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Molecular-dynamics simulations of the stability of amorphous silicon

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We have performed molecular-dynamics simulations as a first step towards understanding the Staebler-Wronski effect in amorphous silicon, utilizing classical silicon potentials and computer-generated amorphous silicon structures. A localized hot spot is used to model the nonradiative transfer of photoexcited carrier energy to the lattice. This leads to structural degradation in *a*-Si networks in which weak Si—Si bonds are broken and dangling bonds are produced, requiring a threshold energy of about 0.8–1.0 eV. Thermal annealing of an *a*-Si model with coordination defects is also described.

An outstanding problem in solar-cell technology is the Staebler-Wronski (SW) effect[1] or the light-induced degradation in amorphous hydrogenated silicon (*a*-Si:H). As the light exposure time increases there is an increase in the density of gap states that saturates[2] at a value of the order of 10^{17} cm^{-3}. These structural changes are metastable and can be annealed out by heating. While many aspects of the SW effect have been extensively studied experimentally,[3] a number of basic questions on the microscopic atomic mechanisms underlying the SW effect remain unanswered and several different interpretations have been proposed. It has been proposed that the SW effect is related to the breaking of weak Si—Si bonds and creation of metastable dangling-bond defects.[3] Another view is that the SW effect involves changes in the charge states of already existing charged dangling bonds in *a*-Si:H.[4] An alternative view is that impurities in *a*-Si:H can lead to metastable defect centers.[5] It has also been suggested that the SW effect is caused by the simultaneous creation of pairs of dangling-bond and floating-bond defects.[6]

In this paper our aim is a first step towards understanding the stability of amorphous silicon, and identifying microscopic structural changes underlying light-induced degradation. The results presented here may also be relevant for annealing phenomena and understanding the differences between *a*-Si models developed under different theoretical preparation methods. Our approach is based on the development of molecular dynamics (MD) simulations for silicon with both classical and electronic-structure-based models. MD simulations have computer-generated amorphous silicon (*a*-Si) (Ref. 7) models by both melt-quenching and deposition simulations, that have had much success in describing structural, vibrational,[8] and void properties.[9–11] A complementary approach, pioneered by Wooten, Winer, and Weaire (WWW), generated[12] an *a*-Si model, by disordering a diamond silicon structure by bond-switching rearrangements. In contrast to the extensively studied models for Si-Si interactions, the Si-H model potentials are still in an early stage of development. Hence in this paper we will focus on models of *a*-Si that do not contain H as a first step towards understanding mechanisms for the SW effect, and anticipate that the present results will guide future work with *a*-Si:H models. In this paper we discuss three classes of models: (i) the four-coordinated WWW model, (ii) an *a*-Si model with a substantial density of overcoordinated defects, and (iii) crystalline silicon. MD simulations were performed with the Stillinger-Weber potential.[13]

A common view is that the nonradiative recombination of photoexcited carriers in band-tail states is responsible for metastable-defect formation in *a*-Si:H. We adopt this ansatz in this paper. This is consistent with structural degradation caused also by electron irradiation or excess carrier generation in *a*-Si:H. Modeling the transfer of recombination energy to the system is a difficult electron-phonon-interaction problem. We model the energy transfer simply, by assuming that the recombination creates a local "hot spot" or a local region of a few excited atoms in the network.[14] We emphasize that this is a weak decay channel that can lead to interesting consequences, compared to the dominant channel of radiative decay. In fact, Weeks, Tully, and Kimmerling[15] have argued that nonradiative carrier-recombination energy can be largely coverted into vibrational energy that is localized in the vicinity of a defect. Creation of a hot spot may be enhanced in *a*-Si by defects that have strongly localized gap states to which the photoexcited band-tail carriers can decay.

In the MD simulations we create a hot spot by providing an excess kinetic energy to a local region and allow the system to dynamically evolve and equilibrate. Typical equilibration times are 5000–7000 time steps (18.5–26

ps). Resulting structural changes are examined in detail. The variables we have studied in this dynamical simulation are (i) the extent of the locally excited region, (ii) the spatial location of the hot spot, and (iii) the amount of excitation energy, which can be less than or on the order of the band gap (1.7 eV). A simple approach to (i) is to provide excess energy to a single bond, i.e., two bonded atoms, as opposed to an extended atomic cluster.

We first tested our approach with crystalline silicon. Local excitations of energy 1.7–8.0 eV in *c*-Si failed to induce structural changes. This is consistent with the Frenkel pair energy for a vacancy-interstitial pair being 8.0 eV in *c*-Si, and involving an even larger energy barrier for structural changes. The perfect crystal without any impurities or defects would then not show light-induced structural changes. In contrast the energy surface of *a*-Si has a number of nearby local minima separated by small energy barriers, and hence structural changes are much more readily induced, as discussed below.

We first consider the WWW model, which was relaxed at zero temperature to a local minimum with the Stillinger-Weber potential. The WWW model has 216 atoms with periodic boundary conditions. The WWW model may be a realistic representation of a defect-free region of an experimental *a*-Si film. The most significant result is that structural changes are very spatially dependent on the location of the hot spot. Choosing an excitation region at random usually leads to equilibration and no structural changes. We have identified two local regions of the WWW network where excitation-induced structural changes are possible. Both of these local regions involve weak Si—Si bonds or weakly bonded Si sites.

The first region [Fig. 1(a)] involves a weak bond ($R = 2.53$ Å, where the mean bond length is 2.35 Å) between two atoms one of which (atom 126) is the most weakly bound site in the model with a site energy $E_s = -3.30$ eV, substantially higher than the average site energy of -4.07 eV for the WWW model ($E_s = -4.33$ eV for the crystal). The bond angles and bond lengths are highly strained on this atom. Creation of a hot spot on this bond and equilibration broke the 122—126 bond creating two dangling bonds on these sites [Fig. 1(a)].

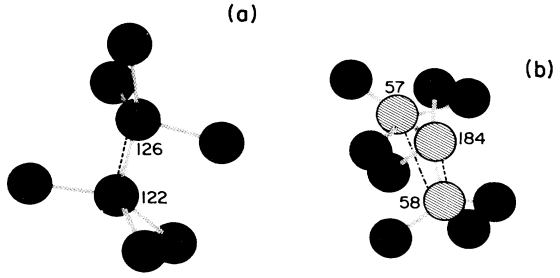

FIG. 1. (a) Defect center involving a weak Si—Si bond between atoms 122 and 126 (dashed line), which is broken after the local excitation process. Atom 126 is very weakly bound with a site energy of -3.30 eV. (b) A metastable configuration that can be altered on excitation, by creation of a new bond between 58 and 57 (dot-dashed line) and elimination of the bond between 58 and 184 (dashed line).

Some shearing motion of this bond is also involved. Resulting atomic displacements are shown in Fig. 2(a). This bond-breaking process requires an excitation-energy threshold of about 1.0 eV, and no changes are observed with a lower energy of 0.4 eV. The energy for the broken-bond configuration was only 0.14 eV higher than the initial state. The structural change decreases the bond-angle and bond-length distortions (Fig. 2) on these sites (122, 126) which are now more than 3.0 Å apart. To accommodate this local strain relief, atoms in the vicinity of these two sites have sizable displacements [0.1–0.4 Å, Fig. 2(a)] and an overall increase in the strains of these atoms. We have performed electronic-structure calculations with the Chadi model[16] which confirm that the final configuration does have two localized gap states, primarily localized on each dangling bond, that would give electron-spin resonance (ESR) signals. In each of these states there is a mixing of 7% and 4% of the wave function of the other nearby dangling bond.

The time scales of our molecular-dynamics simulation are limited to being between 10 and 100 ps. Over substantially longer times it may be possible for one of these dangling bonds to diffuse away from the local region of Fig. 1(a), resulting in isolated dangling-bond defects. Annealing at 300–330 K rebonded the 122-126 atom pair illustrating the metastability of this configuration. The annealing did, however, lead to extra floating bonds in the region away from this defect center. We feel that these

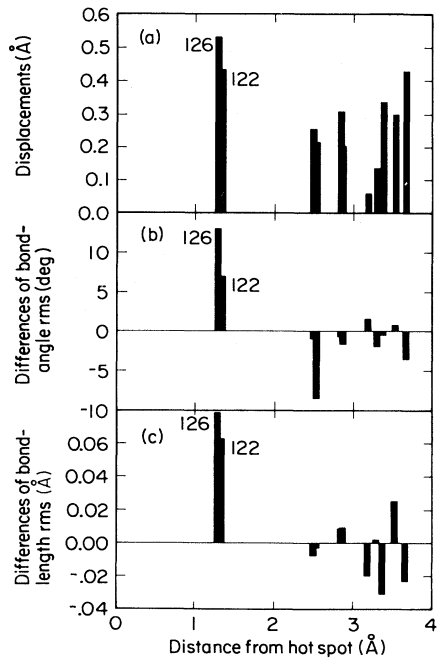

FIG. 2. Structural changes after local excitation in the region in Fig. 1(a) illustrated by (a) atomic displacements, (b) changes in bond-angle distributions, and (c) changes in bond-length distributions on atoms around the excitation region. Plotted in (b) and (c) are differences between initial and final values so that positive bars indicate a relaxation and negative bars an increase of the strain. Distances are from the center of the 122-126 bond.

floating bond defects are an artifact of the present Si model, which may unphysically favor overcoordinated configurations. The bond-breaking change could not be produced by extended-cluster excitations (five atoms around 126), or exciting different bonds on 126 and 122.

The second site [Fig. 1(b)] involves breaking a weak bond on one site (atom 58) and formation of a new bond between 58 and 57, leading to a pair of nearby dangling and floating bonds and an energy lowering of 0.8 eV. This change can also be induced by excitations of as low as 0.4 eV on a number of different sites spatially separated from this region. The floating bond does not migrate over time scales of 40 ps, although longer-time behavior is hard to infer with the molecular-dynamics simulation. The formation of a similar pair of dangling and floating bonds (FB) was proposed by Pantelides[6] to be a fundamental defect reaction underlying the light-induced degradation. It was proposed[6,17] that the FB could migrate, leaving isolated defects, whereas annealing would require defect reactions with H. However, we found that this structural change could also be thermally induced by heating the sample to 300–350 K, suggesting that this change is due to a poorly relaxed local region of the original network, unrelated to degradation processes.

The above results indicate a limited number of atomic sites at which structural degradation changes are possible, a concept suggested by the observed saturation of the light-induced-defect density in *a*-Si:H. These results are independent of the method of preparation of *a*-Si and the Si potential used. Simulations of a melt-quenched *a*-Si model (generated by Biswas, Grest, and Soukoulis[7] utilizing a different Si potential) showed similar results for breaking of weak bonds and a threshold energy of 1.0 eV for excitation-induced structural changes. The bond breaking process was also very spatially dependent affecting weakly bonded Si sites. Similar behavior is also observed at higher temperature. Local excitations of the WWW model at 325 and 590 K also resulted in breaking of weak bonds, with decrease of energy thresholds and larger number of defects with increasing temperatures.

Further multiple local excitations in the vicinity of the site in Fig. 1(a) increased the number of coordination defects, accompanied by an energy lowering of the network, suggesting an annealing of the structure. To systematically examine the stability of the WWW model, we thermally annealed the WWW model by equilibrating it at various temperatures up to 1250 K. We then performed steepest-descent quenches at various temperatures to extract inherent structures, free from thermal disorder. The potential energy of these inherent structures (Fig. 3) is minimized for the 1040 K anneal temperature, and then rises as the amorphous solid–liquid transition is approached. This transition temperature was determined by Luedtke and Landman[18] (LL) to be 1435 K for rapid heating and about 1082 K for slow heating. The WWW model, although a local minimum of this Si potential,[13] can thus be annealed further by 0.03 eV/atom. The steepest descent configuration from the 1040 K anneal was equilibrated near room temperature (313 K) and had a radial distribution function (Fig. 3) very similar to the slow-cooled *a*-Si obtained by LL (Ref. 10) (also at 300 K) including the weak shoulder at 3.2 Å, but unlike the glass obtained by LL (Ref. 10) which had a distinct peak at 3.2 Å. Our 216-atom configuration was substantially overcoordinated with 27.8% five-coordinated and 1.9% six-coordinated atoms, and no dangling bonds, for the $T=0$ network (or 30.5 and 2.3% at 313 K), using a bond cutoff of 2.95 Å. These defect densities are closer to the densities of over-coordinated defect densities in the LL *a*-Si model (21%) than the LL glass (59%).

Our third class of simulations involved the above annealed over-coordinated *a*-Si model. In all cases, local 1.7-eV excitations on bonds led to a metastable configuration with a somewhat higher energy (0.01–0.06 eV for 216 atoms) than the starting configuration, accompanied by an increase in the number of over-coordinated defects. The starting configuration is a stable local minimum. This is consistent with previous results for the WWW

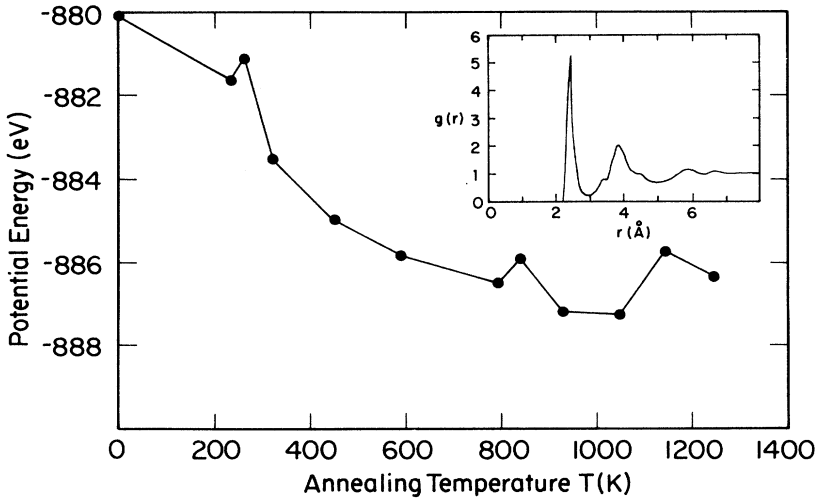

FIG. 3. Potential energies of inherent *a*-Si models as a function of anneal temperature. The steepest-descent quenched *a*-Si model from the 1040-K anneal was equilibrated near room temperature to produce the pair distribution function $g(r)$ in the inset.

model where hot spots also lead to an increase in the number of defects.

In summary we studied the stability of *a*-Si models against local-excitation processes and thermal annealing. Local excitations of the four-coordinated WWW model indicate structural changes that require energy thresholds of 0.8–1.0 eV, and primarily occur on weak Si—Si bonds or weakly bonded Si atoms. We have observed the generation of a metastable pair of ESR-active dangling-bond defects, induced by local excitations on such a weak bond. In contrast, *c*-Si is stable to local excitations as large as 8.0 eV. Further simulations with hydrogenated amorphous silicon networks need to be performed to understand the role of H in light-induced structural changes. H may stabilize the dangling-bond defects found in this work. The role of microvoids also needs to be investigated.

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