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New Microscopic Model of the Staebler-Wronski Effect in Hydrogenated Amorphous Silicon

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New Microscopic Model of the Staebler-Wronski Effect in Hydrogenated Amorphous Silicon

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Abstract. A new microscopic and kinetic model of light-induced metastability in hydrogenated amorphous silicon (a-Si:H) was recently proposed. Carrier recombination excites H from deep Si-H bonds into a mobile configuration, leaving a threefold-coordinated Si dangling bond (DB) defect at the site of excitation – a process long suspected to be an element of metastable DB production. Normally, mobile H are recaptured at DB defects and neither metastability nor net DB production results. However, when two mobile H collide, they form a metastable two-hydrogen complex and leave two spatially-uncorrelated Staebler-Wronski DBs. The model leads to differential equations describing the evolution of the mobile H and DB densities and a variety of new predictions. New directions for improving the stability of a-Si:H are discussed.

INTRODUCTION

Over 20 years ago, Staebler and Wronski (SW) discovered light-induced metastability in hydrogenated amorphous silicon (a-Si:H) (1). The density of neutral threefold-coordinated dangling bond (DB) defects increases by one to two orders of magnitude as a result of illumination or carrier injection (2). These DBs are metastable; they can be annealed away by about 2 hours heating at 150°C (1) . Because DBs act as carrier recombination centers and traps in a-Si:H, the metastable DBs cause significant performance degradation of photovoltaic and other devices made from a-Si:H. Numerous microscopic and kinetic models of the SW effect have been proposed and are reviewed elsewhere (3-5). However, all of these models appear to be incompatible with certain experiments (5-7).

I have recently developed a new "H collision" model of the SW effect (5-7). The microscopic model leads to differential equations describing the evolution of the mobile H and DB densities and to a variety of new predictions. This microscopic and kinetic model is consistent with the main experimental SW results, predicting 1) isolated SW DB defects uncorrelated with H or other DBs, 2) an intrinsic creation mechanism, 3) N_{db}~$G^{2/3}t^{1/3}$ DB creation kinetics at room temperature, 4) light-induced annealing of DBs resulting in saturation at N_{sat}~$G^{1/3}$, 5) N_{db}~$t^{1/3}$ DB creation kinetics at 4.2 K, and 6) N_{db}~$t^{1/2}$ laser-pulse DB creation kinetics. In this paper, I present an abbreviated description of the microscopic model and outline possible directions for improving the stabilized properties of a-Si:H. Rigorous derivations of the main results and predictions are found elsewhere (5-7).

H COLLISION MODEL

In the H collision model (5-7) of the SW effect, DBs are created when light-induced carriers stimulate emission of mobile H from Si-H bonds (normally about 10 at.%), according to:

$$\text{Si-H} \dashrightarrow \text{DB} + \text{Si-H/DB}. \quad (1)$$

The mobile H is labelled here by Si-H/DB because calculations by Biswas et al. (8) show that mobile H break Si-Si bonds and form Si-H bonds as they hop between Si-Si sites. Each broken Si-Si bond reforms as the mobile H hops away. Mobile H is weakly bound compared to H in normal Si-H bonds; mobile H diffuses rapidly through a-Si:H (9).

Mobile H reverts to immobile Si-H through one of two mechanisms. Most often, it retraps to an immobile DB:

$$\text{Si-H/DB} + \text{DB} \dashrightarrow \text{Si-H}, \quad (2)$$

the inverse process to Eqn. (1). Taken together, Eqns. (1) and (2) neither create nor destroy DBs.

Infrequently, H retraps by associating with another mobile H in a metastable complex containing two Si-H bonds in close proximity:

$$\text{Si-H/DB} + \text{Si-H/DB} \dashrightarrow \text{M(Si-H)}_2\,. \quad (3)$$

Eqn. (3) is the key step of SW defect creation. The reaction annihilates two mobile DBs and forms no DBs, consistent with bond-counting constraints. Combining Eqns. (1) and (3), the net reaction leaves DB defects at the sites of the original H excitation according to:

$$2\ \text{Si-H} \dashrightarrow 2\ \text{DB} + 2\ \text{Si-H/DB} \dashrightarrow 2\ \text{DB} + \text{M(Si-H)}_2\ . \quad (4)$$

The created SW DBs appear on the rightmost side of Eqn. (4). The H atoms are slightly less stable in $M(Si\text{-}H)_2$ than in Si-H, and the created DBs are therefore metastable.

NEW DIRECTIONS FOR BETTER STABILITY

The H collision model provides new perspective and therefore suggests new directions that may be taken to improve the stability of a-Si:H materials and devices. Certainly, reduction of H content could reduce the metastability; perhaps this was already observed in the improved stability of hot-wire a-Si:H containing about 1 at.% H (10). However, stabilized defect density increases only as the two-thirds power of H content (5-7), and some H is needed to relieve strain, so this tactic may not yield further dramatic improvements.

A more subtle approach would be to increase the diffusion rate of mobile H. This may increase the retrapping rate of Eqn. (2) and thereby reduce the mobile H concentration. Improved ordering may be a key to this approach. Finally, it may be helpful to grow a-Si:H with "benign" H stored in excess $M(Si\text{-}H)_2$, but without an increase of the DB or isolated Si-H densities. This H would form a reservoir of H that light could liberate (5-7) by the reverse reaction of Eqn. (3). Light-induced annealing of defects by the reverse of Eqn. (4) should then improve stabilized properties.

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REFERENCES

1. D. L. Staebler and C. R. Wronski, *Appl. Phys. Lett.* **31**, 292 (1977).
2. H. Dersch, J. Stuke, and J. Beichler, *Appl. Phys. Lett.* **38**, 456 (1981).
3. H. Fritzsche, in *Amorphous and Microcrystalline Silicon Technology-1997*, 467, edited by E. A. Schiff, M. Hack, S. Wagner, R. Schropp, and I. Shimizu (Materials Research Society, Pittsburgh, 1997), p. 19.
4. M. Stutzmann, in *Amorphous and Microcrystalline Silicon Technology-1997*, 467, edited by E. A. Schiff, M. Hack, S. Wagner, R. Schropp, and I. Shimizu (Materials Research Society, Pittsburgh, 1997), p. 37.
5. H. M. Branz, unpublished.
6. H. M. Branz, *Solid State Commun.* **105/6**, 387 (1998).
7. H. M. Branz, in *Amorphous and Microcrystalline Silicon Technology-1998*, 507, edited by S. Wagner, M. Hack, H. M. Branz, R. Schropp, and I. Shimizu (Materials Research Society, Pittsburgh, 1998), in press.
8. R. Biswas, Q. Li, B. C. Pan, and Y. Yoon, *Phys. Rev. B* **57**, 2253 (1998).
9. H. M. Branz, S. E. Asher, and B. P. Nelson, *Phys. Rev. B* **47**, 7061 (1993).
10. A. H. Mahan and M. Vanecek, in *Amorphous Silicon Materials and Solar Cells*, AIP Conf. Proc., 234, edited by B. L. Stafford (AIP, New York, 1991), p. 195.