Diatomic-Hydrogen-Complex Dissociation: A Microscopic Model for Metastable Defect Generation in Si

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Using first-principles calculations, we demonstrate an explicit reaction pathway for carrier-induced changes in hydrogenated Si through dissociation of paired-H complexes. The complex dissociates through the capture of charge carriers with calculated kinetic barriers for electron- and hole-induced dissociations of 1.1 and 0.9 eV, respectively, in crystalline Si, in general agreement with the experimentally observed activation energies for single-carrier defect creation in hydrogenated *a*-Si. Exciton lowering of the barrier accounts for the low activation energy of light-induced defect formation.

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Structural metastability associated with various forms of hydrogen bonding in Si is a problem of long-standing interest because of the nearly ubiquitous presence of H in crystalline (*c*) and amorphous (*a*) Si as a result of device processing. The presence of carriers, created either electrically or optically, is experimentally known to increase the number of metastable midgap defects in hydrogenated *a*-Si (*a*-Si:H),[1,2] and in hydrogenated polycrystalline Si (poly-Si:H).[3] These changes anneal at temperatures of 150–250 °C, where the material nearly returns to its original state.[1,2] Despite extensive studies, the microscopic origin and mechanism for metastable defect formation is poorly understood. It is generally believed that optical excitation creates Si dangling bonds which act as efficient recombination centers and deep traps, altering the electrical properties of the material.[4,5] From the dependence of the defect-formation kinetics on Fermi-level position, temperature, deposition conditions, and impurity levels, hydrogen-induced-bond reconfiguration is believed to be involved.[6] Recently, the dissociation of a diatomic H complex[7] (H_2^*) (see Fig. 1) into separate H atoms has been suggested to be the mechanism responsible for carrier-induced metastable phenomena.[8] In this model, the carriers, whether electrons, holes, or both, localize on the H_2^* complex, causing dissociation. Once dissociated, the isolated H atoms become trapped at strained Si-Si bonds creating spin-active midgap defects, passivate active dopants, or become attached to impurities. The strained Si-Si bonds and impurities serve as deep traps for the isolated H atoms so they do not recombine or diffuse to the surface. While the initial- and final-state energies were discussed in Ref. 8, the precise energy barriers and specific dissociation pathways and mechanisms remain to be identified. An important consequence of this work is that carriers cause changes in electronic properties of Si containing H by dissociating relatively immobile and inactive H pairs into more mobile and active isolated H.

In this paper, the total energy for the carrier-induced dissociation reaction was calculated from first principles and the reaction pathways were examined. These barriers are in reasonable agreement with experimental defect creation and annealing activation energies. Moreover, our work also indicates that the reaction pathways are kinetically allowed.

We employed an *ab initio* pseudopotential total-energy method within the local-density-functional approximation (LDA).[9] A Wigner interpolation formula was used for the correlation energy.[10] The wave functions were expanded in a plane-wave basis with a kinetic-energy cutoff of 10 Ry.[11] A supercell containing sixteen Si atoms was used to simulate isolated H_2^* complexes. Charge integration over the Brillouin zone was replaced by a discrete sum accurate to within 0.1 eV per cell. The structure was determined using a Hellmann-Feynman energy-minimization scheme.[12] The energies for charged states were calculated with a background charge of opposite sign.[13] The LDA total energies and eigenval-

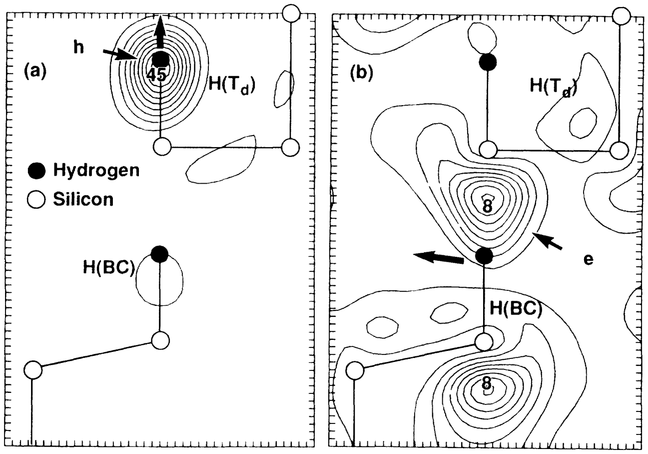

FIG. 1. Atomic positions for an H_2^* complex and charge contours for near-gap H states shown in a (110) plane. The open circles are Si and the solid circles are H atoms. (a) The 1*s* bonding state on the T_d site with a contour spacing of 5. (b) The 1*s* antibonding state on the BC site with a contour spacing of 1. The arrows indicate the dissociation pathways upon capture of charge carriers. The contours are given in units of electron/(320.7 Å^3).

ues were corrected for the well-known band-gap error by projecting each state onto the Si conduction band and using the scissors operator as described in Ref. 14. We found in the present case that the "quasiparticle" energies (i.e., the LDA eigenvalues plus the gap correction) track the transition levels rather closely so that only the electronic contribution to the charged-neutral transition is important. The accuracy of the calculation is estimated to be about 0.2 eV per H pair.

The H_2^* complex, consisting of an H atom at the bond-center (BC) site [H(BC)] and an H atom at the interstitial tetrahedral (T_d) site [H(T_d)] (see Fig. 1), was proposed as a metastable microstructure of H in c-Si.[7] The energy is 0.4–0.45 eV/2H higher than that of an interstitial H_2 molecule.[7,15] In a-Si, the energy difference is expected to be smaller, however, since some of the H_2^* complexes may release preexisting strains among neighboring Si atoms. H_2^* agglomeration gives rise to increased stability.[15] Within the complex, the H(BC) atom has a strong Si-H bond characterized by a local-vibrational-mode frequency (ω) of 2070 cm^{-1} while the H(T_d) atom has a weaker Si-H bond with a vibration of 1480 cm^{-1}.[16] The highest occupied H 1s level is about 0.8 eV below the Si valence-band maximum (VBM) (Fig. 2), and the corresponding wave function is largely localized on the weak Si-H bond [Fig. 1(a)]. In contrast, the lowest unoccupied H 1s antibonding level is about 0.9 eV above the conduction-band minimum (CBM) (Fig. 2), and the corresponding wave function is to a large extent associated with the strong Si-H bond [Fig. 1(b)]. The different energies and characters of the two states lead to distinct microscopic dissociation mechanism for the complexes depending on the carrier type. Holes tend to excite H atoms from the T_d sites while electrons tend to remove H atoms from the BC sites, as shown by arrows in Fig. 1. Eventually both H atoms can leave the complex since the energy barriers for moving a single H atom is reasonably small (~0.2–0.33 eV).[17]

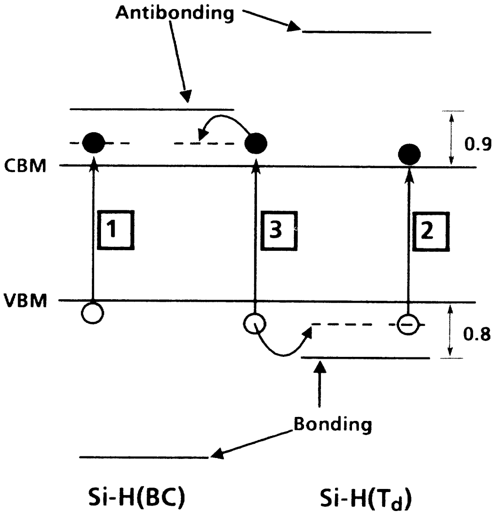

FIG. 2. H levels of the H_2^* complex and possible transitions responsible for light-induced dissociation. In transition 1, the carrier is excited by light (solid arrow) from a nearby Si-Si bonding orbital to the antibonding Si-H(BC) state while in transition 2, the light causes a transition from the bonding Si-H(T_d) to a neighboring Si-Si bond. Transition 3 indicates that light excites electrons and holes via one-photon processes. These carriers then localize near the H_2^* and become captured by the complex. Because of localization of the charges, the transition energies are lower (dashed lines) in all cases as a result of the electron-hole Coulomb interaction.

Our results for the hole-induced dissociation of H_2^* complexes are summarized in Fig. 3, where Fig. 3(a) gives the total energies for the neutral positively ionized complexes and Fig. 3(b) shows the corresponding (+/0) levels. The horizontal axis is the Si-H(T_d) separation along the direction of the Si-H bond. The dissociation of H_2^* complexes can either be direct or be assisted by thermal motion of H atoms. In the former case, H(T_d) captures a hole before it moves significantly away from the equilibrium position. The Si-H bond stretches by almost 50% to reach a new equilibrium. Since the (+/0)

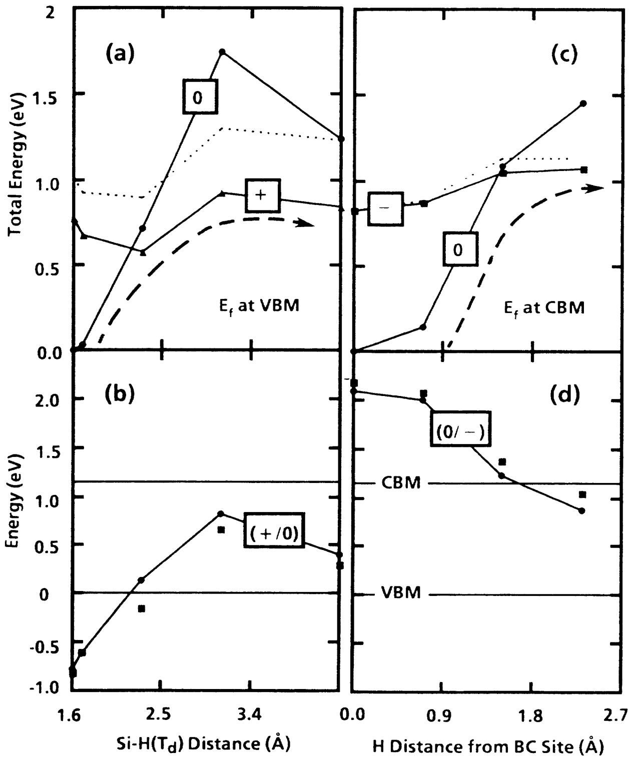

FIG. 3. (a),(c) Total energies and (b),(d) transition levels for H_2^* complexes. (a) and (b) are energies for neutral and positively charged complexes vs Si-H(T_d) separation. (c) and (d) are energies for neutral and negatively charged complexes vs H(BC) displacement. The dotted lines depict the (uncorrected) LDA results for charged states and the arrows indicate the dissociation path. The solid squares are the quasiparticle energies of the electrons.

level at this equilibrium is above the VBM, which is the Fermi level for heavily *p*-doped samples, this ionized configuration is metastable. Only 0.1-eV energy is required to further dissociate the ionized complex. After the dissociation, the H(T_d) diffuses away as a neutral atom and the centered Si atom rebonds to the H(BC) making it positively charged. In the case of dissociation assisted by H thermal motion, thermal excitation causes the Si-H(T_d) bond to stretch, resulting in an increase in the quasiparticle energy of the localized electron [Fig. 3(b)]. If the Si-H(T_d) distance exceeds 2.4 Å, the complex can capture a hole from the VBM and dissociate by excitation over the low energy barrier for the positively charged state as indicated by the arrow in Fig. 3(a). Dynamical effects due to slower motion of the silicon change the barrier heights by less than 0.2 eV. Because the electron relaxation time is much shorter than that of ions, we expect that the direct process is less likely than the thermally assisted process. In either case, the dissociation barrier is 0.9 ± 0.2 eV. From Fig. 3(a), the H complex completely dissociates for a Si-H(T_d) separation of about 3 Å, corresponding to having the H atom at a Si hexagonal interstitial position.

A similar calculation was carried out for electron-induced dissociation and the results are also shown in Fig. 3, where Fig. 3(c) is the total energies of the neutral and negatively charged states and Fig. 3(d) is the corresponding (0/−) level. These energies are plotted against the H(BC) displacement away from the BC site towards the nearest T_d site [Fig. 1(b)]. Because the lowest unoccupied H state is localized at the BC site this atomic path is more effective in lowering the quasiparticle level as well as the total energy than the path discussed for hole-induced dissociation [Fig. 1(a)]. The H(BC) motion in Fig. 1(b) corresponds to an H wagging mode which is much softer than the H stretching mode;[16] thus the (0/−) level in Fig. 3(d) decreases relatively slowly and reaches the CBM at a relatively large H displacement of 1.6 Å. In contrast, the corresponding H displacement for hole-induced dissociation is only 0.6 Å [Fig. 3(b)]. There is no metastable state for electron carriers unless the two H atoms separate completely. The activation energy for electron-induced H-complex dissociation with the Fermi level at the CBM is near 1.1 ± 0.2 eV.

These values agree reasonably well with experimental measurements of defect kinetic barriers in doped *a*-Si:H. For highly 10^{-2}-B-doped *a*-Si:H (produced by a 10^{-2} gas-phase ratio of B_2H_6 to SiH_4 during deposition), the kinetics of defect relaxation has been determined to have an activation energy of about 0.7–0.8 eV.[18–20] For this doping, the Fermi-level position should be close to the VBM in *c*-Si. In 10^{-2}-P-doped *a*-Si:H or with the Fermi level near the CBM in *c*-Si, the activation energy has been determined to be 0.9–1.0 eV.[19,20] These values are in reasonable agreement with the calculated values assuming that the dissociation barrier determines the metastability activation energy. From Fig. 1(a), the Si-H(T_d) bonding state is significantly more localized than the Si-H(BC) antibonding orbital. Such localization, in addition to lowering the energy barrier, increases the probability of ionic motion leading to defect formation. This fact accounts for the greater rate of defect formation by holes than by electrons—a result difficult to explain by rupture of strong Si-H bonds. Furthermore, as the Fermi level is changed towards the midgap doping level for undoped material, experimental data indicate that the kinetic activation energy is about 1.25–1.4 eV,[21,22] in agreement with the approximate 1.3-eV value for dissociation by the reaction $H_2^* \rightarrow H^0(BC) + H^0(T_d)$.[8] Hence, both the doping dependence and the magnitudes of the calculations and experiment are in reasonable agreement.

Of particular interest is that these calculations illustrate a possible mechanism for light-induced defect formation (the Staebler-Wronski effect). Light-induced metastable defect generation has a low activation energy of 0.15–0.4 eV,[22] depending on how the kinetics are analyzed, and the photon energy threshold is as low as 1.2 eV.[23] From Figs. 3(b) and 3(d), it is possible to either optically excite directly the levels responsible for dissociation (transitions 1 and 2, Fig. 2) or create band-tail carriers which then occupy the bonding and antibonding levels (transition 3). In the former case, light excites an electron from the valence-band state associated with the sp^2 bonds of the H(T_d)-bonded Si to the Si-H(BC) antibonding level (transition 1) or from the Si-H(T_d) bonding state to the conduction-band-minimum states associated with the sp^2 antibonding states of the H(T_d)-bonded Si (transition 2). The charge densities of these states indicate significant overlap is necessary for a large optical transition matrix element (Fig. 1). Once the carriers occupy their respective bonding or antibonding states, the activation barrier for either transition 1 or 2 would be only about 0.2 eV (Fig. 3), in accordance with the observed values. Because the relatively localized electron and hole states caused by this transition are only about 1.1 Å apart (Fig. 1), one would expect a strong exciton lowering of the optical energy (dashed lines, Fig. 2) necessary to induce such a transition. Using a dielectric constant of 12, the exciton energy lowering, estimated to be proportional to the electron-hole Coulomb energy, is roughly 0.6 eV. The resulting photon energy threshold for light-induced defect formation would be about 1.5 eV—a value in a reasonable agreement with the observed value of 1.2 eV.[23] Alternatively, defect creation by transition 3 occurs when H_2^* captures photoexcited carriers from a neighboring band-tail state in the presence of the opposite charge located on the Si backbonds. The Coulomb energy reduces the 0.8–0.9-eV energy required to thermally excite the carrier into either the bonding or antibonding state to roughly 0.2–0.3 eV. Upon dissociation, individual H atoms will leave the complexes in a neutral form similar to charge-induced dissociation. The estimated total dissociation activation energy for transition 3 is, therefore, about 0.4 eV including the subsequent diffusion barrier. Regardless of which possibility in Fig. 2 applies, we see that the H_2^*-complex dissociation can account for the low subgap photon energy threshold and the low thermal activation energy, and is consistent with experiments indicating that electron-hole pair formation accelerates defect formation.

This work demonstrates that H_2^* dissociation is a viable model for metastability in silicon-hydrogen systems. The calculations indicate that single carriers cause dissociation of paired H with barriers compatible with experiment. These isolated, interstitial, H atoms diffuse to create midgap defect and passivate dopants. The H_2^*-complex dissociation mechanism also provides an explanation for the low photon energy threshold required for defect generation and the low activation energy for light-induced defects in amorphous Si.

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