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Hydrogen diffusion in a-Si:H stimulated by intense illumination

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Hydrogenated amorphous silicon (a-Si:H) films have been thermally annealed at temperatures in the range 220–270 °C for 24–48 h either under intense visible light illumination (4–16 W/cm^2) or in the dark. After each annealing, the hydrogen-concentration profile was measured with Rutherford-backscattering-spectrometry and elastic-recoil-detection-analysis ion-beam analysis methods. A model is proposed which shows that, in good agreement with our results, the hydrogen-diffusion constant D_{H} is proportional to the power of illumination and also proportional to the loosely bonded hydrogen concentration. Other consequences of the model are discussed.

I. INTRODUCTION

In a-Si:H, hydrogen plays a fundamental role by passivating the Si dangling bonds (DB) which are the principal types of defects in this amorphous structure. The defect density is thus reduced from 10^{19} cm^{-3} to about 10^{15}–10^{16} cm^{-3}.[1] The a-Si:H system has been described as a Si structure in which hydrogen can diffuse relatively easily.[2,3] Moreover, it has long been suspected that hydrogen is related to the metastable defects produced by intense illumination and responsible for the Staebler-Wronski effect (SWE). Several models relating the hydrogen mobility with the defect production have been proposed [Refs. 2–5 of (Ref. 4)]. It is then natural to suppose that illumination has some influence on the hydrogen-diffusion processes through a-Si:H:D films. Indeed Santos, Johnson, and Street[5] and Branz, Asher, and Nelson[6] have observed an increase of the diffusion constant D of deuterium through illumination of a a-Si:H/a-Si:H:D/a-Si:H sandwich structure (annealing temperature T_a range: 200–350 °C). Their results are dark, $5\times10^{-18} \leq D \leq 6\times10^{-16}$ cm^2/s; illumination, $5\times10^{-17} \leq D \leq 4\times10^{-15}$ cm^2/s.

It is also known from previous work[7,8] that, below 300 °C, the rapid effusion of the loosely bound hydrogen out of the film is not likely to occur and that the proportion of this hydrogen phase is large when the substrate temperature T_s during the film deposition is low. More severe SWE occurs in these films where the hydrogen concentration C_{H} may be as high as 20 at. % than in films deposited at higher temperature. One can then deduce that the "SWE defects" take place mainly in this loosely bound phase. On the other hand, one can estimate[9] that at $T_a < 300$ °C and under an illumination of 15 W/cm^2 the ratio $d_i/d_d \approx 2$–5 ($d_{i,d}$ are the defect densities under illumination and in the dark, respectively). Therefore, the influence of illumination on the hydrogen-diffusion constant D_{H} is expected to be observable primarily in a-Si:H films deposited at rather low substrate temperature T_s.

Hydrogenated amorphous silicon (a-Si:H) films have been thermally annealed at temperatures T_a in the range 220–270 °C for 24–48 h either under intense visible-light illumination (4–16 watts/cm^2) or in the dark. After each annealing, the hydrogen concentration profile was measured with Rutherford-backscattering-spectrometry -elastic-recoil-detection-analyses (RBS-ERDA) ion-beam analysis methods. The diffusion constant D_{H} was deduced form this profile. We propose a model which shows that, in good agreement with our results, D_{H} is proportional to the power of illumination and also proportional to the loosely bonded hydrogen concentration. Other consequences are discussed.

II. EXPERIMENT

The experimental setup and method were described in Ref. 4. The main steps of the procedure were as follows.

The undoped a-Si:H films (2 μm thick) were deposited on c-Si wafers with the very-high-frequency–glow discharge (VHF-GD) method,[10] at substrate temperature T_s varying from 100 to 300 °C. Their characteristics are shown in Table I.

Each sample was first annealed at T_s for 1 h and then slowly cooled to room temperature to eliminate stresses in the film and thereby prevent it from "exploding" in subsequent thermal treatments. Then the total hydrogen concentration C_{H} was measured by ERDA which is a nondestructive high-energy ion-beam analysis method. The maximum depth that we could study by ERDA was about 0.8 μm. The measured hydrogen concentration at great depth (≤ 0.8 μm) was always the same as the original concentration. This means that the film could be considered as a half infinite H reservoir and that any hydrogen diffusion in the c-Si substrate could not influence our H-recoil spectra analyses. Our ERDA setup and analyses methods are described in detail elsewhere.[7]

The thermal annealings under illumination or in the

TABLE I. T_s is the substrate deposition temperature, C_H is the total hydrogen concentration.

Sample number	T_s (°C)	C_H (at. %)
1	100	19.4
2	100	21.6
3	200	15.0
4	300	9.6

dark were done in a vacuum chamber ($p < 10^{-6}$ torr). Three thermocouples controlled the film temperature to ensure that temperature gradients did not affect the hydrogen-diffusion process.

The illumination was done by a xenon lamp (Osram 64635) powered by a constant current source. The light power range was 4–16 W/cm^2 (±1 W/cm^2). The annealing temperature T_a range was $220 \le T_a \le 270$ °C. During each annealing, T_a was kept constant (±2 °C) for 24–48 h by regulating the air flow cooling the sample holder. To anneal in the dark, the same procedure was used except that the xenon lamp illuminated (and heated) the back side of the sample holder and not the film itself.

The sample was then transferred into the ERDA scattering chamber ($p < 10^{-6}$ torr). The proton energy spectra were analyzed with our own reconstruction code resulting in C_H profiles from which D_H could be determined.[4]

III. RESULTS

Figure 1 shows a typical hydrogen concentration depth profile as deduced form a hydrogen recoil energy spectrum. D_H is computed from this C_H profile. The dependence of D_H on the annealing temperature T_a and on the illumination power I_0 is shown in Fig. 2. The solid lines are computed with the model of Sec. IV, Eq. (8). The *a*-Si:H samples were deposited at $T_s = 100$ °C. The activation energy E_a and the prefactor $\text{PF}=D_0\eta n/N_H$ [Eq. (8)] have been determined from the Arrhenius plot of Fig. 3. They are $\text{PF}=(6.2\pm1.8)\times10^{-14}$ cm^{4}W^{-1}s^{-1} and $E_a=(0.46\pm0.01)$ eV. We have neglected the hydrogen-diffusion dispersivity $[D_H(t)\propto t^{-\alpha(T)}]$.[7,12,13] Indeed, in the present range of annealing temperatures and that of durations, one can estimate, from the results of Ref. 13, that the variation of D_H due to dispersivity is at most 10% and generally smaller than our error bars.

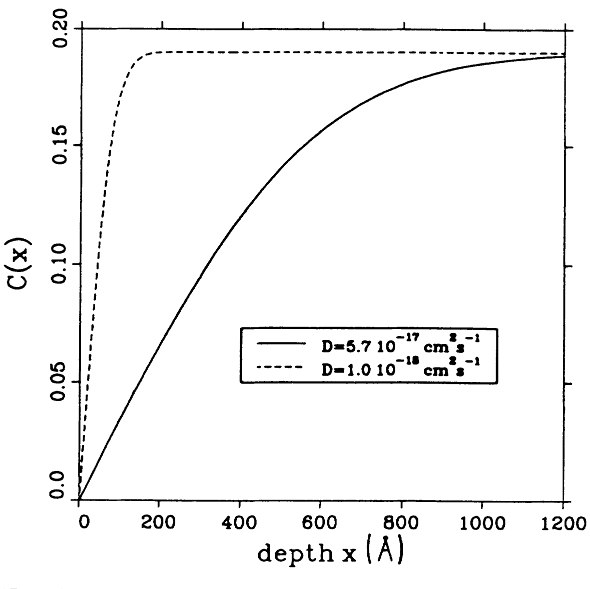

FIG. 1. Hydrogen-concentration depth profiles $C(x)$ in illuminated (——) and not illuminated (— — —) *a*-Si:H films. Deposition substrate temperature $T_s = 100$ °C. Annealing temperature $T_a = 270$ °C.

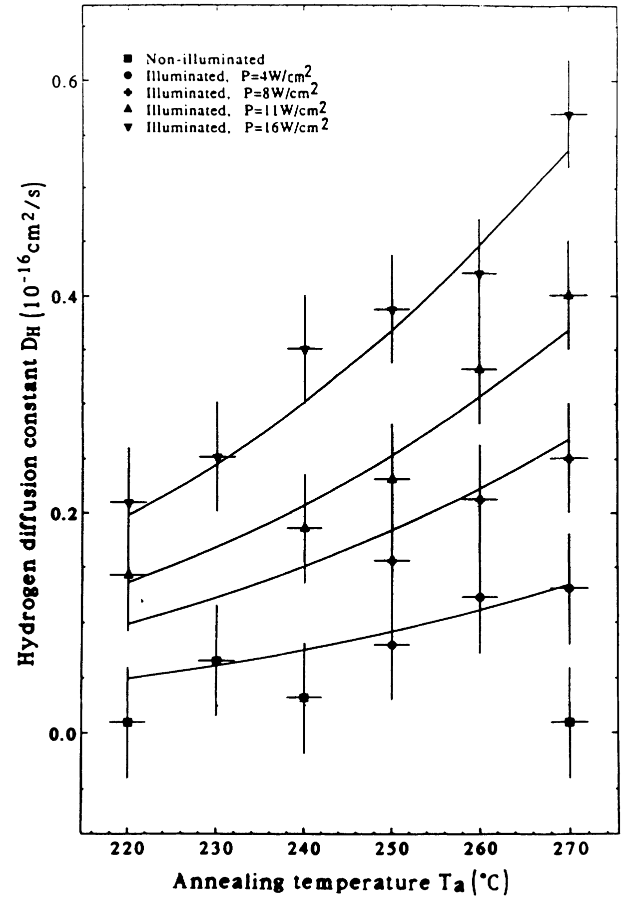

FIG. 2. Temperature dependence of the hydrogen-diffusion constant D_H at different illumination powers in *a*-Si:H deposited at $T_s = 100$ °C. The solid lines are computed with the model of Sec. IV, Eq. (8).

IV. DISCUSSION

We first summarize some relevant characteristics of *a*-Si:H films. Hydrogen is distributed in two phases: a phase of isolated monohydride Si-H diluted in the bulk and a loosely bound phase essentially contained in clusters of monohydride SiH and dihydride SiH$_2$. These H clusters can be considered microvoids whose internal walls are decorated by hydrogen atoms.[11] In the first phase, the hydrogen concentration is more or less con-

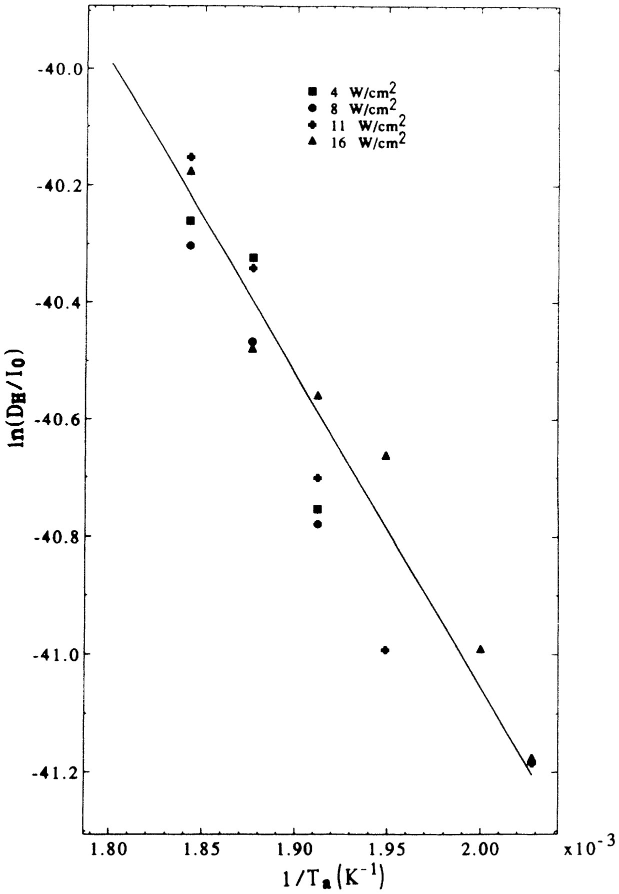

FIG. 3. Arrhenius plot of D_{H} versus $1/T_a$, where T_a is the annealing temperature for different I_0 values.

stant, 3–4 at.% whereas in the second phase it is highly dependent on the conditions of the film deposition, particularly, the substrate temperature T_s: a low T_s results in a large cluster concentration.[7] Hydrogen in this latter phase can effuse from the film through a percolating network of microvoids at annealing temperatures above 300 °C, as shown by Beyer and Tang and co-workers.[8,7]

The hydrogen-diffusion dispersivity ($D_{\mathrm{H}} \propto t^{-\alpha}$) was observed by Street *et al.*[12] and Kakalios and co-workers[3,13] and by Tang and co-workers.[7] The dispersivity was explained by a "multiple trapping model" with an exponential energy density distribution for the traps: ($dn/dE \propto \exp(E/k_B T_0)$).[13] T_0 is the width of this distribution and n the density of traps. Then the dispersivity parameter α is related to T_0 by $\alpha = 1-(T/T_0)$. Tang and co-workers[7] have shown that the dispersivity is closely correlated to the H-cluster density.

The Staebler-Wronski effect, a reversible degradation of the photocurrent under intense illumination,[14] is related to creation and annihilation of DB. The metastability of these defects is explained by the conversion of weak bonds into DB.[2] In this conversion hydrogen should play a critical role; see, for example, Refs. 15 and 16. This metastability (and the saturation of the SWE) was suggested to be a consequence of the H-cluster structure.[7] Santos *et al.*[17] have demonstrated that in illuminated amorphous silicon photogenerated charges, when recombining on defects, facilitate the emission of hydrogen from Si-H bonds. This process is believed to be responsible for the enhancement of the diffusion constant D_{H} with respect to its "dark" value.

The "normal" diffusion of hydrogen in *a*-Si:H is controlled by trapping and releasing from Si-H bonds in H clusters. Free hydrogen atoms diffuse through the matrix from one shallow trap (interstitial site) to the next. It is described by a diffusion coefficient[5]

$$D_{\mathrm{H}} = \frac{N_{\mathrm{H}s} D_{\mathrm{H}s}}{N_{\mathrm{H}}} , \tag{1}$$

where $N_{\mathrm{H}s}$ is the hydrogen density in interstitial sites, $D_{\mathrm{H}s}$ is the diffusion coefficient in the shallow traps, and N_{H} is the total hydrogen density.

$D_{\mathrm{H}s}$ is given by Santos *et al.*,[17]

$$D_{\mathrm{H}s} = D_0 \exp\left[\frac{-(E_s - E_m)}{k_B T}\right] . \tag{2}$$

E_s is the shallow traps energy, E_m is the migration energy, and k_B is the Boltzmann constant. With ERDA, we found that our N_{H} is in the range $2.7\times10^{21} \le N_H \le 5.4\times10^{21}$ H-atoms/cm³. D_{H} can be written as $D_{\mathrm{H}} = D_{\mathrm{H}}$ (ill.)$+D_{\mathrm{H}}$ (dark) (Ref. 18), where D_{H}(ill.) is the contribution due to illumination. The aim of the following simple model is to describe only D_{H}(ill.). When fitting D_{H} to our experimental data, D_{H} (dark) will be neglected since it is of the order of our measurement sensitivity ($\approx 5\times10^{-18}$ cm²/s, see Fig. 2). The density of hydrogen untrapped from H clusters and ready to diffuse (or be trapped again) can be estimated as follows:

$$\frac{dN_{\mathrm{H}s}}{dt} = I_0 \eta \nu n - N_{\mathrm{H}s}\sigma . \tag{3}$$

$dN_{\mathrm{H}s}/dt$ is the number of H atoms released from Si-H bonds (in clusters) per unit time and unit volume. I_0 is the illumination power (W/cm²), η is the number of electron-hole pairs produced by I_0, ν is the frequency of H-release by Si-H bonds, n is the density of Si-H bonds that can be broken by illumination, σ is the frequency of H capture by these traps. η ($\eta \propto G$, the electron-hole generation rate[19,20]), ν and σ are some "average" values taken over complex processes. Integration of (3) gives

$$N_{\mathrm{H}s} = \frac{I_0 \eta \nu n}{\sigma}(1-e^{-\sigma t}) . \tag{4}$$

In Fig. 4, our measurements are made in the saturation domain, i.e., at large t and

$$N_{\mathrm{H}s} = I_0 \eta \nu n / \sigma . \tag{5}$$

Stutzmann, Jackson, and Tsai[21] show that the photocurrent I_{ph} is inversely proportional to the DB ($N_{\mathrm{H}s}$) density. However, the variation of I_{ph} with time is complex (at least at small t) so that it cannot be related to

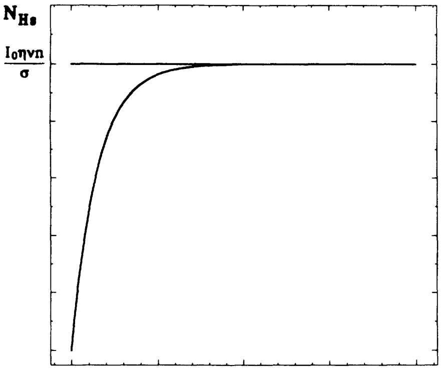

FIG. 4. $N_{\mathrm{H}s}$ as a function of time t in arbitrary units calculated with Eq. (4).

$dN_{\mathrm{H}s}/dt$ in a simple way.

In Eq. (8), $N_{\mathrm{H}s}$ is proportional to I_0. This is in agreement with the conclusion of Santos, Johnson, and Street[5] that the hydrogen release rate by illumination is proportional to the product of the densities of photogenerated electrons and holes. $N_{\mathrm{H}s}$ is also proportional to the density n of Si-H bonds that can be broken by illumination. As was shown by Tang and co-workers[7] n is directly correlated to the H-cluster density. This density becomes small when the film deposition temperature T_s increases beyond about 150 °C. Indeed we did not observe any D_{H} enhancement by illuminating such samples.

With Eqs. (2) and (4), D_{H} can be written

$$D_{\mathrm{H}}=\frac{I_0\eta(\nu/\sigma)n(T_s)}{N_{\mathrm{H}}(T_s)}D_0\exp\left[-\frac{E_s-E_m}{k_BT}\right]. \tag{6}$$

According to Pankove and Johnson,[22] at thermodynamic equilibrium

$$\nu=\sigma\exp\left[-\frac{E_s-E_t}{k_BT}\right], \tag{7}$$

where E_s is the shallow trap energy, E_t is the deep trap energy. Finally, combining Eqs. (6) and (7)

$$D_{\mathrm{H}}=\frac{I_0D_0\eta n(T_s)}{N_{\mathrm{H}}(T_s)}\exp\left[-\frac{E_a}{k_BT}\right]. \tag{8}$$

Three statistical tests have been applied to the data points $[1/T_a,\ln(D_{\mathrm{H}}/I_0)]$, to check the model of Eq. (8).

(i) The F test shows that $\ln(D_{\mathrm{H}}/I_0)$ depends linearly on $1/T_a$.

(ii) The linear correlation coefficient is $r=-0.962$ and the confidence coefficient is >0.999.

(iii) The randomness of the residuals is verified by the "Run test."

Consequently, the sample model of Eq. (8) describes correctly our data. Moreover, our value of $E_a=(0.46\pm0.08)$ eV is in good agreement with the value that can be estimated from the publications of Santos and co-workers[17,23] $(0.32\leq E_a\leq 0.5$ eV).

It is also interesting to note that our E_a value is very close to the activation energy of 0.5 eV for the diffusion of hydrogen in c-Si (Ref. 22, p. 434). This remark suggests that in illuminated a-Si:H, H diffuse mainly from interstitial site to interstitial site without being hindered much by deep traps. This is in accordance with the diffusion scheme proposed by Santos and Jackson[23] and by Jackson and Tsai.[24] Our data are consistent with D_{H} proportional to the illumination power I_0. As a consequence, the mean free path λ of H through the shallow traps as discussed by Santos, Johnson, and Street[5] does not depend on I_0. This is also in agreement with the diffusion scheme just mentioned.

V. CONCLUSIONS

We have systematically measured D_{H} in illuminated a-Si:H films with respect to the annealing temperature and the illumination power. It was found that D_{H} is proportional to the illumination power and to $\exp(-E_a/k_BT)$ with $E_a=(0.46\pm0.08)$ eV. It was also found that the diffusion enhancement is important only in films where the concentration of H clusters is large (low film deposition temperature). A model is proposed which is in good agreement with the experimental results.

This experiment illustrates the possible role of hydrogen in the Staebler-Wronski effect: the photogenerated e-h pairs contribute to free hydrogen from Si-H bonds in the H clusters thus creating DB traps acting as recombination centers for the photogenerated carriers. The H atoms diffusing from interstitial sites to interstitial sites can create more traps by breaking stretched Si-Si bonds (Si-Si+H$\Longrightarrow$Si-H+Si·). This is consistent with the fact that the SWE is more pronounced in high hydrogen concentration.[25]

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