# Effect of hydrogen on the microstructural, optical, and electronic properties of *a*-Si:H thin films deposited by direct current magnetron reactive sputtering

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Device quality hydrogenated amorphous silicon (*a*-Si:H) films have been deposited under a wide range of deposition conditions using dc magnetron reactive sputtering. The total hydrogen content ($C_H$) has been varied from 0 to ~40 at. % by changing the substrate temperature ($T_s$) or hydrogen partial pressure ($P_{H_2}$) independent of other deposition parameters. The films that contain $C_H$ between 10 and 28 at. % have the highest quality. The optical band gap ($E_g$) varies linearly with $C_H$ for all deposition conditions studied. With increasing $C_H$ the dark conductivity at 300 K decreases from $\sim 1\times 10^{-4}$ to $\sim 1\times 10^{-12}$ $(\Omega\ \text{cm})^{-1}$; however, the photoconductivity under AM-1 illumination, for the highest quality films, remains in the 0.8–$3.5\times 10^{-5}$ $(\Omega\ \text{cm})^{-1}$ range. The dark conductivity activation energy ($E_a$) was measured to determine the Fermi-level ($E_f$) position with respect to the conduction band ($E_c$) and a linear correlation between $E_g$ and $E_a$ is found for high-quality films. The films having low hydrogen content ($10 < C_H < 17$ at. %) are slightly *n* type and become intrinsic as $C_H$ is increased. The subgap density of states diminishes with the increase in $E_c - E_f$ (taken to be $E_a$) as the films become intrinsic. In short, the microstructural, optical, and electronic properties of these films vary monotonically with the total hydrogen content. Therefore we propose that $C_H$ is the appropriate structural parameter to correlate changes in the properties of *a*-Si:H.

## I. INTRODUCTION

Reactive sputter deposition of *a*-Si:H has the advantage that the hydrogen content of the films can be independently controlled by adjusting the hydrogen partial pressure ($P_{H_2}$) in the discharge. Bonded hydrogen transforms pure amorphous silicon into an electronic quality material by modifying the microstructure, optical, and electronic properties, especially by eliminating dangling bonds. The photoconductivity, dark conductivity, and dark conductivity activation energy ($E_a$) of reactive sputtered films have been previously reported[1–4] as a function of $P_{H_2}$ in the discharge.

The partial pressure of hydrogen is an important deposition parameter in reactive sputtering. However, it is clear that the hydrogen and argon partial pressures which produce high-quality films by one technique (eg., rf diode,[5] rf magnetron,[6,7] or dc magnetron[4,8]), do not in general yield similar results for the other methods, or even for the same method with a different reactor geometry. Therefore it is difficult to compare results based on this discharge parameter. We prefer to examine the microstructural, optical, and electronic properties of the films on the basis of their total hydrogen content. This structural parameter is justified because the total hydrogen content of the films is uniquely related to the hydrogen bonding, microstructure, and morphology of the films as discussed by Pinarbasi *et al.*[9] and Beyer and Wagner.[10] In previous studies we also reported on the effect of $P_{H_2}$ on the discharge properties, on the optical and electronic properties of the *a*-Si:H.[8]

In this paper, we show that the total $C_H$ is a systematic parameter for magnetron reactive sputter-deposited *a*-Si:H films, whereby microstructural, optical, and electronic properties may be compared. This includes the variations in the band gap, electronic transport properties, and density of states. The films that were grown between 200 and 300 °C with a hydrogen content ($C_H$) between 10 and 28 at. % are all device quality having photoconductivity of 0.8 to $3.5\times 10^{-5}$ $(\Omega\ \text{cm})^{-1}$, a photo (AM-1) to dark conductivity ratio of $10^4$ to $2\times 10^6$, an electron drift mobility of ~0.5 to 2 $\text{cm}^2/\text{V s}$, an electron mobility–recombination lifetime ($\mu\tau$) product of ~1 to $4\times 10^{-7}$ $\text{cm}^2/\text{V}$, a hole mobility–recombination lifetime ($\mu\tau$) of 0.8 to $3.1\times 10^{-8}$ $\text{cm}^2/\text{V}$, and a subgap density of states (DOS) between 0.1 and $1\times 10^{16}$ $\text{cm}^{-3}$.

## II. EXPERIMENTAL APPARATUS AND PROCEDURES

The hydrogenated amorphous silicon films investigated here were deposited in an UHV chamber from a planar, high-purity crystalline silicon target located 15 cm from the substrates. The details of the deposition system and the procedure are described elsewhere.[8] The films were grown over a wide range of deposition conditions: $100 < T_s < 330$ °C, deposition rate 30–200 Å/min, and hydrogen partial pressure 0.1–1.2 mTorr. The argon partial pressure was maintained at 1 mTorr. Three 1 in.-square substrates were simultaneously coated during deposition at a given set of discharge parameters. One was crystalline silicon which was used to determine the hydrogen content and bonding with infrared absorption[11] and hydrogen evolution techniques.[10,12] These films were also used to determine the growth morphology by scanning electron microscopy (SEM) and impurity levels by secondary ion mass spectroscopy (SIMS). The remaining two substrates were 7059 Corning glass. One of these samples was used to determine the thickness, optical absorption coefficient, optical band gap, and index of refraction of the film from reflectance and transmission measurements using a Perkin–Elmer Lambda 9 spectrophotometer. The band gap was calculated from Tauc's plot. Chromium contacts, 1.2 cm long and 0.2 cm apart, were also sputtered onto this film in order to perform conductivity, activation energy, and DOS measurements. Photoconductivities were measured on the annealed films (2 h at 160 °C) under AM-1 illumination (100 mW/cm$^2$) from an ELH lamp. The third substrate had a bottom contact of either sputtered chromium ($\sim$5000 Å) and sputtered unhydrogenated *a*-Si from a phosphorus doped silicon target ($\sim$200 Å), or a glow discharge produced $n^+a$-Si:H layer on 7059 Corning glass obtained from Solarex. After depositing the *a*-Si:H film, chromium dots were sputtered on the Cr/*a*-Si/*a*-Si:H samples to make conductivity measurements through the film; these gave similar results as the planar electrode geometry. The samples on $n^+$ *a*-Si:H were used to make Schottky barrier devices with evaporated semitransparent palladium contacts to perform electron and hole transport measurements.

## III. STRUCTURAL AND OPTICAL PROPERTIES VERSUS HYDROGEN CONTENT

The SIMS analysis of representative films showed that the oxygen, carbon, and nitrogen impurity levels are $<50$, 15, and 5 parts per $10^6$ (ppm), respectively, and are in the range to make high-performance devices.[13] The argon concentration in the films was $<0.1$ at. %. In Fig. 1 (a), we show a cross-sectional SEM micrograph of a film deposited at low $T_s$ (125 °C) and $(P_{H_2}) = 1.0$ mTorr, having high hydrogen content (38 at. %); and in Fig. 1 (b) the micrograph of a film deposited at $T_s = 300$ °C and 0.2 mTorr $P_{H_2}$, having 12 at. % H. The film having the low $C_H$ shows no visible microstructure other than the bright thick line on the micrograph which is associated with breaking of the film. On the other hand, the high hydrogen content film shows clear microstructure, both on the crosssection and top surfaces. Here we emphasize that the substrate temperature also plays an important role in film properties. Our previous paper[9] reported that films grown at $(P_{H_2}) = 1$ mTorr and $T_s = 230$ °C also have a "bumpy" microstructure, but retain acceptable electronic quality. By contrast, lowering $T_s$ to 125 °C produces a film with more enhanced microstructure and poor electronic quality $[\sigma_{ph} = 3.5\times10^{-7} (\Omega\ \text{cm})^{-1}$, $\text{DOS} = 3.4\times10^{16}\ \text{cm}^{-3}]$. While this may simply result from higher $C_H$, earlier reports for glow discharge[14,15] and for reactive sputtered films[16] show that good-quality films are grown above $T_s = 200$ °C. Restricting our attention to the range $T_s = 200$–300 °C, where we have grown high-quality films,[17] we suggest that hydrogen content is the dominant parameter which determines the film properties. We attribute the substrate temperature effect to changes in the total $C_H$. This is reasonable in view of the unique relationship we have reported between $C_H$ and SiH/$SiH_2$ bonding ratio[9] for the same films reported here.

Thermal hydrogen evolution measurements give additional information on the microstructure of the films.[9,10] In Fig. 2, we show the first-derivative hydrogen evolution spectra for the same samples as shown in Fig. 1. While the film having low hydrogen content does not have any hydrogen release at low temperatures ($<400$ °C), the high hydrogen content film shows a large release of hydrogen at $\sim$375 °C. This indicates that the film with high $C_H$ has a large fraction of weakly bonded hydrogen, which we infer to be clustered in sites such as microvoids.[9] Furthermore the sharpness of the peak at 375 °C indicates that its structure is permeable to hydrogen motion at low temperatures.[9,10]

Hydrogen in amorphous silicon increases the band gap mainly by eliminating the states at the top of the valence band, which has been experimentally observed by photoemission studies.[18] The optical band gaps ($E_g$) of our sputtered *a*-Si:H films grown under all the deposition conditions studied are shown in Fig. 3 as a function of total hydrogen content. A least-squares fit to the data gives $E_g = 1.5 + [C_H \times (0.0125 \pm 0.003)]$. We obtained $E_g = 1.35$ eV for a film without hydrogen. The fast initial in-

(a) (b)

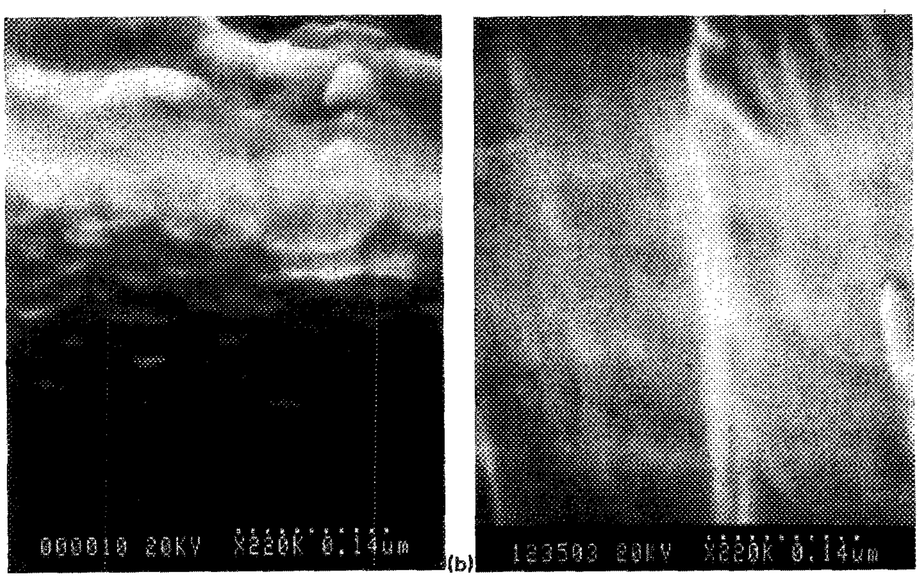


FIG. 1. (a) SEM micrograph showing the surface and cross section of sample 1134 taken at 45° angle to the surface. The top part of the figure is the cross section. (b) SEM micrograph showing the cross section of sample 1235. Samples 1134 and 1235 have 38 and 12 at. % H, respectively.

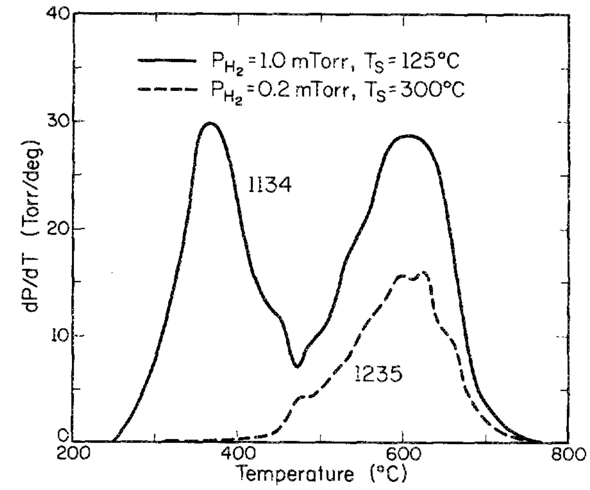


FIG. 2. The first-derivative hydrogen evolution spectra for samples 1134 (38 at. % H) and 1235 (12 at. % H). The spectra are normalized to 1-cm$^3$ $a$-Si:H film and the heating rate $\beta$ was a constant 15 °C/min.

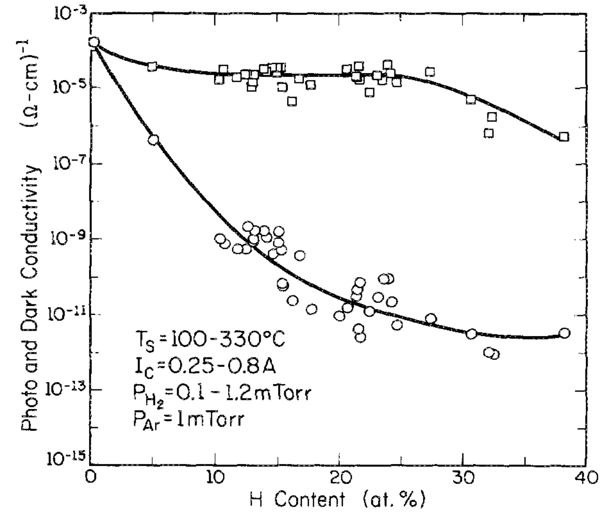


FIG. 4. The photo and dark conductivity of $a$-Si:H films as a function of total hydrogen content. The solid line is drawn as a visual aid.

crease in the band gap is due to the relaxation of the $a$-Si:H network with the hydrogen incorporation.[19] Earlier studies of glow discharge and rf reactive sputtered $a$-Si:H films have given a similar linear relation between $C_H$ and $E_g$.[20] The significance of our work is that it includes structurally and electronically well-characterized films grown over a wide range of deposition conditions.

## IV. ELECTRONIC PROPERTIES VERSUS HYDROGEN CONTENT

The photo and dark conductivities of our $a$-Si:H films for the entire range of deposition conditions are shown in Fig. 4. These films may be separated into three categories. The films in the first category contain $< 10$ at. % hydrogen, and their dark conductivities decrease sharply as hydrogen content increases due to termination of dangling bonds in the band gap. [The film without hydrogen, deposited at $T_s = 230$ °C, has a conductivity of $\sim 1.5 \times 10^{-4}$ $(\Omega\ \text{cm})^{-1}$ both in the dark and under AM-1 illumination.] The second category contains films having $C_H$ between 10 and 28 at. % and are all high-quality films in the annealed state with photoconductivity ranging from $8 \times 10^{-6}$ to $3.5 \times 10^{-5}$ $(\Omega\ \text{cm})^{-1}$. We previously reported[9] that the SiH/$SiH_2$ bonding ratio, evaluated by IR absorption, decreases as hydrogen content increases. The near constancy of the photoconductivity in this range implies that the hydrogen bonding ratio does not directly affect the recombination pathway in the annealed state. This has also been argued by Moustakas.[5] The third category contains the films which were all made at lower substrate temperatures ($T_s < 200$ °C) to incorporate more hydrogen into the films and are of poor quality. The photoconductivity of these films is over an order of magnitude lower than the films containing 10–28 at. % hydrogen. This is mainly due to a higher DOS (discussed below) which reduces the carrier lifetime, but also partly due to the higher band gap which reduces absorption of the AM-1 spectrum. There is approximately eight orders of magnitude decrease in dark conductivity as the hydrogen content increases from 0 to $\sim 40$ at. %.

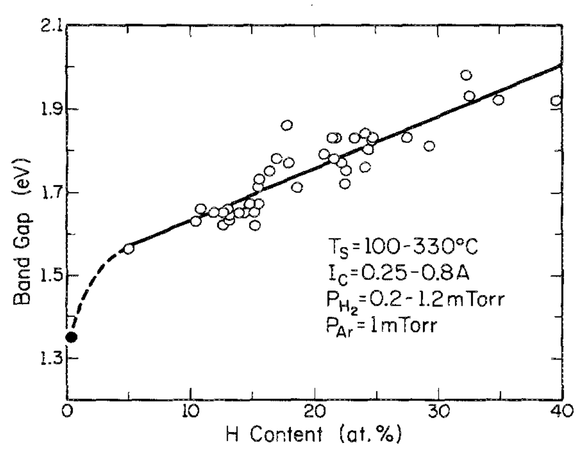


FIG. 3. The optical band-gap variations of magnetron reactive sputtered $a$-Si:H films as a function of total hydrogen content. The solid line is a least-squares fit to the data for films having $5 < C_H < 40$ at. %.

The temperature dependence of the dark conductivity is given as $\sigma = \sigma_0 \exp(E_a/kT)$. $E_a$ is the activation energy and approximately equal to the distance from the Fermi level to the dominant extended band, e.g., $E_c - E_f$,[4,21] and $\sigma_0$ is the preexponential factor. Typical films which show band conduction have $E_a = 0.5$–$0.9$ eV and preexponential constants in the range $10^3$–$10^4$ $(\Omega\ \text{cm})^{-1}$,[21,22] but values from 1 to $10^6$ $(\Omega\ \text{cm})^{-1}$ have been reported.[23] Since the Fermi level is determined mainly by the band-gap states, activation energy measurements reveal that the hydrogen in $a$-Si:H changes the energy distribution, as well as density, of the states in the band gap.

All the films reported here have an exponential dependence of dark conductivity on temperature indicating conduction through extended states. The changes in activation energy as a function of $C_H$ are shown in Fig. 5(a). This dependence was measured from room temperature to $\sim 160$ °C for the films deposited above 200 °C; all these films have $C_H < 28$ at. %. The films with $C_H$ from 10 to 17 at. %

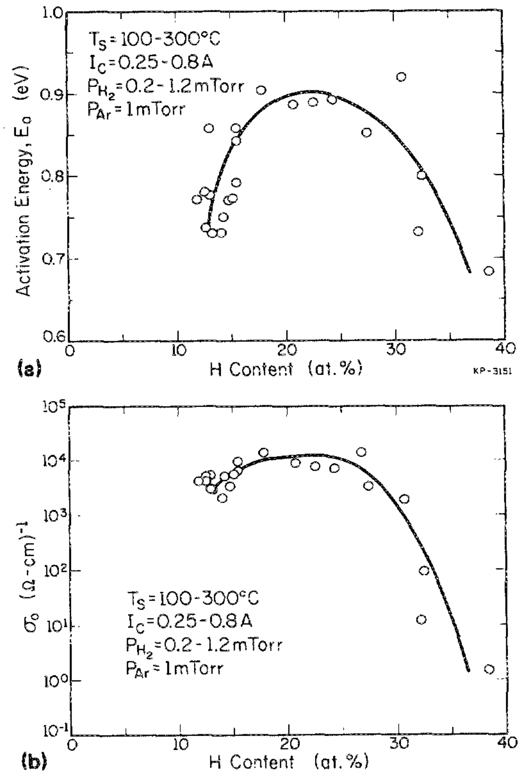


FIG. 5. (a) Dark conductivity activation energy of *a*-Si:H films as a function to total hydrogen content. (b) Preexponential factor as a function of total hydrogen content. The solid lines are drawn as a visual aid.

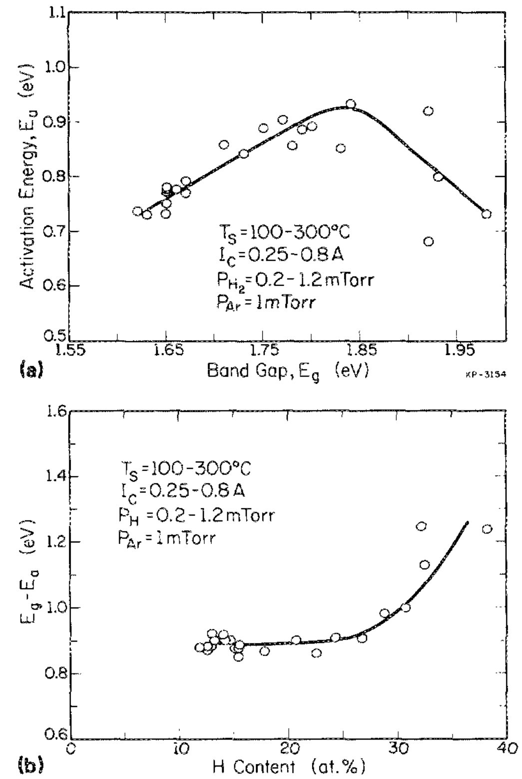


FIG. 6. (a) The activation energy of the films as a function of the band gap. (b) The energy difference between Fermi level and valence band ($E_g$-$E_a$) as a function of total hydrogen content. The solid lines are drawn as a visual aid.

are slightly *n* type. The activation energy for these films starts from ~0.7 eV and increases as the $C_H$ increases. Maximum activation energies are obtained for the films having $C_H$ between 17 and 28 at. % which are intrinsic. The films which were deposited at $T_s$ = 100–160 °C have more than 30 at. % hydrogen and show a sharp decrease in the $E_a$. The maximum temperature used to measure the $E_a$ for these films was kept below the deposition temperature to prevent the occurrence of irreversible microstructural changes.

Similar trends in activation energy have been observed by Moustakas[1] as a function of hydrogen partial pressure. Moustakas also measured the thermoelectric power and found that, except for intrinsic films where ambipolar conduction occurs, electron conduction is dominant for all the films. For a film containing ~30 at. %. H,[24] the thermoelectric power was temperature independent, large, and negative which indicates electron conduction.[1] We propose, by comparison, that our $C_H > 30$ at. % films are also *n* type. In Fig. 5(b) we plot the preexponential factor ($\sigma_0$), which is a material constant, as a function of $C_H$. The $\sigma_0$ rises from ~0.2 to ~$1\times10^4$ ($\Omega$ cm)$^{-1}$ with increasing $C_H$ below 28 at. %; this is essentially constant in comparison with the exponential term in the conductivity. A sharp decrease takes place as $C_H$ goes over 28 at. %. As noted above, the high $C_H$ films are microstructurally inhomogeneous, and we attribute the drop in $\sigma_0$ and $E_a$ to this difference.

Figure 6(a) shows the linear correlation between the increase of the band gap and activation energy for the films having a band gap up to 1.85 eV, in agreement with the work of Solomon *et al.*[22] This band gap value corresponds to ~28 at. % hydrogen, below which good-quality films were grown, and above which there is a sharp decrease in the activation energy. The energy difference between the valence band and the Fermi level is shown in Fig. 6(b).

For selected samples the total hydrogen content, activation energy, $E_a/E_g$ ratio, photoconductivity, and density of satates in the band gap are listed in Table I. The density of states in the band gap is measured by the photoconductivity subgap absorption technique[25] under 10 mW/cm$^2$ red bias light and recently we have obtained similar values by the constant photocurrent method. Returning to Fig. 6(b), for $C_H$ less than ~28 at. %, the distance between Fermi level and the valence band is almost constant (~0.9 eV), as observed by Solomon *et al.*[22] Since the increase in the band gap

TABLE I. Activation energy, $E_a/E_g$ ratio, photoconductivity, and density of states (DOS) in the gap are shown for representative samples with hydrogen content varying from 12 to 38 at. %.

| Sample No. | At. % H | $E_a$ (eV) | $E_a/E_g$ | $\sigma_{ph}$ ($\Omega$ cm)$^{-1}$ | DOS(cm$^{-3}$) |
|---|---|---|---|---|---|
| 1239 | 12.5 | 0.73 | 0.45 | $1.0\times10^{-5}$ | $8.5\times10^{15}$ |
| 1237 | 15.5 | 0.79 | 0.47 | $1.4\times10^{-5}$ | $5.0\times10^{15}$ |
| 1232 | 20.5 | 0.89 | 0.50 | $1.3\times10^{-5}$ | $1.1\times10^{15}$ |
| 1229 | 24.0 | 0.89 | 0.50 | $9.9\times10^{-6}$ | $1.8\times10^{15}$ |
| 1130 | 32.0 | 0.73 | 0.37 | $4.3\times10^{-7}$ | $4.6\times10^{15}$ |
| 1134 | 38.0 | 0.68 | 0.35 | $3.5\times10^{-7}$ | $3.4\times10^{16}$ |

is mainly due to the downward movement of the valence band, we deduce from Fig. 6(a) and 6(b) that the Fermi level sweeps downward approximately 0.25 eV across the band gap when the $C_H$ increases from 10 to 28 at. %. This implies that hydrogen changes the distribution of defect states in the band gap. Two possibilities are (i) hydrogen preferentially eliminates the states at the upper part of the band gap, or (ii) as the band gap increases with increasing hydrogen, new states are created that are closer to the valence band.[7] The details of the process are not clear at the present time, but the decrease in the DOS as hydrogen content increases from $\sim 10$ to 20 at. %, as seen from Table I, along with the downward movement of the Fermi level with valence band suggests the first possibility. From Table I we also observe that the films which are intrinsic ($17 < C_H < 28$ at. %) have the lowest density of states. This is in qualitative agreement with the predictions of Müller's chemical equilibrium DOS model.[26]

The DOS measured by the photoconductivity subgap absorption does not, however, show an inverse relation[27] ($\sigma \alpha$ 1/DOS) with the measured AM–1 photoconductivity, as seen from Table I. The lowest hydrogen content samples have a higher DOS, but comparable photoconductivity, to those films with hydrogen content in the 20–25 at. % range. Evidently the electron recombination kinetics are not fully evaluated by the integrated subgap absorption techniques. We note the published speculations that states in the upper half of the band gap have low electron capture cross sections under light illumination[7] or that the electron lifetime is sensitized by particular hole trapping states.

## V. CONCLUDING REMARKS

We present a detailed set of data on the optical, transport, and electronic properties of the dc magnetron reactive sputtered *a*-Si:H. The films grown at substrate temperatures between 200 and 300 °C have hydrogen contents between 10 and 28 at. %, and are all device quality in the as-deposited state. The optical band gap of the films varies linearly with the hydrogen content for all deposition conditions studied. The photoconductivity of the high-quality films is unchanged with the hydrogen content and stays in the 0.8–$3.5\times 10^{-5}$ $(\Omega\ \mathrm{cm})^{-1}$ range. In the same range dark conductivity decreases about three orders of magnitude. The films that contain between $\sim 17$ and 28 at. % hydrogen are intrinsic; those with less than $\sim 17$ at. % are slightly *n* type. The films deposited at $T_s < 200$ °C are structurally inhomogeneous and have low activation energies and conductivity prefactors. For the good-quality films, as increasing hydrogen content opens the band gap, the Fermi level follows the movement of the valence-band edge and changes the films from slightly *n* type to intrinsic. The net Fermi-level movement is $\sim 0.25$ eV with respect to the conduction-band edge. This suggests that hydrogen not only reduces but also changes the energy distribution of the states in the band gap. The DOS in the gap is the lowest for the intrinsic films ($17 - 28$ at. % H) and increases for both low and high $C_H$ films. These results show that for substrate temperatures of 200–300 °C, the total hydrogen content is a rational parameter upon which to evaluate the properties of high-quality *a*-Si:H films.

## ACKNOWLEDGMENTS

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[a] In memory of John A. Thornton


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