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DISPERSIVE HYDROGEN DIFFUSION IN AN ILLUMINATED UNDOPED a-Si:H FILM AS A FUNCTION OF ANNEALING TEMPERATURE.

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The dependence of the dispersion parameter α and of the time dependent diffusion parameter $D_H(t_L)$ (estimated over a fixed diffusion length L) on annealing temperature T_a was investigated with elastic-recoil detection analysis (ERDA) in an undoped a-Si:H sample. We found that the α dark value increases with T_a as already observed by other groups, and that the illuminated α value also increases. But we observe that $D_H(t_L)$, measured under illumination, deviates from an Arrhenius law, while $D_H(t_L)$ measured in the dark follows an Arrhenius behavior.
The hydrogen diffusion mechanisms under intense illumination are discussed in the framework of existing models.

Keywords: A. semiconductors, thin films, D. trapping, E. ion impact.

1. Introduction

In hydrogenated amorphous silicon (a-Si:H), hydrogen (H) plays a fundamental role by passivating the Si dangling bonds (DB) which are the principal types of defects in this amorphous structure. The a-Si:H system has been described as a Si structure where H can diffuse relatively easily[1,2]. It has long been suspected that H is related to the metastable defects produced by intense illumination and that it is responsible for the degradation of the photo-current in a-Si:H films[3] (Staebler-Wronski effect, SWE).

We first summarize some relevant characteristics of a-Si:H films. The results of thin-film experiments[4,5,6] suggest that H is found in Si-H, $Si\text{-}H_2$, and $Si\text{-}H_3$ groups forming clusters with 5-7 H-atoms, or as Si-H uniformly distributed in Si. The ratio of clustered and isolated H-atoms varies with the deposition method and the processing conditions.

Two different mechanisms have been found to govern the evolution of the H concentration[7]. For the isolated atomic H species, this evolution is driven by a diffusion-limited process (DL) that reaches a maximum at 600°C. For the clustered H, it is controlled by a non-diffusion-limited process (NDL) involving the desorption of molecular H_2 from the clustered phase, followed by a rapid exodiffusion of H_2 through a network of voids in a-Si:H. This "NDL-hydrogen" is expected to be related to the disorder of the a-Si:H microstructure. Tang et al.[8] have suggested that annealing temperatures T_a higher than 300°C modify the energy and/or the spatial distribution of traps resulting from the release of the "NDL-hydrogen" so that the hydrogen diffusion becomes more dispersive.

In the hydrogen glass model proposed by Jackson and collaborators[2,9], the diffusion parameter D_H is expressed as:

$$D_H(t) = D_{00} \cdot (\omega t)^{-\alpha} \qquad (1)$$

where D_{00} is the microscopic diffusion constant, ω plays the role of an attempt frequency for hydrogen atoms to escape the traps. The dispersion parameter α is given by

$$\alpha = 1 - \frac{T_a}{T_0}$$

where T_a is the annealing temperature and $k_B T_0$ is the characteristic energy width of the exponential energy distribution of traps for diffusing hydrogen atoms (k_B is the Boltzmann constant). This distribution is responsible for the dispersion.

In previous papers[10], we have shown that the H-diffusion parameter D_H increases under illumination intensity I ($4 \leq I \leq 16$ W/cm^2, white light) for annealing temperatures in the range $220 \leq T_a \leq 270$°C where the H concentration remains constant. It was found that the diffusion enhancement is important only in films where the concentration of H clusters is large (low film deposition temperature). These findings illustrated the influence of illumination and the possible role of H in the SWE. If T_a is raised above 300°C, releasing the "NDL-hydrogen", we observed that illumination influences the dispersion parameter α of H-diffusion. We presented[11] the first results confirming the influence of intense illumination on the dispersion parameter α, after effusion of the "NDL-hydrogen" at T_a=350°C. These results were observed on two different types of sample and the influence of illumination on the dispersivity of H-diffusion was a function of the film type. These experiments should help to understand the H-trapping-detrapping processes and confirm the role of H played in defects formation in a-Si:H layers.

In this paper, we provide some valuable information on the H-diffusion mechanisms under illumination. Our results suggest that, according to the values of I and T_a, illumination influences the rate of creation and annealing kinetics of metastable defects in a-Si:H films. The H-diffusion mechanisms under intense illumination are discussed within the framework of existing models.

2. Experimental

An undoped a-Si:H sample (2μm thick) was deposited onto a c-Si wafer at the Institut de Microtechnique de l'Université de Neuchâtel (IMT). This film was prepared by the silane-based Very High Frequency-Glow Discharge (VHF-GD) method at low pressure (10^{-2} mbar)[12]. It was deposited at a substrate temperature T_s=250°C. The initial H concentration C_H and the hydrogen concentration profiles after the annealing and illumination periods at temperature T_a=330, 350, 380°C were measured by ERDA, a non destructive high energy ion beam analysis method. Our ERDA set-up is described in detail elsewhere[8]. The initial H concentration was uniform in the film and was found to be C_H=13 at.%.

The thermal annealings under illumination or in the dark were made *in situ* in the ERDA scattering chamber ($p<10^{-7}$ torr). ERDA is particularly suited to the large number of necessary measurements since it is non-destructive and allows to perform successive annealings of the same sample. The time required to rise and lower the temperature was of the order of 1 min., short compared with the annealing periods (>30 min.). The detailed description of our experimental set-up for the control of the sample temperature during annealing in the dark or under illumination has been published[11] elsewhere. Let us summarize the main features. The samples were fixed onto a pure silver holder onto which Cu tubing was soldered in order to allow a temperature control with circulating air. Two thermocouples (TC), protected from direct illumination, were attached to the surface of the film and a third TC measured the sample holder temperature. At any time during the annealings, the three temperatures were within 5°C. In this way we were sure that hydrogen diffusion was not affected by spurious temperature gradients.

The illumination was done with a Xenon lamp (Osram 64635) powered by a constant current source. The sample was first degraded (I=15 W/cm^2) for about 18h at room temperature and then illuminated at the same light power at annealing temperature T_a. This temperature was kept constant (±2°C) 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.

3. Analysis and Results

Figure 1 shows the double logarithmic plot of G(t) (the time integrated diffusion parameter) vs the annealing

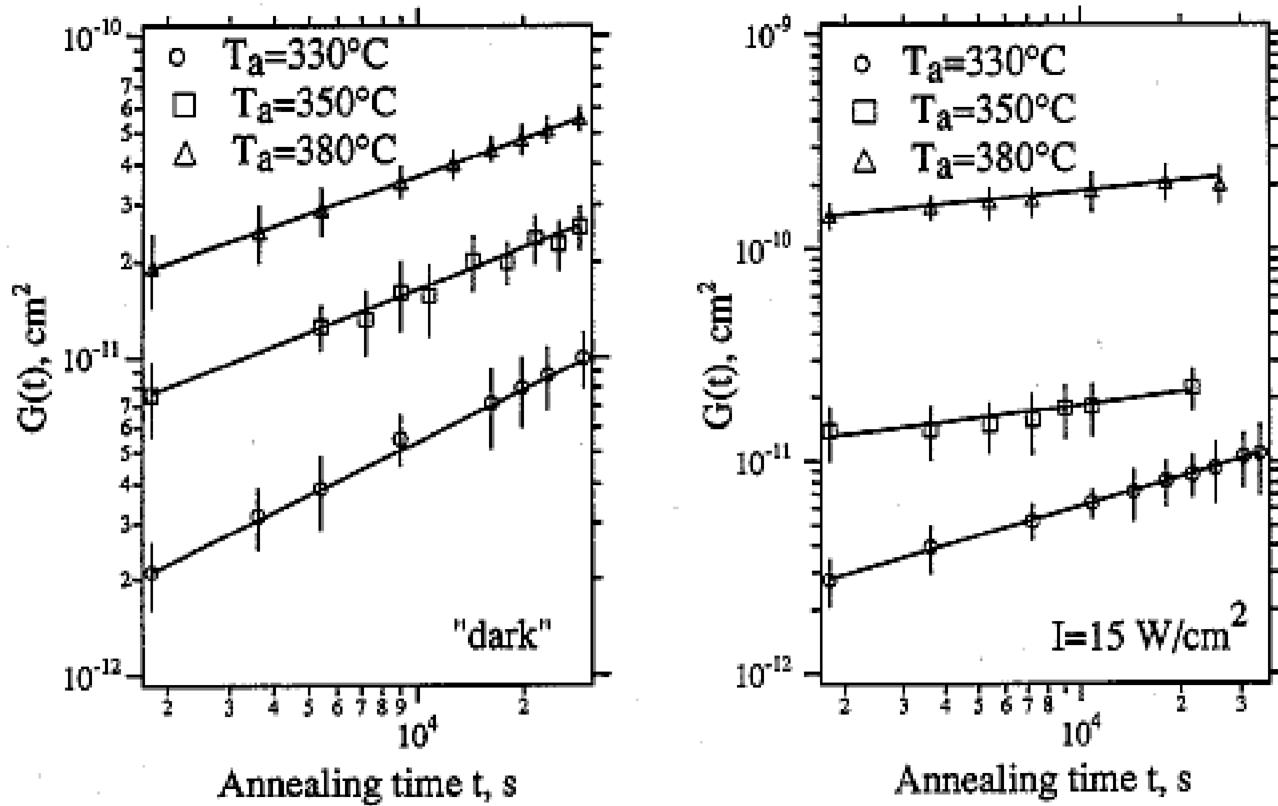

Fig. 1: Time integrated diffusion parameter $G(t, T_a)$ vs the annealing time t in the dark (left) and under illumination (right). The errors bars are estimated from the quality of the fit of the computed ERDA spectrum. The lines are linear best fits to the data.

time t at different annealing temperatures in the dark and under illumination. With equation (1) and

$$G(t) = \int_0^t D(\tau)d\tau$$

one obtains the following relation:

$$G(t) = At^{(1-\alpha)}$$

where $$A = \frac{D_{00}\omega^{-\alpha}}{1-\alpha}$$

From the slopes (1-α) in Fig. 1, the dispersion parameters are deduced and the constant A from the extrapolation to t=1. Table 1 summarizes our results.

Table 1

T_a [°C]	ΔC [% at.]	α ±0.03	$A = \frac{D_{00}\omega^{-\alpha}}{1-\alpha}$
	"dark"		
330	1.5	0.45	$3.40\ 10^{-14}$
350	2.0	0.56	$2.90\ 10^{-13}$
380	2.8	0.61	$1.06\ 10^{-12}$
	I = 15 W/cm^2		
330	1.5	0.54	$8.76\ 10^{-14}$
350	2.0	0.80	$2.92\ 10^{-12}$
380	2.9	0.84	$4.32\ 10^{-11}$

Summary of our results. ΔC, "NDL-hydrogen" concentration; α, dispersion parameter; A, prefactor estimated from the linear best fit of logG(t) vs logt.

For comparison purposes, the diffusion parameter D_H is estimated at a fixed diffusion length L (for example L=1000Å, as in Ref 9):

since $$L^2 = G(t)$$

and $$G(t) = At^{(1-\alpha)},$$

then $$t_L = t(L) = \left(\frac{L^2}{A}\right)^{\frac{1}{1-\alpha}}$$

and finally $$D_H(t_L) = D_L = (1-\alpha)\frac{G(t_L)}{t_L}$$

If $D_H(t_L)$ follows an Arrhenius law, then one can write:

$$D_H(t_L) = D_0 \exp\left(\frac{-E_a}{k_B T_a}\right)$$

where D_0 is a diffusion prefactor, E_a the activation energy for H-diffusion, and T_a the annealing temperature. Figure 2 shows the Arrhenius plot of $D_H(t_L)$ vs $1/T_a$ in the dark and illuminated case estimated for different diffusion lengths.

It is interesting to note that the dependence of $D_H(t_L)$ on $1/T_a$ under illumination is different from the dark case. This effect will be discussed in detail in the following section.

In order to show that the a-Si:H film used in this experiment is standard (from a microstructure point of view), a linear fit of $D_H(t_L)$ measured in the dark estimated at a diffusion length L=1000Å (as is usually used for comparison purposes[9]) vs $1/T_a$ provides an activation energy E_a=1.69±0.1 eV and a diffusion prefactor D_0=3.5 10^{-3} cm^2/s. These values are in good agreement with those obtained by Tang et al.[8] (E_a=1.57 eV, D_0=4.1 10^{-3} cm^2/s) for an a-Si:H VHF-GD prepared sample (T_s=150°C).

4. Discussion and conclusion

It has been shown[10,13,14] that the presence of photogenerated carriers increases both the rate of H hopping and the number of silicon network sites where new defect formation is energetically favorable. Due to the silicon network disorder, there will be a distribution of barriers for H motion, leading to the observed dispersive H motion[8,15,16]. In agreement with Tang et al.[8] we observe that the dispersion parameter α of H-diffusion increases with T_a and is correlated with ΔC, the concentration of the H released by the NDL process. Moreover α is strongly enhanced under illumination for each annealing temperature. As already mentioned, these findings suggest that illumination influences the creation and annealing kinetics of metastable defects in a-Si:H films.

The number of measurements of $D_H(t_L)$ as a function of T_a is not sufficient to develop a phenomenological model of dispersive H-diffusion under illumination. However our experimental results reveal a general, qualitative trend. Figure 2 provides very interesting information. It shows that $D_H(t_L)$, measured under illumination deviates from an Arrhenius law, while $D_H(t_L)$ measured in the dark follows an Arrhenius behavior[9]. It is also interesting to note that for short diffusion lengths (L=200Å), corresponding to short diffusion times, t<15 min., $D_H(t_L)$ vs $1/T_a$ seems to be linear. We can therefore speculate that, after a short time

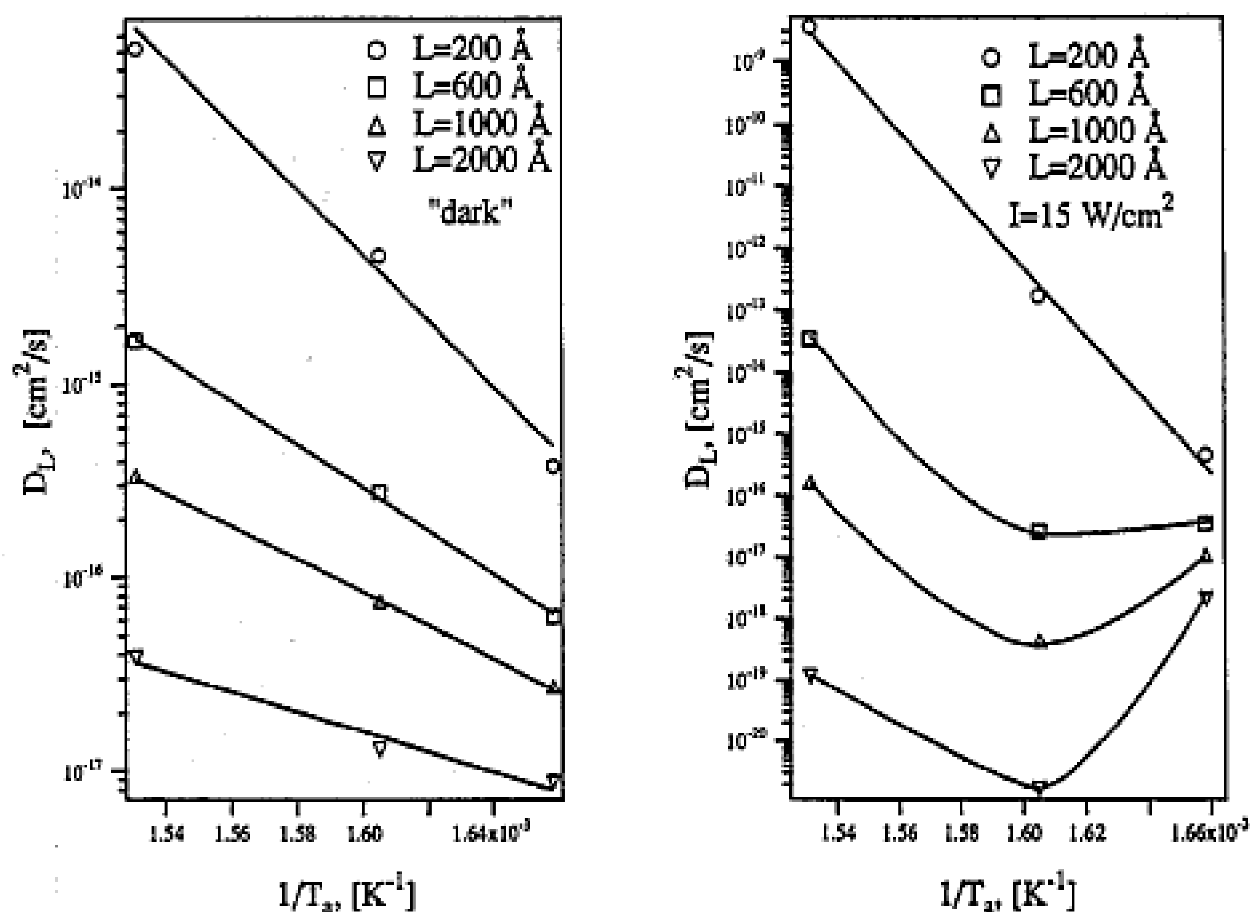

Fig. 2: Arrhenius plot of the diffusion parameter D_H estimated at fixed diffusion lenths L ($D_H(t_L)$=D_L) vs $1/T_a$, where T_a is the annealing temperature. The solid lines are guides to the eye only. It is interesting to note that $D_H(t_L)$ measured under illumination (right) deviates from an Arrhenius law, while $D_H(t_L)$ measured in the dark (left) follows an Arrhenius behavior.

interval, the H interstitial will most likely be trapped in energetically very shallow Si-Si bonds since these shallow states are the most numerous[16]. These shallow states have a short trapping time and the diffusion coefficient is thereby large. On the other hand, for longer diffusion lengths, $D_H(t_L)$ deviates from an Arrhenius law. According to Philibert[17], a non Arrhenius plot can generally be understood in three different ways:

i)- the mechanism of diffusion is unique, but some energy involved in the film (dependent on T_a and I in occurrence) is used to deform the network. We can therefore imagine that the structure relaxes during illumination. The modification of the silicon network would then be responsible for the increase of defects. This explanation might be similar to the model developed by Pantelides[18].

ii)- several diffusion mechanisms are superimposed. The different slopes are then related to the different activation energy corresponding to the dominant diffusion process taking place at the corresponding T_a. This might explain the competing mechanisms of traps production due to illumination and trap reconstruction due to annealing temperature. Depending on which process dominates, creation or anihilation of traps (depending on I and T_a), H-diffusion is more or less perturbed. This might also explain the observation of the linear dependence of $D_H(t_L)$ with $1/T_a$ for L=200Å. Indeed, as shallow sites for H are the most numerous at short times, only one H-diffusion mechanism (interstitial) dominates.

iii)- regions with strong structural inhomogeneities in the a-Si:H matrix might appear during illumination and modify therefore the diffusion mechanism. This is in agreement with previous experimental results confirming that cluster sites rich in dangling bonds and weak bonds seem to be responsible for the metastable defects formation[10,11,19]. The enhanced α value obtained under illumination compared with the dark case suggest that these regions, where strong structural inhomogeneities in the a-Si:H matrix might appear, are probably enlarged under illumination. This would mean that the formation of traps is favored under illumination and that the width of their distribution increases. In a recent paper[20], Fritzsche proposed that photo-induced structural changes occur in a-Si:H in addition to the creation of DB defects.

It is conceivable that these three scenarios for metastable defects formation under illumination, explaining the origin of a non Arrhenius plot for $D_H(t_L)$ occur simultaneously. But the actual data presented in this paper do not allow to further develop a theoretical model. The aim of this note is rather to show a general trend and to suggest a possible route for further work. To get a more precise picture of the intricate connection between H-diffusion and defects formation, it would be necessary to accumulate measurements over a larger range of annealing temperatures and illumination intensities, and on various types of samples (Glow Discharge, Hot Wire samples).

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References

1. R. A. Sreet, in *Amorphous Silicon Semiconductors-Pure and Hydrogenated*, edited by A. Maclam, M. Thompson, D. Adler, and Y. Hamakawa, MRS Symposia Proceedings N° 95 (Material Research Society, Pittsburgh, 1987), p. 13.

2. J. Kakalios and W. B. Jackson, in *Amorphous Silicon and Related Materials*, edited by Hellmut Fritzsche (World Scientific, Singapore, 1988), p. 207.

3. D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).

4. K. K. Gleason, M. A. Petrich, and J. A. Reimer, Phys. Rev. B **36**, 3259 (1987).

5. J. A. Reimer, R. W. Vaughan, and J. C. Knights, Phys. Rev. Lett. **44**, 193 (1980).

6. G. Lucovsky, R. J. Nemanich, and J. C. Knights, Phys. Rev. B **19**, 2064 (1979).

7. W. Beyer, in *Tetrahedrally-Bonded Amorphous Semiconductors*, edited by D. Adler and H. Fritzsche (Plenum, New York, 1985) p. 129.

8. X. M. Tang, J. Weber, Y. Baer, and F. Finger, Phys. Rev. B **41**, 7945 (1990),

X. M. Tang, J. Weber, Y. Baer, and F. Finger, Phys. Rev. B **42**, 7277 (1990),

X. M. Tang, PhD. Thesis, Neuchâtel (1991).

9. W. B. Jackson, Phys. Rev. B **38**, 3595 (1988).

10. O. Greim, J. Weber, X. M. Tang, Y. Baer, and U. Kroll, Solid State Commun. **88**, 583 (1993),

O. Greim, J. Weber, Y. Baer, and U. Kroll, Phys. Rev. B **50**, 10644 (1994).

11. O. Greim, J. Weber, Y. Baer, and Y. Ziegler, Solid State Commun. **93**, 719 (1995).

12. H. Curtins, N. Wyrsch and A.V. Shah, Elec. Lett.

23, 228 (1987).

13. P. V. Santos, N. M. Johnson, and R. A. Street, Phys. Rev. Lett. **67**, 2686 (1991).

14. H. M. Branz, S. E. Asher, and B. Nelson, Phys. Rev. B **47**, 7061 (1993).

15. R. A. Street, C. C. Tsai, J. Kakalios, and W. B. Jackson, Philos. Mag. B **56**, 305 (1987).

16. J. Kakalios, R. A. Street, and W. B. Jackson, Phys. Rev. Lett. **59**, 1037 (1987).

17. J. Philibert, *Diffusion et transport de matière dans les solides*, les éditions de physique, 91944 les Ulis Cedex, France, (1985), p. 43.

18. T. Pantelides, Phys. Rev. Lett. **58**, 1344 (1987).

19. M. Vanecek, A.H. Mahan, B.P. Nelson and R.S. Crandall, 11th E.C. Photovoltaic Solar Energy Conf, Montreux 1992, edited by L. Guimarães et al. (Harwood Academic 1993) p.96.

20. H. Fritzsche, Solid State Commun. **94**, 953 (1995).