RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 7 15 AUGUST 1991-I

Mechanism for the Staebler-Wronski effect in *a*-Si:H

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(Received 31 May 1991)

A mechanism is proposed for the Staebler-Wronski effect in *a*-Si:H. A bridge-bonded H interstitial defect is identified as the annealed state that can form a higher-energy metastable dangling-bond state in the light-soaked state. This defect can account for various features of light-induced degradation. The calculations are based on an *a*-Si:H model containing 10% hydrogen, bonded as the monohydride species. A Si-H two- and three-body interatomic potential has also been developed for the simulations.

The understanding of the Staebler-Wronski (SW) effect[1] in *a*-Si:H is important for both basic-science and solar-energy-conversion applications. Device-quality *a*-Si:H grown under different conditions displays under illumination a metastable increase in the density of defect states in the gap region that can be annealed out by thermal annealing at 150–200 °C.[2] The metastable defects are usually excess silicon dangling-bond spins. The saturated metastable-defect density correlates with the hydrogen content and band gap.[3,4] Despite extensive studies,[1–4] the microscopic mechanisms for the Staebler-Wronski effect remain unclear. Several different mechanisms have been proposed for the SW effect including the breaking of weak Si-Si bonds by nonradiative recombination of carriers,[2,5] the capture of carriers at existing charged dangling-bond sites,[6] the generation of pairs of dangling-bond–floating bond defects,[7] the local metastable states of dopant atoms,[8] the diatomic H complexes in *a*-Si:H,[9,10] and the role of H interstitials in *a*-Si:H.[11] A difficulty in many of the previous studies was the lack of a realistic atomic model of *a*-Si:H. We overcome this difficulty by working with a realistic atomic structural model of *a*-Si:H, containing 10% H, similar to device-quality material. Based on this approach, we propose and analyze a mechanism for the Staebler-Wronski effect in *a*-Si:H that can account for many of the experimental observations. We propose a structure for the defects in both the light-soaked and annealed states.

The calculations in this paper are based on molecular dynamics in which we have developed a Si-H two- and three-body potential. In addition we utilize Si-Si potentials that have had much success in describing properties of *a*-Si.[12] Details of the Si-H potential development will be presented elsewhere. Briefly, the two-body Si-H interaction is

$$V^2_{\text{Si-H}}(r)=[A_1\exp(-\lambda_1 r)+A_2\exp(-\lambda_2 r)]f_c(r)\,, \tag{1}$$

where $f_c(r)$ is the cutoff function.

$$f_c(r)=\begin{cases}1 \text{ for } r\le 1.70\text{ Å}\,,\\ 0.5+0.5\cos[(\pi/0.2)(r-1.7)] \text{ for } 1.70\text{ Å}\le r\le 1.90\text{ Å}\,,\\ 0 \text{ for } r\ge 1.90\text{ Å}\,.\end{cases} \tag{2}$$

The three-body potential which describes Si-Si-H or H-Si-H or even Si-H-Si interactions is

$$V_3(r_{12},r_{13},\theta)=B_{\text{H}}\phi_{1,2}(r_{12})\phi_2(r_{13})(\cos\theta+1/3)^2 \times g_{c1,2}(r_{12})g_{c2}(r_{13})\,, \tag{3}$$

where the subscripts 1 and 2 refer to Si-Si and Si-H interactions, respectively. Here $\phi_1(r)=\exp(-\alpha r^2)$ and $\phi_2(r)=\exp(-\alpha_{\text{H}} r^2)$ are the radial functions, and $g_{c1,2}(r)=[1+\exp(r-r_{c1,2})/\mu_{1,2}]^{-1}$ are cutoff functions.

We use a repulsive H-H interaction V^2_{HH}, similar to that employed by other workers,[13] that prevents H atoms from approaching unphysically close, where

$$V^2_{\text{HH}}=[\epsilon/(1-6\alpha_{\text{HH}})][(6/\alpha_{\text{HH}})e^{\alpha_{\text{HH}}(1-r/\sigma)}-(\sigma/r)^6]\,. \tag{4}$$

H_2 molecular formation is inhibited in this scheme, but that is less important for the purposes of this paper.

The two-body potential $V^2_{\text{Si-H}}(r)$ was fitted to *ab initio* calculations of the energy of H on a Si cluster,[14] whereas the three-body parameters were adjusted to achieve a reasonable description of the energies of SiH_4 and both the amorphous and crystal phases.[15] Although improvements in these parameters may be possible, the present set satisfactorily describes energies of silane and *a*-Si:H models and are adequate for the purposes of this paper. This classical model describes well the collinear Si-H-Si bond-centered H interstitial (BC) in *c*-Si with an Si-H bond length of 1.71 Å and cohesive energy of 0.88 eV, in good agreement with values from *ab initio* calculations[16] of 1.63 Å and about 1.0 eV, respectively. A satisfactory description of the BC H interstitial is important for the conclusions of this paper.

Using these potentials we have considered the *a*-Si:H model containing 10% of H proposed by Guttman and Fong,[17] with 54 Si atoms and six H atoms in monohydride bonding configurations, and periodic boundary conditions. The *a*-Si:H model was relaxed to a minimum of the potential energy with the above potentials at different densities. The lowest-energy configuration occurred at a mass density of 0.92 of *c*-Si, with a root-mean-square (rms) bond angle deviation of 10.5° and rms bond length deviations of 0.10 Å for Si-Si and 0.01 Å for Si-H bonds. In the fully

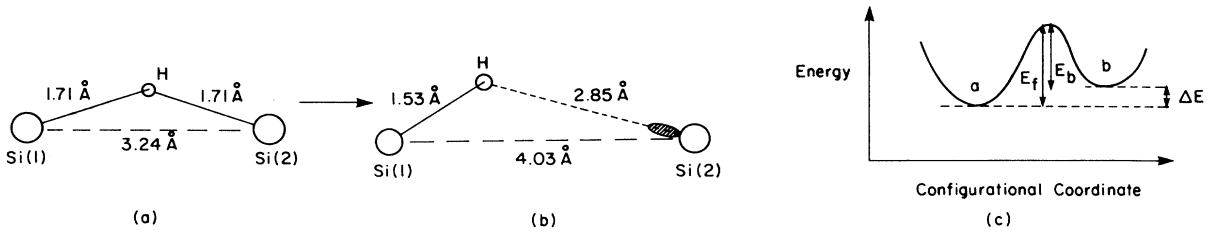

FIG. 1. (a) Schematic diagram of the bridge-bonded (BB) hydrogen configuration and (b) the resulting metastable configuration with a single dangling bond on one Si atom. (c) Schematic energy-level diagram connecting these two configurations.

relaxed configuration all the H atoms were incorporated in monohydride bonding configurations, with no coordination defects, a feature qualitatively similar to device-quality *a*-Si:H. H relaxes the strains and eliminates the large density of coordination defects present in *a*-Si models without H. We found that this *a*-Si:H model was very stable to thermal annealing up to 700 K, and no lower-energy configuration could be produced by quenching or cooling from elevated temperatures. Hence this *a*-Si:H model, devoid of unnecessary defects, was a good starting point for further investigations of the Staebler-Wronski effect.

Experimentally, the light-soaked defect densities reach a saturation value of the order of 10^{17} cm^{-3} so that the Staebler-Wronski defect occurs with a probability of about 10^{-4} to 10^{-5} per atom.[3,4] Hence in computer-generated models of up to a few hundred atoms, the Staebler-Wronski defect is not expected to be present. However it is still possible to "introduce" relevant defects into our finite-size models that are connected to light-induced degradation.

Our crucial observation is that a novel defect can be created in this otherwise stable *a*-Si:H network by introducing an additional H atom. We find that the extra H atom energetically prefers occupying a bridge-bonded (BB) configuration in which it is bonded to two Si atoms with bond lengths of 1.71 Å, and an Si-H-Si bond angle between 140° and 150° [Fig. 1(a)]. The extra H induces large outward displacements of the two Si neighbors. This result is analogous to well-established first-principles theoretical results[16] that H in *c*-Si has the lowest energy when occupying a collinear Si-H-Si bond-centered configuration for positive and neutral charge states. Other authors[9-11,18] have suggested the collinear bond-centered H interstitial in *a*-Si:H, but in contrast to these studies we find that the H interstitial in *a*-Si:H remains off-center in a bridged configuration.

The longer Si-H bond length in both BC H in *c*-Si and the BB H in *a*-Si:H reflects the weaker Si-H bonding compared to Si-H bonds in silane, or monohydride groups in *a*-Si:H (where Si-H is 1.50 Å). We calculate a distribution of energies (Fig. 2) to create a BB H interstitial that lies at least 0.3 eV above the Si-H bond energy (−3.05 eV).

Our key observation is that the H atom can be displaced towards one or the other Si atom resulting in a strong Si-H bond (1.50–1.53 Å) with one Si atom and resulting in a single dangling bond on the other Si atom [Fig. 1(b)]. To accommodate the Si dangling bond the two Si atoms are pushed outwards even further, i.e., relaxation of the amorphous network is essential. The dangling-bond state is a locally stable configuration that has higher energy than the BB state [Fig. 1(c)], with energy differences δE varying from 0.04 eV to 1.2 eV, depending on the particular BB H site examined (Fig. 3). We note that Street has also suggested the existence of the bond-centered H interstitials in *a*-Si:H and the dangling-bond state and their relation to both light-induced degradation and H diffusion.[11] Also a diatomic H complex, containing a bond-centered H interstitial, has been proposed by Jackson and co-workers,[9,10] as an alternative model for the Staebler-Wronski effect.

Since the dangling-bond state is locally stable to structural perturbations we hypothesize that the BB H state is the annealed state of the Staebler-Wronski defect whereas the dangling bond is the metastable-defect state, with these two configurations connected by a two-state energy configuration [Fig. 1(c)]. We find an energy barrier between these two configurations in our calculations. The height of the energy barrier depends on the ability of the amorphous network to relax during the motion of the H between the two configurations. When the H atom and its two neighboring Si atoms move uniformly between their positions in the BB H state to the dangling-bond state we

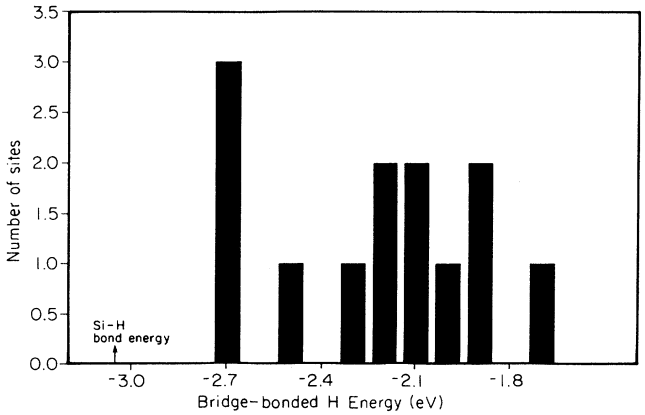

FIG. 2. Distribution of energies to create a bridge-bonded H interstitial at various sites in the *a*-Si:H network. For comparison the energy to put the H in a normal Si-H bond (as in a monohydride) is −3.05 eV.

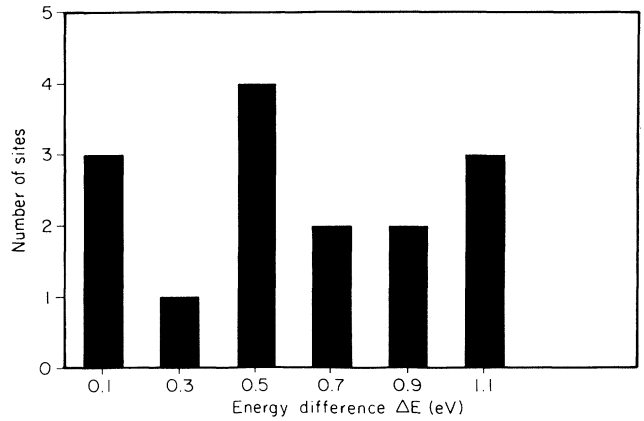

FIG. 3. Distribution of the energy differences between the metastable dangling-bond state and the bridge-bonded H configuration.

estimate an annealing energy barrier E_b of 1.0–2.0 eV, whereas this annealing barrier is reduced to 0.2–0.3 eV when the entire network is allowed to relax. The complete network relaxation may not be possible on the time scales of the H motion, in which case energy barriers of 1.0–2.0 eV are consistent with barriers of 0.9 eV to 1.3 eV obtained from measurements of the annealing of the metastable dangling-bond density.[2]

We note that the energy barrier to defect formation is higher than that for annealing by the energy difference between dangling-bond and BB H state. In general, there is a distribution of barrier heights [E_b and E_f, Fig. 1(c)], and this implies that the kinetics of formation of the metastable defects should follow a stretched exponential behavior, in agreement with theoretical fits of the experimental saturation behavior of light-induced defects.[19]

We hypothesize that a small density N_{BB} of the BB H configurations are frozen in during the growth process. An a-Si:H sample would then have a finite number of such weakly bonded BB H defect centers that could be converted to metastable dangling-bond sites during illumination. The saturation of the metastable-defect density is achieved, when the rates of transition from a to b and from b to a [Fig. 1(c)] are the same. The kinetics of conversion between the two species in the two-level potential diagram can be described by stretched exponential kinetics.[19] During an equilibrium growth process a density N_{BB} of the weakly bonded species may be produced that is given by

$$N_{BB}=N_H \exp(-\delta E/k_B T_s)\,, \tag{5}$$

where T_s is the substrate temperature, and N_H is the total H density. The thermally activated expression (5) is best approached at low substrate temperatures (about 200 °C or below). If we use typical glow-discharge a-Si:H conditions[20] at 200 °C where H concentration is 16.5% or N_H is 8.25×10^{21} cm^{-3}, we estimate a density of BB H to be 4.5×10^{17} cm^{-3} using an average δE of 0.4 eV for the energy difference of the lower-energy group of BB H defects from Fig. 2. We note that even if higher-energy BB H configurations are initially formed the H could switch to adjacent sites in the lower-energy tail of the distribution in Fig. 2, so that lower value of about 0.4 eV for δE is relevant. This estimate of the density of BB H defects is consistent with measured values of the saturation density of the metastable defects. This picture leads naturally to a finite saturation density and a limited number of metastable-defect sites that can be produced during illumination.

During the creation of the metastable dangling-bond state, the charge state of the defect can change. Our tight-binding electronic structure calculations (employing a Chadi-type of model) indicate that the BB H has a defect level in the upper half of the band gap, similar to the result found for bond-centered H in c-Si.[17] If the Fermi level is near midgap (i.e., compensated material) the BB H is unfilled and exists in the positive-charge state. The dangling bond is, however, stable in the neutral charge state. Conversion of the BB H to a dangling bond then involves a change in the charge state of the defect with the capture of an electron and a consequent decrease in the conductivity. Details of the microscopic conversion between these two species will require further studies.

A definite prediction of this model is that the metastable dangling-bond defects should have a H atom in their vicinity. In principle a hyperfine interaction should exist between the H nuclear moment and the dangling-bond spin. However, we expect a distribution of distances between H and the Si dangling bond arising from the range of amorphous environments, and this may lead to a broadening of the electron-spin-resonance line itself rather than a sharp hyperfine feature. The present model leads to a single dangling bond in the light-soaked state in contrast to two dangling bonds in the weak Si bond-breaking model of Stutzmann *et al.*[2] H plays a crucial role in the present model, in contrast to the model of Adler[6] where existing charged dangling bonds trap carriers. Saturation of the light-induced defect densities arise from a finite number of H induced defect sites in the present model. Further experimental studies are needed to study predictions of the BB H model.

In summary, we have described a two-level defect system in a-Si:H consisting of a bridge-bonded H interstitial and a Si dangling-bond defect that can account for various features of the light-induced degradation in undoped a-Si:H including the finite saturation density and metastability properties. The presence of hydrogen and local H motion play a crucial role in both the metastable defect formation and the annealing of these defects.

We thank J. Shinar, K. M. Ho, C. G. Van de Walle, D. Redfield, and B. Min for helpful discussions. We acknowledge support from the Electric Power Research Institute under the amorphous thin-film solar cell program. We also acknowledge an NSF grant of Supercomputer time. Work at the Ames Laboratory, operated by Iowa State University for the U.S. Department of Energy (U.S. DOE) under Contract No. W-7405-ENG-82 was supported by the Director for Energy Research, Division of Material Sciences, U.S. DOE.

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