Electronic stability of the reactively sputtered hydrogenated amorphous silicon thin films: The effect of hydrogen content

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The total hydrogen content (C_H) of reactively sputtered hydrogenated amorphous silicon (*a*-Si:H) films can be independently controlled by adjusting the partial pressure of hydrogen (P_{H_2}) during deposition. We report on the electronic stability of direct-current (dc) magnetron reactive sputtered films deposited at a constant substrate temperature of 230 °C with various P_{H_2}. The films have C_H from ~13 to 28 at. % and similar, device quality properties in the as-deposited state. The photoconductivities of all the films are between 0.9 to 3×10^{-5} $(\Omega\ \text{cm})^{-1}$ under AM-1 (air mass-1) illumination (100 mW/cm^2). The density of deep states (DOS) measured by the constant photocurrent method is $\sim6\times10^{15}$ cm^{-3} for low C_H ($\leqslant15$ at. %) and $\sim2\times10^{15}$ cm^{-3} for high C_H ($\geqslant17$) films. Light induced degradation measurements show a systematic correlation between C_H and the electronic stability; the low C_H films have a slower rate of photoconductivity decrease, and slower DOS increase, than either the high C_H films or one glow-discharge deposited film tested for comparison. In fact the low C_H *a*-Si:H appears superior after just a few hours of light exposure.

I. INTRODUCTION

Light induced degradation of hydrogenated amorphous silicon, or Staebler–Wronski effect (SWE), is of great technological importance. The decrease in photoconductivity and dark conductivity,[1] and the increase in density of states (DOS)[2,3] in the band gap upon light exposure limits the performance of photovoltaic and other devices. Stutzmann *et al.*[4] measured and modeled the degradation kinetics of glow discharge (GD) produced *a*-Si:H. 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.[1]

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 the free carrier recombination events breaks weak Si–Si bonds; and second, these newly created defect states are stabilized, possibly by hydrogen motion which spatially isolates them.[3,4]

Most SWE studies have concerned GD films, and several of them suggest that the hydrogen content (C_H) affects the material stability.[6–8] In this technique, the silicon enters the system on hydrogen rich molecules such as SiH_4 or Si_2H_6. Net rejection of hydrogen occurs at the substrate surface to yield films having C_H in the 10 to 20 at. % range. The substrate temperature is the principle variable which controls C_H. However, changing the substrate temperature affects all the bulk and surface processes during film growth in addition to the steps which causes hydrogen rejection.

In the reactive sputter (RS) deposition method a pure silicon target is sputtered in a mixture of hydrogen and argon gas.[9,10] This is believed to differ fundamentally from GD deposition in that hydrogen incorporated from an incident flux of atomic silicon and hydrogen[11,12] rather than arriving on silane radicals. By adjusting the hydrogen partial pressure in the discharge chamber, the total C_H of the films can be independently controlled. This enables us to study the effect of the hydrogen content on the properties, in particular the electronic stability, of the films deposited at a fixed substrate temperature. This work is the first systematic examination of the light induced degradation on reactively sputtered *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 optical, electronic, and microstructural properties of these films.[13–16]

II. EXPERIMENTAL

Hydrogenated amorphous silicon films were deposited in an ultrahigh vacuum chamber; the partial pressures of O_2, CO, and H_2O were less than 1×10^{-9}, 1×10^{-9}, and 2.5×10^{-9} Torr, respectively.[13] The films were grown using high purity argon and hydrogen gases and a high purity 5×12 in. crystalline silicon target.[13] The total C_H of the films was independently controlled by adjusting the hydrogen partial pressure in the discharge at a constant substrate temperature of 230 °C. The hydrogen partial pressure was increased from 0.2 to 1.2 mTorr and the argon partial pres-

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sure was kept constant at 1 mTorr. Most of the films studied here had thicknesses of 1.2–1.4 μm. The deposition rate was ~30 to 200 Å/min. and controlled by the cathode current (0.25–0.80 A). The C_H and the properties of the films were independent of the deposition rate in this range.[14]

Conductivity measurements were performed using planar post deposited chromium contacts 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. In order to get nearly uniform absorption of the light throughout the volume, low and high pass filters were used to bracket the wavelengths between 620 and 680 nm (1.83 to 2 eV) with a nearly top hat spectrum. This range of photon energies is larger than the band gap of all the films studied. The films were placed on a water cooled stage to keep the temperature constant at ~30 °C throughout the light exposure experiments. The light intensity was 150 mW/cm^2 as measured by a pyroelectric radiometer and the illumination of the sample was uniform. The hydrogen content and bonding are determined from the films deposited on crystalline silicon substrates using infrared absorption. Similar results were obtained with hydrogen evolution measurements.

The DOS of the films is estimated with the constant photocurrent method (CPM).[17] In this method, the photon flux is measured as a function of the photon energy while keeping the photocurrent constant. Then the results are converted to absorption coefficient α by normalizing the reflectance—transmission data at some photon energy where $\alpha d \sim 1$ (d is the film thickness). The integrated absorption is then calculated by subtracting the extrapolated exponential edge, and then integrating the excess absorption. Jackson and Amer[18] correlated the photothermal deflection spectroscopy (PDS) subgap absorption with the electron spin resonance (ESR) signal in *a*-Si:H films. Comparison of CPM data and ESR have shown that the CPM subgap absorption is also proportional to the ESR density. Smith *et al.*[19] determined the proportionality constant to be 1.9×10^{16} cm^{-3}. We have used this constant to estimate the DOS of our films.

III. RESULTS

The total C_H of the films were measured using both infrared absorption and hydrogen thermal evolution techniques.[16,20] The integrated absorption centered at 640 cm^{-1} (I_{640}) is directly proportional to the total C_H of the films by the relation $N_H = I_{640} \times A_{640}$ where N_H (cm^{-3}) is the total number of bonded hydrogen atoms and A_{640} (cm^{-2}) is the constant of the proportionality (oscillator strength). The constant of proportionality for these films was determined to be 2×10^{19} cm^{-2} ($\pm 10\%$) by comparing the I_{640} with the hydrogen evolution measurements.[20] The density of the *a*-Si:H films were taken to be 5×10^{22} cm^{-3}. The integrated absorption of the stretching modes was determined after deconvoluting the absorption into two Gaussians centered around 2000 and 2100 cm^{-1}. Figure 1 shows the ratio of the I_{2100} (dihydride and clustered monohydride content of the films) to the I_{640}, (I_{2100}/I_{640}), as a function of the total C_H of the films. Figure 1 also indicates the ratio of the atomic concentration of hydrogen ($C_{H,2100}/C_H$) in these modes. The

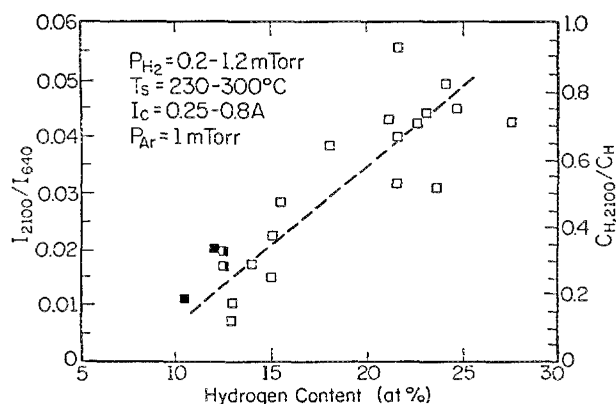

FIG. 1. The ratio of the infrared (IR) absorption intensity at I_{2100} cm^{-1} (the stretching mode of dihydride and clustered monohydride groups) scaled to the absorption intensity at 640 cm^{-1} (the wagging mode, which is proportional to total hydrogen) as a function of C_H. The ratio of the atomic concentrations in these modes is also indicated. The substrate temperature was kept constant at 230 °C for all the films, except the filled and half filled data points which were measured on films deposited at 300 and 275 °C, respectively: the hydrogen partial pressure during deposition was kept constant at 0.2 mTorr for these films.

constant of proportionality of 3.3×10^{20} cm^{-2} was used to calculate the $C_{H,2000}$, which was determined by comparing the low temperature hydrogen evolution peaks and I_{2100}.[16,20] The monohydride concentration of the films, $C_{H,2000}$, (the integrated absorption at 2000 cm^{-1}) can be calculated from $C_{H,2000} = C_H - C_{H,2000}$. These results show that the total C_H of the films correlates uniquely with the hydrogen bonding modes. The low C_H (10 to 15 at. %) films are monohydride rich. The hydrogen concentration in the 2100 cm^{-1} mode increases nearly linearly as the total C_H of the films increases (Fig. 1) and more than half of the hydrogen is in this mode when C_H exceeds ~17 at. %. The films which had 3 and 5 at. % hydrogen had only the 2000 cm^{-1} (monohydride) mode and had poor electronic properties.[16,20]

The annealed state photoconductivity of the films under AM-1 light exposure (100 mW/cm^2) were scattered between 0.9 to 3×10^{-5} (Ω cm)$^{-1}$ but no dependence on C_H was observed. The dark conductivity of the low C_H ($\leqslant 15$ at. %) films is approximately two orders of magnitude larger than the high C_H films, and the Fermi level (distance from conduction band) determined by thermal activation analysis is correspondingly smaller (~0.75 versus ~0.9 eV).[15]

The photoconductivity (σ_{ph}) of the films diminishes with light exposure. The relative reduction in σ_{ph} [$\sigma_{ph}(t)/\sigma_{ph}(0)$] as a function of total C_H for 0.5, 3, and 15 h of red light exposure (150 mW/cm^2) are shown in Fig. 2. The top curve in Fig. 2 shows the relative decrease in σ_{ph} after a 30 min exposure as a function of C_H. The drop in σ_{ph} is ~15%–20% for $C_H < 15\%$, and increases to ~50% for $C_H \geqslant 20\%$. This behavior, a larger reduction in photoconductivity for high C_H films, is emphasized after both 3 and 15 h of light exposure. The relative reduction in photoconductivity is linear for low C_H films ($\leqslant 15$ at. %) and levels off for high C_H films. The results in Figs. 1 and 2 indicates that there is a

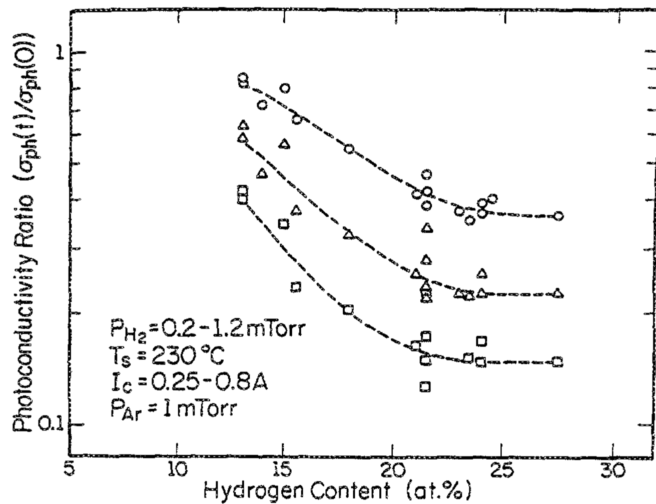

FIG. 2. The reduction in photoconductivity $[\sigma_{ph}(t)/\sigma_{ph}(0)]$ as a function of the total hydrogen content of the films. The degradation studies are done under red light (620–680 nm) with 150 mW/cm^2. This figure shows a strong correlation between hydrogen content and reduction in σ_{ph} of the magnetron reactive sputtered a-Si:H. All samples have similar σ_{ph} in the as-deposited state [$0.9\text{–}3\times10^{-5}$ $(\Omega\ \text{cm})^{-1}$] under AM-1 light exposure and were deposited at a constant substrate temperature of 230 °C. [t = 30 min (○), 3 h (△), and 15 h (□)].

correlation between light induced degradation and the hydrogen bonding of direct-current (dc) magnetron RS films.

We did not observe a large decrease in dark conductivity upon light exposure: the decrease was less than a factor of two for all RS films. We also measured the dark conductivity activation energy of the low and the high C_H films after light exposure and did not observe any significant changes. This indicates that the dark Fermi level does not move upon light exposure, in agreement with the very small decrease in room temperature dark conductivity of the films upon light exposure.

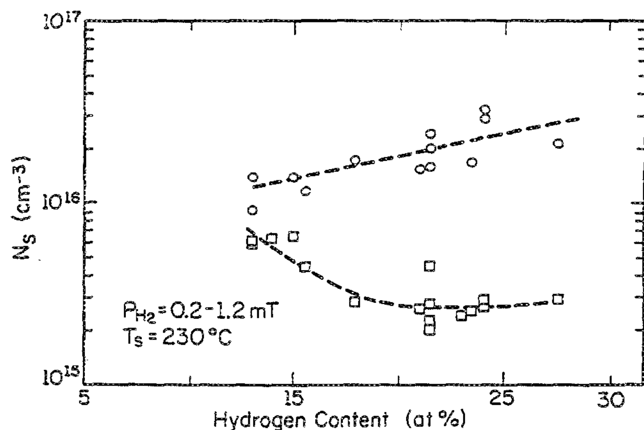

FIG. 3. The total density of defect states as a function of the total C_H for annealed films (□) and after 15 h of light exposure (○). These results indicate that the quality of the material can not be simply judged from the initial properties. These results and those in Fig. 2 indicate that there is a strong correlation between the total C_H and the SWE of the a-Si:H films. All the samples were deposited at a constant substrate temperature of 230 °C.

The DOS in the band gap of a-Si:H increases under light exposure and as a result degrades the carrier transport properties by reducing the carrier lifetimes. This ultimately limits the long term performance of a-Si:H in device applications. To measure the increase in the density of defect states as a function of light exposure time, the DOS was measured for a series of films in the annealed state and after 0.5, 3, and 15 h of light exposure.

The DOS in the annealed state and after 15 h of light exposure is shown in Fig. 3 as a function of total C_H of the films. (For clarity the DOS after 30 min and 3 h of exposure are not shown). In the annealed state, low C_H ($\leqslant$15 at. %) films have a 2 to 3 times higher DOS than the high C_H ($\geqslant$17 at. %) films. After 15 h of light exposure the DOS increases by an order of magnitude for high C_H films; at this stage they have a factor of two higher DOS than the low C_H films. If the quality of the material was simply judged from their properties in the as-deposited state, the high C_H films would be the best choice. However, the increase in DOS only after 15 h of light exposure shows that the quality of a-Si:H films in the as-deposited state cannot be taken alone to judge the electronic quality of the material.

The number of created defect states (ΔN_s) after 30 min and 15 h of light exposure as a function of total hydrogen content of the films is shown in Fig. 4. The ΔN_s increases almost exponentially as a function of total hydrogen content both after 30 min and 15 h of light exposure.

The DOS as a function of the light exposure time is shown in Fig. 5. Long light exposure experiments are done on two representative RS films with low (12 at. %) and high (28 at. %) C_H and a glow discharge produced film (contains ~10 at. % hydrogen).[21] The film with a low C_H was prepared at 0.2 mTorr hydrogen partial pressure and a 300 °C substrate temperature. The film with a high C_H was prepared at 1 mTorr hydrogen partial pressure and a 230 °C substrate temperature. [We find no evidence for a substrate temperature effect, for films deposited between 230 and

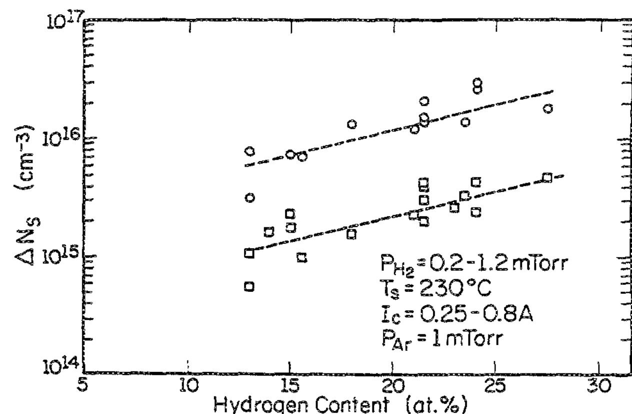

FIG. 4. The number of created defect states after 30 min (□) and 15 h (○) of light exposure as a function of the total hydrogen content. All the samples were deposited at a constant substrate temperature of 230 °C.

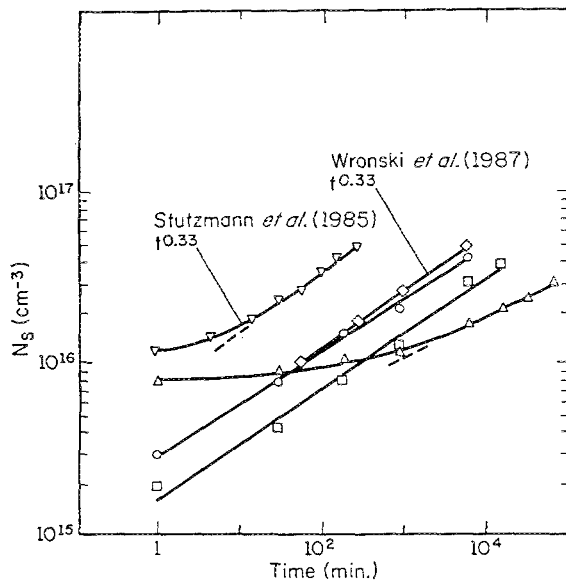

FIG. 5. The DOS (measured by CPM) as a function of the light exposure time at $I = 150$ mW/cm^2 for two representative dc magnetron reactive sputtered films and a glow discharge produced film. The low C_H film is superior against SWE compared to the glow discharge produced films. The SWE results of Stutzmann *et al.* ($I = 200$ mW/cm^2, ESR),[4] and Wronski *et al.* ($I = 50$ mW/cm^2, CPM data)[22] for GD produced films are also shown for comparison. Light intensity does not effect the slope of the curves. 1166, $C_H = 28$ at. %, $N_s \propto t^{0.30}$ (O), 1235, $C_H = 12$ at. %, $N_s \propto t^{0.23}$ (Δ), solarex glow discharge $N_s \propto t^{0.32}$ (□).

300 °C, beyond its influence on C_H: we performed the light induced degradation study for up to 15 h on another low C_H film (13 at. %) which was deposited at 230 °C and 0.2 mTorr hydrogen partial pressure, and found identical behavior.] Low C_H magnetron RS films are evidently more stable against light induced degradation compared to high C_H RS and a device quality glow discharge produced film. The glow discharge produced film and the high C_H reactive sputtered film have a factor of ~3 smaller DOS than the low C_H film in the as-deposited state; however after a few hours of light exposure the DOS for the low C_H film becomes less than the other two films. Further light exposure increases the difference in the DOS between these films since the number of created defect states is less for low C_H films (Fig. 4).

IV. DISCUSSION

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) as shown in Fig. 5. 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 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 change in slopes. If we assume that we will eventually observe the $t^{1/3}$ rule for these films then we must conclude that the SWE susceptibility coefficient, $A_{s\text{-}w}$, is approximately 100× less for 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.[4,22] The details of these results are analyzed elsewhere.[23]

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[24] 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.[25] The band gap of our material changes from 1.62 to 1.85 eV with increasing C_H, 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.[16] 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.[26] Bhattacharya and Mahon[27] 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.*[28] 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.

V. CONCLUSIONS

Independent control of the hydrogen content of the *a*-Si:H films with reactive sputtering technique enables us to study the effect of hydrogen content on the stability of the *a*-Si:H films as well as their other properties. Our results indicate that 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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