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Studies of silicon dihydride and its potential role in light-induced metastability in hydrogenated amorphous silicon

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Recent nuclear magnetic resonance experiments on protons in hydrogenated amorphous silicon (a-Si:H) by T. Su, P. C. Taylor, G. Ganguly, and D. E. Carlson [Phys. Rev. Lett. **89**, 015502 (2002)] have shown that light exposure leads to structures involving two protons separated by 2.3 ± 0.2 Å. In this report, using supercell models of a-Si:H, we show that SiH_2 configurations in the solid state are consistent with these observations. We find an average proton distance of 2.39 Å for SiH_2 structures considered for four different configurations. We also find that the details of basis set and density functional are important for accurately representing these structures. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1943488]

In 1977 Staebler and Wronski reported an experiment on hydrogenated amorphous silicon (a-Si:H),[1] which revealed a marked change in dark photoconductivity after light soaking. Subsequent work showed that defects, most probably dangling bonds, were created by light soaking. Because hydrogenated amorphous silicon (a-Si:H) is a material with technological applications, understanding the phenomenon of light-induced degradation, now named the Staebler-Wronski effect (SWE), has been a major focus.[2] In the intervening thirty years, extensive work in experiment and modeling has been carried out to obtain the microscopic origin and fundamental understanding of light-induced degradation. Disorder in the network, hydrogen concentration and its complex bonding structure and concentration of impurities are some of the material properties that play a role in the SWE.

An experimental clue of importance was recently reported by Su *et al.*,[3] who performed nuclear magnetic resonance (NMR) experiments on protons in a-Si:H and found that the NMR spectrum of light-soaked a-Si:H films show the preferential creation of a H–H distance of 2.3 ± 0.2 Å. Remarkably, this experiment directly connects light soaking to the creation of a specific new structure (or family of structures) in the amorphous matrix. Here, we show that SiH_2 is a possible candidate for the observed proton separation. Zhang *et al.* and Chadi have shown in careful calculations in c-Si:H that a two H interstitial complex, H_2^{**} is another potential candidate for the observed defect.[4,5] Both proposals have the merit that they do not rely on an unlikely conformation found only in specific models, and appear to occur with significant reproducibility, consistent with the well defined experimental distance.

There have been various proposals for the microscopic origins of the SWE. One class of models involves breaking of "weak bonds" which were often unspecified.[6] Another class of models propose the creation of new defects as a result of movement of the original defect.[7] Zafar *et al.* considered a metastability model based upon transfer of H between clustered and isolated phases seen by NMR.[8] Bonding in each of these phases was presumed to be monohydride. In their subsequent work Zafar *et al.* showed that the two-phase image closely accounted for experiments on the thermal changes in the spin density and also the changes caused by evolving hydrogen.[9]

Some current theories combine the electronic and hydrogen energy states and hydrogen diffusion as in the hydrogen collision model of Branz,[10] and the hydrogen flip model of Biswas *et al.*[11] Kopidakis *et al.* then proposed that clustered-phase sites can bind either one or two hydrogen pairs (dihydride bonding).[12] In this line of argument, Zhang and Branz proposed a model that m vacancies of m missing Si atoms, which are fully terminated with Si–H bonds to eliminate DBs and strained Si–Si bonds, provide the paired H reservoir and metastability sites in Si.[13] There are also new findings that reveal a lack of spatial correlation between the defects and hydrogen, the realization that the effectiveness of light induced defects as recombination centers depends on the light exposure conditions, and the observation that it is not only defects which are produced by extended light exposure but also larger structural changes in the material involving the Si network.[2]

There are two possible interpretations of the results of Su *et al.*[3] The simplest interpretation is that some metastable, paired-hydrogen site, perhaps, but not necessarily SiH_2, is formed after the exposure to light. A second interpretation, which cannot be ruled out by the experiments to date, is that some changes in the various NMR relaxation rates after exposure to light allow existing paired-hydrogen sites, such as SiH_2, to become observable in the NMR spectra.

Of particular importance to the latter interpretation, Stutzmann *et al.* have argued that the breaking of weak Si–Si bonds will also promote the diffusion of dangling bonds away from the original site.[6] If the presence of such a dangling bond near a stable, paired-hydrogen site, for which the most logical candidate is SiH_2, allows this site to be seen in the H NMR, then the results of Su *et al.* are also logically explained. Although there are technical reasons why this explanation is not as probable as the formation of metastable, paired-hydrogen sites, it cannot be ruled out. Our simulations strongly support either of these two interpretations.

In our calculations we used the *ab initio* code SIESTA,[14–16] within the local density approximation (LDA) with parametrization of Perdew and Zunger,[17] and the gen-

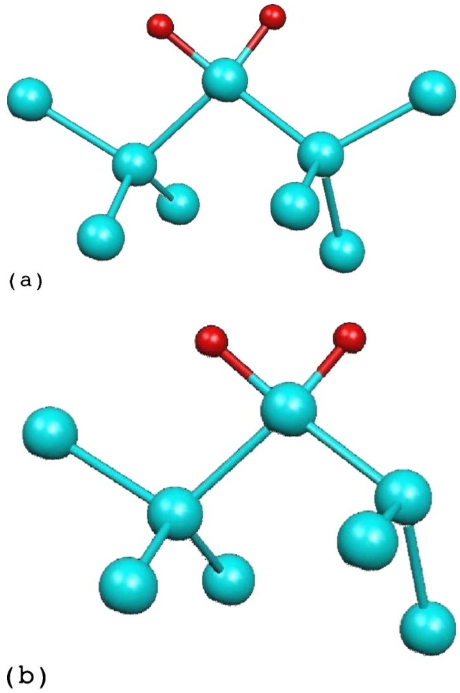

FIG. 1. (Color online) (a) SiH_2 conformation in *a*SiH−70 model and (b) SiH_2 conformation in *a*SiH−72 model with a dangling bond. In the figure the hydrogen atoms are shown in red (smaller in size) and the silicon atoms are shown in cyan (larger in size).

eralized gradient approximation (GGA) with parametrization of Perdew, Burke, and Ernzerhof.[18] Norm conserving Troullier-Martins pseudopotentials,[19] factorized in the Kleinman-Bylander form,[20] were used. For LDA we employed both double ζ polarized basis sets (DZP), where two *s* and three *p* orbitals for the H valence electron and two *s*, six *p*, and five *d* orbitals for Si valence electrons were used, and for comparison a cruder single ζ basis set (SZ), where one *s* orbital for the H valence electron and one *s* and three *p* orbitals for Si valence electrons were used. We used only DZP basis sets for GGA calculations. Details on generation of the basis orbitals are reported in the work of Artacho *et al.* and references therein.[21]

We began with a defect-free 64 atom *a*-Si model,[22] and removed two Si atoms and added eight H atoms to create defect-free (that is, gap state free) structures with SiH_2 present. We named this model *a*SiH−70. Another model is obtained in the same way except that one more Si atom is removed to form *a*SiH−72 (61 Si atoms and 11 H atoms), which includes one dangling bond.[23] We then repeated this supercell surgery at other sites to generate an ensemble of models to obtain some insight into the bonding statistics of SiH_2 conformations in the solid state. The SiH_2 confirmations obtained in the two models are shown in Figs. 1(a) and 1(b). We have considered four configurations for each model in our calculation. Each configuration in the respective models was constructed by selecting different (typically tetrahedral) sites of the SiH_2 conformations in the cell. We performed our calculations of SiH_2 structure and dynamics on each of the four configurations of *a*SiH−70 and also on each of the four configurations of the *a*SiH−72 model. The system was then relaxed using polarization functions (DZP) basis sets on all of the atoms employing a GGA exchange-correlation functional and also using polarized (DZP) and SZ basis sets using the LDA exchange-correlation functional.

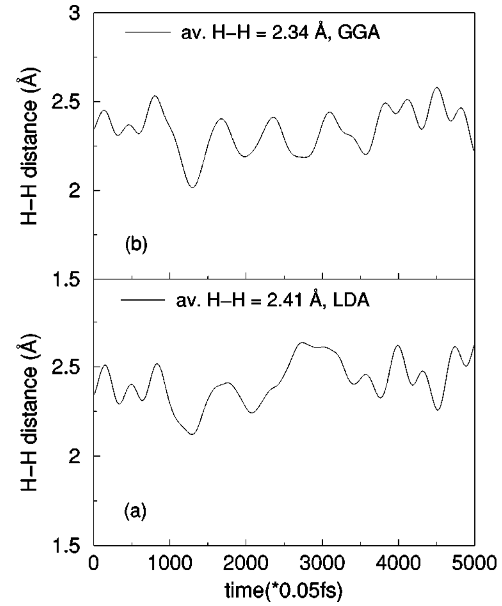

FIG. 2. Thermal MD simulation for the H–H distance in *a*SiH−72 model using a) LDA calculations and b) GGA calculations.

We note that there is a consistent pattern that in the amorphous matrix the proton–proton separation is significantly reduced relative to a gas phase silane molecule with tetrahedral bonds (which produces a separation of 2.45 Å).

We performed thermal molecular dynamics (MD) simulations to estimate the H–H distance at room temperature and to compare to $T=0$. The cells evolved freely for 250 fs (within a time step of 0.05 fs) at a temperature of $T=300$ K. We observed thermal fluctuations in the bond lengths as indicated in Figs. 2(a) and 2(b). We obtained an average H–H distance of 2.41 Å in the case of the LDA calculation and an average H–H distance of 2.34 Å for the GGA calculations for an initial H–H distance of 2.27 Å over a 5000 step MD run.

For the first group of four configurations (*a*SiH−70), our results are summarized in Table I. In all these configurations, for different initial proton distances, we see a consistent approach to near the measured proton–proton separation of (2.3±0.2 Å) as the basis set improves from SZ to more complete DZP. Though the shift is smaller, there is also an im-

TABLE I. H–H distance before and after relaxation for *a*SiH−70 using LDA and GGA exchange correlation functional for four different configurations. The GGA (DZP) calculation is expected to be the most accurate.

Model *a*SiH−70				
		H–H distance after relaxation		
Configurations	H–H distance before relaxation (Å)	LDA (SZ) (Å)	LDA (DZP) (Å)	GGA (DZP) (Å)
1	1.58	2.51	2.40	2.38
2	2.27	2.38	2.36	2.35
3	3.02	2.69	2.46	2.42
4	3.30	2.59	2.47	2.42
Average		2.54	2.42	2.39

TABLE II. H–H distance before and after relaxation for $a\mathrm{SiH}-72$ using LDA and GGA exchange correlation functional for four different configurations. These models contain one dangling bond. The GGA (DZP) calculation is expected to be the most accurate.

Model $a\mathrm{SiH}-72$				
		H–H distance after relaxation		
Configurations	H–H distance before relaxation (Å)	LDA (SZ) (Å)	LDA (DZP) (Å)	GGA (DZP) (Å)
1	1.61	2.39	2.35	2.34
2	2.20	2.59	2.51	2.46
3	2.35	2.34	2.33	2.32
4	3.29	2.56	2.47	2.44
Average		2.47	2.42	2.39

provement in going from LDA to GGA functionals. There is a strong message in these results that high-quality calculations are needed to properly describe the structure.

The same calculation has also been done for the $a\mathrm{SiH}-72$ model, and, the results are given in Table II. As before, a DZP basis set and GGA appears to be necessary. Consistent with the first configuration, $a\mathrm{SiH}-72$ also gives proton separations well within the tolerance of the experiments of Su *et al.*[3]

Most of the aforementioned models of the SWE invoke paired-hydrogen sites. These models associate the SWE with the conversion of isolated H into paired-hydrogen sites, for which SiH_2 must be considered a prime candidate. The experiments of Su *et al.* suggest that light soaking creates structures with a proton–proton separation of about 2.3 Å.[3] Given the remarkably well-defined nature of the observed proton separation, it is natural to expect that the structure(s) causing the feature must not be a very rare conformation. Something like the complex of Chadi,[5] or our SiH_2 proposal here, appear to fulfill that condition—one certainly expects *a priori* that both of these configurations should occur in a-Si:H, though it is not initially obvious with what probability.

Given that the various models proposed,[4–13] all appear to be at least consistent with our calculations for SiH_2, the link between our calculations and the NMR experiments is a very important step. On the other hand, what we have not done is provide any explanation of the light-induced formation of the SiH_2, which is certainly a key missing piece to the puzzle. This is not an easy process to simulate, since the (diffusive) time scales for simulation are presumably vastly longer than what is directly accessible from our simulation. Still, special techniques like the activation relaxation technique exist to track such diffusive motion,[22] and might indicate a plausible path to SiH_2 creation.

Using accurate methods and supercells properly representing the disorder of a-Si:H, we have seen that the SiH_2 is a credible candidate for the proton–proton distance inferred from the work of Su *et al.* We have seen that rather accurate methods (including a double-zeta polarized basis and a GGA) are needed to properly describe the bonding in this system.

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