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Structural disorder induced in hydrogenated amorphous silicon by light soaking

J. M. Gibson[a)]
Departments of Physics and Materials Science, University of Illinois, and Frederick Seitz Materials Research Laboratory, Urbana, Illinois 61801

M. M. J. Treacy
NEC Research Institute, Inc., Princeton, New Jersey 08540

P. M. Voyles
Department of Physics, University of Illinois, Urbana, Illinois 61801

H-C. Jin and J. R. Abelson
Department of Materials Science and Coordinated Science Laboratory, University of Illinois, 1-109 Engineering Science Building, Urbana, Illinois 61801

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We show, using variable coherence transmission electron microscopy, that light soaking of amorphous hydrogenated silicon thin films leads to structural changes. We speculate that the structural changes are associated with instability in the as-deposited material. We suggest that improved immunity to Staebler–Wronski degradation could be achieved by a less-ordered material which is closer to the ideal continuous random network. © *1998 American Institute of Physics.* [S0003-6951(98)02947-7]

The light-induced creation of dangling bond defects in hydrogenated amorphous silicon (*a*-Si:H), called the Staebler-Wronski effect (SWE),[1–3] has proven an obstacle to the widespread technological application of this material. Although the Staebler–Wronski effect saturates with the creation of about $10^{17}/\text{cm}^3$, there is growing indirect evidence that a much larger number of atoms are affected by light soaking.[4–6]

Here, we report that there is a significant structural change in hydrogenated amorphous silicon after light soaking, which we have observed using variable coherence electron microscopy. Our experiments show no such structural change in hydrogen-free silicon. In the light of our previous work on pure amorphous Ge and Si,[7,8] we interpret this result as evidence for a structural instability in the as-deposited *a*-Si:H structure, which has more medium-range order than the continuous random network. We propose that the Staebler–Wronski effect is intimately related to this structural instability.

Electron fluctuation microscopy techniques have high sensitivity to such subtle structural changes. Diffraction, including small angle scattering, and other single-scattering techniques such as extended x-ray absorption fine structure (EXAFS) reveal correlations between pairs of atoms only, as embodied in the radial distribution function (RDF), which is not sensitive to subtle differences between network structures.[7] We have shown that higher-order atomic correlation functions (three and four body), which are measured by variable coherence microscopy,[9] are sensitive to such differences.[7] Specifically, variable coherence electron microscopy can detect correlations at a characteristic length scale of 10–20 Å that fall short of the perfect ordering necessary for strong diffraction. Raman scattering and x-ray absorption near-edge structure may also provide useful information about medium-range order, but the interpretation of these techniques is complicated by the need to know the internal properties of the atoms in order to calculate the vibrational spectrum or electronic density of states. Because variable coherence electron microscopy uses high energy electrons as a probe, the atoms' positions are their most important attribute, supplemented by the well-known atomic scattering factor.

For this experiment amorphous hydrogenated silicon films of varied composition were deposited by reactive magnetron sputtering of a silicon target in argon and hydrogen. This method permits independent control of hydrogen content, and produces material with excellent electronic and optical properties,[10,11] <0.1 at. % argon concentration, and a low void fraction.[12] Films of 20 nm nominal thickness were deposited on commercial aluminum foil at 230 °C. Specimens for transmission electron microscopy (TEM) were picked up with 3 mm Cu grids after dissolving the Al in 20% HCl solution. X-ray microanalysis indicates a barely detectable residue of Al in the form of sparsely separated aluminum oxide particles on the film's surface and <0.1 at. % concentration of any other metal contaminant. Broadband illumination was provided by a 100 W Oriel quartz halogen lamp coupled to a quartz fiber to yield an illumination intensity of $0.4\ \text{W cm}^{-2}$ at the specimen. Specimens were irradiated for 70 000 s (20 h) at room temperature in a water-cooled TEM holder.

Samples were examined in a Hitachi H9000NAR side-entry TEM operating at 200 kV using the variable coherence microscopy method.[9,13] Hollow-cone dark-field images of

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[a)]Electronic mail: j-gibson@uiuc.edu

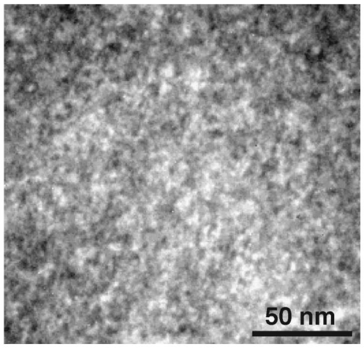

FIG. 1. Typical hollow-cone dark-field micrograph of 20-nm-thick amorphous $Si_{0.85}H_{0.15}$ showing speckle.

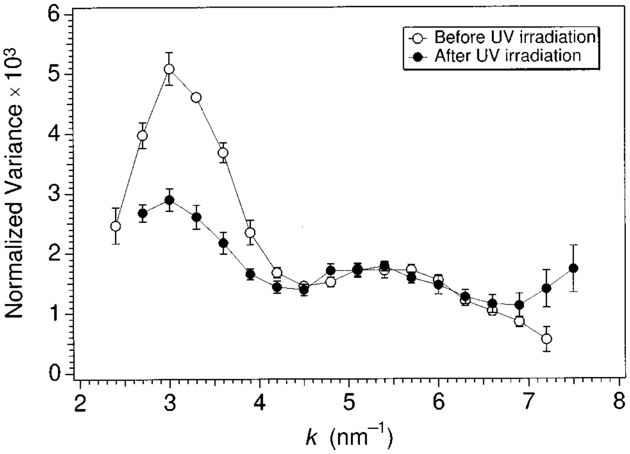

FIG. 2. Plots of the image intensity variance V of the $Si_{0.85}H_{0.15}$ sample, as a function of the hollow-cone scattering vector magnitude k. Open circles are before light soaking, and solid circles are after light soaking.

amorphous materials, such as Fig. 1, exhibit a speckle pattern whose character depends on the scattering vector magnitude, $k=\sin(\theta)/\lambda$, where θ is the hollow-cone illumination semi-angle λ is the electron wavelength. The lateral extent of the scattering coherence volume decreases as $\sim 1/k$. The image resolution imposes a maximum lateral distance over which scattering can be correlated, which we set at 1.6 nm with the objective aperture. In our images speckle arises from statistical scattering fluctuations between volumes typically containing ~1000 atoms, which determines the length at which we probe medium-range order. A perfect crystal would show no speckle at low resolution, since each mesoscopic volume would be scattering identically. A perfectly random atomic distribution would exhibit speckle corresponding to the sampling statistics of small volumes, but this contribution will have little or no k dependence. An amorphous specimen with medium-range order, however, will impose additional k-dependent intensity fluctuations because of local orientation dependencies to the coherent scattering. The variance of the image intensity provides a measure of the speckle, and was recorded from each image, then plotted as a function of the scattering vector magnitude, as in Fig. 2. $V(k)$ is given by

$$V(k)=\frac{\int\int I^2(\mathbf{r},\mathbf{k})d^2\mathbf{r}}{[\int\int I(\mathbf{r},\mathbf{k})d^2\mathbf{r}]^2}-1, \tag{1}$$

where $I(\mathbf{r},\mathbf{k})$ is the image intensity at position $\mathbf{r}$, when the hollow-cone scattering vector magnitude is k. Each point in Fig. 2 represents the average of typically ten measurements from successive scans from different areas plotted with one-standard-deviation error bars. Scans were made from high to low scattering vectors, and vice versa, to reveal any electron dose dependence. We also examined the variance at a fixed scattering vector as a function of time.

Figure 1 shows a typical speckle image from an as-deposited 20-nm-thick a-$Si_{0.85}H_{0.15}$ specimen, taken at $k=3.0\ \mathrm{nm}^{-1}$. Sample (a) was virgin material, and sample (b) was light soaked. Both samples were taken from the same piece of film.

The variance peak amplitude at $3\ \mathrm{nm}^{-1}$ is reduced considerably after light soaking, and is a signature of medium-range order on a length scale of ~1.6 nm. We have demonstrated by modeling[8] that pronounced peaks, such as those observed here, are not consistent with a continuous random network. The differences between Figs. 2(a) and 2(b) indicate that light soaking produces structural rearrangement which reduces medium-range order and involves substantially all the atoms in the sample. The rearrangement is not easily detected in the diffraction pattern because diffraction is sensitive only to pair correlations.[7,9] It is consistent with growing evidence for hydrogen motion during light soaking that involves the creation and annealing of Si–H–Si intermediate bonds.[14–17] A detailed interpretation of the observed change in $V(k)$ will require atomic modeling.

It has been proposed that keV electron irradiation creates similar effects to light soaking.[18,19] The electron beam current density during our experiments was $25\ \mathrm{A\ cm}^{-2}$. A typical image required a 3 s exposure, and an entire series taken from one area required about 20 min, for a total dose of $\sim 3\times 10^4\ \mathrm{Coulomb\ cm}^{-2}$. No pronounced dose dependence was observed for doses between 75 and $10^4\ \mathrm{Coulomb\ cm}^{-2}$, but at higher doses ($>10^5\ \mathrm{Coulomb\ cm}^{-2}$) changes similar to those observed on light soaking began to appear.

The energy deposited by the high energy electron beam is around 10 eV per electron for a 20-nm-thick film, as estimated from Bethe's formula[20] in the very thin film limit. The power density deposited into the sample is thus $230\ \mathrm{W\ cm}^{-2}$. However, the electron illumination is confined to a circular region about one micron in diameter, and the total beam current is 70 nA, yielding a total power of only 0.6 μW. This shows that temperature changes associated with electron irradiation are negligible. Based on earlier published work,[18,19] an exposure of around 1 ms, at the electron dose we use, should be equivalent to our total light dose. If that were the case, e-beam effects should dominate the results, with no discernible contribution from the light soaking.

We see two possible resolutions of this difficulty: (i) Electron and photon irradiation produce distinctly different effects; (ii) The models of defect creation by keV electrons in the literature cannot be simply extended to our experimental conditions. Previous work comparing ultraviolet (UV) and electron irradiation has focused only on the electrically active Staebler–Wronski defects, which are created at densities around $10^{17}\ \mathrm{cm}^{-3}$. It is possible that while defect creation associated with electron and UV irradiation are similar, structural rearrangements are not.

Earlier work noted that electron beam irradiation seemed to be more than 3000 times more efficient than UV irradiation in generating Staebler–Wronski defects.[18,19] Previous e-beam irradiation experiments were performed in a scanning electron microscope, where an intense focused electron beam is scanned rapidly over very large areas; however the modeling assumed uniform illumination. It is known that there is a striking increase in the efficiency of Staebler–Wronski defect production with high-intensity pulsed light beams.[21] There may be a previously undetected dose-rate dependence to the e-beam effect, which would introduce a difference between scanned and flood illumination. Additionally, we study free-standing thin films where surface effects may be more important. Further experiments will be required to resolve these issues.

If the electron-based Staebler–Wronski effect were identical to the light-based effect, then from power density considerations, we would expect to see electron induced changes in about 100 s. We do not detect such changes. The substantial difference in light-soaked and virgin *a*-Si:H samples observed under the same electron dose conditions indicates that there is light-induced structural relaxation.

Recent observations of paracrystalline medium-range order in as-deposited *a*-Si and *a*-Ge suggest an explanation of the light-induced structural changes.[8] Paracrystalline materials comprise strongly deformed grains, less than ~3 nm in size, that are *topologically* crystalline, but diffraction amorphous. The deformation is an elastic relaxation bonding disorder at grain boundaries. On annealing below the recrystallization temperature, grain boundaries are eliminated, removing strained bonds, and the structure transforms into a relatively stable continuous random network. Such a relaxation is not observed in the magnetron-sputtered samples on thermal annealing, perhaps due to the relative ease of homogeneous recrystallization.

We find close parallels between the variance signature of evaporated *a*-Si and the magnetron-sputtered *a*-Si with only 1% hydrogen. The 15% hydrogen sample in Fig. 2, prior to light soaking, also shows a similar paracrystalline signature. It is straightforward to see how a paracrystalline structure can contain many more weak bonds than the continuous random network. According to the weak bond-breaking model, this will lead to greater susceptibility to the Staebler–Wronski effect.[22] As relaxation occurs, a separation between the Staebler–Wronski defects and hydrogen in the structure is observed.[23] Mild thermal annealing at 200 °C reduces the Staebler–Wronski defect concentration,[3] but is not a high enough temperature to significantly relax the paracrystalline structure. Therefore the whole process of Staebler–Wronski defect generation begins again on renewed light soaking.

We speculate that if *a*-Si:H could be produced in the fully relaxed continuous random network state, then the density of weak bonds would decrease Furthermore, without a driving force for relaxation, Staebler–Wronski defects and hydrogen would be less likely to migrate, and more likely to recombine. These effects might minimize photodegradation. It is known that microstructure affects the Staebler–Wronski effect.[14–17] It has been generally assumed that the favorable microstructure is more highly ordered, but there is little evidence for this. We propose that the favorable microstructure is *less ordered*, and more like a continuous random network. We know that high temperature annealing can produce a continuous random network in pure amorphous semiconductors; the challenge is to find a way to reproduce the continuous random network and to maintain hydrogen passivation. Even though disorder may promote stability, it remains to be seen how it affects the initial electrical properties of the material.

This work shows that light soaking of *a*-Si:H leads to structural changes that involve many atoms, and are distinct from any electron beam effects observed at very high doses. We speculate that the structural changes are associated with instability in the as-deposited material, and suggest that a material which is closer to the ideal continuous random network would exhibit improved immunity to Staebler–Wronski effect degradation.

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