Nature of metastable and stable dangling bond defects in hydrogenated amorphous silicon

M.J. Powell a,*, R.B. Wehrspohn b, S.C. Deane a

a Philips Research Laboratories, Redhill, Surrey, RH1 5HA, UK
b Max-Planck-Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

Abstract

We present a new microscopic model for metastable Si dangling bond defect creation in hydrogenated amorphous silicon. Carrier localisation on short, weak Si–Si bonds causes the bond to break. One hydrogen atom from a nearby doubly hydrogenated Si–Si bond (SiHHSi) moves to the Td site of the broken Si–Si bond, leaving the remaining H atom also in a Td site. The net reaction produces two SiHD defects (intimate Si dangling bond and Si–H bond), where both the H atoms are in the Td site. The Td site is energetically favoured over the BC site, for short, weak bonds. The distance between the dangling bonds and the H atoms, in the Td sites, is in the range 4–5 Å. The vast majority of silicon dangling bonds, both metastable and stable, are SiHD, with the H atom in the Td site. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 71.55.Jv; 61.43.Dg

1. Introduction

Metastable Si dangling bond defects are formed in hydrogenated amorphous silicon (a-Si:H), whenever it is illuminated [1] or charge carriers are injected [2]. This is a crucial fundamental property that limits the performance of both solar cells [1] and thin film transistors [2]. We believe these effects have a common cause, and it is of considerable importance to understand this at a microscopic level.

It is well established that dangling bonds are created. The key problem revolves around the role of hydrogen. Previously we have proposed a defect pool model, for the equilibrium properties of amorphous silicon, which can account for a wide range of experimental results [3]. The key element is that there is a thermal equilibrium between weak bonds and dangling bonds according to the reaction, SiHHSi + Si–Si → 2SiHD, where SiHHSi is a doubly hydrogenated weak bond, most probably an amorphous analogue of a H2. The H2 model of SiHHSi is favoured by ourselves, though it is not strictly necessary to specify the microscopic nature of the SiHHSi. Si–Si is a weak bond and SiHD is an intimate dangling bond and Si–H bond. The majority of hydrogen is located in SiHHSi configurations, rather than in isolated SiH, which is
consistent with a negative U for H in a-Si:H and with hydrogenation and dehydrogenation experiments [4].

Light-induced defects, or TFT bias-stress created defects, are non-equilibrium, metastable, defects. Experiments on intrinsic stress dependence of TFT stability, suggest that conversion, from weak bonds to dangling bonds proceeds first by Si−Si bond breaking, stabilised by H, in a fairly local reaction [5], rather than by breaking an Si−H bond and long range diffusion of hydrogen. However, if a broken Si−Si bond is stabilised by inserting a hydrogen atom, to form a SiHD defect, then one might expect a measurable hyperfine broadening of the ESR signal, which has never been observed [6].

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-centred site (BC), but in the tetrahedral site (Td). This is still an SiHD, and the defect is still correctly identified as an intimate Si dangling bond and Si−H bond. 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. The weak bond, which is broken, is a short bond. Stabilisation of a broken short bond by hydrogen in the Td site is favoured over the BC site.

2. New microscopic model

The key features of our model are as follows. Short, weak Si−Si bonds are the precursors for dangling bond defect formation. This is supported by theoretical calculations, which showed that the valence band tail originates from short bonds [7] and also from experiments on the intrinsic mechanical stress dependence of defect formation [8]. 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. When the bond is broken, most bonds will reform immediately, but occasionally, there is a site, where there is another short, weak Si−Si bond, which is doubly hydrogenated (SiHHSi), and which is sufficiently close that one hydrogen atom can move to the site of the broken Si−Si bond. The doubly hydrogenated weak bond (SiHHSi) is most probably the amorphous analogue of the H_2^+, with one H in a BC site and one in a Td site.

Crucial to the argument in this paper is how the energies of the BC and Td sites change for the case of short, weak bonds. The energy of H in the BC site has been calculated to linearly decrease as the Si−Si bond length increased [9], so the energy will be raised for short bonds 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 an Si−Si bond, which is already constrained to be shorter than average. There will be relatively little effect on the energy of the Td site. Therefore, we suggest the energy of the Td site will be energetically favoured, for short, weak Si−Si bonds, compared to average bonds.

Fig. 1 shows the energy of H in the BC site, compared to H in the Td site, for different charge states [10]. For average bonds, the energy of the BC and Td sites, in the neutral state is similar, while the Td site is favoured in the negative charge state and the BC site is favoured in the positive charge state [10]. For short bonds, the energy of the BC site is raised, which means the Td is favoured for a much wider energy range.

![Fig. 1. Energy of hydrogen BC and Td sites in a-Si:H.](image-url)
The broken short bond will be stabilised by inserting a hydrogen atom in the $T_d$ site. Furthermore, the remaining hydrogen atom in the SiHHSi will also assume (or switch to) the $T_d$ site, since the SiHHSi also originates from a short, weak Si–Si bond and the $T_d$ site is energetically favoured. The overall reaction results in the formation of two SiHD defects, where the hydrogen is always in the $T_d$ site and never in the BC site. The hydrogen atoms move a relatively short distance, so this is truly a local model for defect formation. The separation of each hydrogen atom from the dangling bond will be in the range 4–5 Å, which is completely consistent with ESR experiments.

Fig. 2 shows a new calculation of the distant hyperfine ESR broadening, based on a radial distribution function, for a-Si:H, compared to specific ligands with dangling bond-hydrogen separations of 2 Å (BC site) and 4.5 Å ($T_d$ site). The H in $T_d$ ligand is not observable and the experimental data is consistent with a random distribution of hydrogen [11].

Fig. 3 shows one specific example of a local reaction pathway for dangling bond formation. Fig. 3(a) shows the initial state, with a weak bond (WB) and a nearby $H_2$. One Si atom of the WB and one Si atom from the $H_2$ is part of the same low order silicon ring. Carriers reasonably localised on the weak bond, result in the bond breaking. The energy from electron-hole recombination facilitates bond-breaking, for light-induced defect formation, while additional thermal energy is required for electron-induced defect formation. The $T_d$ site of the broken weak bond is close to the $T_d$ site of the nearby $H_2$, so it is possible for the hydrogen atom to switch from the $T_d$ site of the $H_2$ to the $T_d$ site of the WB. This stabilises the broken bond and forms a metastable SiHD. The second H atom in the BC site of the $H_2$ then moves to the $T_d$ site, most easily by bond switching from the left Si atom to right Si atom and then undergoing a H-flip from the BC site to the $T_d$ site of the right Si atom. Biswas and Li [12] proposed the hydrogen flip transition, from the BC site to the $T_d$ site and showed that this could proceed with remarkably low energy. The final (metastable) state, with two...
dangling bonds, both SiHD, with H in Td, is shown in Fig. 3(b).

The whole process is fairly well localised. The energy for the hydrogen bond-switching and flip transitions can be provided from the electron–hole recombination, in the form of phonons. In the case of electron-induced defect creation, the activation energy is around 1.0 eV \[8\]. The energies for H bond switching and flip transitions can easily be lower and thus not rate limiting.

3. Discussion

Staebler and Wronski [1] first suggested that their effect might be due to a structural change, involving hydrogen. Stutzmann et al. [13] proposed that localisation of carriers cause weak silicon–silicon bonds to break and back-bonded H atoms to then switch into the broken bonds to stabilise the defects. In this model, the half-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 stabilising hydrogen atom must come from further away.

Jackson and co-workers [10] suggested that electron–hole recombination (or electron injection) first caused a H\(_2\) to dissociate, by breaking an Si–H bond (rather than an Si–Si bond). The hydrogen atom 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 at least one of the dangling bonds is close to a hydrogen atom, i.e. in a BC site.

Branz [14] proposed a hydrogen collision model, in which electron–hole recombination breaks well separated isolated Si–H bonds (rather than part of an SiHHSi or H\(_2\)). The hydrogen then diffuses, until two diffusing H atoms collide, forming a stable SiHHSi, which could also be a H\(_2\) [15]. This model also involves long range hydrogen diffusion and the statistical probability of random hydrogen collisions has been questioned. This model also requires the vast majority of hydrogen to be in isolated Si–H sites, rather than SiHHSi sites, which is in contradiction to hydrogenation–dehydrogenation experiments [4].

In a development of the Branz model, Biswas [16] proposed a model, where Si floating bonds are the migrating species, rather than H. 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 [17].

Our new model, provides a resolution of the ESR paradox \[6,11\], without the need to postulate long range, low energy, light-induced H diffusion or floating bond diffusion. In reality, it is only necessary to separate the dangling bond and hydrogen atom by 4 Å, for the ESR hyperfine broadening to be negligible. The realisation that short, weak bonds are a very likely precursor for defect creation, leads naturally to a consistent model, which is still a local model, involving few bonding rearrangements in a relatively small local volume.

The same microscopic model is applicable to the stable defects in a-Si:H, which is consistent with our defect pool model \[3\]. In the equilibrium situation, there will be a certain density of stable defects, depending on the valence band tail state distribution, the hydrogen content and the Fermi energy. The defects are predominantly SiHD, with few isolated dangling bonds. Since the valence band tail states are predominantly short, weak bonds, the energetically favoured SiHD has the H in the Td site.

The arguments given in this paper present an interesting possibility. From Fig. 1, there might be a Fermi energy range, for distinctly p-type material, which favours H in the BC site. These are SiHD states labelled as D\(_h\) states in our defect pool paper \[3\]. These SiHD, with H in BC, should show hydrogen hyperfine ESR broadening. Detecting the hyperfine ESR broadening, in this situation, might be difficult due to the \(g = 2.004\) signal from the occupied valence band tail states. However, the same type of states might also be formed, as a
result of bias-stressing with just holes. In this situation, we might expect to form $D_{th}$ states, which are SiHD with H in the BC site. These might be detectable, since there will be no occupied tail states, when the bias-stress is removed, yet the formed defects should remain, until annealed.

4. Conclusion

We propose a new microscopic model for metastable dangling bond formation in hydrogenated amorphous silicon. This is a local model, 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 the metastable defects.

This model is consistent with all known experimental results.

Acknowledgements

The authors acknowledge stimulating and extensive discussions with Martin Stutzmann.

References