Microscopic mechanisms for creation and removal of metastable dangling bonds in hydrogenated amorphous silicon

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We present a microscopic model for metastable Si dangling-bond defect creation in hydrogenated amorphous silicon, which is applicable to both light-induced defect creation in solar cells (Staebler-Wronski effect) and bias-stress-induced defect creation in thin-film transistors. Light or gate bias causes electron-hole pairs or electrons, respectively, to be localized on short, weak Si-Si bonds, which then break. A hydrogen atom, from a neighboring, doubly hydrogenated weak Si-Si bond (SiHHSi) moves to the T_d site of the broken Si-Si bond. The other H atom from the SiHHSi is also located in the energetically favorable T_d site. Overall, the reaction produces two SiHD defects. Each SiHD defect is an intimate Si dangling bond and Si-H bond, where the H atom is in the T_d site, not the BC site. The distance between the dangling bond and the H atom in the T_d site is in the range 4–5 Å, in agreement with ESR data. The majority of silicon dangling bonds, both metastable and stable, exist as SiHD, with the H atom in the T_d site. The microscopic process for defect creation is fairly well localized, requiring only short-range H motion, which proceeds via bond switching between neighboring T_d sites. In contrast, the microscopic process for defect removal during thermal annealing involves reequilibration of H in the a-Si:H network and is a global process involving a large fraction of H atoms. The rate-limiting step for this process is Si-H bond breaking from SiHHSi sites, which accounts for the maximum activation energy of 1.5 eV. We present a revised hydrogen density of states diagram, in line with this process.

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I. INTRODUCTION

Metastable Si dangling bond defects are formed in hydrogenated amorphous silicon (a-Si:H), whenever it is illuminated or charge carriers are injected. This is a crucial fundamental property that limits the performance of both solar cells and thin film transistors. These are, by far, the two most important applications of amorphous semiconductors. In the case of defect creation by illumination, the effect is known as the Staebler-Wronski effect[1] and this is the main fundamental limitation to the efficiency of amorphous silicon solar cells. In the case of thin film transistors, electrons are injected into the channel region of the transistor and this causes Si dangling bonds to be created, which leads to a threshold voltage shift.[2] This is a serious instability, which prevents their use in certain circuit applications. Defect state creation is also observed for unipolar and bipolar current injection in switching diodes.[3] We believe these defect creation reactions have a common cause, and it is of considerable importance to understand this at a microscopic level.

There has been an enormous amount of research on these topics over more than 20 years. In spite of this, there is still no consensus for a microscopic model that can explain all the experimental results. It is well established that dangling bonds are created. The key problem revolves around the role of hydrogen. It is generally considered that H motion probably plays some role in stabilizing the defects, for example, by inserting a hydrogen atom into a broken Si-Si bond to form a SiHD defect (an intimate Si dangling bond and Si-H bond). However a H atom placed at the bond-centered position, would imply that the dangling bond and H atom are separated by about 2 Å, which would lead to a measurable hyperfine broadening of the ESR signal, which has never been observed.[4]

In this paper, we propose a resolution of this problem. We suggest that the hydrogen atom in the SiHD defect is not located at the bond centered site (BC), but in the tetrahedral-like site (T_d).[49] We still refer to this defect as SiHD, and the defect is still correctly identified as an intimate Si dangling bond and Si-H bond. This remains completely consistent with our defect pool model.[5,6] However, the separation of the dangling bond and hydrogen atom is now in the range 4–5 Å and this would be consistent with all ESR experiments. We propose that the weak bond, which is broken, is a short bond, not a long bond. Stabilization of a broken short bond by insertion of hydrogen in a T_d site is favored over the BC site and we propose that the vast majority of dangling bonds in hydrogenated amorphous silicon, both stable and metastable, are SiHD defects of this type.

The process of defect removal, by annealing, is not simply the reverse process to defect creation. Dangling bond defects can only be removed by a process of reequilibration of the silicon-hydrogen network. This is a global process involving a large fraction of the H atoms.

II. KEY EXPERIMENTAL RESULTS

The defect density in amorphous silicon is a thermal equilibrium property and the process of thermal equilibration is mediated by hydrogen motion. This is the so-called hydrogen glass model for a-Si:H.[7] The density of dangling bonds under thermal equilibrium conditions depends strongly on the

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Fermi energy, and not so much on the actual density of hydrogen.

Experiments with thin film transistors showed clearly that not only the density of dangling bonds, but also the energy spectrum of dangling bond defects in the a-Si:H bandgap, depended on the Fermi level. Bias temperature annealing of a-Si:H thin film transistors leads to a threshold voltage shift of both n-channel and p-channel TFT's, with some changes in one of the prethreshold slopes, depending on the sign of the bias. Raising the Fermi level (electron accumulation) leads to more dangling bond states in the lower part of the band gap. Lowering the Fermi level (hole accumulation) leads to more dangling bond states in the upper part of the band gap.[2]

Nickel and Jackson showed that modifying the hydrogen content of a-Si:H, either by hydrogenation or by dehydrogenation has little effect on the dangling bond density.[8] Adding or removing more than 10^{21} hydrogen atoms changes the dangling bond density by less than 10^{17}. This means that hydrogen must exist mainly in paired configurations, and not as isolated Si-H. If hydrogen is only bonded as isolated Si-H, then the addition of one extra H atom to the network would result in the breaking of one Si-Si bond and the formation of one dangling bond. This clearly does not happen. A second hydrogen atom must always accompany the first and result in two SiH bonds. Similarly the removal of hydrogen does not, initially, have much effect on the dangling bond density. Hydrogen atoms are removed in pairs and the majority of hydrogen is therefore located in paired configurations, which we label SiHHSi.[5,6] Hydrogen in Si-Si bonds has a negative correlation energy U_{H}, such that occupancy by two hydrogen atoms has a lower energy (per hydrogen atom), than occupancy by one hydrogen atom. There are a far larger number of SiHHSi states, than isolated Si-H states and the majority of hydrogen exists in SiHHSi states.

The exact microscopic model for SiHHSi is not specified or exactly determined. One possibility is the amorphous analogue of the H_2^* complex in crystalline silicon, where one H atom is located at the bond-centered site and one at the tetrahedral-like site (T_d). Another possibility is a double tetrahedral-like configuration, where both H atoms are in T_d sites. This latter configuration actually has a HSiSiH linear arrangement of atoms, but we stick with the notation "double T_d SiHHSi," in line with previous work.[5,6,9] For both the H_2^* and the double T_d models, there is significant structural relaxation of the original Si-Si bond distance and two well defined Si-H bonds are formed.

The dependence of the dangling bond defect energies on the Fermi level and the role of hydrogen, in the equilibration process, is well described by our defect pool model.[5,6] Here the defect equilibration reaction is shown to be SiHHSi + Si-Si⇔2SiHD. Hydrogen is essential to generate the right entropy. Without hydrogen, we could not account for the intrinsic dangling bond density and its temperature dependence in amorphous silicon.[5] The majority of Si dangling bonds therefore exist as SiHD. Further, independent evidence in support of our defect pool model is provided by DLTS experiments[10] and from quasistatic capacitance-voltage measurements.[11]

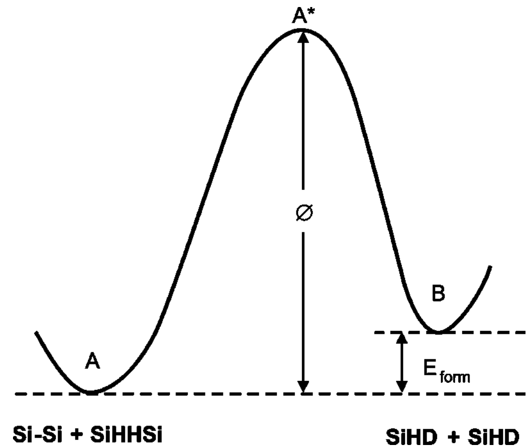

FIG. 1. Energy diagram illustrating the difference between metastable defect formation and thermal equilibrium defect formation processes. State A is the initial state, state B is the final state, after defect formation, state A^* is the intermediate state, during the defect formation process. The energy barrier for defect formation is Φ. The formation energy is E_{form}.

Bias temperature stress (as opposed to bias temperature annealing) is a *nonequilibium* experiment. Here we create new dangling bonds, due to an applied bias, at a lower temperature. We monitor the rate of dangling bond creation. Figure 1 illustrates the difference, between bias annealing and bias stress. There is a potential barrier between the initial state A, which is SiHHSi+Si-Si, and the final state B, which is 2SiHD. The potential barrier represents a third, intermediate, state A^*. In a bias-annealing experiment, we measure the equilibrium situation. We establish an equilibrium population between the states A and B, so the nature of state A^* is immaterial. In a bias-stress experiment, we measure the rate of defect creation, so A^* is significant, since the rate of defect creation is primarily dependent on the barrier to defect creation.

Possible reaction pathways for the defect creation are

$$\mathrm{SiHHSi+Si-Si \rightarrow SiHHSi+2D \rightarrow 2SiHD}, \tag{1}$$

$$\mathrm{SiHHSi+Si-Si \rightarrow 2SiHD+H_{\mathit{i}}+Si-Si \rightarrow 2SiHD}. \tag{2}$$

In Eq. (1), Si-Si bond breaking is the rate limiting step and the barrier state (A^*) is SiHHSi+2D. The broken Si-Si bond is subsequently stabilized by a hydrogen atom from a SiHHSi, which must involve the breaking of a SiH bond. In Eq. (2), Si-H bond breaking is the rate limiting step and the barrier state (A^*) is SiHD+H_i+Si-Si. H_i is a mobile H atom which is successively captured at a (weak) Si-Si bond forming a second SiHD.

Bias-stress experiments on samples with different intrinsic stress, show that the reaction rate is dependent on the Si-Si bond strength and not on the SiH bond density or character, which favors reaction (1) and not reaction (2).[9,12] Furthermore, this dependence showed only for samples with compressive stress and not with tensile stress, which suggests that the Si-Si bonds are short bonds and not long bonds. We therefore conclude that the rate-limiting step for

dangling bond creation is the breaking of short, weak Si-Si bonds and not the breaking of a Si-H bond.

It is possible to measure an activation energy and an attempt frequency for the defect creation process, using the thermalization energy concept.[13] We measured an activation energy of $0.9-1.0$ eV and an attempt frequency of 10^{10} Hz. The activation energy is interpreted as the energy to break the weak Si-Si bond in the presence of excess electrons.[12] The energy is slightly dependent on the electron density, a factor which is anticipated in the full theoretical analysis.[14] The attempt frequency is interpreted as the Si-Si phonon frequency times the probability of finding an electron localized on the Si-Si bond, determined from the localization length of the electron wave function.[15]

The process of defect removal, by thermal annealing, can also be analyzed using the thermalization concept. We measure an activation energy for defect removal in the range $1.1-1.5$ eV, depending on how the defects are formed.[9,16] Most significantly, however, the attempt frequency is 10^{13} Hz, quite different to that for defect creation.[13] This important result suggests that the microscopic mechanism for defect removal is different to defect creation. The attempt frequency for defect removal is consistent with the phonon frequency for Si-H bonds and with a process of Si-H bond breaking. The activation energy of 1.5 eV is very similar to the activation energy of long range H diffusion, suggesting that defect annealing also proceeds by long range hydrogen diffusion. The mechanism is consistent with the emission of H out of SiHHSi sites. Defect annealing is therefore a global process, involving a large fraction of H atoms in the network.

Light-induced creation of dangling bonds has a very low activation energy[17] and can even proceed efficiently at very low temperature.[18] This strongly suggests some localized defect formation process. Light-induced defect creation is not consistent with long-range light-induced hydrogen diffusion, which has an activation energy of 0.9 eV.[19] On the other-hand, annealing of light-induced defects, formed at room temperature, has an activation energy in the range $1.1-1.3$ eV,[17] similar to annealing of bias-stress induced defects.

The experimental correlation of light-induced defect creation with stress in films is not well established. Nonomura *et al.* performed very careful experiments of photo induced expansion, and showed a correlation with intrinsic stress. However, their light-induced defect densities varied little, over the normal range of deposition temperatures.[20] Attempts to measure the effect of externally applied stress on the light-induced defect creation show conflicting results.[21–23] However, our analysis of these experiments[12] suggest that the true stress induced in the amorphous silicon film is quite low and these experiments cannot be compared with the large variations of intrinsic stress in different samples. More importantly, our experimental correlation of bias-stress created defect densities with intrinsic stress is due to the dominant role of the energy barrier for defect creation. For light-induced defect creation, there is a negligible energy barrier and we would not expect the same correlation of light-induced defects with intrinsic stress.

Palinginis *et al.*[24] have studied the defect creation and annealing process in a-(Si,Ge):H alloys, using modulated photocurrent measurements. The experiments monitor the separate time evolution of Si and Ge dangling bonds. They find a clear asymmetry between defect creation and defect annealing. Analysis of the data suggests that the defect annealing is a global process, related to long range hydrogen diffusion, while defect creation is not.

ESR experiments give important information on dangling bond interactions. There is no detectable spin-spin dipolar broadening in conventional ESR, even after light-induced metastable defect creation, which means that dangling bonds are well separated from each other, by at least 10 Å, and could even be randomly dispersed.[25] However, there is a measurable hyperfine broadening of the Si dangling bond signal which increases with hydrogen content. The hyperfine broadening is consistent with a random distant hyperfine interaction with the hydrogen nuclei.[26] The broadening is about $0.4G$, for 2% hydrogen, increasing to $1.3G$ for 18% hydrogen. Most striking is that the line shape hardly changes, at all, when new dangling bonds are created by illumination, where the hydrogen content remains the same.[26] This is consistent with a random distant hyperfine interaction, since the density of hydrogen atoms is much larger than the density of dangling bonds and the mean dangling bond to hydrogen separation is of the same order, as the mean hydrogen-hydrogen separation. This rules out a well-defined ligand for SiHD, where the separation of the dangling bond to hydrogen is less than 4 Å.[26–28] It does not, however, rule out a well-defined ligand, where the separation is more than 4 Å.

NMR experiments give information about local H environments. They show a narrow line and a broad line. Both the narrow line and the broad line are present in high quality device grade a-Si-H, which show no dihydride (SiH_2) modes in the IR spectra. The narrow line is usually interpreted as randomly distributed isolated monohydrides (Si-H).[29] The width of the narrow line gives an estimated H-H separation of 6–8 Å.[30] The broad line is due to clustered monohydrides. PECVD samples with less than 4% hydrogen have no clustered hydrogen.[31] Samples with higher hydrogen content have most of the extra hydrogen in clustered sites, while the concentration in nonclustered sites is more or less constant. The clustered sites in PECVD a-Si:H typically have six hydrogen atoms per cluster and are consistent with hydrogen decorated divacancies.[32] The H-H separation in such clusters is estimated to be 2–3 Å. Hot-wire a-Si:H has larger clusters of typically 14 atoms, and a smaller H-H separation, in spite of an overall lower H concentration.[30]

It is important to distinguish between clustered hydrogen and hydrogen in SiHHSi, which is not clustered hydrogen. Only clusters of SiHHSi would be considered clustered hydrogen. If SiHHSi also exists in the nonclustered phase, then the H-H separation must be 6–8 Å. This is inconsistent with H_2^*, where the H-H separation is 3.4 Å, but is consistent with the double T_d model of SiHHSi, where the H-H separation is 6.4 Å (based on values for H_2^* in crystalline Si). Since hydrogenation experiments in PECVD a-Si:H show hydrogen is also paired for low hydrogen concentrations

FIG. 2. Energy diagram illustrating the defect formation process. States A^* and B^* are intermediate states, between the thermal equilibrium initial and final states A and B. The overall chemical reaction is SiHHSi+Si-Si→2 SiHD. The intermediate states, considering only the Si-Si bond, are Si-Si$\rightarrow D^0+D^-\rightarrow 2D^- \rightarrow 2$ Si$\mathrm{H}D$.

(1–3 %),[33] this suggests that the majority of hydrogen, in the nonclustered phase, consists of SiHHSi, with both hydrogen atoms in T_d sites. Dangling bonds occur mainly in the nonclustered phase.

III. MICROSCOPIC MODEL FOR DEFECT CREATION

The key features of our microscopic model are as follows. Short, weak Si-Si bonds are the precursors for dangling bond defect formation. This is supported by theoretical calculations, which show that the valence band tail is dominated by short bonds in relaxed amorphous silicon.[34] Device-grade amorphous silicon is always under compressive stress which leads to a further weakening of the short bonds. This has been shown by experiments on the intrinsic mechanical stress dependence of defect formation.[12] Compressive stress produces shorter bonds and the rate of defect creation increases. Short bonds most easily occur at highly strained regions of the network.

Dangling bond formation proceeds, first by carrier induced bond breaking of the Si-Si short bonds. The kinetics of the defect formation process are determined by the Si-Si bond breaking step. Originally, it was thought that the rate of defect creation was only dependent on state A and state A^* in Fig. 1. However, recently, we have shown that the backward reaction is always significant, since there is an exponential distribution of barrier heights and some low energy barriers have a significant backward component.[9] Furthermore, a detailed analysis of the reaction kinetics allows us to identify the backward reaction with an intermediate state B^*, associated with two negatively charged dangling bonds.[14]

Figure 2 shows a refined version of Fig. 1 illustrating the defect formation process, for electron induced defect creation. Si-Si bond breaking occurs when a bond is occupied by a single electron. The intermediate state A^* is therefore D^0+D^-. The neutral dangling bond then captures an additional electron lowering the overall energy. State B^* is therefore $2D^-$. This state has a reasonably long lifetime (rough estimate 1 ns) due to the stabilizing presence of two electrons. If there is a doubly hydrogenated silicon bond (SiHHSi) sufficiently close to the broken bond, then there is a small but finite probability (within the lifetime of the $2D^-$ states) that one hydrogen atom can move to the site of the broken Si-Si bond, and form an SiHD. This is the reaction $B^*\rightarrow B$, in Fig. 2. Once the SiHD is formed, the reaction will not be reversed, when electrons are removed, by simply removing the bias.

A similar diagram is appropriate for light-induced defect creation, though in this case, defects are not formed due to a single carrier, but only by a bimolecular process, involving e-h pairs localized on (or very close to) the same weak Si-Si bond. Most of the energy for the barrier $A\rightarrow A^*$ is provided by the energy of the e-h recombination event, leaving a very low effective energy barrier for light-induced defect creation. Defects are formed in a neutral state, so state A^* corresponds to $2D^0$ (or possibly $D^+ + D^-$). The subsequent charge state of the defects (under illumination) depends on electron and hole capture cross sections and on the electron and hole populations. Asymmetries between electron and hole properties, lead to the conclusion that most states will be negatively charged, under illumination in the steady state.[35] This implies that intermediate state B^* is mainly $2D^-$, the same as for electron induced defect creation.[14] Of course many, though not all, of the light-induced SiHD states will become neutral again, in the dark.

The broken short bond is stabilized by inserting a hydrogen atom in the T_d site. Furthermore the other hydrogen atom in the SiHHSi is also located in a T_d site, since SiHHSi has the double T_d configuration. SiHHSi originates from the double hydrogenation of a short, weak bond and the T_d site is energetically favored. The overall reaction results in the formation of two SiHD, where the hydrogen is always in the T_d site and never in the BC site. The hydrogen atom moves a relatively short distance, so this is truly a local model for defect formation.

The separation of each hydrogen atom in a T_d site from the dangling bond can be estimated, as follows. In crystalline silicon, the normal Si-Si bond length is 2.35 Å and the Si-H bond length is 1.48 Å. Without any structural relaxation, this gives a separation of 3.83 Å. Structural relaxation leads to a separation of 4.9 Å, for the distance between the first Si atom and the H atom in the T_d site, for a H_2^* complex, with both H atoms present, according to Chang and Chadi.[36] Isoya *et al.*[27] estimate the distance from the dangling bond to a H atom in the T_d site (labeled the F1 site by Isoya *et al.*) to be 4.6 Å. These published calculations are based on a crystalline Si lattice. We believe the degree of structural relaxation will be greater in a-Si:H, and this will be more significant than the distribution of Si-Si bond lengths. We therefore conclude that in each SiHD, with H in T_d, the separation of the H atom from the dangling bond will be in the range 4–5 Å. This is completely consistent with ESR experiments.[26–28]

Important to the argument in this paper is how the energies of the BC and T_d sites change for the case of short, weak bonds. Figure 3 shows the calculated energy of H in the BC site as the Si-Si bond length is increased.[37] We can

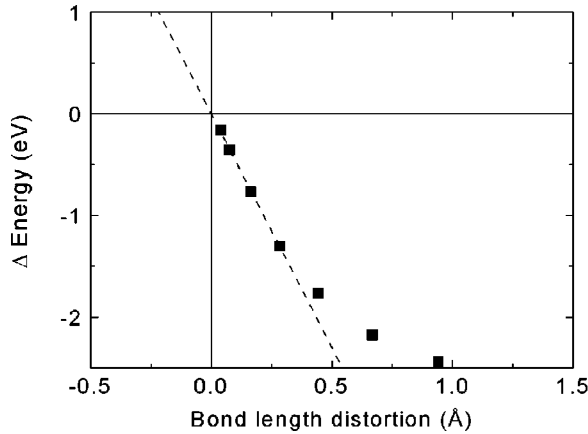

FIG. 3. The energy of the H in BC configuration, as a function of the Si-Si bond length [after van de Walle and Nickel (Ref. 37)]. The energy is reduced for long Si-Si bonds, but conversely it is raised for short Si-Si short bonds.

extrapolate this result and infer that for short bonds, the energy will be raised compared to average bonds. Placing H in an average, Si-Si bond forces the Si-Si atoms apart and this costs strain energy. It must cost more energy to place the hydrogen atom in a Si-Si bond, which is already constrained to be shorter than average. On the other hand, there will be relatively little effect on the energy of the T_d site. Therefore, the energy of the T_d site will be energetically favored, for short, weak Si-Si bonds, compared to average bonds.

Figure 4 shows the energy of H in the BC site, compared to H in the T_d site, for different charge states.[38] The energy of the H in BC and H in T_d, sites in the neutral state has been calculated by Chang and Chadi[36] and van der Walle[39] for crystalline silicon. Chang and Chadi[36] find the T_d site to be the lowest energy, while van der Walle[39] finds the BC site

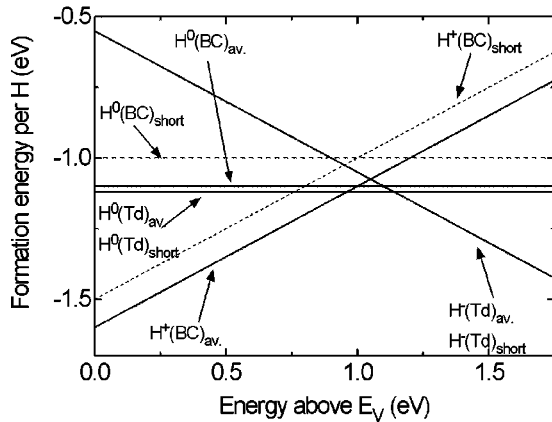

FIG. 4. The energy for different charge states of H in BC sites and H in T_d sites, as a function of the electron Fermi energy. Neutral states are independent of the Fermi energy, but charged states have the total energy raised or lowered by the energy required to move electrons to or from the Fermi energy. The solids lines shows the energies for average Si-Si bonds [after Chang and Chadi (Ref. 36) and van de Walle (Ref. 39)]. The dashed lines show our estimate for the energy of the BC levels for a Si-Si bond length reduction of 1% as compared to an average bond (after Fig. 3).

to be lowest in energy. In both cases the energy difference is about 0.1 eV, which is probably comparable to the accuracy of the calculations. We take the energies to be similar, for a-Si:H, in the neutral state. The BC site is the favored site in the positive charge state and the T_d site is favored in the negative charge state. For short bonds, the energy of the BC sites is raised according to Fig. 3. We find experimentally a bond length compression of about max. 1% for device quality amorphous silicon.[12] This corresponds to a change of about 0.1 eV for the BC sites as compared to the energy of an average bond. The energy of the T_d site is expected not to change significantly. This means that the T_d site becomes the favored site for a wider energy range.

Even without any emphasis on short bonds, the T_d site is favored due to the charge state of the defect. Both defects in the B^* state are negatively charged, whether they are created by electron-induced defect creation or light-induced defect creation. This therefore favors H in the T_d site, rather than H in the BC site, even for average bonds.

The energy levels shown in Fig. 4 are for single H atoms in interstitial sites.[36,39] The energy levels for hydrogen in SiHHSi sites are at a much lower energy, since two strong Si-H bonds are formed, at the expense of one Si-Si bond plus some strain energy. We infer from the hydrogen density of states, to be discussed in Sec. VII, that the energy of the SiHHSi states are at least 1.0 eV lower than neutral H atoms in average BC or T_d sites. We believe that the double T_d configuration, for SiHHSi, must have a lower energy than H_2^*, though there is a need for further calculations to support this.

The same microscopic model, for SiHD, is applicable to the stable defects in a-Si:H, which is consistent with our defect pool model.[5,6] In the equilibrium situation, there will be a certain density of stable defects, depending on the valence band tail state distribution, the Fermi energy, but only weakly on the hydrogen content. The defects are predominantly SiHD, with very few, isolated dangling bonds. Since the valence band states are predominantly short, weak bonds, the energetically favored SiHD has the H in the T_d site. Metastable and stable dangling bonds are indistinguishable. Both are SiHD, with H in T_d sites.

IV. CALCULATIONS OF ESR HYPERFINE BROADENING

We have performed some new calculations of the distant hyperfine ESR broadening, based on a realistic radial distribution function for a-Si:H. Previously the distant hyperfine ESR broadening has only been calculated, using the model of Kittel, which assumes a completely random distribution of hydrogen, without any lattice (network) restrictions.[40]

For a randomly distributed system, the dipolar broadening, $\langle \Delta H^2 \rangle_{av}$ can be written as

$$\langle \Delta H^2 \rangle_{av} = \frac{S(S+1)}{3h^2} f \sum_k B_{jk}^2, \tag{3}$$

where S is the spin, f the hydrogen content, B_{jk} the dipolar hyperfine interaction term, and the sum Σ_k is over all lattice

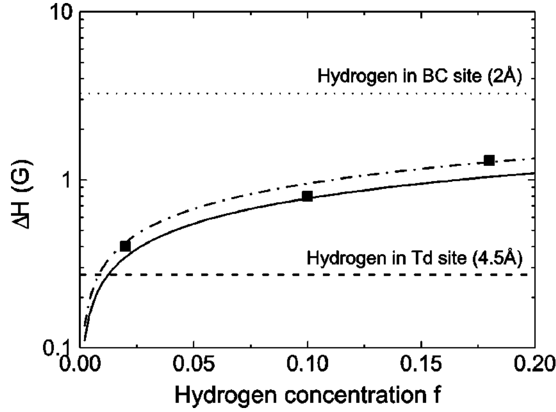

FIG. 5. The calculated ESR hyperfine broadening, due to random distant hyperfine interactions according to two calculation methods. The chain line is calculated for a completely random distribution of hydrogen [using the Kittel method (Ref. 40)]. The solid line is our new calculation based on a realistic RDF for a-Si:H. The horizontal lines indicate the calculated broadening for the H in BC and H in T_d ligands. Data points are from Brandt *et al.* (Ref. 26).

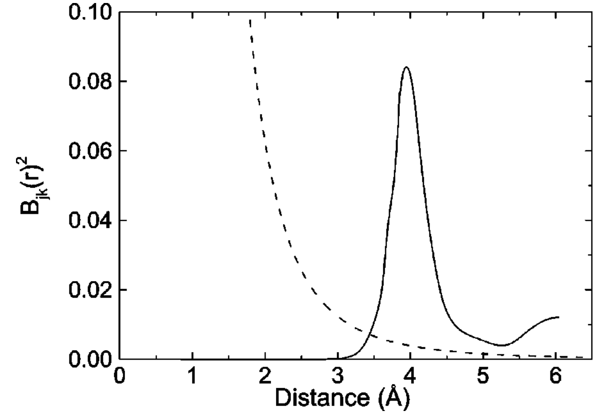

FIG. 6. Relative contribution to the distant ESR hyperfine broadening, from H atoms at different distances from a dangling bond. The peak contribution comes from dangling bond to hydrogen separations of around 4 Å, for the calculation based on the RDF for a-Si:H. The Kittel model (dashed line) implies contributions from unrealistic dangling bond to hydrogen separations.

sites, whether occupied or not.[40] Assuming a continuum of sites, the sum can be replaced by an integral which reads

$$\sum_k B_{jk}^2 \sim [g\mu_B g_N \mu_N (3\cos^2\theta - 1)] \int \frac{1}{r^6} 4\pi r^2 dr$$

$$\sim A \int \frac{1}{r^4} dr. \quad (4)$$

A is a constant containing, μ_B the Bohr magneton, μ_N the nuclear magneton, g the electron g value, g_N the nuclear g value (5.58 for H), and θ the direction cosine. The $1/r^4$ dependence means the nearest hydrogen atom contributes most to the hyperfine splitting.

For a more realistic picture, we have taken into account that hydrogen is situated in well defined positions with respect to the silicon network. We can account for this by using the radial distribution function, to calculate Σ_k

$$\sum_k B_{jk}^2 \sim A \int_0^\infty \frac{1}{r^6} \mathrm{RDF}^2(r) dr. \quad (5)$$

Figure 5 shows our calculation of the distant hyperfine ESR broadening, based on a random distribution of H in an a-Si:H network, defined by a radial distribution function. The result is compared with a calculation, based on the Kittel model,[40] and with some experimental results, from Brandt *et al.*[26] Figure 5 shows that the two calculated results appear to be similar since both exhibit a square root dependence on the hydrogen content f, seen in Eq. (3). However, the calculated results, based on the Kittel model, merely use Eq. (3) with $\Sigma_k B_{jk}^2$ as parameter, which is adjusted to fit the experimental data. Our calculation uses a realistic RDF function to calculate $\Sigma_k B_{jk}^2$, from first principles, using Eq. (5).

Also plotted in Fig. 5, is the calculated hyperfine broadening, for specific ligands, with dangling bond-hydrogen separations of 2 Å (BC site) and 4.5 Å (T_d site). These are not dependent on the hydrogen concentration, since the contribution to the overall broadening is the same for each H atom in a specific ligand. Since the calculated broadening for the H in T_d ligand is less than the contribution from random distant hyperfine broadening, the H in T_d ligand will not be observable in ESR experiments. The H in BC ligand would be observable, so we must conclude that this ligand does not occur. The experimental results are consistent with a random distribution of hydrogen.[26]

Figure 6 shows the relative contribution to the distant hyperfine broadening, from different hydrogen atoms as a function of the individual dangling bond-hydrogen separations. The Kittel model with a completely random distribution of hydrogen, shows that the contribution decays with $1/r^4$ [Eq. (4)], while the model based on realistic radial distribution function shows that the contribution peaks for a dangling bond to hydrogen separation of about 4 Å [Eq. (5)]. This means that randomly distributed H atoms that are around 4 Å from randomly distributed dangling bonds are responsible for the distant hyperfine broadening. This model of the distant hyperfine broadening is more physically realistic than the Kittel model and explains why broadening due to the H in T_d ligand, with a separation of 4–5 Å, cannot be observed.

V. MICROSCOPIC PATHWAY FOR HYDROGEN MOTION IN DEFECT CREATION

Figure 7 shows one specific example of a local reaction for dangling bond formation. In this example, one Si atom of the weak bond and one Si atom of the SiHHSi are part of the same low order (six member) silicon ring. Figure 7(a) shows the initial state, with the WB and the nearby SiHHSi. Carriers reasonably localized on the weak bond, result in the bond breaking [Fig. 7(b)]. For light-induced defect formation, the energy from electron-hole recombination facilitates bond breaking, while additional thermal energy is required for electron induced bond breaking. Figure 7 (b) is consistent

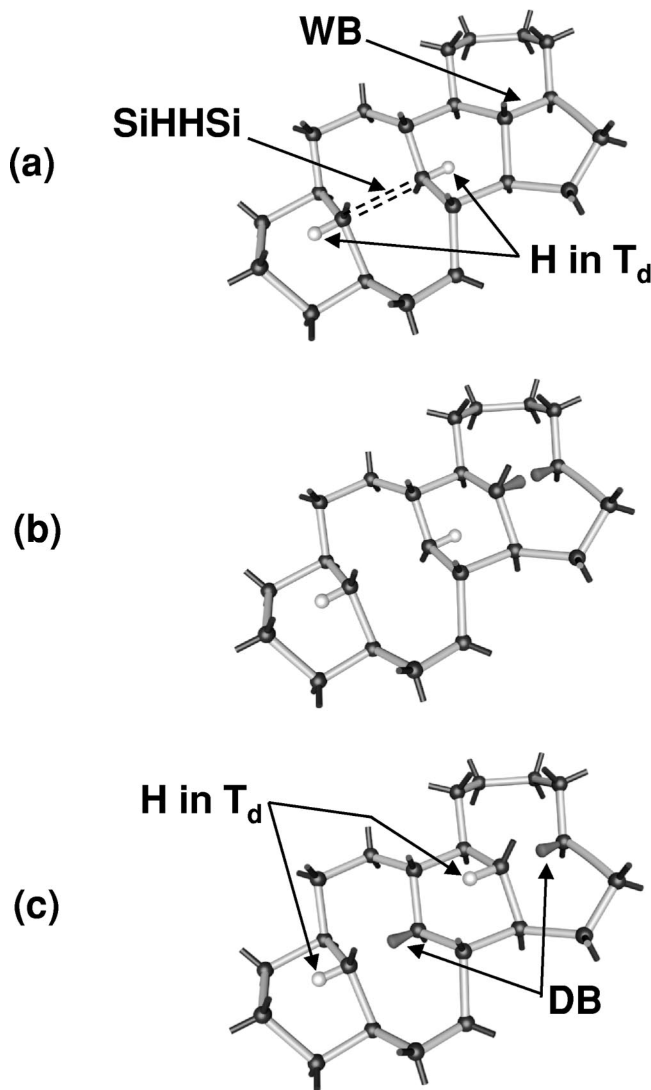

FIG. 7. Microscopic model for metastable dangling bond formation in a-Si:H. (a) The initial (annealed) state where both hydrogen are in the T_d site. (b) Si-Si bond breaking occurs under carrier accumulation or radiation. (c) H bond switching from the T_d site of the SiHHSi to the T_d site of the Si-Si weak bond being the final (metastable) state.

with state B^* in Fig. 2. The T_d site of the broken bond is sufficiently close to the T_d site of the SiHHSi, that it is possible for the H atom to switch from the T_d site of the SiHHSi to the T_d site of the WB [Fig. 7(c)]. This stabilizes the broken weak bond, forming two metastable SiHD. In Fig. 7(c), the distance between the H atom in the T_d site of the broken weak bond and the dangling bond on the nearest Si atom from the SiHHSi is in the range 4–5 Å, similar to the dangling bond to hydrogen separation in each of the two SiHD.

The energy for the hydrogen bond switching can be provided from the electron-hole recombination, in the form of phonons. This accounts for the low activation energy, measured for light-induced defect creation.[17,18] In the case of electron-induced defect creation, the energy for hydrogen bond switching is provided thermally. The energy is far less than the 1.0 eV needed to break the Si-Si bond.[12]

The initial separation of the two dangling bonds in Fig. 7(c) is about 8 Å. However, once the two SiHD are formed, they can move apart, as SiHD, with a relatively low activation energy, measured in the range 0.4–0.5 eV.[41] At room temperature and even down at 100 K, there will be significant separation of SiHD by a process of defect thermalization.[9,16] This is defect thermalization, while the bias is still applied or while the light is still on.

VI. MICROSCOPIC MODEL FOR DEFECT REMOVAL

Once two SiHD dangling bond defects have formed and diffused even slightly apart, there is a very low probability for defect removal via the microscopic pathway which is the exact reverse of the defect creation process. Here we consider the situation when the bias is removed or the light turned off. Defect removal can only proceed by Si-H bond breaking and capture of the H atom at another SiHD. There is no reason for the H atom from one SiHD to move preferentially in the direction of the other SiHD formed in the same local defect creation reaction, as for example shown in Fig. 7. The SiHD is just as likely to diffuse away in any direction. Therefore the annealing process is more complex and involves larger numbers of hydrogen atoms, in a sort of global annealing process. Large numbers of Si-H bonds are broken and reformed and eventually the original broken Si-Si bonds are reformed, with the net effect being the removal of two Si dangling bonds. However, it is highly unlikely that H atoms in SiHD sites will migrate to exactly their original positions, prior to defect creation. Even after only the initial H switching event [Fig. 7(c)], the two SiHD are just as likely to diffuse apart as recombine. This is defect thermalization, with the bias removed or the light off.[9,16]

Defect thermalization eventually leads to reequilibration of the a-Si:H network, as described in the hydrogen glass model of Street.[7] Annealing is not possible at low temperatures and measured activation energies are very similar to the activation energy for hydrogen diffusion. Therefore we believe that defect annealing proceeds by long range hydrogen diffusion, while defect creation does not.

When defects are created, as a result of bias stress, the defects anneal out with a range of activation energies, extending from 1.1 to 1.5 eV, for defects formed at room temperature. The spectrum of activation energies depends on the temperature and bias conditions, during the defect formation process.[9,16] For defects formed at moderate temperatures, the most probable activation energy for defect annealing is around 1.1 eV, increasing with temperature to 1.5 eV, for defects formed under equilibrium conditions.[9] Energies in the range of 1.1 to 1.2 eV have been reported for annealing of defects formed by light soaking at moderate temperatures,[17] very similar to defects formed by bias-stress, at moderate temperatures.

We can understand this result with the aid of a simplified hydrogen density of states diagram (Fig. 8). The hydrogen density of states plots the energy of H in various configurations. The majority of hydrogen is located in SiHHSi sites, while the majority of Si-Si sites are empty of hydrogen. The

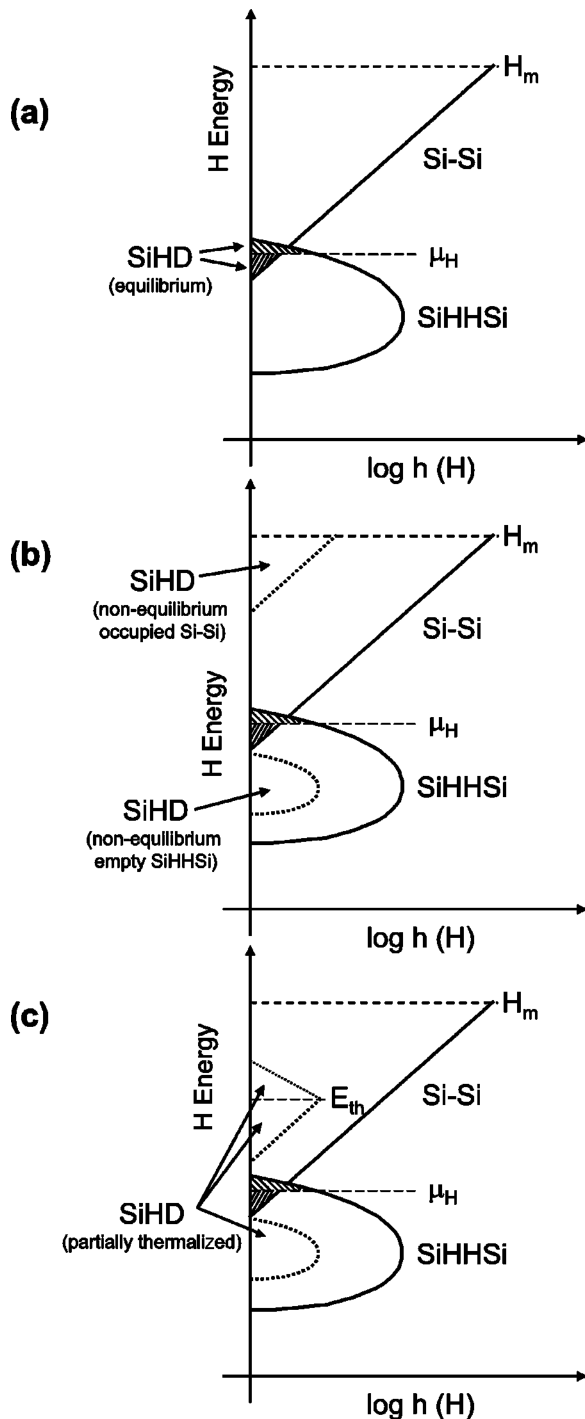

FIG. 8. Simplified hydrogen density of states indicating the creation of equilibrium and nonequilibrium dangling bonds (a) shows the position of the stable SiHD defect states, (b) shows nonequilibrium SiHD states formed by light or bias stress, (c) shows partial thermalization of these states.

hydrogen chemical potential μ_H, marks the demarcation between empty and full states. SiHD states (silicon dangling bond) appears on a hydrogen density of states diagram in two places, as a SiHHSi, with a missing H, and as a Si-Si, occupied by one H. This reflects that there are two possible hydrogen transistions for a SiHD (emission of hydrogen or capture of an additional H), represented by the reactions SiHD→Si-Si+H_i and SiHD+H_i→SiHHSi, respectively. The majority of hydrogen is in doubly occupied SiHHSi sites, with negative correlation energy U_H. However, the few stable SiHD sites in thermal equilibrium have a positive U_H. The stable SiHD are located in those few SiHHSi states above μ_H. These states also appear as the few Si-Si states below μ_H. These states are shown shaded in Fig. 8(a).

In our earlier work,[16] we identified the defect creation process and hence the energy barrier Φ, with a transition on the hydrogen density of states diagram. At that time, we thought the defect creation reaction was rate limited by the breaking of Si-H bonds, as proposed by Jackson,[38,42] and not to the breaking of Si-Si bonds. We now realize that this is incorrect, but the mechanism for defect annealing, proposed, at that time, remains substantially correct.

Strictly speaking, it is not possible to represent our proposed localized defect creation process by a transition on the hydrogen density of states diagram, since the initial defect reaction, Si-Si→2D does not involve a hydrogen transition. However, once the SiHD state is formed, we can indicate it on the hydrogen density of states, for the purpose of subsequent hydrogen transitions. Dangling bonds formed as a result of bias stress are nonequilibrium defects. These defects are not necessarily at the lowest possible energy for the dangling bond defect, immediately after formation. A process, which we call defect thermalization, leads to SiHD migration to progressively more stable sites at a lower energy. This corresponds to thermalization of hydrogen in the Si-Si states within the hydrogen density of states.

On the hydrogen density of states diagram, SiHD defects formed by a local process, at low temperatures, are distributed over a wide energy range of Si-Si sites. Their distribution will be roughly in proportion to the density of available sites [Fig. 8(b)]. Now the process of defect thermalization starts. Those SiHD in shallow states can easily emit the hydrogen to the hydrogen mobility edge, whereupon it will be captured at another Si-Si site. This process continues with progressive excitation of H in SiHD sites at lower energies. This process results in a gradual thermalization of H in the tail of Si-Si states. The distribution of H in the Si-Si states peaks at an approximate thermalization energy E_{th} [Fig. 8(c)]. This is exactly analogous to electron thermalization in a tail of conduction band states. When dangling bond defects are formed at room temperature there is already some defect thermalization.

It is important to note that defect thermalization is not annealing. The defects are not annealed until hydrogen is captured at a SiHD site, which is a much rarer event. However, there will be some progressive annealing of defects during the thermalization process. This accounts for measured activation energies having a continuum from 1.1 to 1.5 eV. If the defects had been formed at lower temperatures, we would expect to record lower energies for some defect annealing. The process of defect removal, for metastable SiHD defects, is by emission of H from one SiHD site, followed by capture of the H, at another SiHD site. This is basically the process described by Branz, in his hydrogen collision model.[43] We believe this process is not applicable to defect

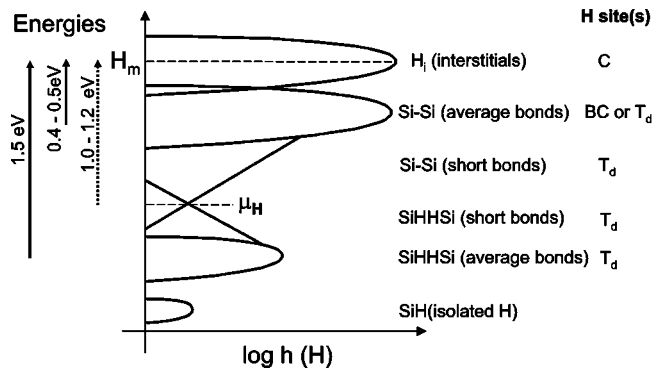

FIG. 9. A hydrogen density of states model for hydrogenated amorphous silicon. Transition energies indicated on the left, nature of the states and hydrogen configuration on the right.

creation, but it is applicable to defect annealing.

As defect removal progresses, the thermalization energy falls towards μ_H, until it becomes more probable for emission of H from SiHHSi states than it is for emission of H from the few remaining SiHD (occupied Si-Si). This occurs before the thermalization energy actually reaches μ_H. Full thermal equilibrium can only be achieved with the participation of a substantial fraction of hydrogen in the SiHHSi sites. This requires excitations of H from doubly occupied SiHHSi, which are actually defect forming reactions, in order to promote eventual defect annealing. Full thermal equilibration has an activation energy of 1.5 eV, the same as the activation energy for H diffusion, which proceeds by the same mechanism. Full thermal equilibrium annealing of metastable defects can only be reached with annealing activation energies of 1.5 eV, which is the SiHHSi energy, i.e., the energy to emit one hydrogen out of a SiHHSi site. Defects formed by bias annealing, under thermal-equilibrium conditions, also require the full 1.5 eV for annealing.[9,16]

VII. HYDROGEN DENSITY OF STATES

Figure 9 presents our new improved hydrogen density of states diagram, with some of the significant transition energies labeled. We introduce some distinctions between different types of states, in order to aid interpretation of significant experimental results.

First, we distinguish between mobile hydrogen interstitials and hydrogen in Si-Si sites. Hydrogen is only truly mobile when excited to interstitial sites, such as the *M* site or the C site, as defined for crystalline Si.[36] These states are at higher energy than the bonded hydrogen in the BC or the T_d sites. Singly occupied hydrogen in T_d (or BC) sites requires $0.4-0.5$ eV to diffuse around the network. This energy corresponds to the activation energy for atomic hydrogen diffusion, from a plasma source.[41] Bulk hydrogen diffusion has a higher activation energy since it requires the majority of hydrogen to diffuse, which is located in SiHHSi sites. The activation energy for this process is 1.5 eV.[41]

Previously the hydrogen diffusion activation energy of 1.5 eV has been identified with the energy between the hydrogen chemical potential and the hydrogen mobility edge.[44] However, this is only true for full thermal equilibrium diffusion. In practice, hydrogen is unlikely to be in thermal equilibrium and the measured 1.5 eV activation energy more likely corresponds to the SiHHSi energy level. We can estimate the energy of the hydrogen chemical potential, to be $1.0-1.2$ eV, below the hydrogen mobility edge, from the known density of the Si-Si, SiHHSi, and SiHD states.

The short weak Si-Si bonds form a tail of states, where the characteristic energy of the tail is $2E_{v_0}$.[5,6] The exponential tail is visible on both the Si-Si states and the SiHHSi states. E_{v_0} is the characteristic energy of the valence band tail states. The short weak Si-Si bond states all have H in the T_d site, when occupied by a single H. Stable SiHD states are all located on short bonds, in those few Si-Si states below μ_H. The same states also appear as those few empty SiHHSi states above μ_H.

Hydrogen located in an average Si-Si bond (BC or T_d site) will require only $0.4-0.5$ eV to remove the hydrogen to the hydrogen mobility edge. This would be the energy corresponding to theoretical calculations of the stability of a (average) H in T_d site.[45] In contrast, a thermal equilibrium stable SiHD state requires an energy corresponding to $E_m - \mu_H$ to remove the H atom, i.e., $1.0-1.2$ eV. Therefore H in T_d, for SiHD, in short weak Si-Si bond sites can be quite stable. Full thermal equilibration requires H to be excited out of average SiHHSi sites, which requires the full 1.5 eV.

VIII. PREVIOUS MICROSCOPIC MODELS FOR DEFECT CREATION

Staebler and Wronski[1] first suggested that their effect might be due to a structural change, involving hydrogen. Stutzmann *et al.*[17] proposed that localization of carriers cause weak silicon-silicon bond to break and a back-bonded H atom then switched into the broken bond to stabilize the defect. In this model, half the formed dangling bonds would have a back bonded H atom bonded to the same silicon atom. Experimentally, the dangling bonds are fully back bonded to Si atoms, so any stabilizing hydrogen atom must come from further away.

Jackson[38,42] suggested that electron-hole recombination (or electron injection) caused a H_2^* to dissociate, by breaking a Si-H bond (rather than a Si-Si bond). The hydrogen then diffuses away and is captured at a weak Si-Si bond, by inserting in the bond-centered position, and forming a second dangling bond. This model involves long-range hydrogen diffusion and as described by Jackson, has at least one of the dangling bonds close to a hydrogen atom, i.e., in a BC site.

Branz[43] proposed a hydrogen collision model, in which electron-hole recombination breaks well separated isolated Si-H bonds (rather than part of a SiHHSi or H_2^*). The hydrogen then diffuses, until two diffusing H atoms collide, forming a stable SiHHSi, which could also be a H_2^*.[46] The metastable dangling bonds are then located on isolated sites, originating from isolated Si-H bonds. This model requires the preferential breaking of isolated Si-H bonds, over Si-H bonds in SiHHSi, which requires the Si-H energy level to be higher than the SiHHSi energy level, in the hydrogen density of states. This model also involves long-range hydrogen dif-

fusion and the statistical probability of random hydrogen collisions has been questioned. The hydrogen collision model was developed, by Branz, as a way to overcome the perceived problem with models involving local hydrogen motion via H bond switching or long range hydrogen diffusion, where the diffusing H atom was trapped in a Si-Si BC site. Branz dismissed all these models as being inconsistent with hyperfine ESR experiments. However, in this paper, we have shown that a model for Si-Si bond breaking, with local hydrogen motion, can be perfectly consistent with hyperfine ESR experiments and considerably better with respect to accounting for other experimental data.

In a development of the Branz model, Biswas proposed a new model, where Si floating bonds are the migrating species, rather than H.[47] Floating bonds are expected to be highly mobile and when two floating bonds collide, they give a metastable configuration, with well separated dangling bonds. In this model, there is no direct involvement of hydrogen, at all. However, there is no experimental evidence for highly mobile floating bonds. In fact, it has been shown that defect diffusion, which includes floating bond diffusion, is less pronounced than hydrogen diffusion.[48]

IX. CONCLUSION

We propose a microscopic model for metastable dangling bond formation in hydrogenated amorphous silicon. This is a local mechanism, involving hydrogen motion over relatively short distances. The formed defects are SiHD defects, in which there is always an intimately associated hydrogen atom with each dangling bond. The hydrogen atom is located at the T_d site of a broken short, weak Si-Si bond and the dangling bond is on the other Si atom. The separation of the dangling bond and hydrogen atom is 4–5 Å. Thermal equilibrium stable defects are also SiHD and are indistinguishable from metastable defects. Defects are annealed by a process involving long range hydrogen diffusion. This process is a global reequilibration, involving a substantial fraction of hydrogen atoms in the network.

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[49] Note that the tetrahedral-like position (T_d) in amorphous silicon forms a strong Si-H bond, together with some Si network motion, in contrast to crystalline silicon, where the tetrahedral site is commonly attributed to a weakly bound interstitial state. An alternative notation, for this site could be the antibondinglike (AB) site. However, to be in-line with previous publications, we refer to it as a tetrahedral-like site.