated after full relaxation with a steepest-descent algorithm. The total energy includes the electronic, lattice, and Coulomb energies associated with charge-transfer effects, and, most importantly, includes the large structural relaxation energy that would not be accounted for by approximating energies from differences in one-electron levels. We have systematically studied insertion of H into distinct Si-Si bonds with H from a Si-H site. We utilize our computer generated *a*-Si:H model[8] of 272 atoms with periodic boundary conditions, containing both SiH and SiH_2 species.[11]

Light-induced defects have a low probability (10^{-5}, for a saturated defect density $N_{\text{sat}} \sim 10^{17}$), implying that such a defect site is highly improbable in a finite-size model of a few hundred atoms. A manifestation of this problem is the occurrence of weak bonds with extensions

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of at most 0.15 Å in our *a*-Si:H configuration. To overcome this problem we systematically created strained *a*-Si:H configurations by expanding the periodic unit-cell dimensions in increments between 1.5% and 6.5%. The dilated unit-cell dimensions are held constant, while all the Si and H atoms are allowed to locally relax with a steepest-descent minimization. While the Si-H bonds do relax to their original bond length, the Si-Si bonds are uniformly expanded in the dilated cells, resulting in considerably weaker Si-Si bonds and in the systematic generation of defect sites that have low probability in the original relaxed cell.

The formation energies of reaction (1) have been calculated at more than 70 different sites (Fig. 1). The defect formation energy of (1) strongly correlates with the Si-Si bond length (Fig. 1), indicating that the bond length is the primary factor determining the defect formation energy. For the narrow range of bond lengths in the original cell ($\Delta R < 0.15$ Å), (1) has a large formation energy of 2–3 eV and is not favored. However, at weaker Si-Si bond sites (in the dilated cells) the formation energy reduces dramatically to < 1.0 eV for weaker bonds with $\Delta R > 0.3$ Å. Remarkably, the defect formation energy scales almost linearly with the bond-length deviation, over the large variations of the bond length, and is approximately given by

$$E = 2.5 \text{ eV} - \alpha \Delta R, \quad (2)$$

where $\alpha \approx 6.3$ eV/Å. The linear relation allows extrapolation to the region of low formation energy. This scaling behavior also extends to the region of small bond lengths and large formation energies ($\Delta R < 0$ in Fig. 1). Notably, the *ab initio* calculations of Tarnow and Street[12] of formation energies of (1) caused by angular distortions of a Si-Si bond also fall on our scaling line (Fig. 1), lending further confidence to the scaling result. Also, *ab initio* calculations of Van de Walle and Street[13] for H insertion into a normal bond in *c*-Si yield a value of 2.5 eV, in excellent agreement with our calculations [at $\Delta R = 0$ in (2)]. A recent *ab initio* calculation by Van de Walle and Nickel[14] also shows the linear dependence on the bond length in *c*-Si, with a value of $\alpha = 4.6$ eV/Å. Generally somewhat larger atomic relaxation and larger α is expected in *a*-Si:H where atoms may more easily accommodate the H-induced defect.

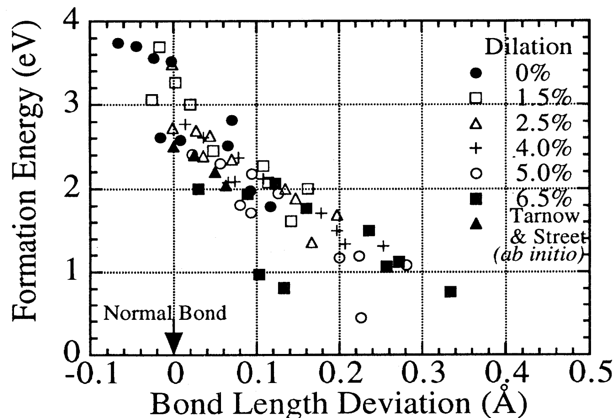
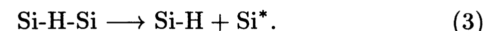


FIG. 1. Formation energy for the reaction (1) that creates a dangling bond as a function of the weak Si-Si bond-length deviation. The different symbols illustrate the calculations in the original cell (0%), and the cells that were dilated by 1.5–6.5 %. *Ab initio* calculations of Ref. 12 are also shown. Formation energies scale well with bond-length distortions.

In contrast, the same formation energies plotted against the root-mean-square (rms) bond angle distortion at the Si-Si site do not show any significant correlation (Fig. 2). This is because reaction (1) requires a large expansion of the weak Si-Si bond to accommodate the H, a process that is favored simply by having a larger Si-Si bond length. Also, no correlation of the defect formation energy was found with the magnitude of the average bond angle on the two Si sites. Reaction (1) always results in a single unpaired electron spin at the initial Si-H site. The Si-H-Si complex involves an asymmetric noncollinear configuration of the H between the two Si atoms. When the initial Si-Si bond length is close to the *c*-Si value, the resulting Si-H-Si configuration is the distorted analog of the bond-center configuration found in *c*-Si, and has an unfilled state near the conduction-band tail. However, when the initial Si-Si bond length is elongated, resulting in low formation energy defects, the Si-H-Si complex also results in a singly occupied state near midgap, or another dangling bond at the Si site that is somewhat coupled to the complex,



$$\text{Si-H-Si} \longrightarrow \text{Si-H} + \text{Si}^{*}. \quad (3)$$

The two resulting neutral dangling bonds are spatially separated and do not significantly interact, consistent with electron-spin resonance measurements. A few special cases were found where the defect formation energy is significantly below the scaling line (points in Fig. 1). These involve occurrence of two weak Si-Si bonds on the same Si atom, allowing extra freedom for the H to rebond into a lower energy state.

Assuming the linear relation between the formation energy and the bond-length deviation, as suggested by Fig. 1, we can then obtain the defect formation energy distribution from the Gaussian bond-length distribution.[15,16] The density of Si-Si bonds with an

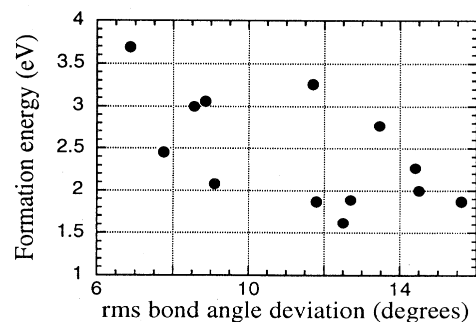


FIG. 2. Dangling-bond formation energy of (1), in the undilated cell, as a function of the rms bond angle deviation from the tetrahedral angle, illustrating no significant correlation. The six bond angles for the two Si atoms in the Si-Si site are used.

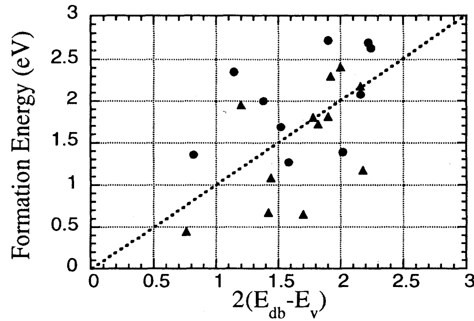


FIG. 3. The formation energy of the metastable defects formed through Eq. (1), as a function of twice the difference in one-electron energies of the dangling bond (E_{db}) and depleted valence-band tail state (E_v), for the two cells with 5% (triangles) and 2.5% (circles) dilation. The procedure for extracting (E_v) is described in the text.

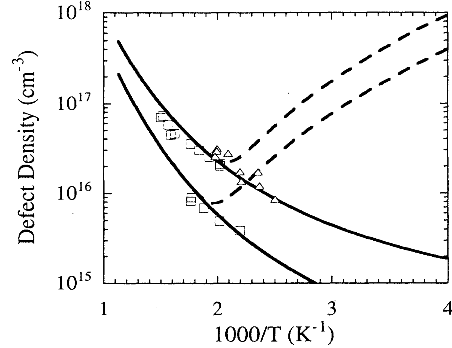


FIG. 4. Thermal-equilibrium (solid line) and light-induced (broken line) densities as a function of temperature, predicted from a rate equation [Eq. (4)]. The measured equilibrium defect densities (squares) for two samples are from Ref. 4, whereas the measured defect density (triangles) is from Ref. 17. The values of σ (300 K) = 0.075 and 0.07 Å are used for the upper and lower curve, respectively, together with values of other parameters in the text. Light-induced defect densities are predicted from the H-relocation mechanism.

extension of ΔR is $N(\Delta R) = \frac{N_0}{\sqrt{2\pi\sigma}} e^{-\Delta R^2/2\sigma^2}$. Here N_0 is the density of Si-Si bonds. The standard deviation of bond lengths σ has been measured to be 0.062 – 0.065 Å at room temperature.[15] Our a-Si:H models indicate the spread of bond lengths for longer bonds ($\Delta R > 0$) exceeds that for short bonds ($\Delta R < 0$). Hence a somewhat larger $\sigma = \sigma^+ \approx 0.065 - 0.075$ Å can describe elongated bonds that have $\Delta R > 0$.

Since the H concentration in device quality samples is substantial, there are always hydrogen atoms available on Si-H sites located within 3–4 neighbor shells around a weak Si-Si bond (unless the H content is lower than 1–2%). Creation of this dangling-bond defect from (1) involves very short-range H motion and not long-range H diffusion. Hence such a defect can be annealed out by only local atomic rearrangements. The relocation of H from a Si-H site to the Si-Si involves the H surmounting local energy barriers to attain a transport state with energy E_{tr}, followed by trapping at the weak-bond site — a complex process which needs to be studied with further dynamical simulations.

Previous defect equilibria models[3,4] of thermally induced defects are based on conversion of band tail states of weak Si-Si bonds into midgap dangling bonds. The formation energy was estimated by the difference in the one-electron energies, together with an additional entropy gain on dangling-bond formation. The density of thermal defects correlated with the slope of the valence-band tail in agreement with experiment. We examine this approach by extracting an approximate valence-band tail state energy (E_v) of the Si-Si bond that is removed by reaction (1) by subtracting the sum of one-electron energies of valence-band tail states before and after reaction (1). More precisely, E_v represents a region from which the valence-band tail states are most strongly depleted. The calculated defect formation energy differs substantially from the difference ($E_{db} - E_v$) of one-electron energy levels (dotted line in Fig. 3), since there is large lattice relaxation and lattice strain energy accompanying the H insertion. Notwithstanding the absence of correlation with the actual formation energy, the difference in one-electron energy levels nevertheless falls in the same range. This may partially explain why the previous defect equilibration approaches[3,4] were successful. To calculate the defect density, we need (i) to take the calculated formation energies from tight-binding simulations and (ii) to use the distribution of weak bond lengths in a-Si:H, rather than the valence-band tail state energies. The valence-band tail or the Urbach energy may be more closely coupled to the bond angle disorder, rather than the distribution of bond lengths, appearing in the H-induced reaction here.

The temperature-dependent defect density resulting from the equilibration between Si-H bonds and the Si-bonding network is determined by applying thermal-equilibrium defect expressions[4] to our defect formation energies, and found to be of the order of 10^{16} around 400 K (Fig. 4) for values of σ (300 K) from 0.07 to 0.075 Å. The annealed-state defect density is, in fact, a measure of the bond-length standard deviation σ. The predicted defect density agrees well with previous work[3,4] and measured thermal-equilibrium values,[4,17] including small calculated activation energies (of 0.15–0.25 eV from a linear approximation to the measurement region in Fig. 4).

The saturated light-induced defect density results from a balance between light-induced creation and light-induced and thermal annealing of the defects.[18,19] Light-induced processes are beyond the scope of the present calculations. A qualitative estimate of light-induced defects may, however, be obtained by using the rate equation approach[18] with (a) both light-induced creation (A) and light-induced annealing (B) terms dependent on free-carrier densities,[5] and (b) thermal generation to the H-transport energy E_{tr}, involving a thermal annealing energy barrier ($E_{\mathrm{tr}} - E$), where E is the defect formation energy. The saturated defect density requires solving

$$N_{\text{sat}} = \int_0^{E_{\text{tr}}} \frac{2[\frac{A}{N_{\text{sat}}^2} + \nu_0 \exp(-\frac{E_{\text{tr}}}{kT})]N(E)}{\frac{A}{N_{\text{sat}}^2} + \frac{B}{N_{\text{sat}}^2} + \nu_0 \exp(-\frac{E_{\text{tr}}-E}{kT}) + \nu_0 \exp(-\frac{E_{\text{tr}}}{kT})} dE, \quad (4)$$

where ν_0 is the phonon frequency ($\sim 1.4 \times 10^{13}$ Hz) and $E_{\text{tr}} = 1.5$ eV, obtained from hydrogen diffusion measurements.[1] In evaluating $N(E)$ with Eq. (2), we use an Einstein model for the temperature dependence of σ, $\sigma^2(T) = \sigma_0^2 + \frac{\hbar^2}{Mk\theta_E}\coth(\frac{\theta_E}{2kT})$, where $\theta_E = 700$ K is the Einstein temperature calculated from the optical phonon frequency and σ_0 is from structural disorder. The equilibrium defect density (Fig. 4) can be simply extracted from (4) by setting $A = B = 0$.

Values of A and B of $(6.3 \times 10^{14})^2$ for AM1.5 illumination were derived from previous rate equations.[18] The calculated N_{sat} shows a minimum at 450–500 K, above which the thermal term dominates. At low temperature the defect density gradually rises above 10^{17}. A significant difference from previous approaches[18,19] is that the present pool of defects is not limited to a single total value, but has an energy and density distribution. The approach in Fig. 4 and (4) is valid only at higher temperature (above approximately room temperature), otherwise the decrease of the nonradiative efficiency at lower temperature would have to be incorporated. Other rate equations may need to be developed for more accurate comparisons with experiment,[19,20] as well as more quantitative evaluation of the light-induced processes. Although results in Fig. 4 illustrate trends rather than quantitatively accurate densities, this model does allow a direct estimate of the saturated defect density. Annealing barriers are in the range of 1.1–1.3 eV (assuming E_{tr} to be 1.5 eV), in agreement with measurements.[5,19]

In summary, our calculations show the energy of H-insertion reaction into a weak Si-Si bond scales linearly with the bond length of the weak Si-Si bond. We have developed a procedure to systematically generate low probability configurations with our tight-binding calculations and finite-size models. Short-range H motion and rebonding creates dangling-bond defects with single unpaired electron spins, and a low thermal activation energy. These defects can account for several aspects of temperature-induced and light-induced defect densities. The defect density is controlled by the standard deviation of the bond-length distribution — a quantity that characterizes the "quality" of the sample, and which should be probed with further measurement techniques.

This research was supported by the Iowa Energy Center and by the Electric Power Research Institute under the amorphous thin-film solar-cell program. We acknowledge valuable discussions with S. Wagner and collaborations with C.M. Soukoulis and I. Kwon.

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