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# Microscopic mechanism for dopant activation in hydrogenated amorphous silicon

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A microscopic model for doping activation and passivation, in both *n*- and *p*-type hydrogenated amorphous silicon (*a*-Si:H) is proposed explaining the variation of doping efficiency with bias and thermal history and the activation energies and kinetics of dopant activation.

Unlike crystalline silicon, amorphous materials should be difficult to dope because the dopant atom, being less constrained by the surrounding network, is free to adopt a coordination which does not move the Fermi level. Surprisingly, it was discovered that hydrogenated amorphous silicon (*a*-Si:H) could be readily doped both *n*- and *p*-type with the incorporation of dopant atoms.[1] Furthermore, the doping efficiency is affected by Fermi-level position,[2] thermal and bias history,[3-5] and illumination.[6,7] Despite significant study of various aspects of doping and its technological importance, the microscopic doping mechanism remains unclear, and the doping properties of *a*-Si:H are unique among amorphous materials. In this paper, a microscopic model based on recent progress in understanding H passivation of dopants in crystalline silicon is proposed to explain doping activation and passivation in *a*-Si:H.

Previous models proposed that dopant activation and passivation occurs through threefold to fourfold coordination changes involving breaking and switching of dopant-Si or dopant-H bonds[8-10] ignoring dopant passivation mechanisms known to occur in crystalline Si (*c*-Si). In the case of B in *c*-Si, the H atom inserts between the B and a neighboring Si atom, bonding to the Si, and passivating the B acceptor level.[11-14] In the case of P, the H is located in an antibonding site forming a bond with the Si atom, breaking the P—Si bond, and removing the P donor level (Figs. 1 and 2).[12-14] It is unlikely that these effects only occur in *c*-Si since the local configuration for fourfold dopants in *a*-Si:H should be nearly the same. Furthermore, breaking and switching of dopant-Si and dopant-H bonds requires on the order of 2 eV or the improbable association of weak bonds with Si—H bonds.[8-10] Defect kinetic studies indicate that the barriers are on the order of 0.7–0.8 and 0.9–1.0 eV for dopant passivation in heavily B- and P-doped material, respectively.[7,15]

It is proposed in this paper that doping and the position of the Fermi level in *a*-Si:H is determined by the equilibration between H passivated and unpassivated fourfold dopants according to the following model. Some fraction of the dopants enter into a fourfold coordinated site while others reside in threefold sites. The relative numbers are determined by the total energies of formation and the kinetics during growth. Once the material is deposited, the number of threefold and fourfold coordination sites remain more or less fixed for temperatures less than 400 °C with threefold sites probably predominating. The relative doping efficiency of the fourfold sites is determined by passivation through the presence of H as in the

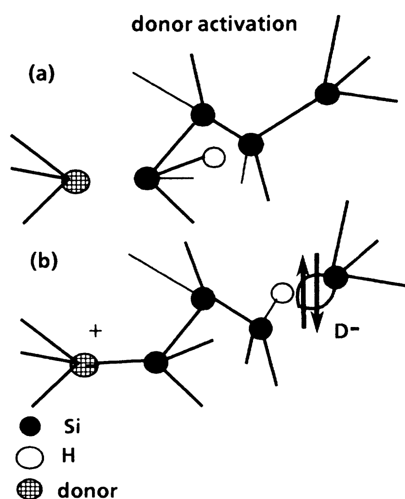


FIG. 1. Schematic of donor activation in *n*-type *a*-Si:H where (a) represents the initial, passivated configuration and (b) the final, activated configuration.

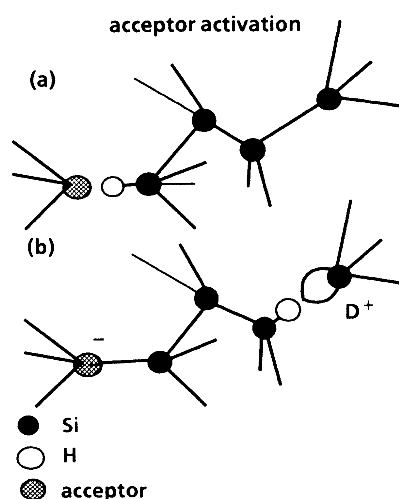


FIG. 2. Schematic of acceptor activation in *p*-type *a*-Si:H where (a) represents the initial, passivated configuration and (b) the final, activated configuration.

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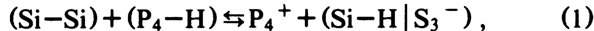
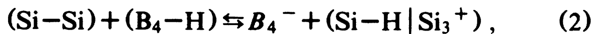
case of $c$-Si. Considering $n$-type material first, it is proposed that the number of active phosphorus dopants is determined by the model depicted in Fig. 1. A fourfold P atom is passivated by an H in the $T_d$ site (near the antibonding site). Through either the capture of an electron or thermal dissociation, the H atom becomes an interstitial and migrates with a diffusion energy of 0.1–0.2 eV (Ref. 16) to a weak Si–Si bond site forming a dangling bondlike defect. This defect captures a carrier, while the fourfold donor becomes positively charged (ionized) $P_4^+$ as an active, unpassivated donor (Fig. 1).

This process can be represented by the reaction



$$(\text{Si}-\text{Si})+(\text{P}_4-\text{H}) \leftrightarrows \text{P}_4{}^{+}+(\text{Si}-\text{H}\,|\,\text{S}_3{}^{-})\,, \quad (1)$$

where $P_4$–H represents a passivated fourfold P atom, (Si–Si) represents a weak Si–Si bond, (Si–H|$Si_3^-$) represents the negatively charged defect created by H breaking a weak Si–Si bond. The annealing process occurs either by a reversal of this reaction or more likely, an H from the dissociation of a two-H-atom complex,[17] denoted by $H_2^*$, creating two isolated H atoms which passivate activated dopants. Thermal equilibrium, determined by the relative energies of the initial and final states, is eventually established. An analogous reaction holds for acceptor activation in $p$-type material as well. The configuration changes responsible for acceptor activation are shown in Fig. 2. The reaction describing the acceptor activation energy is



$$(\text{Si}-\text{Si})+(\text{B}_4-\text{H}) \leftrightarrows B_4{}^{-}+(\text{Si}-\text{H}\,|\,\text{Si}_3{}^{+})\,, \quad (2)$$

where $B_4$–H is a passivated boron. Passivation is dominated by $H_2^*$ dissociation.

The two-H-atom complex $H_2^*$ proposed by Chang and Chadi,[13–17] is formed by an H atom in the bond-centered configuration, H(BC), and another in the adjacent $T_d$ position, H($T_d$). The Si–Si bond is broken and replaced by two reasonably strong Si–H bonds. Consequently, there is no midgap states associated with this complex—only occupied and unoccupied states near the respective band edges. Heuristically, the complex can roughly be viewed as the intimate association of two charged defects: H+(BC) and H−($T_d$). When the defects lie adjacent to each other, charge is transferred back making each H neutral. This complex can diffuse with an activation energy of 1.0 eV or dissociate.[13,17] These complexes can in turn coalesce into larger lower-energy complexes.[18] Based on infrared and nuclear-magnetic-resonance studies and the energetics, it is estimated that there are roughly $10^{18}$–$10^{20}$ isolated complexes per $cm^3$ and $10^{21}$ per $cm^3$ H atoms in the larger complexes.[18] Primarily, the isolated complexes are involved in the metastable phenomena.

The implications of these reactions compare well with experiment. In particular, the total energies of these configurational changes have been calculated for $c$-Si and can be compared to the observed activation energies. It is assumed in the following that the effect of disorder in $a$-Si:H broadens levels into bands but that the average or most probable energy remains approximately the same as in $c$-Si. In Fig. 3, the total energies of formation from local-density calculations[13,14,16] are presented as a function of Fermi-level position in $a$-Si:H. Since the band gap

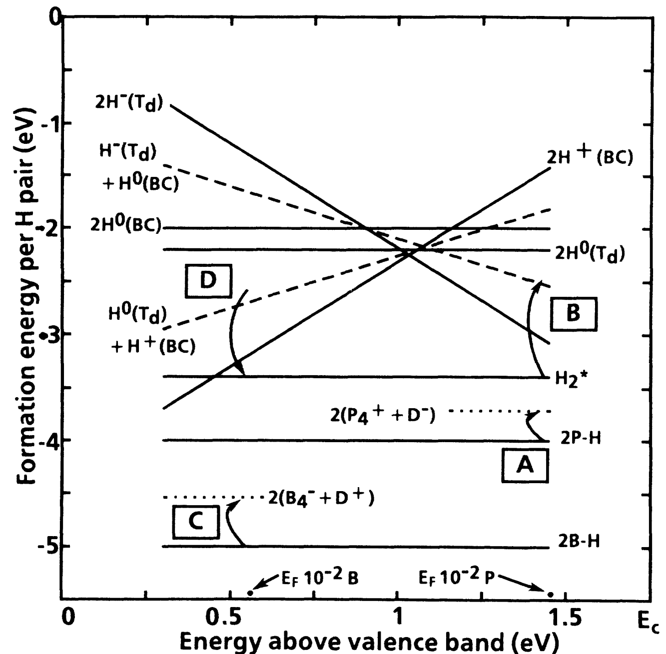



FIG. 3. Calculated total formation energies of various pairs of H configurations in $c$-Si relative to 2H atoms in the vacuum from Refs. 12 and 13 as a function of Fermi level in $a$-Si:H. BC denotes the bond-centered site, $T_d$ is the interstitial tetrahedral site, $H_2^*$ is an H(BC)–H($T_d$) bound pair, and B–H and P–H denote passivated dopants. Transitions $A$ and $C$ represent the energy necessary for dopant activation in equilibrated $10^{-2}$ B- and P-doped $a$-Si:H, respectively. Transitions $B$ and $D$ represent the energy barriers required for $H_2^*$ dissociation and passivation of active dopants in B- and P-doped material, respectively.

of $a$-Si:H is 0.6 eV larger than $c$-Si, 0.3 eV has been added to valence and conduction band to refer the Fermi energy to $a$-Si:H band edges. Other means of correcting the band-gap difference, effects due to disorder, uncertainties in the calculations give an estimated uncertainty on the order of 0.3 eV in the energies in the following discussion.

Using the energy diagram in Fig. 3, a number of consequences of this model follow which are in good agreement with experiment. The total-energy difference for the dopant activation reaction (1) is the energy required to dissociate a passivated complex into neutral species minus the electronic energy gained by redistributing charge. The former energy for $(P_4\text{-H}) \rightarrow P_4^0 + H^0(T_d)$ is 0.9 eV $[=(2E_{H^0(T_d)} - 2E_{P\text{-}H})/2]$, and the electronic energy of 0.75 eV is gained from taking an electron from the donor transition level ($E_c - 0.1$ eV ) to the defect (0/−) transition at $E_c - 0.85$ eV.[15] Hence, the total energy cost for fourfold P activation is $0.9 - 0.75 = 0.15$ eV independent of Fermi-level position ($\frac{1}{2}$ transition $A$ energy in Fig. 3). These energies are in good agreement with those found for doping equilibration in P-doped material,[7,15] where the formation energy (represented by $U_p + U_d$ in Ref. 15) is 0.9 eV and the electronic energy gain was estimated to be 0.75 eV. Of course, the addition of disorder broadens all the levels into distributions which affects the equilibrium

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in a known way.[19]

Furthermore, passivation kinetics are also in agreement. If a sample reaches equilibrium at a temperature above the equilibration temperature, the number of activated donors increases with an activation energy of 0.25 eV representing the total energy difference.[15] If the film is brought rapidly to lower temperatures as in rapid thermal quenching, an excess number of activated $P_4$'s exist. Hence, the number of donors determined by hyperfine measurements should increase, consistent with observations.[10] These activated donors become passivated by dissociation of $H_2^*$ complexes according to $2e + H_2^* \rightarrow e + H^-(T_d) + H^0(BC) \rightarrow 2H^-(T_d)$ (transition *B*, Fig. 3). In $10^{-2}$ P-doped *a*-Si:H, under equilibrium conditions, the Fermi energy is located 0.28 eV below the conduction band or at $E_v + 1.5$ eV.[15] Hence, the $H_2^*$ dissociation activation energy at this Fermi-level position is 0.85 eV. Since the diffusion activation energies for both $H^-$ and $H^+$ are very low (0.1–0.2 eV),[16] the donors are passivated with an activation energy barrier of roughly 0.95–1.05 eV in good agreement with the observed range of values of 0.9–1.0 eV.[7,15,20,21] Furthermore, since the $H_2^*$ dissociation energy depends on Fermi level, the passivation rate decreases as the P-doping level decreases also in agreement with experiment.[15,20]

If the sample is illuminated, defects created by $H_2^*$ dissociation lower the Fermi energy.[22] Lowering the Fermi level decreases the rate of dopant passivation and therefore the equilibrium number of activated dopants increases. This light-induced effect has been observed in the effect of illumination on picosecond absorption measurements as well as hyperfine measurements in doped material.[6,10] Finally, this model explains the missing H hyperfine splitting of the neutral-donor electron-spin resonance.[22] According to Fig. 3, and $H_2^*$ complex in the neighborhood of the P donor is unstable to the formation of a passivated donor and a midgap defect. Hence, the only neutral donors which have a spin signal are those without H nearby. The proposed microscopic model thus accounts quantitatively for the observed kinetics and doping equilibrium as well as a number of other previously observed phenomena in *n*-type material.

The detailed experimental investigation of the formation energies and electronic relaxation energies for *p*-type *a*-Si:H have not been undertaken. Presumably, transition *C*, Fig. 3 represents the energy required for dopant activation. The annealing kinetics, however, have been studied. Because the equilibrated Fermi level in *p*-type material is at $E_v + 0.45$ eV,[22] the $H_2^*$ dissociation barrier for the reaction $2h + H_2^* \rightarrow h + H^+(BC) + H^0(T_d) \rightarrow 2H^+(BC)$ (transition *D*, Fig. 3) is 0.7 eV giving a passivation activation energy including diffusion of 0.8–0.9 eV. This agrees well with the observed values of 0.7–0.8 eV in heavily *B*-doped material.[7,15] The 0.15-eV lower barrier for passivation by $H_2^*$ dissociation explains why equilibration is 300 times faster in $10^{-2}$ B- than in $10^{-2}$ P-doped material at room temperature in agreement with experiment.[15] The fact that $H_2^*$ becomes unstable for a Fermi-level position below $E_v + 0.4$ pins the Fermi level, making it difficult to stably dope the Fermi level below this point.[22] Thus, the energetics of the dopant passivation calculated for *c*-Si agree rather well with the observed kinetics in *a*-Si:H, suggesting that a single mechanism underlies both forms of Si as well as polycrystalline silicon. Moreover, other calculations yield similar results.[14,16] Unlike previous models proposed for *a*-Si:H, the total-energy calculations for this model are known and are in agreement with previous experiments.

The presence of $H_2^*$ complexes along with the passivation reactions discussed in this work can account for many other puzzling aspects of amorphous Si. The complexing accounts for the clustered H component indicated by the broad nuclear-magnetic-resonance component,[23] the effect of doping on H diffusion and H evolution,[24] and doping passivation in micro- and polycrystalline Si.[25] Furthermore, $H_2^*$ explains the creation and annealing of metastable defects. These aspects are discussed in other publications.[18]

In summary, this model quantitatively accounts for a number of aspects of dopant activation in *a*-Si:H and provides an explanation to a number of observations concerning doped *a*-Si:H. With this microscopic model, doping activation in the presence of hydrogen for both *a*-Si:H and *c*-Si, are treated in a consistent, unified manner. Therefore, it should be considered as a viable model for doping activation in *a*-Si:H.

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