

Role of hydrogen complexes in the metastability of hydrogenated amorphous silicon

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A microscopic model for metastability in hydrogenated amorphous silicon (a -Si:H) involving two-hydrogen-atom complexes is proposed. Metastable-defect formation occurs when this complex dissociates creating two interstitial H atoms which form Si dangling-bond-like defects at weak-bond sites. Annealing occurs when the H atoms reform complexes.

Metastable-defect formation in hydrogenated amorphous silicon (a -Si:H) is an interesting phenomenon of significant technological importance. Whenever carriers are introduced, either by light, doping, or current, the density of defects with a spin signature characteristic of a Si dangling bond increases.¹ Despite intensive investigation, the microscopic mechanism remains unclear.

Various models based on changes in hybridization of existing dangling bonds,² impurities,³ or silicon-silicon bond breaking have been proposed.^{1,4-10} The first two are not widely accepted since long-time stability and lack of dependence on impurities are difficult to understand.^{1,11} Among the Si-Si bond-breaking models, bond breaking through H-bond rearrangements is perhaps most widely proposed because of the connection between H and metastability. H is known to change its bonding configuration at temperatures below 150°C from diffusion measurements, and high defect densities remain in unhydrogenated silicon even at 550°C.^{1,4-10} Despite the large number of models, a major problem for H-induced Si-Si bond-breaking models is to explain how carriers accelerate the rupture of Si-H bonds known to exist from infrared measurements. When both holes and electrons are present, the activation energy for defect formation is only 0.15 eV. Because the Si-H bond requires 2.0-2.1 eV for rupture and diffusion and the bonding and antibonding states are 2-3 eV from the band edges,^{12,13} most H-bond-breaking models have assumed an improbable close association of a weak Si-Si bond with a Si-H bond. This association reduces the energy barrier for rupture to the observed value of 1.4 eV and/or traps carriers near the Si-H bond to assist in rupture.^{7,10} Another difficulty is that these models often require that two H atoms insert into a single weak Si-Si bond to account for defect annealing.¹⁰ Because the Si-H bond distance is 0.15 nm and a strong H-H interaction, this configuration is high in energy.¹³

In this paper it is argued that a two-atom complex form of H (denoted by H_2^*), proposed by Chang and Chadi for c -Si,¹² explains many of the features of metastability including the observed activation energies and kinetics of metastability. This complex is formed by a neutral H atom in the bond-centered (BC) site and another in an adjacent tetrahedral site (T_d) near the antibonding site (see Ref. 12) as indicated in Fig. 1(a). The H atoms break the Si-Si bond and form strong Si-H bonds with stretching frequencies in the 2000-cm⁻¹ region. This H_2^* complex is lower in energy than most other configurations except Si-

H at a vacancy (requiring a preexisting dangling bond) or an H^+ in a BC site in strongly p -type silicon.^{12,14} The complex has a barrier to diffusion of 1.0 eV in undoped Si (Ref. 12) and therefore can also form larger complexes which are even lower in energy (Fig. 2).¹⁵ This pair can roughly be viewed as an intimate association of the charged defects H^+ (BC) and H^- (T_d) which because of close proximity are lower in energy. In the process of forming, the intimate pair charge is transferred by making both H atoms approximately charge neutral.

It is proposed that metastability in a -Si:H occurs when this complex dissociates either thermally or through light-induced carriers into isolated atomic H configurations (H^0 , H^+ , and H^- in undoped, p -type, and n -type a -Si:H, respectively) which diffuse rapidly to other

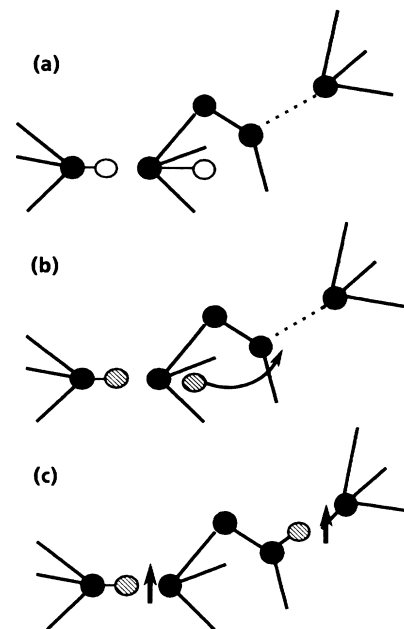


FIG. 1. Schematic of H_2^* dissociation steps responsible for metastable defect formation. (a) Initial H_2^* complex (solid circles, Si; open circles, complexed H atoms). (b) Complex dissociation into H^0 (BC) and H^0 (T_d) which diffuse rapidly to traps at a deep 1H state (shaded circles, uncomplexed H; dotted line, weak Si-Si bond). (c) H atoms create midgap dangling-bond states (arrows). Annealing occurs when H atoms reform complexes.

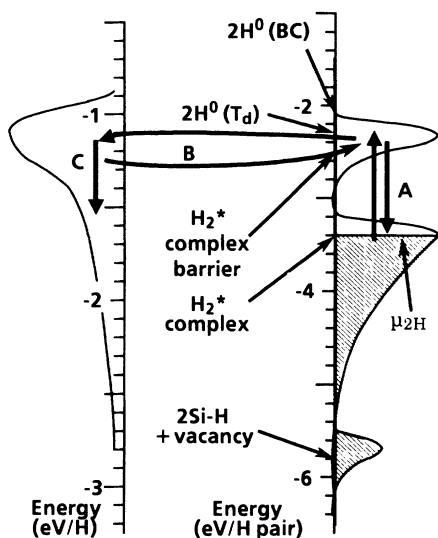
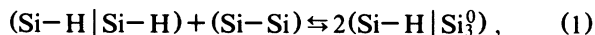


FIG. 2. Calculated total energies of various H configurations in *c*-Si relative to atomic H in the vacuum from Refs. 12 and 14. On the left- (right-) hand side is a schematic sketch of the 1H (2H) density of states. Diffusion occurs by transition *A* or by pair dissociation (transition *B*), diffusion and recomplexing. Metastability occurs when individual H atoms trap and do not recomplex (transition *C*) and annealing occurs when H atoms reform complexes.

weak Si–Si bond sites creating midgap defects. Annealing occurs when these isolated H atoms recomplex either with the same or different H atoms.

The reaction for metastability can be written as



where the Si–H bond of the H_2^* complex is indicated explicitly in the first term, the second term denotes a weak Si–Si bond, and the right-hand side denotes an unpaired or isolated H associated with a weak Si–Si bond creating a dangling bond (see Figs. 1 and 2). The system evolution can be described in terms of hopping in the 2H density of states on the right-hand side of Fig. 2. H_2^* periodically dissociates, and because of the high mobility of the resulting atomic H, the complex usually reforms. Every so often a pair dissociates into separate H atoms indicated by the transition to the 1H density of states on the left-hand side of Fig. 2. These highly mobile species then trap and detrap in the 1H density of states depicted on the left-hand side of Fig. 2 until they reach a deep 1H state (weak Si–Si bond) creating dangling bonds or midgap states. The metastable sites available to H atoms are limited by the fact that many of the lowest weak-bond sites are already occupied by H_2^* complexes (H_2^* and H compete for the same sites) and because of thermal detrapping and recomplexing reactions for 1H configurations. Hence, the energy position of the single H's will be sufficiently deep to prevent significant detrapping during illumination, i.e., > 1 eV for temperatures of 25 °C. The annealing process occurs when trapped H forms a new H_2^* complex.

The implications of this model compare favorably with experiment. In the following discussion, the total forma-

tion energies of these complexes calculated in *c*-Si are used to estimate the expected kinetics of the proposed model in *a*-Si:H and compared with experiment. In Figs. 2 and 3, these total energies computed by total-energy calculations in Ref. 14 for various H configurations versus Fermi level are depicted. In order to approximately reference the energies to the Fermi level in *a*-Si:H with its 0.65-eV larger gap, 0.3 eV has been added to the valence and conduction bands. The results are only slightly affected if the band-gap difference is added differently. The total uncertainties because of calculations, Fermi energy positions, and affects of disorder are on the order of 0.3 eV. Despite these uncertainties, there is reasonable quantitative agreement between calculations and experiment. The light-induced case is considered first, followed by the charge-induced case.

In the case of light-induced metastability, the H_2^* complex is dissociated by trapping electrons and holes in or near the H_2^* complex. While the occupied and unoccupied states associated with an isolated complex are on the order of 0.5–1 eV from the band edges in *c*-Si, they are near or in the band-tail states in *a*-Si:H with its larger band gap of 1.8 eV.¹⁵ The dissociation may occur when electron-hole pairs become trapped in the band-tail states associated with H_2^* complexes. This type of dissociation would only occur if electrons and holes existed in the same spatial region, a requirement necessary for recombination. This feature is in concordance with observations that recombination is required for light-induced defect formation.¹⁶ Trapping an extra electron and a hole in an H_2^* complex results in a small probability of creating a $\text{H}^0(\text{BC})$ and $\text{H}^0(\text{T}_d)$ (transition *A* in Fig. 3 or transition *B* in Fig. 2). The total formation energy surface for these species are flat allowing the H atoms to readily diffuse apart with an activation energy of 0.2 eV or less.¹³ This small activation energy agrees well with the 0.15-eV activation energy observed for light-induced defect generation.⁷

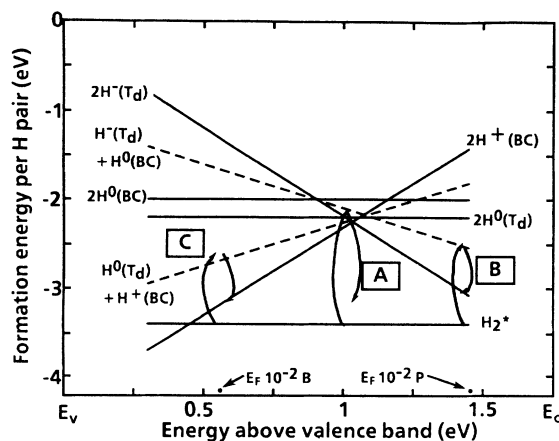


FIG. 3. Calculated total energies of various 2H configurations in *c*-Si vs Fermi-level position in *a*-Si:H from Ref. 14. Arrows indicate the transitions for pair dissociation in undoped (*A*), 10^{-2}P (*B*), and 10^{-2}B (*C*) doped *a*-Si:H. Note that barrier heights and final-state energies decrease relative to the H_2^* energy as the Fermi level moves away from midgap.

Annealing occurs by recomplexing either by further dissociation of H_2^* (transition A in Fig. 3) or possibly by thermal detrapping and recomplexing of isolated H configuration. In undoped material, the activation energy for this process is roughly 1–1.2 eV (Figs. 2 and 3) in good agreement with the annealing energy of light-induced defects.^{7,17} For low-temperature illumination, the isolated H traps into high-energy states which anneal away rapidly by thermal release and recomplexing. High-temperature illumination results in H trapped in deeper traps; the corresponding annealing process takes longer and the activation energy moves to higher energies in agreement with light-induced annealing experiments.¹⁷ Steady-state conditions occur when the rate of dissociation balances the recomplexing as the concentration of atomic H builds up. The kinetics of the process will exhibit nonexponential decays due to the distribution of barriers both for complex dissociation and atomic-H trapping and release. If these barriers are approximately exponential, the decays will exhibit the observed stretched exponential time dependence.^{18,19}

Consider next the impact of changing the Fermi level in this model either by doping, current, or charge accumulation in metal-insulator-semiconductor devices. Moving the Fermi level from midgap affects metastability through two processes: (i) lowering the H complex dissociation energy and (ii) reducing 1H total-energy levels which create midgap electronic states relative to the H_2^* complex energies. The former effect primarily increases the rate of defect formation while the latter increases the equilibrium defect density. In the case of dissociation by a single carrier type, the total-energy barrier for dissociation of a H_2^* complex is due to the capture of a single carrier in the complex, dissociation and diffusion, and finally capture of a second carrier by the neutral 1H configuration. The energy barrier depends on the Fermi-level position and must include the 0.1–0.2-eV diffusion energy for the isolated H. The Fermi level under annealing conditions is the Fermi-level position for equilibrated material: $E_c - 0.25$ for $10^{-2}P$ and $E_c + 0.5$ for $10^{-2}B$ a -Si:H (Fig. 3).²⁰ In the case of P-doped material, the H_2^* complex dissociates according to the reaction $H_2^* + 2e \rightleftharpoons H^-(T_d) + H^0(BC) + e \rightleftharpoons 2H^-(T_d)$ (transition B, Fig. 3). The barrier for this process is approximately $0.8 + (0.1-0.2) = 0.9-1.0$ eV. The rate of dissociation decreases if the doping levels are decreased. This activation energy for defect generation and dependence on carrier density agrees very well with observed defect creation rates in both n -type doped material and in electron accumulation layers of metal-insulator-semiconductor devices.¹⁹⁻²² For p -type material, H_2^* dissociation occurs by the reaction $H_2^* + 2h \rightleftharpoons H^0(T_d) + H^+(BC) + h \rightleftharpoons 2H^+(BC)$. Because the dissociation energy of H_2^* drops to near zero for degen-

erately doped p type, this fact prevents efficient p -type doping in a -Si:H and pins the Fermi level at $E_c + 0.45$ eV in equilibrated p -type material.²³ The barrier energy for the intermediate state is $0.5 + (0.1-0.2) = 0.6-0.7$ eV (transition C, Fig. 3). This estimate is in reasonable agreement with defect annealing activation energies of 0.7–0.8 eV in B-doped material.^{20,21} The effect of this metastable H passivation effect on dopants and doping efficiency, neglected above, will be discussed in future work.

The decrease of the final energy of isolated H configurations relative to H_2^* complex states as the Fermi-level moves from midgap occurs because many of the atomic H states result in midgap states. Consequently, if the Fermi level increases above the (0/–) or below the (+/0) electronic transition level for the induced gap state, the formation energy for the 1H configurations (on the left-hand side of Fig. 2) will decrease in energy relative to 2H states on the right-hand side which do not create midgap states. Hence, the equilibrium density of midgap defects will increase whenever the Fermi level shifts towards the band edges in a -Si:H. When the Fermi level returns to midgap, these atomic-H induced states are no longer energetically favorable; the H recomplexes removing the midgap defects.

Numerous other aspects of amorphous silicon can be explained by the presence of H_2^* complexes. For example, the correlation between the Urbach edge and equilibrium defect densities²⁴ occurs because the Urbach edge distribution reflects the weak Si–Si bonds energy distribution which directly affect the distribution dissociation and trapping energies for H_2^* complexes and isolated H atoms. The equilibrium and kinetics Eq. (1) are consistent with those previously used to account for aspects of metastability.^{7,10,20} The formation of groups of H_2^* complexes can also account for the broad line component in nuclear magnetic resonance indicating a clustered form of H which is not SiH_2 and yet the linewidths (and therefore the inter-H distances) are nearly independent of deposition or annealing.²⁵ These aspects will be discussed in future work. Therefore, H complex formation explains many features of metastability in a -Si:H and is consistent with c -Si models. The H complex provides a low-energy means for inserting H into Si and breaking Si–Si bonds without creating dangling bonds. Total-energy calculations indicate that the energetics of the model are approximately consistent with experiment. Therefore, the H complex model should be considered as a viable possibility to explain metastability in a -Si:H.

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¹See for example, *Stability of Amorphous Silicon Alloy Materials and Devices*, Proceedings of an International Conference on Stability of Amorphous Silicon Alloy Materials and Devices, AIP Conf. Proc. No. 157, edited by B. L. Stafford and E. Sabisky (AIP, New York, 1987), and references therein.

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