

Atomistic Origins of Light-Induced Defects in *a*-Si

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We present an atomistic model of light-induced defects (the Staebler-Wronski effect). The model is based in part on our observations of molecular-dynamics simulations with an *ab initio* code and requires a change in the charge of a well-localized state in the gap, such as a dangling bond, to nucleate a defect. The defects are formed at weak-bond sites in the network following a rearrangement caused by the change of the charge of the localized state.

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An understanding of the phenomenon of light-induced defects in *a*-Si:H, the Staebler-Wronski (SW) effect [1], is arguably the most important problem in research on *a*-Si insofar as both photovoltaic devices and basic science are concerned. Briefly, the effect is that device-quality *a*-Si:H, grown under a variety of different conditions, displays an increase in the number of defects under illumination by light [2,3]. These defects are associated with localized states in the gap of the material which manifest themselves in a number of ways, the most important being that they shorten the recombination time for electron-hole pairs. The number of defects eventually saturates under intense illumination and the samples can be dark annealed back to their original condition. The induced defects are thought to be threefold coordinated Si atoms or dangling bonds and recent experiments show that these defects are virtually identical to the native dangling bonds and that they are created at least 5–8 Å from H atoms [4]. It has not been possible to determine whether the light-induced defects and only these defects are the ones dark annealed out or whether the samples after the dark anneal are only the same as the original samples on the average.

Despite extensive experimental work and theoretical modeling [1–13], the microscopic origins of the effects are unclear. There are several competing theories of the kinetics of the process and models of the microscopic origins. Basically, there are two types of microscopic models for the origin of the light-induced defects. One class of models is based on the idea of breaking “weak” Si-Si or Si-H bonds [2,9,10], although an exact or quantum-mechanical description of a weak bond has not been offered, nor have any details of how or why a weak bond breaks. The second class of models has the new defects being created by the movement of a defect [12–15] such as impurities, native defects, or an H that is bonded in a special way. In many of the models the weak bonds are broken when an electron-hole pair recombines, although the microscopic details of this process have not been addressed. In other models impurities or specially bonded

H atoms move extensively, giving rise to the new defect. Here, again, details as to how or why this happens remain to be worked out. In this Letter we are mainly concerned with the microscopic origins rather than the kinetics on a more macroscopic scale. We perform a detailed study of the effects of changes in defect charge states on the structural and electronic properties of *a*-Si. Since our primary tool is first-principles molecular dynamics (in which interatomic forces are computed directly from the electronic structure), we have properly included the quantum-mechanical effects like charge states, the role of the Fermi level, etc. Interestingly enough, this work has some of the flavor of both types of models described above. One result of our study is that a light-induced defect is nucleated by a localized defect state, probably a dangling bond but possibly an impurity atom. Another conclusion is that weak bonds are broken in connection with changes in defect charge state, and that the whole process is exceedingly nonlocal and involves a rather massive reorganization of the material in the vicinity of the defect. This is in agreement with recent preliminary NMR evidence suggesting that up to 1000 H atoms are significantly displaced for each new light-induced defect [16]. This feature of the process involving large relaxation effects encompassing many atoms is, we believe, unique to our description.

The simulations were performed using Sankey’s *ab initio* molecular-dynamics code which has been extensively described elsewhere [17]. The essential approximations are (1) nonlocal, norm-conserving pseudopotentials, (2) a slightly excited local-orbital basis set of four orbitals per site, and (3) the Harris functional implementation of the local-density approximation. The accuracy of the method for Si is very high as is extensively documented elsewhere [18–20]. In earlier work we have shown that classical molecular-dynamics simulations based on angular-dependent forces yield rather poor forces when applied to defects states [19,21] in *a*-Si although they do a rather good job in *c*-Si. In fact we showed that such codes yield forces that are in error by order of 10 times the force

change when one changes the charge state of a dangling bond [19–21]. Since these codes are classical, they cannot describe changes in the system or a defect state when its charge is changed.

Our simulation involves three steps. First we remove (or add) an electron to our supercell. Since the supercell has a dangling-bond state at the Fermi level, in effect this changes the charge state of a dangling-bond state. This change of charge causes the anisotropic forces near the dangling bond to change and the amorphous network starts to move to accommodate these changed forces. In the real material this change in the charge state of a localized state could be due to an electron ejected from the localized state to the conduction band by a photon, or it could be that the photon kicks an electron up from the valence band to the conduction band and then the electron drops into an impurity state. *It is vital that the change in charge take place in a localized state because otherwise there will not be any substantial change in any of the forces.* That is, the process must be nucleated by a localized state. A change in the charge of the valence band causes a very small change in forces because the states are so extended. For the same reason we have found that we cannot simulate the SW effect in supercells with a large number of defects because banding among the impurity states leads to states that are too delocalized.

The second step is to let the system evolve freely without either adding or taking away energy. We found that what started out as a very local disturbance of the atoms kept propagating outward. Furthermore, as the disturbance propagated out, several new defects states were formed and more on this will be given later in this Letter. After times of 200–500 fs, the disturbance had propagated across our supercell of 63 Si atoms. This time scale is obviously controlled at least in part by our sample size and is one aspect of the work that should be investigated more thoroughly.

The third and final step is to replace the removed electron (or hole) so that the charge of the cell was the same as in the beginning and then to quench the sample. In an actual sample this corresponds to returning to local charge neutrality by electron-hole recombination. Upon quenching, some, but not all, of the new defects disappear. Thus we are left with new defect states that consisted of threefold coordinated Si atoms that gave rise to states in the energy gap. These new defects are situated at atomic sites where there was originally a considerable bond-angle and/or bond-length distortion. One could take this to be the definition of a strained bond. There is no way that one can simulate the dark anneal of a sample since the time scales involved make this impossible on any computer with any code in the foreseeable future.

Some of the results of one series of simulations are shown in Table I. Configuration 0 was the initial sample that was characterized as the 63-atom, two-defect sample in earlier work [20–22]. We removed an electron from

TABLE I. Essential properties of one series of computer-simulated light-induced defects.

	Configuration				
	0	1	2	3	4
Number of geometrical defects	2	2	4	4	4
Time in fs	0	100	200	400	200
Number of spectral defects	3	3	6	5	6
Temperature (K)		200	200	200	300

this sample and let it freely evolve starting at a temperature of $T=200$ K. Configurations 1, 2, and 3 evolved for times of 100, 200, and 400 fs, respectively, before the removed electron was returned. Longer times than this lead to similar results. For configuration 4 we let the sample with the removed electron evolve for 200 fs but at a fixed temperature of $T=300$ K. Again, this caused no essential difference.

As we extensively discuss elsewhere [23], there are two inequivalent definitions of “defects” in α -Si which we must present to explain our results. First, a spectral defect is defined as a localized state in the gap where a measure of localization for an eigenvalue E is defined as

$$Q(E) = N \sum_i (q_i)^2,$$

where the sum is over the N atoms in the supercell and q_i is the fraction of the charge on the i th atom. The sum of the q 's is, of course, 1. We have taken $Q > 2$ to be the definition of a localized state. We note that a perfectly extended state will have $Q=1$. A geometrical defect consists of an Si atom that is not fourfold coordinated [20,21]. The definition of a neighbor depends upon the choice of a coordination radius; however, slight changes in the coordination radius almost always shift the defects between threefold dangling bonds and fivefold floating bonds.

There were 126 bonds in our 63-atom system. We monitored the separation of all these pairs over 300 time steps (about 600 fs) following the electronic transition. The initial bond lengths were all between 2.3 and 2.78 Å, although almost all of them were less than 2.5 Å. While a bond 2.78 Å long is severely strained, it is considerably shorter than the next longer pair which had a length of 3.3 Å. For convenience we arbitrarily define a short or normal bond to be one which is less than 2.5 Å long, and a long or strained bond one between 2.5 and 2.8 Å in length. A pair more than 3.0 Å apart is considered to be broken.

Earlier we have reported on dynamical fluctuations [23,24] of geometrical defects in α -Si supercells of the present 63-atom sample and the 216 WWW (Wooten-Weaire-Winer) sample [25]. These fluctuations did not lead to any significant shifts in the energy eigenvalues, nor to any significant change in the localization of any of the states. This type of behavior was also observed in the present simulation except that in this case, as noted

above, some of the energy eigenvalues did change as did their localization. After 300 time steps, we found that 54 normal bonds remained normal in the sense that their lengths had never exceeded 2.5 Å. There were 32 strained bonds which remained strained (but not broken). Another 29 bonds, initially badly strained, became normal (healed): Their lengths, while oscillating, showed an unmistakable tendency to relax towards smaller values with a diminishing oscillation amplitude. Finally, we found 10 broken bonds in the sense that their lengths increased to more than 3.0 Å, and 9 newly formed bonds in the sense that their lengths, while initially greater than 3.0 Å (and therefore not bonding at all at the beginning of our run), became less than 2.5 Å after some 100 time steps. Thus there was a significant rearrangement of the atoms in the sample. The 10 broken bonds and 9 new bonds led to an increase of only two geometrical defects.

The bond-breaking pattern is interesting. Two of the bonds snapped quite quickly. These bonds were both severely strained at the beginning of the run, so it is not surprising that they broke first. They also remained as the new defects when the sample was eventually quenched to $T=0$. The rest of the bonds that were eventually broken stayed longer and only started to break after about 100 fs. These resembled the fluctuations mentioned earlier as dynamical fluctuations in stable systems. What is surprising is that some of the broken bonds were initially normal, whereas some of the strained bonds became healed. Apparently it is not possible to predict which bonds will break on the basis of their initial strength. It is apparent from an animation of the trajectories of selected pairs that the breaking process is almost never a simple matter of monotonically increasing radial distances; the two partners undergo complicated lateral motions.

As the defect density grows, the defect states hybridize and become much less localized. This will prevent the initial nucleation by changing the charge state of a localized state. Such an effect was clearly observed in our simulation in samples with a large number of defects. We note that this can be one of the contributing factors to the saturation or the nonlinear quenching of the SW effect under high light intensities and over long times.

While we believe that the present study provides substantial insight into the microscopic nature of the SW effect, some improvements and extensions will ultimately be considered. One inadequacy is the finite size of our supercell, 63 Si atoms in this case. It is quite possible that the time scale of the reorganization of the Si atoms is being controlled by the sample size. Eventually we hope to investigate this point by employing larger supercells. Another problem is that all good *a*-Si is hydrogenated and our simulations are on unhydrogenated material. Plans are now being made to repeat the simulations on *a*-Si:H. Since the amount of H in a sample unequivocally correlates with the SW effect [5-7], clearly the presence of H is important. On the other hand, ex-

periments also show that new defects are not created near H atoms and that the new defects are no different from original ones [4]. This raises a number of difficulties with theories that explicitly require H motion in the formation of new defects. It is quite possible that the H is vital but in a rather passive role of stabilizing the sample or in decreasing the number of defects and thereby increasing their localization as our results suggest [20,21]. Further, recently observed light-enhanced diffusion of H [7] is consistent with our results of a rather large restructuring of the amorphous network. This restructuring would be expected to cause a substantial H movement. In any case, simulations with H are very time intensive on a computer because one must use time steps about $\frac{1}{20}$ as long as for *a*-Si due to the small mass of H. In lightly doped samples, the SW effect does not seem to correlate with the amount of dopant atoms; in heavily doped samples there are more light-induced defects generated as the doping is increased [2,8]. This might be explained since only a small fraction of dopants lead to a localized state in the gap and that is what our model requires. Simulations with dopants in the supercells are also being considered.

The most important conclusion from this study is the massive reorganization that occurs following an electronic transition in *a*-Si. Most previous theories of the SW effect are based on the breaking or the switching and reconnection of one or at most two weak bonds. Our work shows that such a picture is overly simplistic. At the very least, during the relaxation, many bonds may be broken and reconnected, even though the final net result might be one or two broken bonds. Because the relaxation is spatially highly nonlocal, there is no way to predict the specific bond that will be broken when all is settled. Unlike a crystal, an amorphous solid is in a metastable state with a considerable amount of internal energy associated with local strains. This makes the massive structural reorganization energetically possible.

In summary, we have presented a model for the formation of light-induced defects that is in part suggested by the results of our *ab initio* molecular-dynamics simulations. The model is both quantum mechanical in nature and quite detailed, in contrast to much of the previous work in which the actual mechanism for defect formation is vague and sometimes classical.

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