

Atomistic origins of metastability in amorphous silicon PV materials

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ABSTRACT

We propose a novel atomistic mechanism for metastability in hydrogenated amorphous silicon (a-Si:H) using molecular dynamics simulations. The model involves rebonding at both Si and H sites. The driving force is the non-radiative recombination of excited electron-hole pairs that breaks weak silicon bonds and generates dangling bond-floating bond pairs. The transient floating bonds annihilate. Isolated dangling bonds including charged defects are found. The kinetics of degradation is simulated with coupled rate equations which shows saturation behavior similar to experiment. The model accounts for major experimental features of the Staebler-Wronski effect including ESR data, the $t^{1/3}$ kinetics of defect formation, two types of metastable dangling bond defects and hysteretic $\mu\tau$ annealing measurements.

1. Introduction

The understanding and characterization of metastability or light-induced degradation i.e. Staebler-Wronski (SW) effect[1] is one of the most actively pursued research areas in solar cell research. Light-soaking of hydrogenated amorphous silicon (a-Si:H) produces metastable dangling bonds with mid-gap states and properties indistinguishable from native dangling bonds. The defects can be annealed at temperatures between 180-200 C. Despite extensive experimental characterization of metastability, the microscopic origin of the SW-effect is still intensely debated.

2. Theoretical Model

We have developed a very promising model for the atomistic mechanisms underlying metastability in a-Si:H, that can account for major experimental features of the SW effect. The basic features of this model are:

- 1) Non-radiative recombination of photo-excited carriers (e-h pairs) that break weak Si bonds with a very low energy barrier.
- 2) The production of dangling bond (DB) and floating bond (FB) pairs from weak Si-bond breaking.
- 3) Migration of floating bonds, which are a mobile species [2], to leave behind isolated dangling bonds.
- 4) Recombination/annihilation of the transient floating bonds defects.

3. Results

We describe each step in detail. In our tight-binding molecular dynamics simulations we frequently find a weak silicon bond (WB, Fig. 1) can stretch and create a dangling bond on site c. It is not favorable to have a dangling bond on d. Site d forms a new bond with site x (d-x). Site x is now

five-coordinated but d remains four-coordinated. The Frenkel pair of DB and FB is separated by more than 4 Å and stabilized. The Frenkel pair is the analog of the vacancy- interstitial pair of c-Si.

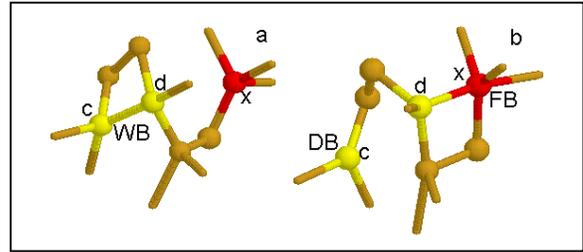


Fig. 1 Breaking of a weak bond to produce a dangling bond floating bond pair

The calculated energy barrier to break the weak Si-bond has a low value of ~ 0.85 eV for the ground state of the electronic system.[3] This barrier is much lower than the ~ 2 eV to break a silicon bond, since the energy cost in breaking bond c-d is compensated by the energy gain in simultaneously forming the new bond d-x.

Weak silicon bonds can trap a hole in a valence band tail level. A photoexcited electron can be captured in the vicinity of the hole. Non-radiative electron-hole (e-h) recombination provides a very low energy path for bond-breaking. The energy barrier for bond-breaking in this excited e-h state (exciton state) is remarkably lowered to ~ 0.35 eV due to the crossing of electronic levels in the gap[3]. Only a single e-h pair can drive Si-bond breaking, whereas 2 e-h pairs are necessary for SiH bond-breaking[4]. The weak silicon bonds are spatially separated from H, since the network is very relaxed in the vicinity of an SiH site. Hence the DB and H are separated by more than 4 Å as the spin echo measurements infer.

The second step is the migration of the FB, which are known to be mobile[2]. Their diffusion involves a bond-switching process from one Si-site to another. There are analogies with the diffusion of self-interstitials in c-Si.

In the third step the FB's annihilate. The common process is when a FB recombines with an existing Si DB, converting it to a four-coordinated site.

When the FB is close to an SiH site, a configuration that must occur frequently, the H can move into the FB site and convert it to a four-coordinated and a new Si-H bond. A secondary dangling bond DB' is left behind at the original site of the H. In the energetically favorable configurations we find that the secondary DB' is substantially separated from the H (>4 Å).

Floating bonds are a transient species and not appreciable in the long-time steady state[3,5] FB's are the analog of mobile H in the H-collision model.[6]

We have developed a quantitative description [5] of the kinetics in this network-rebonding model. The saturated defects consist primarily of dangling bonds (density of 10^{16} – 10^{17} cm^{-3}). There is an accompanying small density of floating bonds (10^{15} cm^{-3}). However the FB's have states in the valence band which are filled (and negatively charged) and do not contribute to the ESR signal. The ESR signal is dominated by the neutral D0 states.

By charge neutrality, the FB's remove charge from the DB states, leading to a small density of positively charged dangling bonds (D+). The saturated state is described by a large density of D0 and small density of charged defects: D+ and FB-. The D+ defects are very strong recombination centers for photoexcited electrons with large capture cross sections, and strongly affect the $\mu\tau$ product. The observed hysteresis of $\mu\tau$ can be directly explained by the presence of the two types of defects: D0 and D+.[3] The initial anneal of D+ generates a large increase in $\mu\tau$ but small change in optical absorption α . The anneal of the D0 defects decreases α with small change in $\mu\tau$.

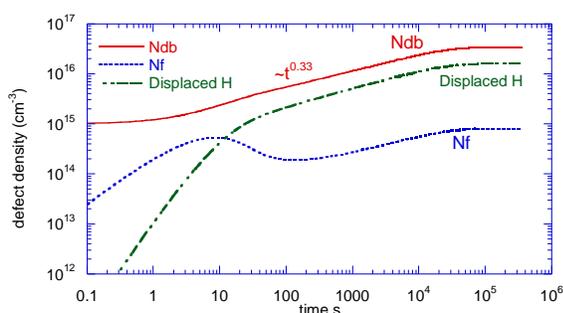


Fig. 2 Solution of rate equations showing the density of the defects as a function of time during light-soaking.

The creation of defects involves short range H rearrangements, not long-range motion. However the annealing of the metastable defects long-range H-motion occurring at elevated annealing temperatures.

In summary we have found a new mechanism for metastability involving bonding rearrangements of Si and H. This is driven by breaking of weak silicon bonds from non-radiative recombination of excited e-h pairs. Major experimental features of the SW effect can be understood within this framework. The instability is intimately related to the amorphous nature of the network and is expected to be reduced in more ordered (or more crystalline) materials. Further work in this project will focus on development of models of mixed phases where nano-crystalline inclusions are embedded in an amorphous matrix. This 'edge' material grown with H-dilution is experimentally known to be more stable and its higher stability will be investigated with similar theoretical simulations.

4. Acknowledgements

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