Hydrogen in a-Si:H : its diffusion under illumination and its influence on the formation of silicide.

Submitted to the Institute of Physics
for the obtention of
the degree of
Doctor of philosophy in Physics
at the Neuchâtel University

by

Olivier Greim

June 8 1995.

(This is a short summary of the thesis manuscript)

IMPRIMATUR POUR LA THÈSE

Hydrogène dans le a-Si:H : sa diffusion sous illumination
et son influence dans la formation de silicure

de M. Olivier Greim

UNIVERSITÉ DE NEUCHÂTEL

FACULTÉ DES SCIENCES

La Faculté des sciences de l'Université de
Neuchâtel sur le rapport des membres du jury,

Messieurs Y. Baer, J. Weber, A. Shah et L. Schlapbach
(Fribourg)

autorise l'impression de la présente thèse.

Neuchâtel, le 21 juin 1995

Le doyen:

H.-H. Nägeli

Hydrogen in a-Si:H : its diffusion under illumination and its influence on silicide formation.

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. 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 (Staebler-Wronski effect, SWE). Several models relating the H mobility with the defect production have been proposed. It is natural to suppose that illumination has some influence on the H-diffusion processes through a-Si:H films.

The aim of our study was to provide an experimental confirmation on the role of H in the SWE and to develop a model explaining the results and therefore improve the comprehension of the mechanisms responsible for the electronic instability of a-Si:H films.

A number of a-Si:H films have been thermally annealed at temperature T_a in the range 220-270°C for 24-48h either under intense visible-light illumination intensity I ($4 \leq I \leq 16$ W/cm^2) or in the dark for comparison purposes [1,2]. After each annealing, the H concentration profile was measured with Rutherford-backscattering-spectrometry and elastic-recoil-detection-analysis (RBS and ERDA) ion-beam analysis methods. We showed that H-diffusion is faster under illumination than in the dark. These results have been observed only in films which were deposited at low substrate temperature (T_s=100°C). These findings are consistent with other measurements showing that films with high H concentration (i.e. with a large weakly bonded H phase) have poor electronic proprieties under illumination and that the SWE is more pronounced in this type of samples. This experiment illustrates the possible role of H in the SWE: the photogenerated e-h pairs contribute to free H from Si-H bonds 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. The good agreement between the phenomenological model which we developed to explain our results and between our data confirm the validity of the hypothesis used for this model.

We have also investigated the variation of the dispersion parameter α of hydrogen diffusion ($D_H \sim t^{-\alpha}$) as a function of illumination intensities (I=8 and 15 W/cm^2) at different annealing temperatures T_a>300°C when the weakly bonded H concentration has effused [3]. After this H phase effusion, the structure is modified in a non-reversible way and remains rich in defects. The measure of α is then characteristic of the disorder in the a-Si:H film. The α value in the illuminated case was compared to the α dark value. We found that α increases with I. Our results suggest that illumination influences the creation and annealing kinetics of metastable defects in a-Si:H. We also observed that the modifications of the micro-structure in a first type of illuminated sample (Hot Wire, HW) are not as large as in a second type of sample (Very High Frequency Glow Discharge, VHF-GD). We conclude that hydrogen is well diluted in the HW sample and that the number of potential deep traps is smaller than in the VHF-GD sample.

Though the link between the SWE and the H diffusion under illumination is complex, we provided the first experimental confirmations of the connection between H diffusion and the influence of illumination on the creation of defects.

In a second part of this work, we studied the influence of H in silicide formation in a-Si:H films [4]. The rate $K(T_a)$ of Ni_2Si formation in a-Si:H films of various H concentrations was measured. We have found that Ni_2Si formation is limited by diffusion and that the activation energy E_a is strongly correlated to the structure and to the H concentration in the film. It is natural to suppose that $K(T_a)$ must be related to the diffusion velocity of the main diffusing species (Ni in our case) through the Ni_2Si new layer to the a-Si:H film where a reaction takes place. We thus showed that Ni_2Si formation is completely governed by the diffusion of Ni through the more or less defect rich structure of the silicide layer depending on the nature of the a-Si:H substrate.

The diffusion of metallic impurities is also of interest in applications, a subject which is not well documented. We got a-Si:H films implanted with metallic impurities (Ni, Pd, Au and Cu) at Sao Paolo University. Heat treatments have been performed. Surprisingly, no diffusion has been observed though it is well known that these impurities diffuse easily in c-Si and a-Si. These results suggest that H, by filling all the possible sites, stops the diffusion. These preliminary results have to be confirmed.

a-Si:H is technologically important. Therefore, the knowledge of the microscopic film behavior during the various processes (illumination, thermal annealing and diffusion, metallic contacts formation and stability) is also important. Our work gave valuable information on the role played by H-complex in these processes. To improve the understanding of these mechanisms we suggest to pursue this type of investigation.

The complete manuscript, in the form of a PhD thesis, has been deposited at the library of the Physics Institute of the Neuchâtel University.

Solid State Communications, Vol. 88, No. 8, pp. 583-585, 1993.
Printed in Great Britain.

0038-1098/93$6.00+.00
Pergamon Press Ltd

ENHANCEMENT OF HYDROGEN DIFFUSION IN a-Si:H THROUGH INTENSE ILLUMINATION

O. Greim, J. Weber, X.-M. Tang and Y. Baer
Institut de Physique de l'Université, CH-2000 Neuchâtel, Switzerland
U. Kroll
Institut de Microtechnique de l'Université, CH-2000 Neuchâtel, Switzerland

(*Received* 6 *September* 1993, *acccpted* 5 *October* 1993 *by P. Wachter*)

Hydrogenated amorphous Silicon (a-Si:H) films have been thermally annealed at temperatures in the range 220°C to 270°C for 48 hours, either under intense visible light illumination (15 watts/cm^2) or in the dark. After each annealing, the hydrogen concentration profile was measured with RBS-ERDA ion beam analysis methods. Substantial enhancement of the hydrogen diffusion constant D was observed in the illuminated samples. To our knowledge, this is the first observation of this effect directly in a-Si:H films. Our results are in agreement with others obtained with a-Si:H/a-Si:D/a-Si:H sandwiches by SIMS (Secondary Ion Mass Spectroscopy).

1. Introduction

It is known that through intense illumination one observes a degradation of the photo current in a-Si:H films (Staebler-Wronski effect, SWE[1]). This is due to the production of metastable defects (dangling bonds, DB). SWE is reversible by thermal annealing at 200°C[1]. It is strongly suspected that the presence and mobility of hydrogen play an important role in SWE. Some models have been proposed[2-5]. It is natural to suppose that illumination has some influence on the hydrogen diffusion processes through a-Si:H films. Indeed Santos et al.[6] and Branz et al.[7] have observed an increase of the diffusion constant D of deuterium through illumination of a a-Si:H/a-Si:D/a-Si:H sandwich structure (annealing temperature T_a range: 200 to 350°C. Their results are:

dark: $5\ 10^{-18} \leq D \leq 6\ 10^{-16}$ cm^2/s
illumination; $5\ 10^{-17} \leq D \leq 4\ 10^{-15}$ cm^2/s

It is also known from previous works[8,9] 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% than in the 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[10] that at T_a<300°C and under an illumination of 15 W/cm^2 the ratio $d_i/d_d \approx 2$ to 5 ($d_{i,d}$ are the defect densities under illumination and in the dark respectively). Therefore, if one wants to observe the influence of illumination on the hydrogen diffusion constant D, one should start with a-Si:H films deposited at rather low T_s and anneal them (for many hours) in the dark and under illumination in the temperature range $200°C \leq T_a \leq 300°C$.

2. Experimental

The a-Si:H films were deposited on c-Si wafers at the Institut de Microtechnique de Neuchâtel (IMT) with the Very High Frequency Glow Descharge (VHF-GD) method[12]. Their characteristics are shown in Table 1

Table 1

Film type	T_s°C	C_H at.%	R
1	100	19.4	0.63
2	100	21.6	0.63
3	200	15.0	0.27
4	300	9.6	0.14

T_s: substrate deposition temperature,
C_H: total hydrogen concentration.
R: a film microstructure parameter. It is determined by IR absorption measurements from the 2000 and 2080 cm^{-1} stretch mode. A higher R value means a higher concentration of H-clusters and of Si-H on internal surfaces with respect to the total H-content[12,13,14].

Each sample was first annealed at T_s for one hour and then slowly cooled down to eliminate stresses in the film and prevent it from "exploding" in subsequent thermal treatments. Then the total hydrogen concentration C_H was measured by Elastic Recoil Detection Analysis (ERDA) which is a non destructive high energy ion beam analysis method. Our ERDA set-up is described in detail elsewhere[8].

The thermal annealings under illumination or in the dark were done in a vacuum chamber ($p<10^{-6}$ torr). The samples were fixed onto a pure silver holder cooled with circulating air. Two thermocouples (TC) protected from direct illumination measured the temperature of the film itself 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 light power was 15 W/cm^2. The illumination heated the sample up to a predetermined value of T_a ($220°C \leq T_a \leq 270°C$). This temperature was kept constant (± 2°C) for 48 hours by regulating (PID controller) the air flow cooling the sample holder.

The sample was then transferred into the ERDA scattering chamber ($p<10^{-6}$ torr) for the C_H profile measurement.

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 proton energy spectra were analyzed with our own reconstruction code resulting in C_H profiles. Since we observed that the C_H profiles of the films as produced were uniform, the profiles after diffusion should obey the Fick's equation solution[15]:

$$\frac{(C(x) - C_s)}{(C_o - C_s)} = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

where:
$C(x)$ is the C_H profile as a function of x, the distance from the film surface. C_s is the value of C_H at the film surface. In our case $C_s=0$. C_o is the H concentration for large x (or anywhere before diffusion), D is the H diffusion constant and t is the annealing (at T_a) duration (in our case 48 hours).

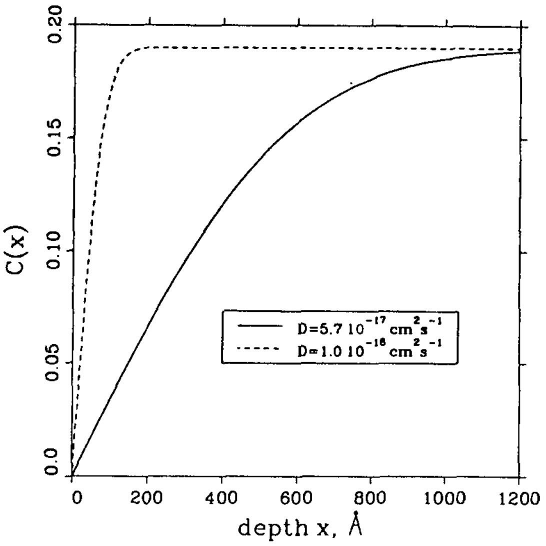

Fig.1: Hydrogen concentration depth profiles C(x) in illuminated (——) and not illuminated (- -) a-Si:H films, Annealing temperature T_a=270°C.

3. Results

Figure 1 shows the profiles C(x) as determined from the measurements at T_a=270°C (see Table 2).

Table 2

Film type	T_a °C	D_{illum} 10^{-17}cm^2/s	D_{dark} 10^{-17}cm^2/s
1	220	2.1	0.1
2	230	3.0	0.66
2	240	3.9	0.32
1	270	5.7	0.1
3	300	52.8	53.0
3	350	104.0	104.0
4	300	48.0	48.0

Film type: see Table 1 for more details.
T_a: annealing temperature.
$D_{illum,dark}$: hydrogen diffusion constant D in illuminated and not illuminated films respectively. The uncertainty in the D values is 0.5 10^{-17} cm^2/s.
Light power: 15 W/cm^2 for 48 hours.

D_{illum} and D_{dark} are plotted In Figure 2 versus T_a.

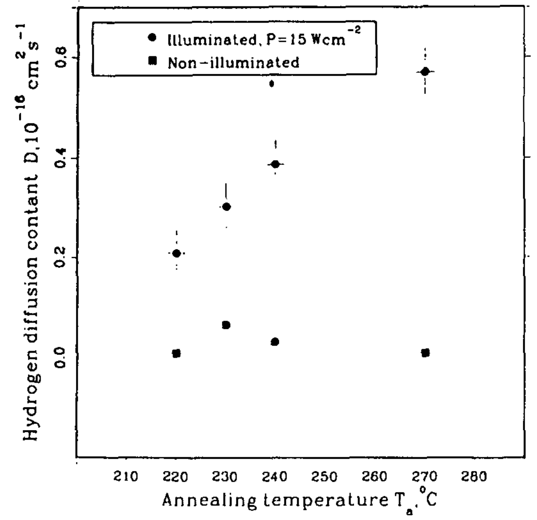

Fig.2: Hydrogen diffusion constant D versus annealing temperature T_a. Light power: 15 W/cm^2.

4. Discussion and Conclusion

To our knowledge, this work for the first time demonstrates, directly in a-Si:H film, the enhancement of hydrogen diffusion through intense illumination.

The inspection of Table 2 suggests that the metastable defects responsible for the SWE are present essentially in the loosely bound hydrogen phase. We did not observe an enhancement of D in samples of type 3 and 4 which were produced at higher T_s and had therefore smaller C_H and R values (Table 1). This is in agreement with the fact that the photo current degradation is smaller when T_s is high ($\geq$ 200°C) and, consequently, C_H is small (a few percent)[16]. This is also in agreement with the results found by Jackson et al.[17] which show that the number of H-clusters becomes larger when C_H increases.

The results of ref.10 allow us to speculate that, for not too high a light power, D_{illum} should reach a maximum in the range $200°C \leq T_a \leq 300°C$. Hence, one might expect to obtain some information about the rate of formation (by light) and passivation (by temperature) of the metastable defects. Work along this line is in progress.

Acknowledgment- Fruitful discussions with prof. Vanececk (Praha University) are gratefully acknowledged.

References

1. D.L. Staebler and C.R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).
2. M. Stutzmann, W.B. Jackson and C.C. Tsai, Phys. Rev. **B32**, 23 (1985).
3. R.A. Street and K. Winner, Phys. Rev. **B40**, 6236 (1989).
4. H. Dersh, J. Stuke and J. Beichler, Appl. Phys. Lett. **38**, 456 (1980).
5. S. Zafar and E.A. Schiff, Phys. Rev. **B40**, 5235 (1989).
6. P.V. Santos, N.H. Johnson and R.A. Street, Phys. Rev. Lett. **67**, 2686 (1991).
7. H.M. Branz, S.E. Asher and P. Nelson, Phys. Rev. **B47**, 7061 (1993).
8. X.-M. Tang, PhD Thesis, Neuchâtel (1991) and
X.-M. Tang, J. Weber, Y. Baer and F. Finger, Solid State Commun. **74**, 171 (1990).
9. W. Beyer in "Thetrahedrally-Bonded Amorphous Semiconductors", D. Adler and H. Frietzsche eds., Plenum Press New York. 1985 p. 129.
10. P.V. Santos, W.B. Jackson and R.A. Street, Phys. Rev. **B44**, 12800 (1991).
N. Huta, M. Isomura and S. Wagner, Appl. Phys. Lett. **60**, 1462 (1992).
11. H. Curtins, N. Wyrsch and A.V. Shah, Elec. Lett. **23** 228 (1987).
12. F. Finger et al., J. Appl. Phys. **71**, 5665 (1992)
13. M.H. Brodsky, M. Cordona and J.J. Cuomo, Phys. Rev. **B16**, 3556 (1977).
14. E. Bhattacharya and A.H. Mahan, Appl. Phys. Lett. **52**, 1587 (1988)
15. J. Philibert, "Diffusion et transport de matière dans les solides", les éditions de physique, Les Ulis, France, 1986.
16. S. Veprek, O. Ambacher and M. Vanecek, Mat. Res. Soc. Symp. Proc. **258**, 45 (1992)
17. W.B. Jackson, P.V. Santos and C.C. Tsai, Phys. Rev. **B47**, 9993 (1993)

PHYSICAL REVIEW B VOLUME 50, NUMBER 15 15 OCTOBER 1994-I

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

O. Greim, J. Weber, and Y. Baer
Institut de Physique de l'Université, Rue Breguet 1, CH-2000 Neuchâtel, Switzerland

U. Kroll
Institut de Microtechnique de l'Université, Rue Breguet 2, CH-2000 Neuchâtel, Switzerland

(Received 16 May 1994)

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, $5\times10^{-18}\leq D\leq6\times10^{-16}$ cm^2/s; illumination, $5\times10^{-17}\leq D\leq4\times10^{-15}$ 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 $d_i/d_d\approx2$–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

0163-1829/94/50(15)/10644(5)/$06.00

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 $220 \leq T_a \leq 270$ °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 $\mathrm{PF} = D_0 \eta n / N_H$ [Eq. (8)] have been determined from the Arrhenius plot of Fig. 3. They are $\mathrm{PF} = (6.2 \pm 1.8) \times 10^{-14}$ cm^{4}W^{-1}s^{-1} and $E_a = (0.46 \pm 0.01)$ 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.

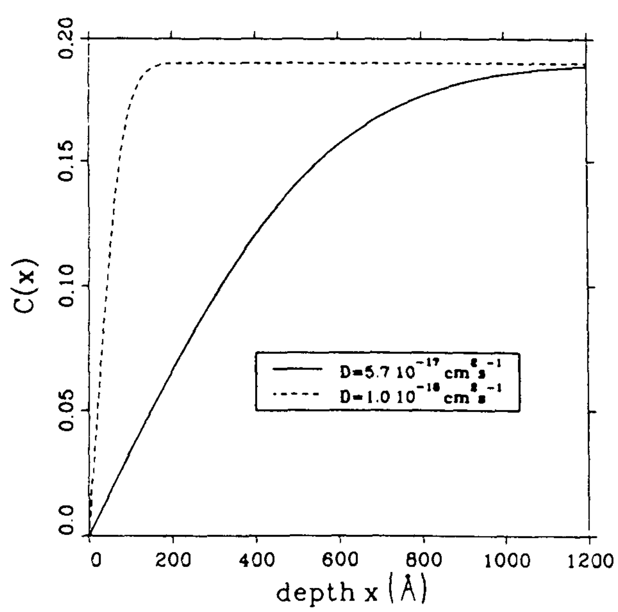

FIG. 1. Hydrogen-concentration depth profiles $C(x)$ in illuminated (——) and not illuminated (– – –) a-Si:H films. Deposition substrate temperature $T_s = 100$ °C. Annealing temperature $T_a = 270$ °C.

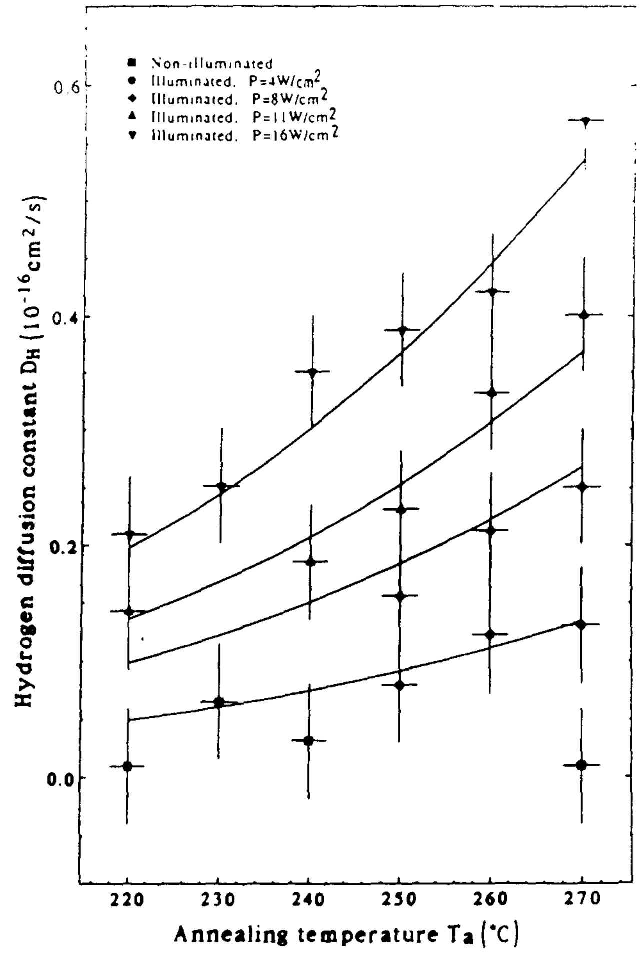

FIG. 2. Temperature dependence of the hydrogen-diffusion constant D_H at different illumination powers in a-Si:H deposited at $T_s = 100$ °C. The solid lines are computed with the model of Sec. IV, Eq. (8).

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-

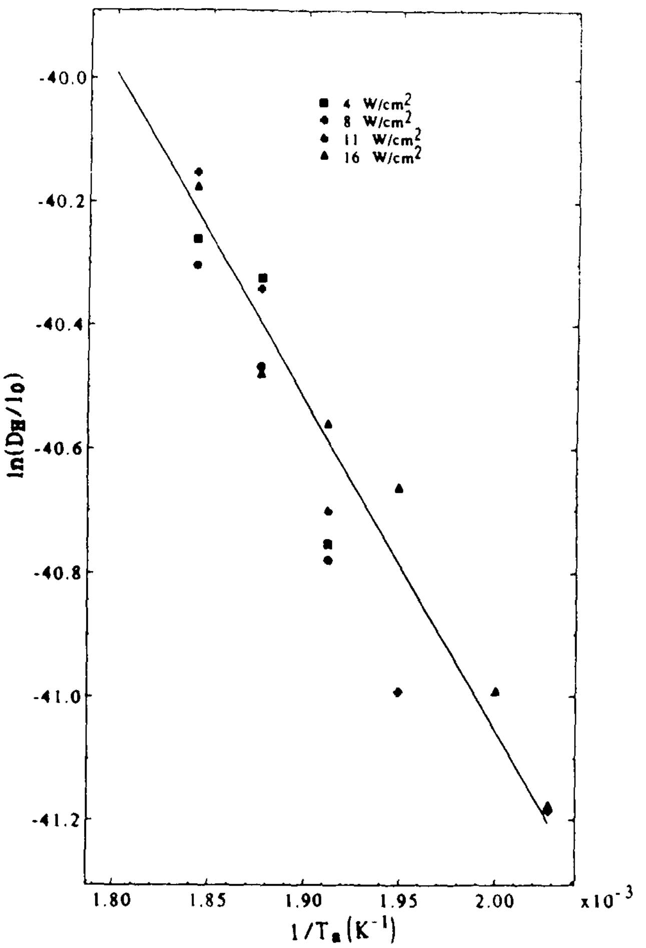

FIG. 3. Arrhenius plot of D_H versus $1/T_a$, where T_a is the annealing temperature for different I_0 values.

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 ($D_H \propto t^{-\alpha}$) 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: ($dn/dE \propto \exp(E/k_BT_0)$).[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]

$$D_H = \frac{N_{Hs} D_{Hs}}{N_H} , \tag{1}$$

where N_{Hs} is the hydrogen density in interstitial sites, D_{Hs} is the diffusion coefficient in the shallow traps, and N_H is the total hydrogen density.

D_{Hs} is given by Santos *et al.*,[17]

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

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/cm^3. D_H can be written as $D_H = D_H$ (ill.)$+D_H$ (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 ($\approx 5\times10^{-18}$ cm^2/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:

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

dN_{Hs}/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/cm^2), 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

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

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

$$N_{Hs} = I_0 \eta \nu n / \sigma . \tag{5}$$

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

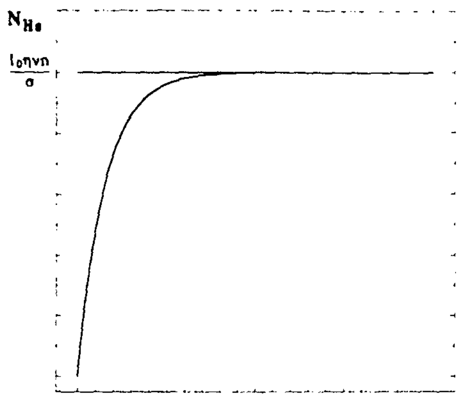

FIG. 4. N_{Hs} as a function of time t in arbitrary units calculated with Eq. (4).

dN_{Hs}/dt in a simple way.

In Eq. (8), N_{Hs} 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_{Hs} 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

$$D_H = \frac{I_0 \eta (\nu/\sigma) n(T_s)}{N_H(T_s)} D_0 \exp\left[-\frac{E_s - E_m}{k_B T}\right] . \tag{6}$$

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

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

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

$$D_H = \frac{I_0 D_0 \eta n(T_s)}{N_H(T_s)} \exp\left[-\frac{E_a}{k_B T}\right] . \tag{8}$$

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

(i) The F test shows that $\ln(D_H/I_0)$ 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 $E_a = (0.46 \pm 0.08)$ 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 $\exp(-E_a/k_B T)$ with $E_a = (0.46 \pm 0.08)$ 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$\Rightarrow$Si-H+Si·). This is consistent with the fact that the SWE is more pronounced in high hydrogen concentration.[25]

ACKNOWLEDGMENTS

Fruitful discussions with Professor Vanecek (Praha University) and W. Beyer (Forschungszentrum Jülich) are gratefully acknowledged.

---

[1] M. H. Brodsky and R. S. Title, Phys. Rev. Lett. **23**, 581 (1969).

[2] R. A. Street, in *Amorphous Silicon Semiconductors—Pure and Hydrogenated*, edited by A. Maclam, M. Thompson, D. Adler, and Y. Hamakawa, MRS Symposia Proceedings No. 95 (Material Research Society, Pittsburgh, 1987), p. 13.

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

[4] O. Greim, J. Weber, Y. Baer, and U. Kroll, Solid State Commun. **88**, 583 (1993).

[5] P. V. Santos, N. H. Johnson, and R. A. Street, Phys. Rev. Lett. **67**, 2686 (1991).

[6] H. M. Branz, S. E. Asher, and P. Nelson, Phys. Rev. B **47**, 7061 (1993).

[7]X.-M. Tang, Ph.D. thesis, Neuchâtel, 1991; X.-M. Tang, J. Weber, Y. Baer, and F. Finger, Solid State Commun. **74**, 171 (1990); Phys. Rev. B **41**, 7945 (1990); **42**, 7277 (1990).

[8]W. Beyer, in *Thetrahedrally-Bonded Amorphous Semiconductors,* edited by D. Adler and H. Frietzsche (Plenum, New York, 1985), p. 129.

[9]P. V. Santos, W. B. Jackson, and R. A. Street, Phys. Rev. B **44**, 12 800 (1991); N. Huta, M. Isomura, and S. Wagner, Appl. Phys. Lett. **60**, 1462 (1992).

[10]F. Finger *et al.*, J. Appl. Phys. **71**, 5665 (1992).

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

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

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

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

[15]S. Zafar and E. A. Schiff, Phys. Rev. B **40**, 5235 (1989).

[16]W. B. Jackson, Phys. Rev. B **41**, 10 257 (1990).

[17]P. V. Santos, N. M. Johnson, R. A. Street, M. Hack, R. Thompson, and C. C. Tsai, Phys. Rev. B **47**, 10 244 (1992).

[18]J. Philibert, *Diffusion et Transport de Matière dans les Solides* (Les Éditions de Physique, les Ulis Cedex, France, 1985), p. 43.

[19]Nobuhiro Hata, Gantam Ganguly, and Akihisa Matsuda, Appl. Phys. Lett. **62**, 1791 (1993).

[20]I. Balberg and Y. Lubianiker, Phys. Rev. B **48**, 8709 (1993).

[21]M. Stutzmann, W. B. Jackson, and C. C. Tsai, Phys. Rev. B **32**, 23 (1984).

[22]*Hydrogen in Semiconductors and Semimetals,* edited by J. L. Pankove and N. M. Johnson (Academic, San Diego, 1991), Vol. 34, p. 113.

[23]P. V. Santos and W. B. Jackson, Phys. Rev. B **46**, 4595 (1992).

[24]W. B. Jackson and C. C. Tsai, Phys. Rev. B **45**, 6564 (1992).

[25]S. Veprek, O. Ambacher, and M. Vanecek, in *Amorphous Silicon Technology,* edited by P. G. Le Comber, M. J. Thompson, V. Hamakawa, and A. Madan, MRS Symposia Proceedings No. 258 (Materials Research Society, Pittsburgh, 1992), p. 45.

Pergamon

Solid State Communications, Vol. 93, No. 9, pp. 719-723, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0038-1098/95 $9.50+.00

0038-1098(94)00868-X

INFLUENCE OF INTENSE ILLUMINATION ON DISPERSIVE HYDROGEN DIFFUSION IN a-Si:H.

O. Greim, J. Weber and Y. Baer
Institut de Physique de l'Université, Rue Breguet 1, CH-2000 Neuchâtel, Switzerland
Y. Ziegler
Institut de Microtechnique de l'Université, Rue Breguet 2, CH-2000 Neuchâtel, Switzerland

(Received 21 November 1994, accepted for publication 25 November 1994 by P.Wachter)

With elastic-recoil detection analysis (ERDA) we have measured the variation of the dispersion parameter α of hydrogen diffusion in undoped a-Si:H as a function of illumination intensities I (I=8 and 15 W/cm^2) at an annealing temperature T_a=350°C. The α value in the illuminated case was then compared to the α dark value. We found that α increases with I. To our knowledge, this is the first observation of this effect. The hydrogen diffusion mechanisms under intense illumination for both film types are discussed in the framework of existing models.

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

1. Introduction

Hydrogen transport in hydrogenated amorphous silicon (a-Si:H) has been studied by many authors with different techniques[1-8]. The results of thin-film experiments[9-11] suggest that hydrogen is found in Si-H, Si-H_2, and Si-H_3 groups forming clusters with 5-7 hydrogen atoms, or as Si-H uniformly distributed in Si. The ratio of clustered and isolated hydrogen atoms varies with the deposition method and the processing conditions.

Two different mechanisms have been found to govern the evolution of the hydrogen concentration[2]. For the isolated atomic hydrogen species, this evolution is driven by a diffusion-limited process (DL) that reaches a maximum at 600°C. For the clustered hydrogen, 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 void network in a-Si:H. This "NDL-hydrogen" is expected to be related to the disorder of the a-Si:H microstructure. Tang et al.[6] have suggested that annealing at temperatures T_a higher than 300°C modifies 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[12,13], the diffusion parameter D is expressed as:

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

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. This distribution is responsible for the dispersion.

This paper presents the first results confirming the influence of intense illumination on the dispersion parameter α, after effusion of the "NDL-hydrogen". These results will be discussed in the framework of existing models, and some conclusions will be proposed about the hydrogen diffusion mechanisms under intense illumination for two types of films.

2. Experimental

Two undoped a-Si:H samples ($2\mu m$ thick) were deposited onto c-Si wafers at the Institut de Microtechnique de Neuchâtel (IMT). The first film was prepared by the silane-based VHF-glow discharge (VHF-GD) method at low pressure (10^{-2} mbar)[14], and the second one by the hot wire (HW) technique[15]. Their characteristics are shown in Table 1.

The initial hydrogen concentration C_H and the hydrogen concentration profiles after the annealing and illumination periods at temperature $T_a=350°C$ were measured by Elastic Recoil Detection Analysis (ERDA) which is a non destructive high energy ion beam analysis. Our ERDA set-up is described in detail elsewhere[6]. 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 suitable to the large number of needed measurements since it is not destructive and allows to perform successive annealings of the same sample. The time required to rise and to lower the temperature was of the order of 1 min. which is short compared with the annealing periods (>30min.).

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.

Table 1

Film type	T_S [°C]	C_H [at.%]	R
VHF-GD	250	13	0.20
HW [a]	350	10	0.16

T_S: substrate deposition temperature,

C_H: total hydrogen concentration,

R: a film microstructure parameter. It is determined by IR absorption measurements from the 2000 and 2080 cm^{-1} stretch modes. A high R value means a high concentration of H-clusters with respect to the total hydrogen content[16, 17].

[a] It has been suggested by M. Vanecek and co-workers[18] that HW material should be more stable than VHF-GD samples with respect to light induced degradation. Hence a smaller influence of intense illumination on H-diffusion should be expected.

The illumination was done with a Xenon lamp (Osram 64635) powered by a constant current source. The light intensities I, were 8 and 15 W/cm^2. The sample was first degraded (I=8 or 15 W/cm^2) for about 18h at room temperature and then illuminated at the same light power at the annealing temperature $T_a=350°C$. 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

Despite the fact that the hydrogen diffusion parameter $D_H(t)$ is time dependent, the hydrogen concentration depth profile C(x,t) in the annealed (dark and illuminated) a-Si:H films can still be described by an error function[19]:

$$C(x,t) = C_0 \operatorname{erf}\left(\frac{x}{2\sqrt{G(t)}}\right) \qquad (1)$$

where t is the annealing time, x the depth and

$$G(t) = \int_0^t D(\tau)d\tau \qquad (2)$$

The prefactor C_0 is the hydrogen concentration at large depth which remains constant in the range of our annealing times. C_0 and G(t) are determined by fitting C(x,t) to the proton energy spectra recorded after the different annealing and illuminating periods. Details of this procedure through our reconstruction code can be found in Ref 6.

If we assume that time dependence of the diffusion parameter is given by $D_H(t)=D_{00}(\omega t)^{-\alpha}$, one obtains the following relation from Eq. (2):

$$G(t) = \frac{D_{00}\omega^{-\alpha}}{1-\alpha} t^{(1-\alpha)} = A t^{(1-\alpha)} = \frac{D_H(t)}{(1-\alpha)} t$$

The logarithmic plot of G vs t shown in Figure 1 provides

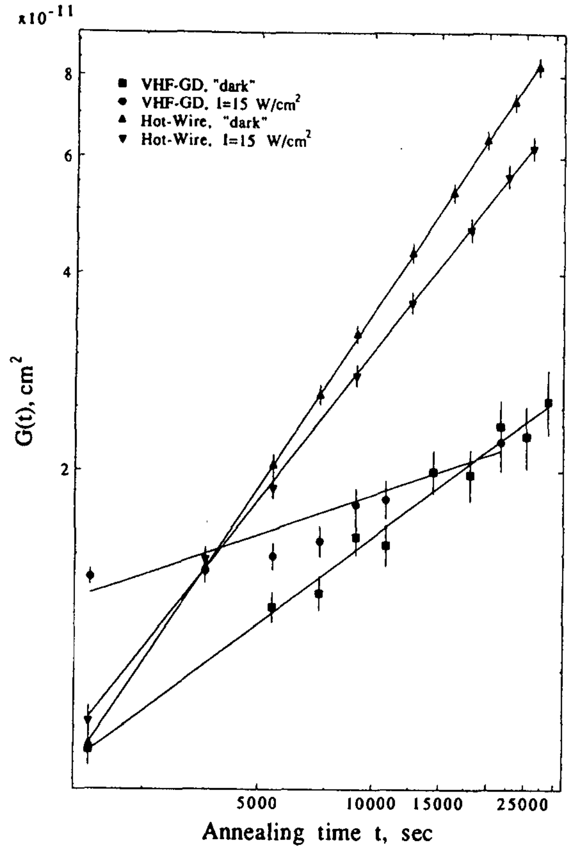

Fig.1: Time integrated diffusion parameter G(t, I) vs the annealing time t. The errors bars are estimated from the quality of the fit of the computed ERDA spectrum. I is the illumination intensity. The lines are linear best fits to the data.

the experimental confirmation of the functional form of G(t). It yields the dispersion parameter α from the slope (1-α) and the constant term $A=D_{00}\omega^{-\alpha}/(1-\alpha)$ from the extrapolation to t=1.

For comparison purposes, the diffusion parameter D_H is estimated at a fixed diffusion length L (for example L=1000Å, as in Ref 12):

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

Table 2 summarizes our results.

The value α=0.56 for the VHF-GD sample annealed in the dark at T_a=350°C agrees with the values given by Shinar et al.[5] and Tang et al.[6], for the same annealing conditions and type of sample.

It is interesting to note that the HW sample does not contain (in the limit of our measurement sensitivity ±0.5 % at.) a loosely bound "NDL-hydrogen" phase, although C_H=10 % at.. This fact suggests that the hydrogen is well diluted and that the amount of H-clusters is very small. Indeed the R parameter value confirms that the proportion of $Si\text{-}H_2$ and $Si\text{-}H_3$ is very small. This explains the small α value found for this sample. As will be discussed later, α is characteristic of the disorder in the structure.

4. Discussion and conclusion

Our results suggest that illumination influences the creation and annealing kinetics of metastable defects in a-

Table 2:

Summary of our results. C_H, initial hydrogen concentration; ΔC, "NDL-hydrogen" concentration; α, dispersion parameter; T_0, characteristic temperature in the relation $\alpha = 1 - \frac{T_a}{T_0}$ (Ref. 4); A, prefactor estimated from the linear best fit of lnG(t) vs lnt.

Film type	Illumination intensity [W/cm^2]	C_H [% at.]	ΔC [% at.]	α	T_0 [K]	$A = \frac{D_{00}\omega^{-\alpha}}{1-\alpha}$
VHF-GD	"dark"	13	2	0.56±0.03	1416	$2.90\ 10^{-13}$
VHF-GD	8	13	2	0.73±0.03	2307	$1.66\ 10^{-12}$
VHF-GD	15	13	2	0.8±0.03	3115	$2.92\ 10^{-12}$
HW	"dark"	10	0	0.12±0.02	708	$1.10\ 10^{-14}$
HW	15	10	0	0.26±0.02	842	$3.22\ 10^{-14}$

Si:H films. Some groups[7, 8, 20] have already shown that illumination enhances the hydrogen diffusion constant in a-Si:H at annealing temperatures $200°C \leq T_a \leq 300°C$. The model of hydrogen motion which was suggested by these results is that a hydrogen atom hops off a weak Si-H bond, travels briefly as an interstitial, and falls into a new bonding configuration, either a pre-existing dangling bond or a strained Si-Si bond[21]. The process then continues as the hydrogen hops off its new bonding site. The presence of photogenerated carriers increases both the rate of hydrogen hopping and the number of silicon network sites where it is energetically favorable for hydrogen to form new defects[22]. Due to the silicon network disorder, there will be a distribution of barriers for hydrogen motion, leading to the observed dispersive hydrogen motion[3, 4, 6].

The present results clearly demonstrate that the hydrogen diffusion becomes more dispersive whith increasing illumination intensity for both types of samples. Assuming that α obeys the same temperature dependence $\alpha = 1 - T_a/T_0$ under illumination, we observe that $k_B T_0$ rises dramatically when the illumination intensity is increased. The presence of photogenerated carriers enhances the number of free hydrogen atoms as well as the probability for hydrogen to be more deeply trapped.

For short diffusion lengths (L=200Å), corresponding to short diffusion times, t<15 min., we observe in Table 3 that D_L is enhanced through illumination. This is due to the fact that, at short times, the hydrogen interstitial will most likely be trapped in energetically very shallow Si-Si bonds since these shallow states are the most numerous[4]. These shallow states have a short trapping time and the diffusion coefficient is thereby large at short times. This effect is more pronounced for the VHF-GD sample than for the HW sample. This is in agreement with our results[20] for hydrogen diffusion at low temperature where the dispersivity is negligible (Tang et al.[6] have shown the dependence of α vs T_a, the annealing temperature). Indeed, we have shown[20] that D_H is enhanced under intense illumination ($200<T_a<270°C$) in samples which are rich in loosely bound hydrogen. This effect is much less important in the HW sample where ΔC, -the "NDL-hydrogen" concentration- is insignificant (see Table 2). For longer diffusion lengths (L=1000Å) we can observe that D_L becomes smaller as I_0 is increased. This is due to the fact that the number of defects goes up as shown by the α value. The probability that a hydrogen atom will fall in a deeper trap is enhanced and consequently D_L decreases.

Alternatively, the diffusion coefficient is given by[7, 23]

$$D = \nu\lambda^2/6$$

where ν is the H-excitation rate and λ the H-mean free path. If we assume a constant diffusion path $\lambda = 10Å$[7], (more work is needed to clarify this issue!) and use D_L at L=1000Å, this formula provides the excitation rate value. The double logarithmic plot of G(t) vs t then yields the constant term A and therefore $D_{00}\omega^{-\alpha}$ (see Table N°2). By substituting the excitation rate ω by ν, it is then possible to estimate the microscopic diffusion constant D_{00}. These values are summarized in Table 3.

With the assumption that the diffusion path λ is constant, we find that D_{00} agrees with the order of magnitude given by other groups[5, 12]. We observe that

Table 3:

The diffusion parameter D_L, computed according to Ref. 12 for a diffusion length L=200Å, resp. L=1000Å; D_{00}, estimated microscopic diffusion constant, see text for more details.

Film type	Illumination intensity [W/cm^2]	$D_{L=200Å}$ [cm^2/s]	$D_{L=1000Å}$ [cm^2/s]	D_{00} [cm^2/s]
VHF-GD	"dark"	$4.52\ 10^{-15}$	$7.52\ 10^{-17}$	$2.25\ 10^{-14}$
VHF-GD	8	$4.13\ 10^{-14}$	$6.86\ 10^{-18}$	$8.12\ 10^{-15}$
VHF-GD	15	$1.66\ 10^{-13}$	$4.25\ 10^{-19}$	$7.79\ 10^{-16}$
HW	"dark"	$4.35\ 10^{-15}$	$2.81\ 10^{-15}$	$1.03\ 10^{-14}$
HW	15	$4.38\ 10^{-15}$	$1.41\ 10^{-15}$	$2.88\ 10^{-14}$

D_{00} decreases when the light intensity is increased in the case of the VHF-GD prepared sample, but that D_{00} seems to increase or stay of the order of the D_{00} dark value in the case of samples prepared by the HW technique. We can speculate that the microscopic local environment of the illuminated HW sample structure is not subjected to large modifications since hydrogen is well diluted and the number of potential deep traps is smaller than in the VHF-GD sample.

More work is needed to clarify the issue of whether the diffusion path is dependent on light intensity or not. It would be necessary to study the hydrogen diffusion constant D_H for the hydrogen in the diluted phase (in the same conditions as decribed in this paper) over a wider range of annealing temperatures and under a fixed illumination intensity. If D_H exhibits an exponential activated (Arrhenius) behavior we could use the relations resulting from the connection between time dependent transport and the Meyer-Nedel relation for multiple trapping dominated processes[12]. These relations are very useful to explain the microscopic transport properties on the basis of experimental results. We would be able to find independently the microscopic diffusion constant D_{00} and therefore determine whether λ is constant or not.

References

1. D. E. Carlson and C. W. Magee, Appl. Phys. Lett. **33**, 81 (1978).

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

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

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

5. J. Shinar, R. Shinar, S. Mitra, and J.-Y. Kim, Phys. Rev. Lett. **62**, 2001 (1989).

6. 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).

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

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

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

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

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

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

13. J. Kakalios, and W. B. Jackson, in *Amorphous Silicon and Related Materials*, edited by H. Fritzsche (World Scientific, Singapore, 1989).

14. H. Curtins, N. Wyrsch and A.V. Shah, Elec. Lett. **23**, 228 (1987).

15. H Wiesmann, A.K. Ghosh, T. McMahon, and M. Strongin, J. Appl. Phys. **50**, 3752 (1979).

16. M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B **16**, 3556 (1977).

17. E. Bhattacharya and A. H. Mahan, Appl. Phys. Lett. **52**, 1587 (1988).

18. 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.

19. J. Crank, *The Mathematics of Diffusion* (Clarendon, Oxford, 1975) Chap. 2.

20. 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, accepted for publication in Phys. Rev. B.

21. R. A. Street et al. Phys. Rev. B **37**, 4209 (1988).

22. W. B. Jackson, Phys. Rev. B **41**, 1059 (1988).

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

Pergamon

Solid State Communications, Vol. 90, No. 8, pp. 475-478, 1994
Elsevier Science Ltd
Printed in Great Britain
0038-1098(94)$7.00+.00

0038-1098(94)E0223-X

SILICIDE Ni_2Si FORMATION IN a-Si:H

O. Greim, J. Weber and Y. Baer
Institut de Physique de l'Université, CH-2000 Neuchâtel, Switzerland
U. Kroll
Institut de Microtechnique de l'Université, CH-2000 Neuchâtel, Switzerland

(Received 24 February 1994, accepted for publication 14 March 1994 by P.Wachter)

The rate K of Ni_2Si formation in a-Si:H films of various Hydrogen concentrations was measured. We have found that K^2 is proportional to the time and that the activation energy E_a is strongly correlated to the structure parameter R and to the Hydrogen concentration C_H in the film. C_H is very small in the Ni_2Si and in Ni layers but does not change in a-Si:H itself.

1. Introduction

The kinetics and the role of Hydrogen in silicide formation in hydrogenated amorphous Silicon films (a-Si:H) is not much documented in the literature. Some authors did not find any influence of H on the rate of silicide formation in a-Si:H as opposed to crystalline c-Si. For example, Rhodes et al[1] found this to be the case for Pd_2Si. Hung et al[2] found that a Hydrogen concentration $C_H \approx 12$ % does not play any role in Ni_2Si formation. On the other hand, other researchers have observed a strong influence of the film micro structure (and C_H) on the diffusion of Sn, Fe, Pt and Pd[3,4]. Hung et al.[2] have measured the activation energy E_a for Ni_2Si to be 1.4 ±0.1 eV. This result is within the range published by Nicolet: $1.3 \geq E_a \geq 1.5$ eV for Ni_2Si in c-Si[5]. In this note, we show that $E_a(Ni_2Si)$ in a-Si:H is strongly correlated to the film initial Hydrogen concentration C_H and to the micro-structure parameter R. This means that H-concentration or micro-structure (or both) are crucial for the silicide formation. Simultaneously, the H-concentrations in Ni_2Si and Ni layers were measured and found to be very small.

2. Experimental

The a-Si:H films were deposited onto c-Si <100> wafers at the Institut de Microtechnique de Neuchâtel (IMT) with the Very High Frequency Glow Discharge (VHF-GD) method[6]. Their characteristics are shown in Table 1

The 2µm thick films were then etched in a 3% HF solution and carefully rinsed in deionised water. In a UHV evaporation chamber ($p \leq 2\ 10^{-9}$ torr) they were annealed at T_s for one hour and then slowly cooled down to avoid stress in the film. During the Ni evaporation, the samples were kept at room temperature. A Ni/c-Si sample was prepared in the same way for comparison purposes.

Table 1

Film number	T_s (°C)	C_H (at.%)	R
1[a]	50	18.7	0.35
2	100	19.4	0.63
3	200	11.5	0.27
4[a]	250	11.0	0.17
5	300	8.3	0.14

[a] : previous results[6]
T_s: substrate deposition temperature,
C_H: total Hydrogen concentration.
R: a film micro structure parameter. It is determined by IR absorption measurements from the 2000 and 2080 cm^{-1} stretch mode. A higher R value means a higher concentration of H-clusters and of Si-H on internal surfaces with respect to the total H-content[6,7,8].

The annealings for silicide formation were performed in our RBS-ERDA scattering chamber ($p \approx 10^{-7}$ torr). They consisted in a succession of periods lasting a few minutes at carefully measured and stabilised (± 1 °C) temperatures T_a ($270°C \leq T_a \leq 330°C$). It should be noted that the temperature rise and fall times were negligible with respect to the annealing duration itself. After each period, the silicide thickness and the C_H profile were measured with RBS and ERDA. A detailed description of the experimental set-up and method can be found elsewhere[9].

3. Results

As expected from earlier measurements[10] and the "Walser and Bené rule"[5], the Ni_2Si phase was the first to grow. Figure 1a shows a succession of RBS spectra as observed after each annealing period. The analysis of these spectra gives the stoichiometry depth profile and the thickness XM (in "molecules"/cm^2) of the Ni_ySi layer. It was found that y=2±0.1. The error in the determination of X was ±0.03 10^{18} molecules/cm^2. Using the known density of this silicide phase, XM can be transformed into a length X. Figure 1b shows that, at each temperature T_a, X is proportional to $\sqrt{t}$, i.e. $X=\sqrt{K(T)t}$ where t is the annealing duration. This means that the Ni_2Si formation is limited by a "diffusion" process and not by a "chemical process" as in the $CrSi_2$ case[5]. The Arrhenius plot of the rate of silicide formation $K(T)=K_o\exp(-\frac{E_a}{kT_a})$, from which the activation energy E_a can be determined, is shown in Fig. 1c. Figure 2 shows a typical proton energy spectrum as obtained by ERDA. Its analysis gives the Hydrogen concentration profile. Our results are presented in Table 2.

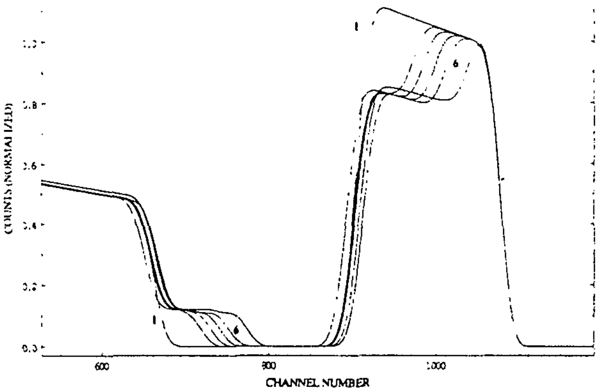

Fig.1a: RBS spectra (film No 2). The progress of Ni_2Si formation is clearly visible. Annealing temperature T_a=300°C. As deposited (spectrum 1) and after annealing for 2,4,6,10 and 14 min. (spectrum 6).

4. Discussion and Conclusion

Our result for E_a c-Si, (1.39 ± 0.1) eV, is inside the range of previously published values (1.3 - 1.5) eV[5]. E_a decreases as C_H and/or R decrease from 1.62 eV to about 1.04 eV as C_H decreases from 19.4 to about 10 at.%. E_a in c-Si lies between these two

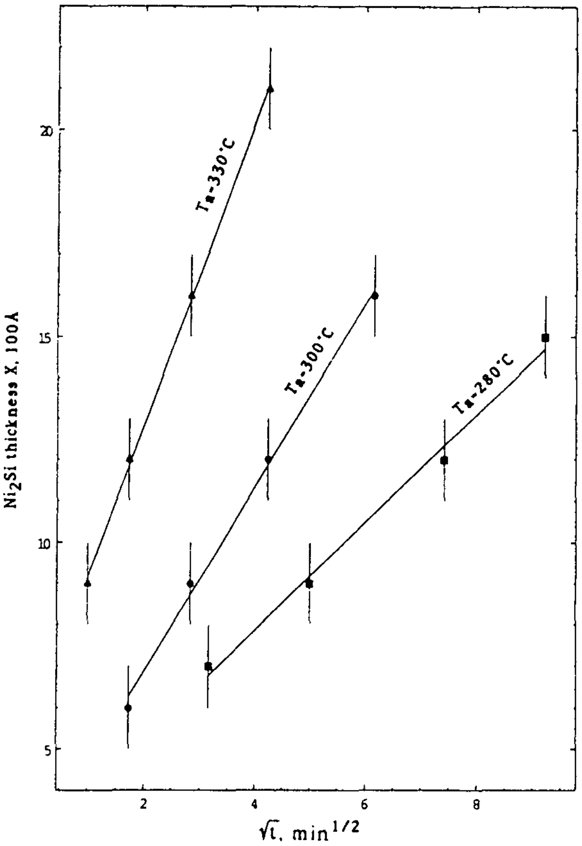

Fig.1b: Thickness of Ni_2Si as a function of square root of annealing duration t for film No 3.

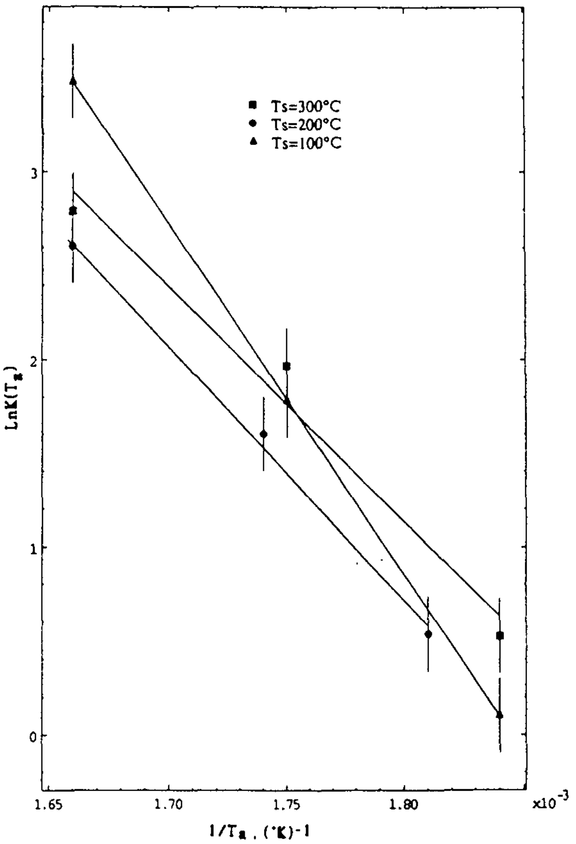

Fig.1c: Arrhenius plots of the rate K of Ni_2Si formation as a function of $1/T_a$ for films 2,3 and 5.

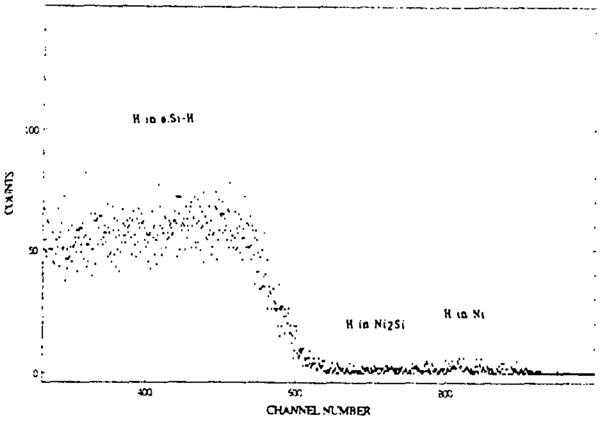

Fig.2: Typical proton energy spectrum as obtained by ERDA after annealing for 25 min. at 270 °C. Film No 2.

Table 2

Film type	T_s (°C)	C_H at.% in a-Si:H	C_H at.% in Ni	E_a (eV)	R
1 a-Si:H	50	18.7	1.5	1.46	0.35
2 a-Si:H	100	19.4	1.0	1.62	0.63
3 a-Si:H	200	11.5	1.0	1.17	0.27
4 a-Si:H	250	11.0	1.5	1.04	0.17
5 a-Si:H	300	8.3	1.5	1.09	0.14
c-Si				1.39	

Film type: see Table 1 and text for more details.
T_s: substrate deposition temperature.
C_H in Ni_2Si is always smaller than 1 at.%.
(E_a,R) linear correlation coefficient r=0.942
(E_a,C_H) linear correlation coefficient r=0.950

extreme values. This might explain the results of Hung et al.[2].

The very low values of C_H in the metal and silicide layers are most probably due to the fact that the H-diffusion constant D_H in Ni et Ni_2Si is much larger than in a-Si:H. For example, D_H in Ni at about 300°C is of the order of 10^{-6} cm^2/s (ref.11). This is 9 order of magnitudes larger than in a-Si:H[12]. On the other hand, we observed that the C_H profiles in annealed a-Si:H substrates remain essentially the same as they were before any thermal treatment. One can then suppose that the networks of micro-voids, responsible for the usual Hydrogen effusion[10], are obstructed by the silicide and metal layers.

To understand the decrease of E_a with C_H and R we have to consider the diffusing species. It has been shown with markers and radio-tracer ^{31}Si that Ni is the diffusing species in c-Si and a-Si [5,13]. Moreover Coffa et al.[14] have shown that the diffusion of Ni in a-Si proceeds by jumps from one interstitial site to another and is slowed down by defects. This has also been observed by Ottaviani et al.[15] and Chung et al.[16]. Therefore we think that when C_H is large in a-Si:H, the structure has a larger defect density than in c-Si resulting in a larger activation energy E_a. On the other hand, when C_H is relatively small, the density of micro-voids is reduced, Hydrogen is well diluted in the bulk and possible defects are thus passivated. This means that Ni atoms can diffuse more easily and form Ni_2Si.

The linear correlation between E_a and R and between E_a and C_H.is very strong (see Table 2). In both cases the confidence coefficient is 0.985. It is not clear whether **both** the micro-structure **and** Hydrogen influence the silicide formation. Measurements of such processes in a-Si:H films of different micro-structures (voids size) but with similar C_H profiles should help in solving this problem. Work along this line is in progress by using films produced in atmosphere of SiH_4 diluted with Ar[17].

Acknowledgement- Fruitful discussions with Dr. X.-M. Tang (CSEM, Neuchâtel) are gratefully acknowledged.

References

1. H.E. Rhodes, G. Apai, L. Rivaud, L.S. Hung and J.W. Mayer, Mat. Res. Soc. Symp. Proc. Vol 70, p. 387 (1986).

2. L.S. Hung, E.F. Kennedy, C.J. Palmstrom, J.O. Olowolafe, J.W.Mayer and J. Rhodes, Appl. Phys. Lett. **47**, 236 (1985).

3. V.Kh. Kudoyarova, G.S. Kulikov, E.I. Terukov and K.K. Khodzaev, J. Non-Cryst. Solids **90**, 211 (1987).

4. W. Beyer, C.E. Galls, J. Herion, W. Losch and H. Wayner, J. Non-Cryst. Solids **97-98**, 951 (1987).

5. M.-A. Nicolet and S.S. Lau in VLSI Electronics: Microstructure Science, Vol. 6, Academic press (New York, 1983).

6. F. Finger et al., J. Appl. Phys. **71**, 5665 (1992)

7. M.H. Brodsky, M. Cordona and J.J. Cuomo, Phys. Rev. **B16**, 3556 (1977).

8. E. Bhattacharya and A.H. Mahan, Appl. Phys. Lett. **52**, 1587 (1988)

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

10. X.-M. Tang, PhD thesis, Neuchâtel, 1991.

11. J. Vôlk and G. Alefeld in "Topics in Applied Physics" vol 28, Hydrogen in Metals I, Chap. 12, Springer Verlag (Berlin, 1978).
12. X.-M. Tang, J. Weber, Y. Baer and F. Finger, Phys. Rev. **B41**, 7945 (1990) and Phys. Rev. **B42**, 7277 (1990).
13. R. Pretorius, Proceedings of the Symposium on Thin Film Interfaces and Interactions, J.E.E. Baglin and J.M. Poate ed. (The Electrochemical Society, Princeton, 1980).
14. S. Coffa, J.M. Poate, D.C. Jacobson, W. Frank and W. Gustin, Phys. Rev. **B45**, 8355 (1992).
15. G. Ottaviani et al., Thin Solid Films **47**, 187 (1977)
16. N. Cheung, S.S. Lau, M.-A. Nicolet, J. W. Mayer and T.T. Sheng, Proceedings of the Symposium on Thin Film Interfaces and Interactions, J.E.E. Baglin and J.M. Poate ed. (The Electrochemical Society, Princeton, 1980).
17. U. Kroll et al., Mat. Res. Soc. Symp. Proc. Vol **258**, p. 135 (1992).

List of publications:

[1] *Enhancement of hydrogen diffusion in a-Si:H through intense illumination*, O. Greim, J. Weber, X.-M. Tang Y. Baer, U. Kroll, Solid State Commun. 88, 583, (1993).

[2] *Hydrogen diffusion in a-Si:H stimulated by intense illumination*, O. Greim, J. Weber, Y. Baer, U. Kroll, Phys. Rev. B 50, 10644, (1994).

[3] *Influence of intense illumination on dispersive hydrogen diffusion in a-Si:H,* O. Greim, J. Weber, Y. Baer and Y. Ziegler, Solid State Commun. 93, 719, (1995).

[4] *Silicide Ni_2Si formation in a-Si:H*, O. Greim, J. Weber, Y. Baer, U. Kroll, Solid State Commun. 90, 475, (1994).

The complete manuscript, in the form of a PhD thesis, has been deposited at the library of the Physics Institute of the Neuchâtel University.