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 \times 10^{-3} (\Omega \text{ cm})^{-1} \text{ under AM-1 (air mass-1)} illumination (100 mW/cm^2). The density of deep states (DOS) measured by the constant photocurrent method is \( \sim 6 \times 10^{15} \text{ cm}^{-3} \) for low \( C_H < 15 \text{ at. %} \) and \( \sim 2 \times 10^{15} \text{ cm}^{-3} \) for high \( C_H > 17 \text{ films} \). 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 Staelber-Wronski effect (SWE), is of great technological importance. The decrease in photoconductivity and dark conductivity, and the increase in density of states (DOS), in the band gap upon light exposure limits the performance of photovoltaic and other devices. Stutzmann et al. 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.

Various mechanisms have been suggested for the creation of these defect states in \( a-Si:H \). The widely recognized “bond breaking” model 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.

Most SWE studies have concerned GD films, and several of them suggest that the hydrogen content \((C_H)\) affects the material stability. In this technique, the silicon enters the system on hydrogen rich molecules such as SiH\(_4\) or Si\(_2\)H\(_6\). 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 cause hydrogen rejection.

In the reactive sputter (RS) deposition method a pure silicon target is sputtered in a mixture of hydrogen and argon gas. This is believed to differ fundamentally from GD deposition in that hydrogen incorporated from an incident flux of atomic silicon and hydrogen 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.

II. EXPERIMENTAL

Hydrogenated amorphous silicon films were deposited in an ultrahigh vacuum chamber; the partial pressures of O\(_2\), CO, and H\(_2\)O were less than 1 \times 10^{-9}, 1 \times 10^{-9}, \text{ and } 2.5 \times 10^{-9} \text{ Torr, respectively.} \text{ The films were grown using high purity argon and hydrogen gases and a high purity 5 \times 12 \text{ in. crystalline silicon target.} \text{ The total } C_H \text{ 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 press-}
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 photocurrent measurements used only the red portion of the spectrum from an EN11 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/cm² 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 \( \alpha \) 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 \textit{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.

\section*{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 \( N_{H2} = I_{640} \times A_{640} \) where \( N_{H2} \) (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 \( 2 \times 10^{13} \) cm⁻² (±10%) by comparing the \( I_{640} \) with the hydrogen evolution measurements.\(^{20}\) The density of the a-Si:H films were taken to be \( 5 \times 10^{22} \) 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 \( I_{200} \) (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 constant of proportionality of \( 3.3 \times 10^{20} \) 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 \( C_{H,2000} = C_H - C_{H,2100} \). 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 photocconductivity of the films under AM-1 light exposure (100 mW/cm²) were scattered between 0.9 to 3 × 10⁻³ (Ω cm)⁻¹ but no dependence on \( C_H \) was observed. The dark conductivity of the low \( C_H \) (<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 photocconductivity (\( \sigma_{ph} \)) of the films diminishes with light exposure. The relative reduction in \( \sigma_{ph} \) (\( \sigma_{ph} (t)/\sigma_{ph} (0) \)) as a function of total \( C_H \) for 0.5, 3, and 15 h of red light exposure (150 mW/cm²) are shown in Fig. 2. The top curve in Fig. 2 shows the relative decrease in \( \sigma_{ph} \) after a 30 min exposure as a function of \( C_H \). The drop in \( \sigma_{ph} \) is ~15–20% for \( C_H < 15 \), and increases to ~50% for \( C_H > 20 \). This behavior, a larger reduction in photocconductivity for high \( C_H \) films, is emphasized after both 3 and 15 h of light exposure. The relative reduction in photocconductivity is linear for low \( C_H \), films (<15 at. %) and levels off for high \( C_H \) films. The results in Figs. 1 and 2 indicates that there is a
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.

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 $C_H$ (<15 at. %) films have a 2 to 3 times higher DOS than the high $C_H$ (>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 ($\Delta N_s$), 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 $\Delta N_s$ 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). 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

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**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/cm². This figure shows a strong correlation between hydrogen content and reduction in $\sigma_{ph}$ of the magnetron reactive sputtered $a$-Si:H. All samples have similar $\sigma_{ph}$ in the as-deposited state [$0.9-3 \times 10^{-8}$ (Ω 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 (□)).

**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 cannot 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.

**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.
that we will eventually observe the $t^{1/3}$ rule for these films then we must conclude that the SWE susceptibility coefficient, $A_s = 2$, is approximately $100 \times$ 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.\cite{22,23} The details of these results are analyzed elsewhere.\cite{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\cite{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.\cite{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.\cite{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.\cite{26} Bhattacharya and Mahon\cite{27} reported that material with greater SiH$_3$ content (which they associate with void density) is more susceptible to light induced defect creation. Kakalios et al.\cite{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 de 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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