Reduced Staebler–Wronski effect in reactively sputtered hydrogenated amorphous silicon thin films

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The kinetics of light-induced defect generation or the Staebler–Wronski effect (SWE) have been measured on device quality hydrogenated amorphous silicon (*a*-Si:H) films having hydrogen contents (C_H) of ~10–28 at. %. The films were deposited with direct current (dc) magnetron reactive sputtering. The low C_H films have a density of defect states (DOS) ~7 to 10×10^{15} cm^{-3} which is three to five times higher than the high C_H films. Under light exposure, the DOS for low C_H films increases slower than that of the high C_H or glow discharge produced films; in fact it is smaller after a few hours of light exposure. These measurements show that low C_H dc magnetron reactively sputtered *a*-Si:H appears to be more stable material for sensitive applications such as solar cells.

Staebler and Wronski discovered that the electronic properties of hydrogenated amorphous silicon (*a*-Si:H) degrade when the material is exposed to light,[1] now known as the Staebler–Wronski effect (SWE). They observed a decrease in photoconductivity and dark conductivity of the films upon exposure which was subsequently correlated with an increase in the density of midgap defect states.[2,3] The degradation is reversible. Annealing the films at 150–200 °C for 1–2 h restores the electronic properties that the films possessed before illumination. Light-induced degradation limits the usefulness of *a*-Si:H in solar cells and photoreceptors, and SWE-resistant material is required to make practical devices.

Stutzmann *et al.*[4] measured and modeled the degradation kinetics of *a*-Si:H and showed that the density of dangling silicon bond defect states (DOS) in the gap increases as $t^{1/3}$ (t is light exposure time) for glow discharge (GD) produced films in silane. Various mechanisms have been suggested for the creation of these defect states in *a*-Si:H. The widely recognized "bond breaking" model[5] postulates two stages: first, the energy liberated by free-carrier recombination events breaks weak Si—Si bonds and then these newly created defect states are stabilized, possibly by hydrogen motion which spatially isolates them.[3,4]

Most SWE studies have concerned GD films; several of them suggest that the hydrogen content (C_H) affects the material stability.[6–8] This work is the first systematic examination of the light-induced degradation on reactively sputtered (RS) *a*-Si:H. All samples are device quality in the as-deposited state and span a range of C_H. We have previously reported the details of deposition and the optical, electronic, and microstructural properties of these films.[9–12]

[a)] This work was carried out while the author was in the Department of Materials Science and Engineering, and the Coordinated Science Laboratory of the University of Illinois at Urbana–Champaign.

Here we focus on the SWE in two representative films with low (12 at. %) and high (28 at. %) C_H. The film with low C_H was prepared at 0.2 mTorr hydrogen partial pressure in argon and a 300 °C substrate temperature. The film with high C_H was prepared at 1 mTorr hydrogen partial pressure in argon and a 230 °C substrate temperature. The argon partial pressure for all depositions was 1 mTorr. We find no evidence for a substrate temperature effect (for films deposited between 230 and 300 °C) beyond its influence on C_H; we performed the light-induced degradation study for up to 100 h on other low C_H films (~13 at. %) which were deposited at 230 °C and 0.2 mTorr hydrogen partial pressure, and found identical behavior.[10,13]

Conductivity measurements were made using coplanar chromium contacts deposited on top of the film and defining a gap of 0.2 cm. The light exposure and photoconductivity measurements used only the red portion of the spectrum from an ENH slide projector lamp. Low and high pass filters were used to bracket the wavelengths between 620 and 680 nm (1.83–2 eV) with a nearly top hat spectrum. This range of photon energies is larger than the Tauc band gap of all the films studied. The light intensity was 150 mW/cm^2 as measured by a pyroelectric radiometer and the areal illumination of the sample was uniform. The films were placed on a water-cooled stage to keep the temperature constant at ~30 °C. The low and high C_H sputtered films and a GD-produced film had thicknesses of ~1.6, 1.0, and 1.2 μm, respectively.

We calculated the volume generation rate (G) for reactively sputtered films using $G=F(1-R)(1-\exp\alpha d)/d$ and integrating between 620 and 680 nm; $F(\lambda)$, $R(\lambda)$, $\alpha(\lambda)$, and d are the photon flux (photons/cm^2), reflection coefficient, absorption coefficient (cm^{-1}), and sample thickness (cm), respectively. The use of near-band-gap light produces a roughly uniform G throughout the sample. For the high C_H film the G for the topmost 0.2 μm (~6×10^{20} cm^{-3}) is ~40% higher than the bottom 0.2

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μm. For the low C_H film, which has higher absorption coefficients, the topmost 0.2 μm has about an order of magnitude higher $G(\sim 4\times 10^{21}\ cm^{-3})$ than the bottom 0.2 μm (which is still comparable to the G for the bottom 0.2 μm of the high C_H film). This is obviously not "uniform." However, previous studies have shown that the defect generation rate proceeds as G^2; thus the low C_H films should degrade more rapidly since their average G is a factor of ~ 2 higher than high C_H films,[10] whereas in fact they degrade much more slowly.

The photoconductivity (σ_{ph}) of the films as a function of the light exposure time is shown in Fig. 1. For comparison, Staebler–Wronski effect studies were also performed on a high quality glow discharge produced a-Si:H film ($C_H \sim 10$ at. %).[14] All three films have nearly the same σ_{ph} in the as-deposited state, but the reduction in σ_{ph} as a function of the length of light exposure is different. Both the GD film and the high C_H RS film show a similar rapid degradation in σ_{ph} compared to the low C_H RS film. Similar degradation in the σ_{ph} of GD films has been observed by other groups.[4,15] After 100 h of light exposure, σ_{ph} for the low C_H film is $\sim$three times higher than the σ_{ph} of the other two samples. Four other RS films with low and high C_H (not shown for clarity) have been measured for exposure times exceeding 100 h and closely follow the trend shown in Fig. 1. This indicates that the degradation in σ_{ph} of the RS films is systematically related to their total C_H.[10,13]

The DOS in the band gap of a-Si:H increases with light exposure and degrades the carrier transport by reducing the free-carrier lifetimes. This ultimately limits the long-term performance of a-Si:H in device applications. We have measured the increase in DOS using the constant photocurrent method (CPM).[16,17] Figure 2 shows the increase in DOS as a function of the light exposure time for the same GD and RS films discussed above. There are two key results. First, we observe a crossover in the DOS for these films. In the annealed state, the low C_H film has a DOS approximately three times larger than the high C_H and a GD film. The rate of increase in the DOS for the low C_H film is markedly lower

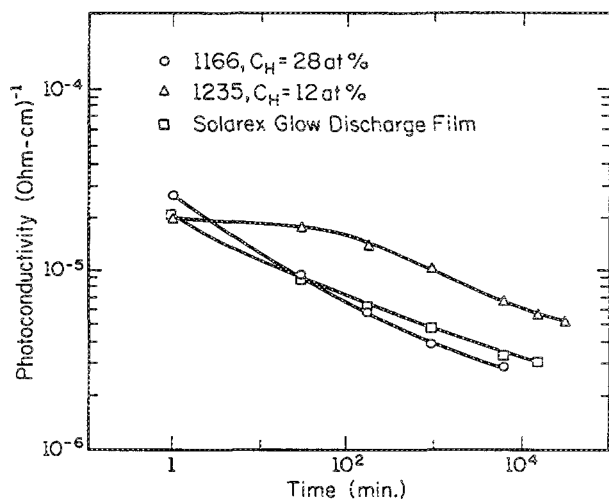

FIG. 1. Reduction in σ_{ph} as a function of the light exposure time for a low and a high C_H reactively sputtered film, and a glow discharge deposited a-Si:H film.

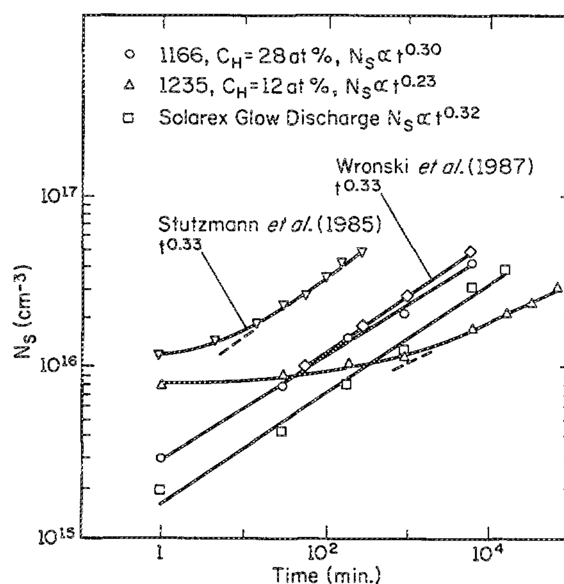

FIG. 2. Increase in DOS (measured by CPM) as a function of the light exposure time at $I = 150$ mW/cm^2 for two representative RS films and a GD film. The low C_H film is superior against SWE compared to the GD films. The SWE results of Stutzmann *et al.* [$I = 200$ mW/cm^2, ESR Ref. (4)] and Wronski *et al.* [$I = 50$ mW/cm^2, CPM data Ref. (16)] for GD films are also shown for comparison. Light intensity does not affect the slope of the curves.

than the other films so that after few hours of light exposure the DOS for low C_H RS film becomes lower than the other two films. Further light exposure increases the differences between the more stable low C_H and the less stable high C_H and the GD films.

The crossover in Fig. 2 is a clear indication that the defect creation kinetics must be fundamentally different for low C_H films. In Stutzmann's model, the initial DOS affects the initial rate of defect creation by a shunting mechanism. Recombination events proceed either through band tails, which create defects with a probability $A_{S\text{-}W}$, or through midgap states which dissipate the pair energy without defect creation. A large initial DOS will dominate the recombination traffic and reduce the defect formation rate. However, if the recombination pathways and the $A_{S\text{-}W}$ coefficients are identical in two films with different initial DOS values, then they must asymptotically approach the same DOS vs t behavior at long times. The low C_H RS film has a lower DOS for long times. We note then that the initial DOS is not a reliable indicator of a-Si:H quality in terms of stability.

The second key result is that the exposure time dependence of the defect creation of the RS films is different from that of GD films. This is shown in Fig. 2. The low C_H film has a $t^{0.23}$ dependence of the DOS on exposure between 100 and 1000 h (the longest time examined). The slope is determined from the last four data points. The high C_H film shows a faster degradation with DOS proportional to $t^{0.3}$. Stutzmann *et al.* predict a $t^{1/3}$ dependence which is inconsistent with our results for low C_H RS films. It is possible that the RS films will take on the $t^{1/3}$ dependence with longer exposure; however, our results do not indicate a significant evolution in slopes. If we assume that we will eventually observe the $t^{1/3}$ rule for these films, then we must conclude that the susceptibility coefficient $A_{S\text{-}W}$ is $\sim 100\times$ less for

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films with a low C_H compared to high C_H films. Identical light exposure experiments on a high quality GD film yielded a $t^{0.32}$ dependence. This result is in accordance with the Stutzmann *et al.* model and the results reported by other groups.[4,18]

A more quantitative measure of light exposure is the total number of photons absorbed by the material. In the spectral range used here, the low C_H films have ~twofold higher generation rate than the high C_H films due to their smaller optical band gaps, i.e., they have larger optical absorption coefficients.[11] Figure 3 shows the increase in DOS as a function of the number of photons absorbed (generation rate × exposure time). When quantified in this fashion, the crossover (Fig. 2) occurs even earlier in the exposure.

Our degradation results may be interpreted within the bond-breaking model as evidence that either the Si—Si bond-breaking step, or the broken bond stabilization, or both are enhanced in high C_H films. Skumanich and Amer[19] measured a variety of films and suggested that the rate of defect creation increases with the band gap, i.e., with the energy released per band-to-band recombination event. In accord with this idea, Kolodzey *et al.* reported very low rates of defect formation in low band-gap *a*-Si,Ge:H,F alloys.[20] The band gap (Tauc gap) of our material changes from 1.62 to 1.85 eV with increasing C_H,[11] which agrees with the trend of increasing degradation.

Alternatively, the broken bond stabilization may be favored in high C_H material. We reported that as C_H increases above 15 at. %, the additional H goes into dihydride modes and the microstructure becomes void-rich.[12] Both aspects have been associated with increased susceptibility to degradation. Carlson's model of degradation involves the motion of hydrogen in the internal surfaces of microvoids and proposes that increasing the density (lowering the void content) of the material should increase the stability of *a*-Si:H.[21] Bhattacharya and Mahon[22] reported that material with greater SiH_2 content (which they associate with void density) is more susceptible to light-induced defect creation. Kakalios *et al.*[23] associate the motion of hydrogen with the annealing of the defect states in *a*-Si:H which indicates that hydrogen is involved in the degradation process. Our results are in agreement with these assertions.

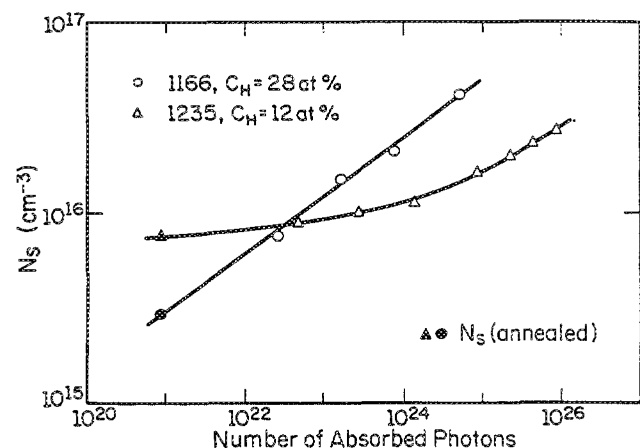

FIG. 3. Increase in DOS is shown as a function of the number of absorbed photons (generation rate × exposure time) during light exposure. Compared to Fig. 2 the crossover in DOS for RS films occurs earlier in the light exposure.

In conclusion, the total C_H of dc magnetron reactively sputtered films has a strong effect on the stability of these films against SWE. Low C_H films are more stable against SWE compared to high C_H films or typical GD films. Noting that the low C_H films have the highest DOS in the annealed state, our results show that the initial DOS is not a reliable indicator of *a*-Si:H quality in terms of stability. For light exposure times of 1000 h, the DOS in the low C_H sputtered films increases only as $\sim t^{0.23}$, which cannot be accounted for by the kinetic model of Stutzmann *et al.*

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[1] D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **39**, 292 (1977).
[2] I. Hirabayashi, K. Morigaki, and S. Nitta, Jpn. J. Appl. Phys. **19**, L357 (1980).
[3] H. Dersch, J. Stuke, and J. Beichler, Appl. Phys. Lett. **38**, 456 (1981).
[4] M. Stutzmann, W. B. Jackson, and C. C. Tsai, Phys. Rev. B **32**, 23 (1985).
[5] J. I. Pankove and J. E. Berkeyheiser, Appl. Phys. Lett. **37**, 705 (1980).
[6] T. Shimizu, M. Kumeda, A. Morimoto, H. Yokomichi, and N. Ishii. J. Non-Cryst. Solids **77-78**, 377 (1985).
[7] M. Ohsawa, T. Hama, T. Akasaka, T. Ichimura, H. Sakai, S. Ishida, and Y. Uchida, Jpn. J. Appl. Phys. **24**, L838 (1985).
[8] S. Nakano, H. Tarui, H. Haku, T. Takahama, T. Matsuyama, M. Isomura, M Nishikuni, N. Nakamura, S. Tsuda, M. Ohnishi, and Y. Kuwano, *19th IEEE Photovoltaics Specialist Conference Proceedings* (IEEE, New York, 1987), p. 678.
[9] M. Pinarbasi, L. H. Chou, N. Maley, A. Myers, D. Leet, and J. A. Thornton, Superlatt. Microstruct. 3, 331 (1987).
[10] M. Pinarbasi, Ph.D. thesis, University of Illinois at Urbana-Champaign, 1989.
[11] M. Pinarbasi, N. Maley, M. J. Kushner, A. Myers, J. R. Abelson, and J. A. Thornton, J. Vac. Sci. Technol. 7, 1210 (1989).
[12] M. Pinarbasi, N. Maley, N. A. Myers, and J. R. Abelson, Thin Solid Films **171**, 217 (1989).
[13] M. Pinarbasi, M. J. Kushner, and J. R. Abelson (unpublished).
[14] Glow discharge sample and its hydrogen content estimation were provided by Dr. Charles Fortman of Solarex Corporation, Newtown, PA 18940.
[15] A. G. Kazanskii, E. P. Milichevich, and V. S. Vaslov, J. Non-Cryst. Solids **97&98**, 787 (1987).
[16] M. Vanacek, J. Kocka, J. Stuchlik, Z. Kozisek, O. Stika, and A. Triska, Solar Energy Mater. **8**, 411 (1983).
[17] Z. E. Smith, V. Chu, K. Shepard, S. Aljishi, D. Slobodin, J. Kolodzey, and S. Wagner, Appl. Phys. Lett. **50**, 1521 (1987).
[18] C. R. Wronski, Z E. Smith, S. Aljishi, V. Chu, K. Shepard, D. S. Shen, R. Schwartz, D. Slobodin, and S. Wagner, AIP Conf. Proc. **157**, 70 (1987).
[19] A. Skumanich and N. M. Amer, Appl. Phys. Lett. **52**, 643 (1988).
[20] J. Kolodzey, R. Schwarz, S. Aljishi, V. Chu, D. S. Shen, P. M. Fauchet, and S. Wagner, Appl. Phys. Lett. **52**, 477 (1988).
[21] D. E. Carlson, Appl. Phys. A **41**, 305 (1986).
[22] E. Bhattacharya and A. H. Mahan, Appl. Phys. Lett. **52**, 1587 (1988).
[23] J. Kakalios, R. A. Street, and W. B. Jackson, Phys. Rev. Lett. **59**, 1037 (1987).

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