IMPRIMATUR POUR LA THÈSE

La diffusion de l'hydrogène et la formation de siliciure dans a-Si:H

de Monsieur Xiao-Ming Tang

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 2 septembre 1991

Le doyen :

Cl. Mermod

LA DIFFUSION DE L'HYDROGÈNE ET LA FORMATION DE SILICIURE DANS a-Si:H

Résumé de la thèse presentée à la faculté des Sciences
de l'Université de Neuchâtel pour l'obtention
du grade de docteur ès Sciences
par

Xiao-Ming TANG
diplomé de l'Université d'Ingénieurie Hydraulique
et Électrique de Wuhan
de la République Populaire de Chine

26 mars 1991

Les articles suivant font partie intégrante de cette thèse:

(1). X.-M.Tang, J.Weber, F.Finger and V.Viret "ERA-measurement of the H-concentration in a-Si:H as a function the annealing temperature" Helv. Phys. Acta. 63 (1990) 499

(2). X.-M.Tang, J.Weber, Y.Baer and F.Finger "Hydrogen diffusion in a-Si:H" Solid State Commun. 74 (1990) 171

(3). X.-M.Tang, J.Weber, Y.Baer and F.Finger "Dispersive diffusion of Hydrogen in a-Si:H: Influence of the film deposition temperature" Phys.Rev. B42 (1990) 7945

(4). X.-M.Tang, J.Weber, Y.Baer and F.Finger "Annealing-temperature influence on the dispersive diffusion of Hydrogen in undoped a-Si:H" Phys.Rev. B43 (1990) 7277

(5). X.-M.Tang, J.Weber, Y.Baer and F.Finger "The Dispersive diffusion of Hydrogen in undoped a-Si:H" Physica B.170 (1990) 146

(6). X.-M.Tang, J.Weber, Y.Baer and M.Favre "Silicide formation for Cu on a-Si:H" Helv. Phys. Acta. 62 (1990) 253

Le text complet de la thèse est déposé à l'Institut de Physique, Université de Neuchâtel.

SUMMARY

The influence of the a-Si:H films microstructure and of the annealing temperature on the hydrogen dispersive diffusion, has been systematically studied by the ERDA and RBS methods.

The results of some measurements of silicide formation in metal(Cu, Ni and Cr)/a-Si:H systems are also presented.

1 INTRODUCTION

Il y a quelques années, le silicium amorphe (a-Si) était considéré comme un matériel peu utilisable du point de vue des applications. En effet, produit par sputtering, il avait une grande densité de défauts et donc pas de bonnes propriétés semiconductrices. Puis, la méthode de CVD assisté par plasma, autrement dit la décomposition du gaz silane (SiH_4) dans une décharge luminescente (glow-discharge, GD) a été développée et a permis d'obtenir du silicium amorphe hydrogéné a-Si:H. Ses propriétés, grâce à l'incorporation de l'hydrogène, changent dramatiquement. De plus il peut être dopé de type n ou p. L'application de a-Si:H devient donc une réalité, avec un grand potentiel de possibilités car il peut être produit à relativement peu de frais.

Depuis lors, de très nombreux travaux de recherche expérimentale et théorique ont été effectués sur ce matériau. Un domaine important de recherche tant du point de vue fondamental que des applications des systèmes à base de a-Si:H est celui du rôle de l'hydrogène dans la structure atomique, la structure électronique et les mécanismes de dopage. Les études menées jusqu'à maintenant mettent en évidence d'intéressants phénomènes chimiques et physiques anormaux. Parmi ceux-ci, on peut citer l'effet Staebler-Wronsky (S-W)[1] et la diffusion dispersive de l'hydrogène. Dans l'effet S-W, la photoconductivité ainsi que la conductivité d'obscurité (dark) de a-Si:H diminuent après que l'échantillon ait été illuminé pendant un certain temps. C'est là un état métastable car les caractéristiques originales du matériau peuvent être recrées par un recuit à une température supérieure à 150°C. La plupart des modèles d'explication de l'effet S-W proposés sont basés sur le mouvement de l'hydrogène. La diffusion dispersive de l'hydrogène a été récemment découverte par Street et al. et Kakalios et al. [2,3]. Ils ont observé que la constante de diffusion de l'hydrogène dans a-Si:H décroît selon une loi en puissance de t:

$$D(t) \propto t^{-\alpha}$$

pour une température de recuit constante. Un modèle est proposé [3] par analogie avec celui qui rend compte de la diffusion dispersive électronique.

La localisation et la dynamique de l'hydrogène dans le silicium amorphe est un sujet de recherche important, actuel et poursuivi par d'autres groupes utilisant diverses techniques.

Dans ce travail, nous avons étudié la diffusion de l'hydrogène en utilisant la méthode ERDA (Elastic Recoil Detection Analysis). Les films de a-Si:H ont été préparés par la technique VHF-GD [4,5].

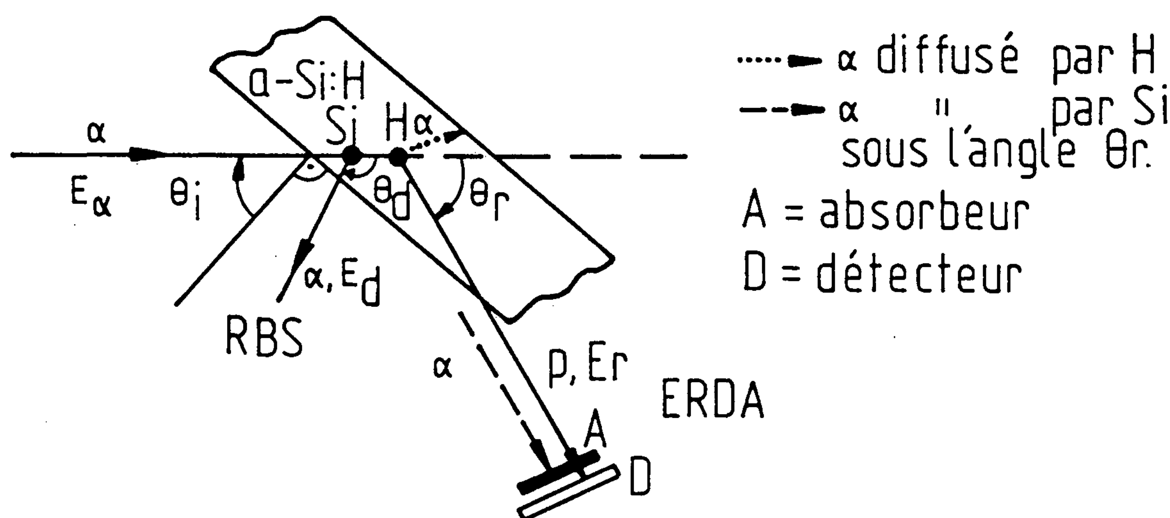
Nous nous sommes intéressés de manière systématique à l'influence de la microstructure des couches et de la température de recuit sur la variation du paramètre de dispersion α.

Nous avons aussi exploré l'influence de l'hydrogène sur la formation de siliciures dans les systèmes Métal/a-Si:H (Métal: Ni,Cu et Cr) en combinant les méthodes RBS et ERDA. RBS permet de déterminer l'épaisseur et la stoechiométrie des couches de siliciure successives tandis que ERDA fournit la concentration d'H dans ces diverses

couches.

La technique ERDA a été développée relativement récemment [6,7]. Elle est basée sur la diffusion élastique d'une particule (par ex. α) par une autre particule plus légère (proton, deuton...). Cette dernière, dite particule de recul, est émise vers l'avant. Si les conditions géométriques sont convenablement choisies, elle peut sortir de l'échantillon. Sa détection devra donner une information sur son énergie. Le taux de diffusion élastique est proportionel à la densité de particule légère. Les particules incidentes et de recul perdent de leur énergie pendant les parcours dans le materiau par chocs inélastiques avec les électrons des atomes du materiau. Donc, le spectre d'énergie des particules recul peut fournir l'information sur la concentration d'atome légère (hydrogène) en profondeur. Notre code RECTRA permet un ajustement du spectre ERDA calculé au spectre expérimental par la méthode de minimalisation du χ^2 [8]. Nous pouvons ainsi obtenir le profil de concentration de H. La technique ERDA est une méthode non destructive et particulièrement bien adaptée à notre accelérateur van de Graaff de 3 MeV.

Fig.1: Technique ERDA



2 DISPOSITIF EXPERIMENTAL

Notre dispositif expérimental est montrée dans le figure 2:

Le faisceau de particules α est fourni par notre accélérateur électrostatique du type van de Graaff (High Voltage Engineering). Le domaine d'énergie se situe entre 0.8 et 3 MeV. La stabilité en énergie est meilleure que 1%.

Le diamètre du faisceau de 0.1 mm est réalisé par un collimateur composé des diaphragmes C_1 à C_4.

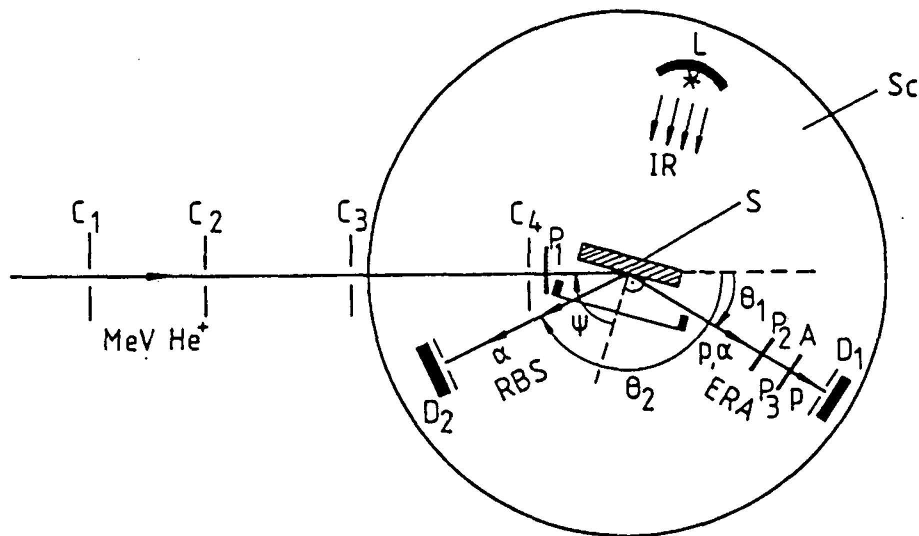
Le porte-échantillon se compose d'une plaque d'Ag pur soudée sur un tube en U en acier inox. Un fluide caloporteur (eau, air comprimé) circulant dans le tube d'acier inox permet de refroidir rapidement l'échantillon après la période de recuit.

La température de l'échantillon est contrôlée par deux thermocouples Fe-Constantant.

Le chauffage de l'échantillon (jusqu'à 600°C) est assuré par une lampe infrarouge à focalisation qui illumine la face arrière du porte-échantillon. Pendant le recuit, la température de l'échantillon est maintenue constante à mieux qu'un degré par un régulateur qui agit sur l'alimentation de la lampe, le signal de référence étant la tension aux bornes d'un des thermocouples.

La chambre à diffusion se compose d'une enceinte à vide poussé (p $\sim 10^{-7}$ Torr). Tous les recuits sont fait sous vide.

Fig.2: Installation expérimentale



Sc : scattering chamber (p~10^{-7} torr)

$C_{1,2,3,4}$: collimater Ø ~ 0.1 mm

S : sample

D1 : ERDA detector

D2 : RBS detector

IR : infrared lamp for " in-situ " annealing

A : Al (10 μm) absorber

3 RESULTATS EXPERIMENTAUX

a). Stabilité de l'hydrogène dans a-Si:H.

La concentration d'hydrogène initiale dans les films de a-Si:H non dopé produits par la méthode VHF-GD, dépend des conditions de la déposition (par ex. température du substrat,Ts). Cette concentration reste stable et uniforme pour des température de recuit de l'échantillon inféfrieures à 300°C. Au voisinage de 300 °C, le processus d'effusion rapide de l'hydrogène faiblement lié a lieu. Il n'est pas limité par la diffusion (voir article 1 et 2), et on l'appel processus NDL (non diffusion limited)

b). Diffusion dispersive de l'hydrogène

Un autre processus intervenant pendant le recuit est celui de diffusion atomique contrôlé par la diffusion, appelé processus DL (diffusion limited). Il est négligeable à basse température (pour des temps de recuit de l'ordre de 30 minutes à quelques heures) mais il devient dominant et mesurable à des températures $T_a > 350$ °C lorsque le film a perdu son hydrogène faiblement lié (processus NDL). Nous avons étudié systématiquement le processus DL et en particulier son caractère dispersif.

Dans notre cas, la concentration de l'hydrogène C(x,t) du film après un recuit de duré t, est donné par:

$$\frac{C-C_s}{C_o-C_s} = erf\left[\frac{x}{2\sqrt{G(t)}}\right]$$

où:

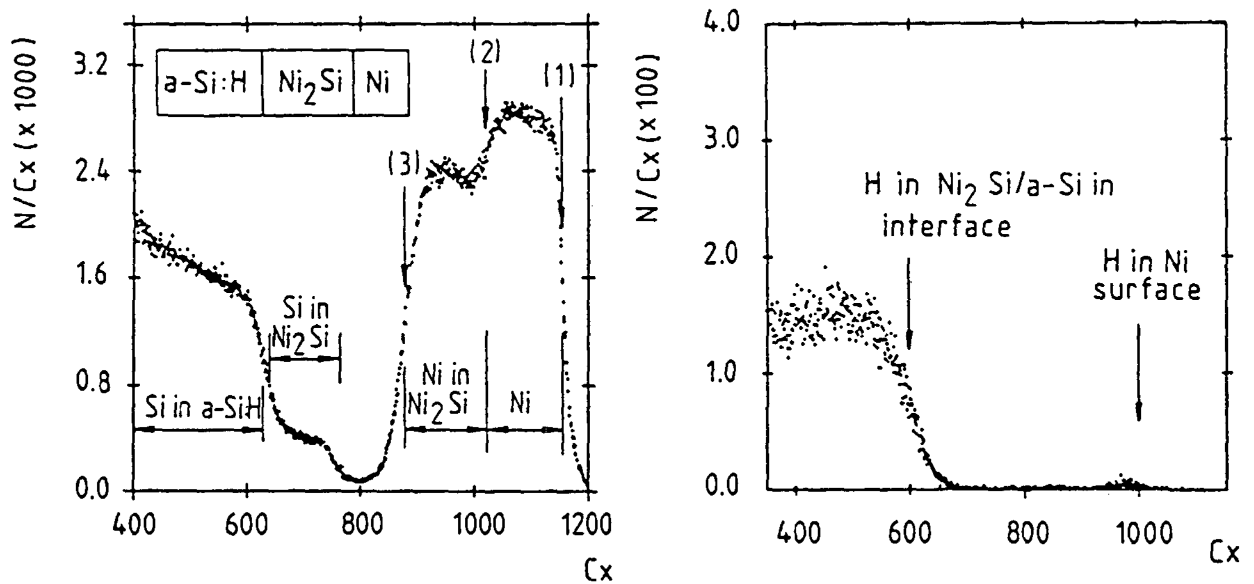
$$G(t) = \int_0^t D(\tau)\, d\tau$$

$$erf(z) = \frac{2}{\sqrt{\Pi}} \int_0^z e^{-u^2} du$$

Co et Cs sont les concentrations à grande profondeur et en surface respectivement.
Pour la diffusion normale, D est indépendant de t, car G(t) = D.t.
Par contre nos résultats expérimentaux montrent que dans a-Si:H:
i) $G(t) = A.t^{1-\alpha}$, autrement dit que $D(t) \propto t^{-\alpha}$, où α est le paramètre de dispersivité à température de recuit Ta constante. α augmente losque la température de déposition Ts diminue, c'est-à-dire losque ΔC, la concentration de l'hydrogène faiblement lié augmente (voir article 3 et 5).
ii) à condition de déposition constante, α augmente lorsque Ta augmente (voir article 4 et 5).
Ce dernier résultat ne peut pas être expliqué par le modèle de " Multiple-Trapping" dans le quel α = 1 - Ta/To où To est une valeur qui caractérise la distribution d'énergie des trappes. Nous avons proposé une explication possible (voir article 4).

c). La formation du siliciure dans les systèmes métal/a-Si:H

De tels systèmes sont utilisés dans certaines applications du a-Si:H. Il est important d'étudier le comportement de l'hydrogène dans la couche métallique simultanément à la formation de siliciure. La combinaison des techniques RBS et ERDA s'adapte bien à cette exigence (voir Fig. 3)



(1) Ni surface
(2) Ni/Ni_2Si interface
(3) Ni_2Si/a-Si:H interface

Fig. 3 : spectres RBS (à gauche) et ERDA obtenus simultanément.
Echantillon: Ni/a-Si:H, T_a=300°C. Durée du recuit t = 15 min.

Nous avons pu faire des études préliminaire de la formation de siliciure et des variation simultanées du profil d' hydrogène lors des recuits successifs de quelques systèmes ME/a-Si:H/c-Si avec ME = Cu, Ni, Cr. Les résultats concernant la formation Cu_4Si sont publiés (voir article 6). Pour le sysème Ni/a-Si:H, nous avons étudié deux séries d'échantillons de Ni/a-Si:H/c-Si pour des températures de déposition de a-Si:H de 50 et 250 °C resp. et des températures T_a de recuit de 270, 295, 300, 330 et 360 °C. C'est le Ni_2Si qui se forme le premier. Quand la couche de Ni est complétement épuisée, commence la formation de NiSi dans l'interface entre Ni_2Si

et a-Si:H. Sa vitesse de croissance est plus faible que celle du Ni_2Si. Ce processus est limité par la diffusion. Par contre, la formation de siliciure de $CrSi_2$, dont le seuil se situe au voisinage de T_a = 380 °C, est contrôlé par la vitesse de la réaction chimique comme dans le cas c-Si [9].

d). Comportement de l'hydrogène dans le substrat a-Si:H, dans les couches de siliciures et les films métalliques:

Dans les systèmes Ni/Ni_2Si/a-Si:H et Ni_2Si/NiSi/a-Si:H, recuits entre 27 et 360°C, la concentration d'hydrogène C_H dans le substrat amorphe ne subit pas de modification contrairement à ce qui se passe dans les couches de a-Si:H vierges d'impuretés métalliques.

Pour les autres systèmes avec Cu ou Cr, les résultats préliminaires ne permettent pas de confirmer cette observation.

Nous n'avons pas observé d'hydrogène dans les couches de Ni et de Ni_2Si des systèmes Ni/a-Si:H et Ni/Ni_2Si/a-Si:H entre 25 et 360°C, cet élément est présent dans le film de Cr des échantillons de Cr/a-Si:H. A 25 °C, C_H = 1 % at. et à 400°C, C_H=0.2 % at.

Le processus NDL consiste en la désorption de l'hydrogène H_2 présent dans les clusters et son effusion le long d'un réseau de "micro-voids" jusqu'à la surface du film de a-Si:H. Une explication possible du fait que nous n'avons pas observé de processus NDL serait que les couches métalliques et de siliciure peuvent interrompre ce réseau. Donc les molécules ne peuvent pas sortir de a-Si:H. Par contre nous pensons que les atomes de H relachés pendant la formation de siliciure restent à l'état atomique et peuvent ainsi diffuser rapidement dans les siliciures et couches métalliques. En effet, les constantes de diffusion de H y sont beaucoup plus grandes que dans a-Si:H. Par ex. D est de l'ordre de 1.10^{-6} $\frac{cm^2}{s}$ dans Ni (T env. 300°C) et dans Cu (T env. 200°C) [10]. C'est 9 ordres de grandeur plus grand que dans le a-Si:H. Ceci peut aussi expliquer pourquoi il n'y a pas d'H dans Ni et Ni_2Si où la solubilité de H est faible.

4 REMERCIEMENTS

Je tiens à exprimer ma profonde reconnaissance au Professeur Y. Baer, directeur de thèse, qui m'a permis d'effectuer ce travail sous sa direction et m'a procuré aide et conseils.

Je tiens aussi à exprimer ma profonde reconnaissance au Dr. J. Weber avec qui j'ai collaboré étroitement et qui m'a constamment donné son aide et des conseils précieux, tout au long de ce travail.

Je remercie Mr. le Professeur A. Shah et le Dr. F. Finger de l'IMT de Neuchâtel pour de fructueuses discussions et pour leur collaboration indispensable en four-

nissant régulièrement les échantillons de a-Si:H.

Je tiens aussi à exprimer ma gratitude au Professeur H. Beck pour les longues discussions qui me furent d'une très grande utilité.

J'exprime aussi ma reconnaissance au Professeur P. Martinoli pour la période fructueuse durant laquelle je travaillais sous sa direction dans le domaine de la physique des basses températures.

5 REFERENCES

(1). Staebler et Wronsky, Appl.Phys.Lett. 31 (1977) 292.

(2). R.A. Street, C.C.Tsai,J.Kakalios and W.Jackson, Philos.Mag. B56 (1987) 305.

(3). J.Kakalios, R.A.Street and W.B.Jackson, Phys.Rev.Lett 59 (1987)1037. W.B.Jackson, Phys.Rev.B38 (1988) 3595. J.Kakalios and W.B.Jackson in Amorphous Silicon and related materials,ed. H.Fritzsche, World Scientific, Singapore 1989,p207.

(4). F.Finger, V.Viret, A.Shah, X.-M. Tang, J.Weber and W.Beyer MRS Sympo. Proc. V192, "Amorphous Silicon Technology-1990", Eds. by P.C.Taylor et al., 583

(5). F.Finger, U.Kroll,V.Viret, A.Shah,W.Beyer,X.-M. Tang,J.Weber, A.Howling and Ch.Hollenstein submited to J. Appl. Phys.

(6). A. Turos et O. Meyer, Nucl. Inst. Meth. B4 (1984) 92.

(7). F.Paszti et al.,Nucl.Inst. Meth. B15 (1986) 486.

(8). P.R.Bevington, Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill 1969.

(9). M.-A. Nicolet et S.S.Lau dans VLSI Electronics:Microstructure Science, Vol.6, Academic Press 1983.

(10). J.Völkl and G.Alefeld in Topics in Applied Physics vol 28, Hydrogen in Metals I, Chap.12, Springer Verlag 1978.

Helv. Phys. Acta
Vol. 63, 1990 Herbsttagung der SPG/SSP

ERA-MEASUREMENT OF THE H-CONCENTRATION IN a-Si:H AS A FUNCTION OF THE ANNEALING TEMPERATURE

X.-M. Tang, J. Weber, Institut de Physique de l'Université,
rue Breguet 1, CH-2000 Neuchâtel
F. Finger, V. Viret, Institut de Microtechnique de l'Université,
rue Breguet 2, CH-2000 Neuchâtel

Abstract : we have measured by the Elastic Recoil Analysis method (ERA) the concentration profiles of hydrogen in amorphous silicon a-Si:H between 25 °C and 500 °C. Up to 280 °C, the H-concentration is constant and uniform in depth. From 280 to 305 ° C there is a fast "H-evaporation". Above 350 ° C, the H-evolution is governed by a diffusion process.

1. Introduction

The hydrogen concentration in amorphous silicon films is known to play an important role in the electronic properties of this material [1]; it should also be important in the silicide formation and/or diffusion processes [2]. From hydrogen evolution studies on undoped a-Si:H films it is concluded [1] that, depending on the preparation conditions and particularly on the substrate temperature Ts, hydrogen "evaporates" from a-Si:H with different rates at temperatures around 300 °C and 600 ° C. Each peak is related to different hydrogen phases [3]. One can expect, for a-Si:H samples prepared at a moderate temperature Ts, two domains of H-concentration: one below and one above 300 °C. One expects also that, in the first domain, the concentration profiles will not depend on the temperature. The purpose of this experiment was to confirm these two domains with respect to the in depth H-concentration profiles.

2. Experimental procedure, data analysis and results

The a-Si:H thin films were prepared by the Silane based VHF-Glow Discharge method (VHF-GD) recently developed [4,5]. Films of about 5 μm thickness were deposited on polished

Si<100> wafers. We have used the Elastic Recoil Analysis (ERA) method to determine the H-concentration profiles. Simultaneously, the He beam current was measured and the scattered α were detected (RBS). The samples were fixed onto a samples holder that could be heated by IR radiation. Samples were annealed for 30 min. at 14 different temperatures between 25 °C and 500 ° C. The measured profiles show that up to 280 °C the H-concentration is uniform in depth and constant. At 305 ° C the concentration has dropped by a few at. % but is still uniform. This situation persists up to 350 ° C. Above 350 ° C, the profiles are no longer uniform, the surface region being the first to be hydrogen depleted. This indicates that the H-evolution is then controlled by a diffusion process in concordance with [1].

3. Aknowledgment

This work has been supported by the FNSRS.

4. References

[1] W. Beyer, in "Tetrahedrally-Bonded Amorphous Semiconductors", D. Adler and H. Fritzscher, eds., Plenum Press, New-York (1985), p. 129.

[2] X.-M. Tang, J. Weber, Y. Baer and M. Favre, Helv. Phys. Acta 62 (1989) 235.

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

[4] H. Curtins, N. Wyrsch and A.V. Shah, Elec. Lett. 23 (1987) 228.

[6] M. Favre, H. Curtins and A.V. Shah, J. Non-Cryst. J. Non-Cryst. Sol. 97/98 (1987) 731.

Solid State Communications, Vol. 74, No. 3, pp. 171-174, 1990.
Printed in Great Britain.

0038-1098/90$3.00+.00
Pergamon Press plc

HYDROGEN DIFFUSION IN a-Si:H *

X.-M. Tang , J. Weber and Y. Baer

Institut de Physique de l'Université, CH-2000 Neuchâtel, Switzerland.

F.Finger

Institut de Microtechnique de l'Université, CH-2000 Neuchâtel, Switzerland.

(Received 24 November 1989 by P. Wachter)

We have measured, by ERA, the hydrogen diffusion constant D_H at 400°C in five undoped a-Si:H/c-Si thin films. The deposition temperatures of these films were successively 50, 100, 150, 200 and 250°C so that the corresponding nominal H-concentrations were ranging from 18 to 11 at.% After having annealed the samples, we have measured the H-concentration profiles which allowed us to determine the diffusion constant D_H. We have found that the higher the deposition temperature, the larger is D_H. We suggest that this behaviour is likely to be attributed to the variation of the cluster concentration in the films.

1. Introduction

The motion of hydrogen in a-Si:H is believed to play an important role in the kinetics of the metastable defects. It has been studied by different authors and with various techniques [1-5]. The results of some experiments [6,7] suggest that there are two different hydrogen environments. In one case it forms clusters of $\equiv Si-H$, $=Si=H_2$ and $-Si\equiv H_3$ groups the size of which is 5-7 H atoms [8]. In the other case it is atomic hydrogen ($\equiv$Si-H) dissolved in the bulk. Beyer et al.[1,2,3] have observed two types of hydrogen behaviour upon heat treatments. The evolution of the atomic hydrogen is driven by a diffusion limited (DL) process and reaches a maximum at 600°C. The evolution of the other hydrogen type is controlled by a non diffusion limited (NDL) process generally attributed to the desorption of molecular hydrogen from the $=Si=H_2$ and $-Si\equiv H_3$ groups followed by a rapid exodiffusion of H_2 through a-Si:H. Using the SIMS technique, Carlson et al. [4] have measured the deuterium profiles after annealing a-Si:H/a-Si:D/a-Si:H samples in the 250 to 400°C temperature range. They have thus determined the activation energy E_a and the prefactor D_o to be respectively 1.5 eV and 1.2×10^{-2} cm^2/s. Street et al. and Kakalios et al. [5,9] have found that the diffusion constant D_H, measured in the same temperature range, is almost three orders of magnitude larger in p-doped a-Si:H than in undoped a-Si:H and that the diffusion constant decreases with the duration of the annealing process (dispersivity). In this paper, we present the results of our ERA (Elastic Recoil Analysis) study of the hydrogen diffusion in undoped a-Si:H films deposited by glow discharge . The ERA method is particularly well suited for this type of experiment since it is not destructive. A succession of annealings of the same sample can thus be made.

* This work has been supported by the SNFSR

2. Experimental

The undoped a-Si:H films (1 to 2 µm thick) were prepared by the Silane based VHF-Glow Discharge (VHF-GD) method [10,11]. During the depositions, the Si<100> backings were kept at a constant temperature T_s which is known [6,8] to influence the hydrogen content and the micro-structure of the films. In order to investigate the diffusion mechanisms as a function of these parameters, we have measured 5 undoped a-Si:H films produced at T_s = 50, 100, 150, 200 and 250°C. Our experimental set up is shown in Fig.1. Both ERA [12] and RBS [13] methods could be used simultaneously. ERA consists in measuring the energy spectrum of the protons which have been elastically hit by incident alphas (from our 3 MeV Van de Graaff electrostatic accelerator) and recoil in the direction defined by θ_1. The energy spectrum is a function of the incident beam intensity, of the H-concentration profile which is to be determined,of the (α,p) cross section $\sigma(E_\alpha, \theta_1)$ [14] and of the energy loss of alphas and protons along their paths in the film [15]. The unknown beam intensity could be measured by detecting the alphas elastically scattered by Silicon nuclei in the direction defined by the angle θ_2. The incident beam current was also measured by the transmission Faraday cup. We have checked our ERA procedure by measuring the H-concentration profile of a hydrogen standard. Annealings could be made in situ by means of the IR lamp. The annealing temperature could be kept constant within ± 2°C and could be reached in less than 60 s. At the end of the annealing period, the sample was cooled down in less than 60 s by air flow in the sample holder.Thus, successive annealing cycles (at the same temperature) of the same sample could be done.

The ERA energy spectrum of each sample was first measured in order to determine (see sect.3) the nominal H-concentration profiles. They were found to be uniform. Each sample was then annealed at 400°C for 30 min. and the energy spectrum measured. Note that during this

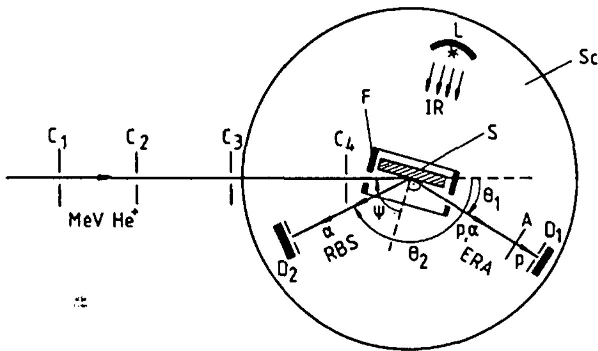


Fig. 1: The experimental set-up. C_1 to C_4: beam collimator (He beam dia. 0.2 mm); Sc: scattering chamber for ERA and RBS, $p = 10^{-7}$ torr; S: sample; F: transmission faraday cup; L: IR lamp; $\psi = 75°$, $\theta_1 = 19°$ and $\theta_2 = 150°$; D_1 and D_2 :Si surface barrier detectors. A: Al absorber (10 μm).

heat treatment above 300°C, hydrogen evaporates very rapidly from the H-clusters by NDL process so that the hydrogen content of the film is lowered. The effusion of the remaining hydrogen is then limited by diffusion so that the H-concentration will be depleted firstly in the sample surface [16].

3. Analysis and Results.

In order to obtain the concentration profile from the proton energy spectrum it is necessary to fit a computed energy spectrum to the experimental one. We did the computations through our RESTCA code which subdivides the film thickness in up to 250 distinct thin slabs, each one having its own chemical composition (up to ten different elements). This code includes in particular: the stopping cross sections [15], the instrumental resolution (15 to 20 keV), the energy straggling [13], the (α ,p) cross section [14], the incident alpha beam intensity and the H-concentration profile H(x) given by (1) which is the solution of the diffusion equation corresponding to our experimental conditions [17]:

$$C_H(X) = C_0 . \mathrm{erf} \left[\frac{x}{2\sqrt{D_H . t}} \right] \qquad (1)$$

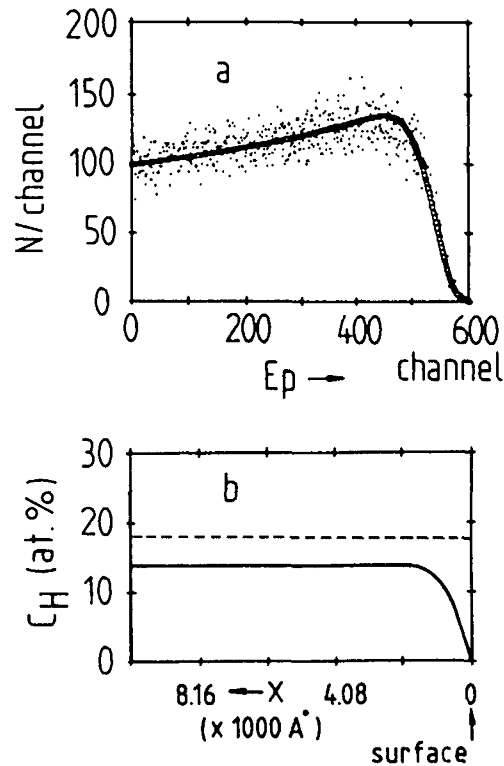


Fig. 2: a) the experimental (•) and computed (□) ERA spectra of sample ASiH50, after annealing at 400°C for 30 min. $E(He^+) = 2.9$ MeV. b) the fitted H-concentration profile C(x) (—). Also shown is the nominal concentration profile (---).

where $C_H(x)$ is the H-concentration in function of the depth x, t is the annealing time and D_H is the diffusion constant. The prefactor C_o is the homogeneous H-concentration at large x value. (The assumed film density was 4.9×10^{22} at./cm^3 [18]). The beam intensity was obtained separately by analysing the corresponding RBS alpha-energy spectra (the Si(α,α)Si cross section is known to be of the Rutherford type in our energy range). The parameter C_o was

Table 1: T_s: the film deposition temperature; C_{H_0}: the nominal H-concentration; C_D: the H-concentration at large depth after annealing at 400°C for 30'; D_H: the H-diffusion constant; C_{ND} : the H-concentration (NDL process) ($C_{H_0} - C_D$).

Sample	T_s °C	C_{H_0} at.%	C_D at.%	C_{ND} at.%	D cm^2/s
ASiH50	50	17.7	13.3	4.4	1.3×10^{-14}
ASiH100	100	17.4	13.9	3.5	1.5
ASiH150	150	16.0	12.3	3.7	1.8
ASiH200	200	13.8	12.4	1.4	1.9
ASiH250	250	11.5	11.1	0.4	2.5

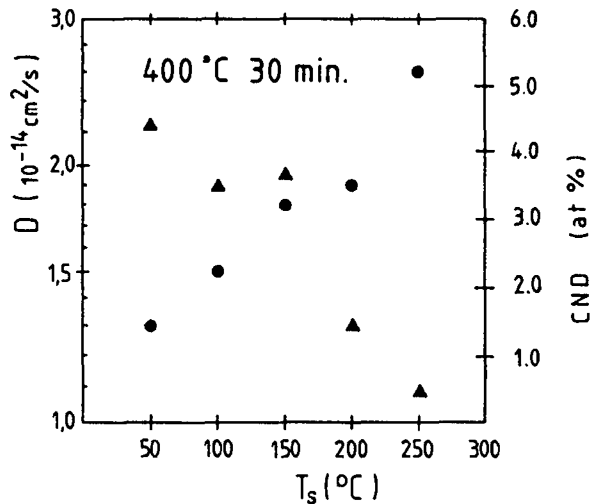


Fig. 3: The H-diffusion constant D_H (•) and the hydrogen concentration C_{ND} (▲) (NDL process) in function of the deposition temperature T_s.

obtained by fitting the computed spectra to the experimental ones at large depth and the diffusion constant D_H by fitting in the surface region. Fig.2a shows the experimental and computed energy spectra (sample ASiH50) and Fig.2b shows the resulting H-concentration profile as computed by formula (1) with the relevant parameters C_0 and D_H ; also shown in this figure is the nominal H-concentration profile which is uniform (C_{H_0}).

The results are the following: the nominal hydrogen concentrations of our five samples were constant throughout the studied depth (1 µm). Their values are listed in column C_{H_0} of Table 1. In this table, C_D is the parameter C_0 of formula (1) for the 400°C annealed samples that is the concentration, at large depth, of the hydrogen participating to the DL process. D_H is the fitted diffusion constant and C_{ND} is the concentration of the evaporated hydrogen during the NDL process ($C_{ND} = C_{H_0} - C_D$)

In Fig.3, D_H and C_{ND} are plotted versus the deposition temperature T_s. The order of magnitude of D_H agrees with the value obtained by Carlson et al. [4]. However one should note that our experiment shows that D_H is a function of T_s (the lower the temperature T_s the lower the diffusion constant D_H) and that the concentration C_{ND} decreases with T_s. This is discussed further in sect. 4.

4. Discussion and conclusion

As explained in section 1, two types of hydrogen exist in a-Si:H : the fast NDL effusion type of hydrogen bound as =Si=H2 and -Si≡H3 in the clusters (initial concentration C_{ND}) which is easily eliminated by a fast effusion mode [19,20] and atomic hydrogen with an initial concentration C_D which is modified by diffusion in the annealing procedures. The H-concentration C_{ND} is reduced by a factor 0.1 when the deposition temperature of the films is increased from 50 to 250°C whereas C_D is only reduced by a factor of 0.83. The first type of hydrogen is very quickly released in heat treatment at 400°C. Since the content of clusters in the film is directly related to the concentration C_{ND} of the fast effusion type hydrogen [21-23], the differences of the diffusion constant D_H in the samples prepared at various T_s can be unambiguously attributed to the variation of the cluster concentration. Fig.3 demonstrates the correlation of D_H with C_{ND} as a function of the deposition temperature T_s of the films. The clusters appear to hinder the diffusion process of atomic hydrogen. Qualitatively, on can anticipate the following mechanism: during annealing, the NDL effusion leaves dangling bonds in the clusters which become more efficient traps for the migrating atomic hydrogen so that an increase of the diffusion constant D_H is observed when a raise of T_s lowers the concentration C_{ND}.

In conclusion, we have shown that ERA is a powerful and non-destructive method allowing us to investigate the different types of hydrogen in a-Si:H. In undoped films prepared by glow discharge we have shown that the diffusion of atomic hydrogen decreases when the concentration of trapping clusters is raised by a lowering of the deposition temperature. Another challenging consequence of the presence of clusters in a-Si:H is the dispersive diffusion of hydrogen [5,9]. Our preliminary results of measurements of D_H in function of the duration of the annealings at 400°C provide the first indication of this phenomenon in undoped a-Si:H. More detailed experimental work and calculations are under way on this subject.

Acknowledgement - We thank L. Schlapbach (University of Fribourg) for the hydrogen standard.

REFERENCES

1 W. Beyer and H. Wagner, J. Phys. Colloq. (Paris), V42, C4, (1981) 783
2 W. Beyer and H. Wagner, J. Appl. Phys. 53 (1982) 8745
3 W. Beyer in "Tetrahedrally-Bonded Amorphous semiconductors" D.Adler and H. Fritzsche eds., Plenum Press N.-Y. 1985 p.129
4 D. E. Carlson and C. W. Magee, Appl. Phys. Lett. 33 (1978) 81
5 R. A. Street, C. C. Tsai, J. Kakalios and W. B. Jackson, Phil. Mag. 56 (1987) 305
6 J. A. Reimer, R. W. Vaughan and J. C. Knights, Phys. Rev. Lett. 44 (1980) 193
7 G. Lucovsky, R. J. Nemanich and J. C. Knights, Phys. Rev. B19 (1979) 2064
8 K. K. Gleason, M. A. Petrich and J. A. Reimer, Phys. Rev. B36 (1987) 3259
9 J. Kakalios, R. A. Street and E. B. Jackson, Phys. Rev. Lett. 59 (1987) 1037
10 H. Curtins, N. Wyrsch and A. V. Shah Elec. Lett. 23 (1987) 228

11 M. Favre, H. Curtins and A. V. Shah, Non-Cryst. Sol. **97/98** (1987) 731
12 F. Paszti, E. Koti, G. Mezey, A. Manuaba, L. Pocs, D. Hildebrandt and H. Strusny, Nucl. Inst. Meth in Phys. Res. **B15** (1986) 486
13 W. K. Chu, J. W. Mayer and M.-A. Nicolet, Rutherford Backscattering Spectrometry, Academic Press 1978.
14 H. Wang and G. Q. Zhou, Nucl. Inst. Meth. in Phys. Res. **B34** (1988) 145.
15 J. F. Ziegler and H. H. Andersen, The Stopping and Ranges of ions in matter, vol. 3 and 4, Pergamon Press 1977.
16 X. M. Tang, J. Weber and F. Finger To be published in Helv. Phys. Acta
17 J. Philibert "Diffusion et transport de matière dans les solides", Les éditions de physique, Les Ulis, France, 1986.
18 K. Kubota et al., Nucl. Inst. Meth. **168** (1980) 211.
19 T. Sakurai and H. D. Hagstrum Phys. Rev. **B14** (1976) 1593
20 P. John , B. C. Cowie and I. M. Odeh Phil. Mag. **B49** (1984) 559
21 J. C. Knights and M. J. Thompson in "The physics of hydrogenated amorphous Silicon", J. D. Ivannopoulos and G. Lucovsky eds. Springer Verlag NY 1984, Chap. 2 and 4.
22 D.K. Biegelsen, R.A. Street, C. C. Tsai and J. C. Knights, Phys. Rev. **B20** (1979) 4839.
23 T. Sakka, K. Toyota and M. Iwasaki, Appl. Phys. Lett. **55** (1989) 1068

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 11 15 APRIL 1990-I

Dispersive diffusion of hydrogen in *a*-Si:H: Influence of the film deposition temperature

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

F. Finger
Institut de Microtechnique de l'Université, CH-2000 Neuchâtel, Switzerland

(Received 23 January 1990)

We have measured by the method of elastic-recoil detection analysis the dispersion parameter a of hydrogen diffusion in undoped *a*-Si:H. We find that a lowering of the deposition temperature of the films increases the value of a. This variation can also be clearly correlated with the increase of the initial concentration of weakly bound hydrogen, which is expected to reflect the disorder of the microstructure. These results will certainly contribute to the elucidation of the dispersive character of the diffusion of hydrogen in the different types of amorphous silicon.

The motion of hydrogen in hydrogenated amorphous silicon (*a*-Si:H) has been studied by many authors with different techniques.[1-7] The results of thin-film experiments[8-10] suggest that hydrogen is found in $\equiv$Si$-$H, $=$Si$=H_2$, and $-$Si$\equiv H_3$ groups forming clusters with 5-7 H atoms, or as $\equiv$Si$-$H uniformly distributed in the bulk. The ratio of clustered and isolated hydrogen atoms varies with the deposition method and the processing conditions. A recent study[8] shows that the substrate temperature T_S and/or the hydrogen content during the film deposition control the microstructure and the density of the film: the lower T_S, the higher the cluster concentration. However, the mean number of hydrogen atoms in the clusters remains constant. Two different mechanisms have been found in the evolution of the hydrogen concentration.[2] For atomic hydrogen, this evolution is driven by a diffusion-limited (DL) process that reaches a maximum at 600 °C. For the clustered hydrogen, it is controlled by a non-diffusion-limited (NDL) process involving the desorption of molecular hydrogen H_2 from the clustered $=$Si$=H_2$ and $-$Si$\equiv H_3$, followed by a rapid exodiffusion of H_2 through a void network in *a*-Si:H.

The dispersive character of the atomic hydrogen diffusion was found by Street *et al.*[3] and Kakalios *et al.*[4] in doped *a*-Si:H/*a*-Si:D/*a*-Si:H multilayers produced by glow discharge (GD). By using the secondary-ion-mass spectroscopy (SIMS) method they have observed that the diffusion constant D is a function of the time t of the form $D(t) \sim t^{-a}$. a is defined as the dispersion parameter. In the "hydrogen-glass" model of Jackson and coworkers[4,11,12] this relation is expressed as

$$D(t) = D_{00}(\omega t)^{-a}, \quad (1)$$

where D_{00} is the microscopic diffusion constant and ω is the H attempt frequency. In this model the dispersion parameter depends on the annealing temperature T and on the width $k_B T_0$ of the trap distribution in the following manner: $a = 1 - (T/T_0)$. Very recently Shinar *et al.*[5] also have studied by SIMS undoped rf-sputtered *a*-Si:H/(*a*-Si:D or *a*-Si:H:D)/*a*-Si:H multilayers. They have observed a dispersive diffusion of hydrogen corresponding to $a = 0.75$ which is much larger than the value of 0.2 obtained by Kakalios *et al.*[4]

In our previous study of undoped *a*-Si:H films,[6,7] we have observed that an annealing above 300 °C induces an uniform drop of the H concentration resulting from the fast NDL transport process and that the diffusion constant of atomic H increases with the deposition temperature of the films. So far, a clear correlation between the preparation conditions determining the microstructure of the film and the amplitude of the dispersion in the transport of atomic hydrogen has never been demonstrated. In this Rapid Communication, we show that for *a*-Si:H prepared by glow discharge, the dispersion parameter depends unambiguously on the substrate temperature T_S during the film deposition and/or on the initial concentration of clustered hydrogen.

Undoped *a*-Si:H samples were prepared by the silane-based VHF-glow-discharge method.[13,14] The *a*-Si:H films (1-2 μm thick) were deposited on Si(100) wafers kept at the different temperatures $T_S = 50$, 100, 150, 200, and 250 °C. The H concentration profiles were measured before and after the annealing periods at 400 °C by the method of elastic-recoil detection analysis (ERDA).[15] The ERDA method consists in measuring the energy spectrum of protons which have been elastically hit by the incident α-particles produced by our Van de Graaff accelerator and recoil in the forward direction. The proton energy spectrum is a function, in particular, of the H-concentration profile to be determined and of the α-beam intensity, which is obtained from the Si signal measured simultaneously by the Rutherford backscattering spectroscopy (RBS). The experimental setup is described elsewhere in detail.[6] When compared to SIMS, ERDA has the advantage of being nondestructive so that the evolution of the H concentration can be measured on the same sample after the different heat treatments. The annealings could be made *in situ*, the time required for the temperature changes being of the order of 1 min, which is short compared to the annealing periods ($\geq$ 30 min).

Despite the fact that the hydrogen diffusion constant $D(t)$ is time dependent, the hydrogen concentration profile $C(x,t)$ in the annealed *a*-Si:H films can still be de-

 © 1990 The American Physical Society

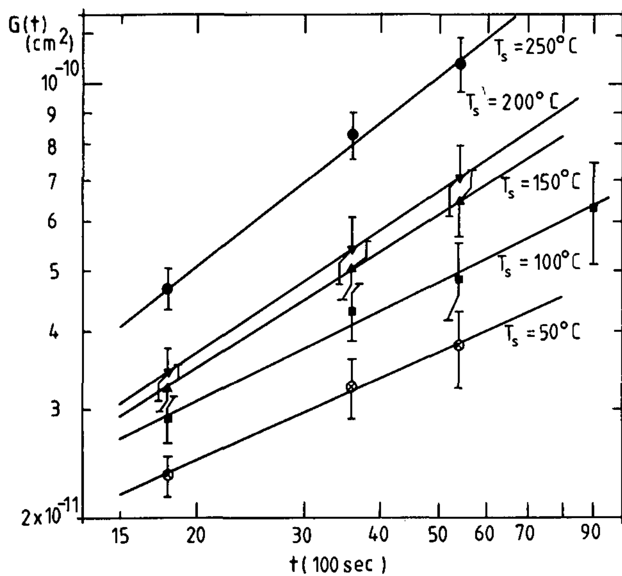


FIG. 1. $G(t,T_S)$ of Eq. (2) vs the annealing time t. The error bars are estimated from the quality of the fit of the computed ERDA spectrum. T_S is the sample deposition temperature. The lines are linear fits to the data.

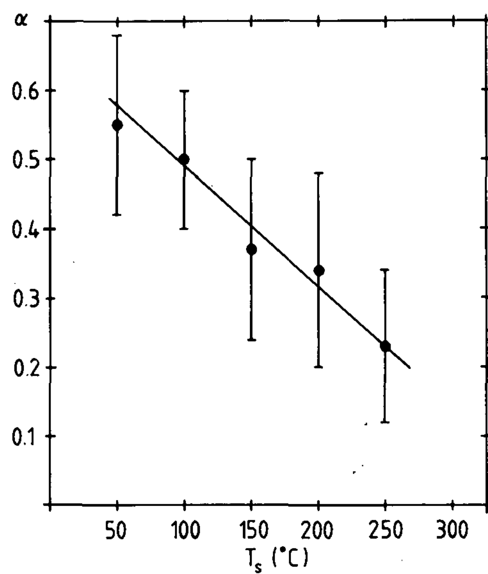


FIG. 2. Dispersion parameter α vs deposition temperature T_S. (The line is only a guide to the eye.)

scribed by an error function:[16]

$$C(x,t)=C_0 \operatorname{erf}\frac{x}{2\sqrt{G(t)}}, \tag{2}$$

where t is the annealing time and

$$G(t)=\int_0^t D(\tau)d\tau. \tag{3}$$

The prefactor C_0 is the H concentration at large depth which remains constant in the range of our annealing times.[6] C_0 and $G(t)$ are determined by fitting $C(x,t)$ to the proton spectra recorded after the different annealing periods. Details of this procedure through our reconstruction code RETSCA and one example can be found in Ref. 6. If we assume that the diffusion constant has the time dependence given by Eq. (1), one obtains immediately from Eq. (3) the following relation: $G(t)=D_{00}\times\omega^{-\alpha}t^{1-\alpha}/(1-\alpha)$. The double logarithmic plot of G vs t shown in Fig. 1 provides the experimental demonstration of this functional form of $G(t)$. It yields the dispersion parameter α from the slope $(1-\alpha)$ and the constant term $D_{00}\omega^{-\alpha}$ from the extrapolation to $t=1$. The different values of the diffusion constant are listed in Table I. A new issue of this study is that α appears to decrease systematically when the deposition temperature T_S of the film is raised. As shown in Fig. 2, this dependence is important but the uncertainty of the experimental values does not allow us to extract its precise form.

The temperature T_S controls the microstructure of the films which can be indirectly characterized by ERDA measurements. After the first heat treatment at 400 °C, the concentration C_0 at great depth remains practically constant within the experimental uncertainty and does not show an important spread among the different samples (see Table I). The nominal hydrogen concentration C_{00} measured before any annealing process includes this atomic hydrogen concentration C_0 and the loosely bound hydrogen concentration $\Delta C=C_{00}-C_0$ which is quickly released from the clusters before the diffusion measurements. Therefore, we can assume that ΔC is proportional to the initial cluster concentration and can be considered as a qualitative measure of the disorder of the films. The values listed in Table I show that ΔC increases when T_S is lowered. This means that the formation of traps is favored and that the width of their distribution is likely to be enlarged. Within the model of Kakalios and Jackson,[4,11] one can simply relate α to the characteristic temperature T_0 which has been calculated at our annealing temperature of 400 °C for the different samples (see Table I).

TABLE I. Summary of the results. T_S, sample deposition temperature; C_{00}, initial hydrogen concentration; C_0 hydrogen concentration at large depth [Eq. (2)]; $\Delta C=C_{00}-C_0$, loosely bound hydrogen concentration; α, dispersion parameter; $D(t)$, mean hydrogen diffusion constant during the annealing period t; T_0, characteristic temperature in the relation $\alpha=1-T/T_0$ (Ref. 4).

Sample number	T_S (°C)	C_{00} (at.%)	C_0 (at.%)	ΔC (at.%)	α	D(30 min) (10^{-14} cm²/s)	D(60 min) (10^{-14} cm²/s)	D(90 min) (10^{-14} cm²/s)	T_0 (K)
1	50	17.7	12.6	5.1	0.55	0.59	0.41	0.32	1500
2	100	17.0	12.4	4.6	0.50	0.80	0.60	0.45	1350
3	150	16.0	11.8	4.2	0.37	1.13	0.88	0.76	1070
4	200	13.8	12.2	1.6	0.34	1.25	0.99	0.86	1020
5	250	11.5	11.1	0.4	0.23	2.00	1.77	1.54	870

It is interesting to consider the variation of α as a function of ΔC shown in Fig. 3. These two quantities are clearly correlated so that we obtain a confirmation that the density and/or the depth of the traps associated with the sites left by the weakly bound hydrogen (clusters, microvoids)[8,17,18] are strongly influencing the dispersive mechanism. One has to remember that in all samples, the remaining concentration of atomic hydrogen involved in the diffusion is practically the same.

Shinar *et al.*[5] have obtained $\alpha = 0.75 \pm 0.15$ from measurements of undoped rf-sputtered *a*-Si:H films (with C_{00} between 17 and 19 at.%) annealed in the temperature range of 275–375 °C. Their values of ΔC lie between 5.5 and 5.8 at.% (samples 27 and 29 of Ref. 5) so that these results are in good agreement with ours. Street *et al.*[3] and Kakalios *et al.*[4] have studied *p*-doped GD *a*-Si:H films deposited at 150 °C and annealed at 200 °C. They have obtained $\alpha = 0.2$. Furthermore, in these doped samples, they measure a diffusion constant 3 orders of magnitude larger than in undoped materials.[3] One should note that in our measurements (and those of Shinar *et al.*), the annealing temperature was higher than in the measurements of Kakalios *et al.* At 200 °C there is practically no evolution of the loosely bound hydrogen which is released only above about 300 °C (Refs. 2, 6, and 7). This process results in the modification of the film microstructure which, we believe, consists in an increase (proportional to the original cluster and microvoids concentrations) of the density of traps and/or of their depth. This might explain the relatively large α values obtained by us and by Shinar *et al.* Another possible contribution to these differences is the influence of the B doping on the microstructure[8] or on the position of the Fermi level in the hydrogen diffusion.[19]

In addition to its nondestructive character, the ERDA method provides the advantage that in such diffusion studies, the hydrogen profile can be directly measured, avoiding the use of deuterium in multiple-layer films[4,5] and, therefore, eliminating the possible uncertainty arising from the larger size of deuterium. Our results yield a direct experimental demonstration that the dispersive diffusion of H in *a*-Si:H depends strongly on the particular preparation conditions of the films which determine, in a wide range, the concentrations and types of defects responsible for this phenomenon. This aspect as well as the influence of the annealing temperature on α will have to be taken carefully into consideration in further experimental studies and comparisons between measurements and theoretical models.

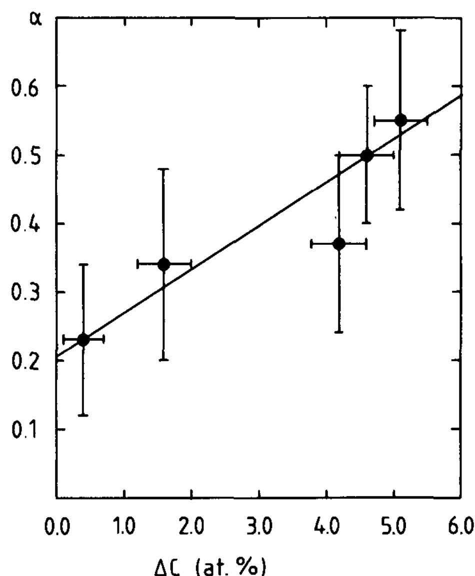


FIG. 3. Dispersion parameter vs the concentration of loosely bound hydrogen ΔC. (The line is only a guide to the eye.)

The Swiss National Science Foundation is gratefully acknowledged for financial support.

[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, Solid State Commun. (to be published).

[7] X.-M. Tang, J. Weber, and F. Finger, Helv. Phys. Acta. (to be published).

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

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

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

[11] W. B. Jackson, Phys. Rev. B **38**, 3595 (1988).

[12] J. Kakalios and W. B. Jackson, in *Amorphous Silicon and Related Materials*, edited by H. Fritzsche (World-Scientific, Singapore, 1989), p. 207.

[13] H. Curtins, N. Wyrsch, and A. V. Shah, Electron. Lett. **23**, 228 (1987).

[14] M. Favre, H. Curtins, and A. V. Shah, J. Non-Cryst. Solids **97/98**, 731 (1987).

[15] F. Paszti, E. Kóti, G. Mezey, A. Manuaba, L. Pócs, D. Hildebrandt, and H. Strusny, Nucl. Instrum. Methods Phys. Res. Sect. B **15**, 486 (1986).

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

[17] D. L. Williamson, A. H. Mahan, B. P. Nelson, and E. S. Crandall, Appl. Phys. Lett. **55**, 783 (1989).

[18] A. H. Mahan, D. L. Williamson, B. P. Nelson, and R. S. Crandall, Phys. Rev. B **40**, 12024 (1989).

[19] W. Beyer, J. Herion, and H. Wagner, in *Proceedings of the Fourth International Photovoltaic Science and Engineering Conference, Sydney, 1989* (The Institution of Radio and Engineers, Edgecliff, Australia, 1989), Vol. 1, p. 255.

PHYSICAL REVIEW B VOLUME 42, NUMBER 11 15 OCTOBER 1990-I

Annealing-temperature influence on the dispersive diffusion of hydrogen in undoped a-Si:H

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

F. Finger
Institut de Microtechnique de l'Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland

(Received 18 July 1990)

We have measured by the method of elastic-recoil detection analysis the variation of the dispersion parameter α of hydrogen diffusion in undoped a-Si:H as a function of the annealing temperature T_a between 350 and 470 °C. We found that α increases with T_a. We suggest a mechanism which can explain this result, as well as the variation of α with the film-deposition temperature reported earlier.

The hydrogen transport behavior in hydrogenated amorphous silicon (a-Si:H) has been extensively studied in the last few years. In particular, two different hydrogen evolution mechanisms have been observed.[1,2] The first one is the non-diffusion-limited (NDL) evolution process (maximum rate near 300 °C). The second one is the diffusion-limited (DL) process (maximum rate near 600 °C). Generally, the dispersion in transport processes (i.e., the diffusion coefficient D is a function of t, the annealing time) occurs whenever there is an energy distribution of traps and/or a random distribution of hopping-site separations.[3]

The dispersive diffusion of hydrogen was first reported by Street *et al.*[4] and by Kakalios, Street, and Jackson[5] in p-type a-Si:H/a-Si:D/a-Si:H multilayers produced by glow discharge (GD). They found that the diffusion constant D decreases with the annealing time t according to a power-law dependence form: $D(t) \sim t^{-\alpha}$, where α, the dispersion parameter, was determined to be ≈ 0.2 for an annealing temperature $T_a = 200$ °C. Nearly two years later, Shinar *et al.*[6] published their results on the hydrogen dispersive diffusion in undoped rf-sputtered a-Si:H multilayers. The value they obtained for the dispersion parameter α was 0.75. The H concentration in the film was high and the annealing temperatures were in the 275–355 °C range.

In the hydrogen glass model proposed by Jackson and collaborators,[7,8] the diffusion constant D is expressed as

$$D(t) = D_{00}(\omega t)^{-\alpha}, \tag{1}$$

where D_{00} is the microscopic diffusion constant, ω is the attempt frequency of H atoms to escape the traps, and α the dispersion parameter which is given by

$$\alpha = 1 - T_a/T_0, \tag{2}$$

where T_a is the annealing temperature. kT_0 is the characteristic energy width of the exponential energy distribution of traps for diffusing H atoms. This distribution is responsible for the dispersion.

Recently, we have systematically studied the dependence of α on the deposition temperature T_s of undoped a-Si:H films produced by glow discharge.[9] We have found that a lowering of T_s from 250 to 50 °C increases the value of α from 0.23 to 0.55 for a fixed annealing temperature $T_a = 400$ °C. This variation was clearly correlated with the increase from 0.4% to 5.1% of the initial concentration of the NDL hydrogen which, in turn, is expected to be related to the disorder of the a-Si:H microstructure. We have suggested that annealing at temperatures T_a higher than T_{NDL} (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 this paper, we present measurements of the dispersion parameter α as a function of the annealing temperature T_a and propose a description of the nature of the traps and of their evolution with the deposition and the annealing temperatures. The samples were prepared by the silane-based very-high-frequency (VHF) -glow-discharge method.[10,11] The a-Si:H films (1–2 μm thick) were deposited onto Si(100) wafers kept at the temperature $T_s = 150$ °C. We have used the elastic-recoil detection analysis (ERDA) method to measure the hydrogen concentration profiles[12] at different annealing temperatures and annealing times. This method is particularly suitable to the large number of needed measurements (about 25 in this case) since it is not destructive and allows us to perform successive annealings on the same sample. ERDA consists in measuring the energy spectrum of protons which have been elastically hit by incident MeV α particles produced by our van de Graaff accelerator and recoil in the forward direction. The annealings could be made in the scattering chamber. The time required for the temperature changes was of the order of 1 min which is short compared with the annealing periods (> 30 min).

Proton energy spectra were computed through our RETSCA code and fitted by χ^2 minimalization to experimental spectra in order to obtain the hydrogen concentration depth profiles and the value of the dispersion parameter. The experimental setup and the data analysis method are described in detail elsewhere.[2] Figure 1 shows a plot of the dispersion parameter α versus the annealing temperature T_a in the range 350 to 470 °C. It is seen that α increases with T_a. It should be noted that, nevertheless, the diffusion coefficient D_L increases with T_a as shown in

 © 1990 The American Physical Society

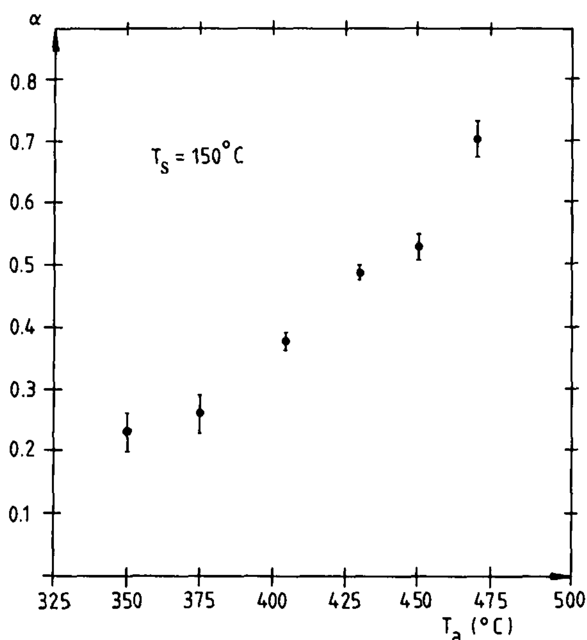


FIG. 1. Dispersion parameter α vs the annealing temperature T_a. The error bars are computed by means of the $\Delta\chi^2=1$ procedure.

TABLE I: Summary of the results. T_a, annealing temperature; α, dispersion parameter; ΔC, NDL hydrogen concentration; T_0, characteristic temperature [Eq. (2)]; D_L, diffusion coefficient computed according to Ref. 7 for a diffusion length $L=1000$ Å.

T_a (°C)	α	ΔC (at.%)	T_0 (K)	D_L (10^{-15} cm^2/s)
470	0.75	4.9	2560	160.0
450	0.53	5.4	1540	59.0
425	0.49	5.3	1370	8.7
400	0.38	4.9	1090	3.2
375	0.26	5.1	880	2.9
350	0.23	3.8	810	1.3

Table I where we summarize our results. In this table, T_0 is computed from Eq. (2); ΔC is the concentration of the hydrogen released by the NDL process which remains practically constant (about 5%) except for the somewhat smaller value at $T=350$ °C; D_L is the diffusion coefficient computed, as in Ref. 7, for a diffusion length $L=1000$ Å.

The increase of the dispersion parameter α implies a modification of the energy and/or of the spatial distribution of the traps. According to Reimer and coworkers,[13,14] the hydrogen of a-Si:H occurs as Si—H in the dilute phase and as Si—H, and Si$=$H$_2$ groups in the clustered phase. The hydrogen clusters can be thought of as a collection of H atoms decorating the inner wall of microvoids. Their size is fairly small with 5-7 atoms and it remains constant as a function of the initial hydrogen concentration. As generally found for a-Si:H prepared by GD from SiH$_4$, the lowering of the deposition temperature T_s increases the initial hydrogen concentration so that a high cluster concentration is expected at low T_s. The NDL evolution of hydrogen is generally attributed to the desorption of molecular hydrogen from the —Si—H and —Si$=$H$_2$ groups of the hydrogen clusters, followed by a rapid exodiffusion through a percolation network of the hydrogen cluster interconnections.[1] We argue that these interconnections are interrupted and disappear during the NDL evolution.

This process should result in an increase of the dangling-bond (DB) density comparable to ΔC which is of the order of 10^{21} cm^{-3}. The comparison of this number with electron-spin-resonance (ESR) results[15] suggests that there is a reconstruction process occurring after the release of the NDL hydrogen so that Si—Si weak bonds (WB) are formed (e.g., stretched Si—Si bonds or modified angle of the Si—Si bonds). On the other hand, one can expect that during the annealing, especially above 300 °C, DB are thermally generated by breaking of WB (a mechanism occurring also in the bulk but at a much lower rate). The distribution of DB and WB depends on the competition between these generation and reconstruction processes so that one observes the equilibrium concentration realized at the annealing temperature.[16] Because the NDL hydrogen evolution is related to Si—H and Si$=$H$_2$ groups present in the clusters, we suggest that the DB are mostly present in the cluster sites and the WB mostly around these sites and that the cluster sites act as trapping centers (TC). The isolated DB (in the bulk) can also trap H atoms but with a capture radius much smaller than the one of the clusters enriched with DB and WB. The TC density is proportional to the cluster density and, therefore, is controlled by the deposition conditions, as, for example, the substrate temperature T_s. On the other hand, the TC local structure is determined by the annealing temperature T_a. In addition, one can expect that the clusters influence locally the structure of the bulk in such a way that a change of their density modifies the DB and WB energy distribution. The hydrogen dispersive diffusion picture may then be as follows: The excited hydrogen atoms diffuse interstitially through the Si lattice. When they are near a cluster site rich in DB and WB, their motion is delayed by the trapping and escape mechanisms. This delay is determined by the DB and WB energy distribution and density. Thus, the dispersion of the hydrogen diffusion depends on the hydrogen cluster density and structure.

By some aspects this picture is similar to the "hydrogen mediated model" of Zafar and Schiff[17] but, in addition, it explains why the dispersion parameter α increases with the annealing temperature T_a which controls the competing mechanisms of trap production and reconstruction. When T_a rises, the defects (DB and WB) thermal generation is enhanced so that the trap density and depth increase. The hydrogen diffusion is thus more dispersive and α increases as shown by our measurements (Fig. 1).

Finally, the increase of T_0 (Table I) is also explained: When the annealing temperature T_a is raised, the defects thermal generation process is enhanced and the proportion of DB and the highly stretched WB increases. Therefore,

if the energy distribution of the traps (DB and WB) is exponential in and around the clusters, we can expect that its characteristic energy width kT_0 becomes larger.

In conclusion, we have measured the variation of the dispersion parameter α as a function of the annealing temperature. In the range 350 to 470 °C, α increases with T_a. A mechanism is proposed that explains the variation of the dispersion parameter α with the film deposition and annealing temperatures.

The Swiss National Science Foundation is gratefully acknowledged for financial support. One of us (F.F.) acknowledges the support of Swiss Federal Research Grant No. OFEN-EF-REN-87-90.

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

[2] X.-M. Tang, J. Weber, Y. Baer, and F. Finger, Solid State Commun. **74**, 171 (1990).

[3] T. Tiedje, in *The Physics of Hydrogenated Amorphous Silicon II,* Topics in Applied Physics Vol. 56, edited by J. D. Joannopoulos and G. Lucousky (Springer-Verlag, Berlin, 1984).

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

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

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

[7] W. B. Jackson, Phys. Rev. B **38**, 3595 (1988).

[8] J. Kakalios and W. B. Jackson, in *Amorphous Silicon and Related Materials,* edited by H. Fritzscher (World Scientific, Singapore, 1989).

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

[10] H. Curtins, N. Wyrsch, and A. V. Shah, Electron. Lett. **23**, 228 (1987).

[11] F. Finger *et al.*, in Proceedings of the MRS Spring Meeting, Symposium O, San Francisco, 1990 (unpublished).

[12] F. Paszti, E. Kóti, G. Mezey, A. Manauaba, L. Pócs, D. Hildebrandt, and H. Strusny, Nucl. Instrum. Methods Phys. Res. Sect. B **15**, 486 (1986).

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

[14] Karen K. Gleason, Mark A. Petrich, and Jeffrey A. Reimer, Phys. Rev. B **36**, 3259 (1987).

[15] D. K. Biegelsen, R. A. Street, C. C. Tsai, and J. K. Knights, Phys. Rev. B **20**, 4839 (1979).

[16] Z. E. Smith and S. Wagner, in *Amorphous Silicon and Related Materials* (Ref. 8), p. 409.

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

Physica B 170 (1991) 146–148
North-Holland

The dispersive diffusion of hydrogen in undoped a–Si:H

X.-M. Tang[a], J. Weber[a], Y. Baer[a] and F. Finger[b]
[a]*Institut de Physique de l'Université, CH-2000 Neuchâtel, Switzerland*
[b]*Institut de Microtechnique de l'Université, CH-2000 Neuchâtel, Switzerland*

We have measured the dispersion parameter α as a function of the annealing temperature in three samples deposited under different conditions. α increases with the temperature and the initial hydrogen concentration. The rate of variation of α with the annealing temperature seems to depend strongly on the deposition conditions. More data will be taken to elucidate this behaviour.

1. Introduction

The hydrogen transport behaviour in hydrogenated amorphous silicon (a–Si:H) has been extensively studied in the last few years. In particular, two different hydrogen evolution mechanisms have been observed [1, 2]. The first one is the non-diffusion limited (NDL) evolution process (maximum rate near 300°C). The second one is the diffusion limited (DL) process (maximum rate near 600°C, depending on the film thickness).

Generally, the dispersion in transport processes (the diffusion coefficient D is a function of t, the annealing duration) occurs whenever there is an energy distribution of traps and/or a random distribution of hopping site separations [3].

The dispersive diffusion of hydrogen was first reported by Street et al. [4] and by Kakalios et al. [5] in p-type a–Si:H/a–Si:D/a–Si:H multilayers produced by glow discharge (GD). They found that the diffusion constant D decreases with the annealing duration t according to a power-law dependence form: $D(t) \sim t^{-\alpha}$ where α, the dispersion parameter, was determined to be $\approx$0.2 for an annealing temperature $T = 200$°C. Nearly two years later, Shinar et al. [6] published their results on the hydrogen dispersive diffusion in undoped RF-sputtered a–Si:H multilayers. The value they obtained for the dispersion parameter α was 0.75. The H concentration in the film was high and the annealing temperatures were in the 275–355°C range.

In the hydrogen glass model proposed by the Xerox group [7, 8], the diffusion constant D is expressed as:

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

where D_{00} is the microscopic diffusion constant, ω is the H attempt frequency, and α, the dispersion parameter, is given by

$$\alpha = 1 - (T_a / T_0) . \qquad (2)$$

T_a is the annealing temperature. kT_0 is the characteristic energy width of the exponential energy distribution of traps for diffusing H atoms. This distribution is responsible for the dispersion.

Recently, we have studied the dependence of α on the deposition temperature T_s and on the annealing temperature T_a of undoped a–Si:H films deposited by glow discharge [9]. On the one hand, we have found that for a fixed temperature T_a (400°C), α decreases when T_s increases (from 50 to 250°C), that is, in these samples, when the initial concentration of the NDL-hydrogen decreases from 5.5% to 0.4%. On the other hand, we have observed that, for

0921-4526/91/$03.50 © 1991 – Elsevier Science Publishers B.V. (North-Holland)

samples deposited at 150°C, α increases (by a factor 3) with T_a (350°C < T_a < 470°C). The conclusion was that the variation of the dispersion parameter is strongly correlated with the behaviour of the a–Si:H layer microstructure as a function of the NDL-hydrogen concentration and/or the annealing temperature. We have proposed a mechanism in which the H-cluster plays a dominant role.

2. Experiment and analysis

Three sets of samples were prepared by the silane based VHF-glow-discharge method [10, 11]. For the first and second set, the a–Si:H films (1–2 μm thick) were deposited onto Si (1 0 0) wafers kept at temperatures T_s = 250 and 150°C, respectively. For the third set, the deposition temperature T_s was 200°C and silane was 50% diluted in hydrogen gas. We have used the ERDA (elastic recoil detection analysis) method to measure the hydrogen concentration profiles [12] at different annealing temperatures and durations. This method is particularly suitable to the necessarily large number of measurements since it is not destructive and allows successive annealings to be performed with the same sample. ERDA consists in measuring the energy spectrum of protons which have been elastically hit by incident MeV alphas produced by our Van de Graaff accelerator and recoil in the forward direction. The annealings could be made in the scattering chamber. The time required for the temperature changes was of the order of one minute, which is short compared to the annealing periods (>30 min).

Proton energy spectra were computed through our RETSCA code and fitted by χ^2 minimalization to experimental spectra to obtain the hydrogen concentration depth profiles, the value of the dispersion parameter and ΔC the concentrations of the NDL-hydrogen. The error bars were computed through the $\Delta\chi^2 = 1$ procedure. The experimental set up and the data analysis method are described in detail elsewhere [2].

3. Results and discussion

Our results are depicted in fig. 1. It is seen that:

- The larger ΔC in a set of samples, the larger is the dispersion parameter α (in agreement with our earlier measurements [9]).
- In each set of samples, α increases with T_a (also in agreement with ref. [9]) but, apparently, with different rates.
- There is no cross-over of the three sets of α-values up to 470°C.

This last fact indicates that the microstructures of the three sets of a–Si:H samples remain different and are therefore strongly determined by the initial microstructure as we discussed before [9]. Concerning the rate of change of α versus the annealing temperature T_a for different T_s and/or ΔC, further experiments are needed in order to see whether there is a clear tendency. In any case, the rate of change of α versus T_a should be a valuable parameter in the understanding of the hydrogen diffusion process in a–Si:H.

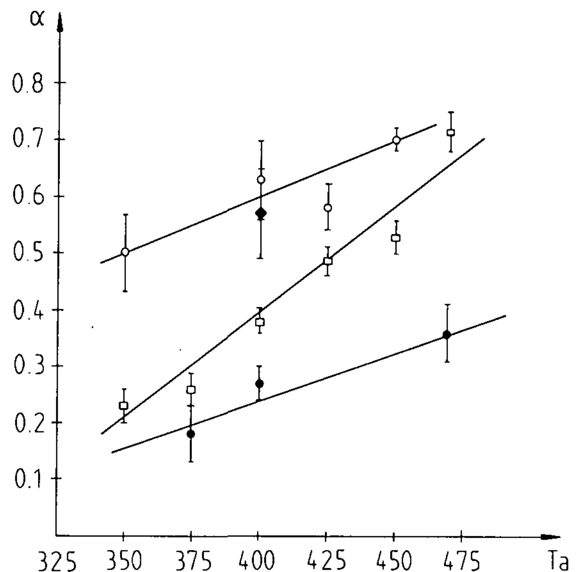


Fig. 1. The dispersion parameter α vs. the annealing temperature T_a. ● T_s = 250°C, $\Delta C \approx$ 1.2%, SiH_4. □ T_s = 150°C, $\Delta C \approx$ 4.9%, SiH_4. ○ T_s = 200°C, $\Delta C \approx$ 5.6%, $1SiH_4 + 1H_2$. ◆ T_s = 50°C, $\Delta C \approx$ 5.5%, SiH_4 [9]. T_s: deposition temperature, ΔC: NDL-hydrogen concentration. The solid lines are guides to the eye.

Acknowledgement

The Swiss National Science Foundation is gratefully acknowledged for financial support. F. Finger acknowledges the support of the Swiss Federal Research Grant OFEN EF-REN 87/9.

References

[1] W. Beyer, in: Tetrahedrally-Bonded Amorphous Semiconductors, eds. D. Adler and H. Fritzsche (Plenum, New York, 1985) p. 129.
[2] X.-M. Tang, J. Weber, Y. Baer and F. Finger, Solid State Commun. 74 (1990) 171.
[3] T. Tiedje, in: The Physics of Hydrogenated Amorphous Silicon II, Topics in Applied Physics, Vol. 56 (Springer, Berlin 1984) ch. 6.
[4] R.A. Street, C.C. Tsai, J. Kakalios and W.B. Jackson, Phil. Mag. 56 (1987) 305.
[5] J. Kakalios, R.A. Street and W.B. Jackson, Phys. Rev. Lett. 59 (1987) 1037.
[6] J. Shinar, R. Shinar, S. Mitra and J.-Y. Kim, Phys. Rev. Lett. 62 (1989) 2001.
[7] W.B. Jackson, Phys. Rev. B 38 (1988) 3595.
[8] J. Kakalios and W.B. Jackson, in: Amorphous Silicon and Related Materials, ed. H. Fritzscher (World Scientific, Singapore, 1989) p. 207.
[9] X.-M. Tang, J. Weber, Y. Baer and F. Finger, Phys. Rev. B 41 (1990) 7945.
X.-M. Tang, J. Weber, Y. Baer and F. Finger, Phys. Rev. B 42 (1990) 7945.
[10] H. Curtins, N. Wyrsch and A.V. Shah, Elec. Lett. 23 (1987) 228.
[11] F. Finger, V. Viret, A. Shah. X.-M. Tang, J. Weber and W. Beyer, MRS Symposium Proc. Vol. 192, Amorphous Silicon Technology-1990, eds. P.C. Taylor et al. (1990) p. 583.
[12] F. Paszti, E. Kóti, G. Mezey, A. Manuaba, L. Pócs, D. Hildebrandt and H. Strusny, Nucl. Instrum. and Meth. B 15 (1986) 486.

Helvetica Physica Acta
Vol. 62 (1989)
0018-0238/89/030235-04$1.50+0.20/0
(c) 1989 Birkhäuser Verlag, Basel

SILICIDE FORMATION FOR Cu ON a-Si:H

X.-M. Tang, J. Weber and Y. Baer, Institut de Physique de l'Université, rue Breguet 1, CH-2000 Neuchâtel
M. Favre, Institut de Microtechnique de l'Université, rue Breguet 2, CH-2000 Neuchâtel

Abstract : we have measured by Rutherford Backscattering Spectrometry (RBS) the rate of formation of CU_4Si in a-Si:H at four temperatures between 160 °C and 200 °C. The results show that the Cu_4Si thickness is proportional to $t^{1/2}$ indicating that the process is controlled by diffusion.

1. Introduction

The silicide formation in monocrystalline Si (c-Si) has been extensively studied and is well documented [1]. It is not the case for micro- and nanocrystalline Si (µc-Si and nc-Si resp.) and amorphous Silicon (a-Si), although these materials are of great technological importance [2]. The diffusion of metallic ions implanted in a-Si has been investigated [3,4] and the formation of Pd_2Si in a-Si:H has been reported without indication of its kinetics [5]. Nemanich et al. [5] and Vanecek [6] have suggested that hydrogen in a-Si:H might be important in the silicide formation and/or diffusion processes. To our knowledge, the present work is the first systematic study of the kinetics of silicide and of the diffusion processes in nc-Si:H and a-Si:H. a-Si:H is unstable above 600 °C [7] but this difficulty could be overcome by choosing Cu which is a fast diffuser in Si [4,5]. Cu-silicide formation and diffusion processes are expected to occur much below the 600 °C limit [4,5]. We report here the results of our investigations in Cu_4Si formation in a-Si:H substrates of - as produced - hydrogen concentration. We have used the Rutherford Back Scattering (RBS) technique [8] which is well adapted to this type of study.

2. Experimental

The a-Si:H/c-Si substrates were prepared by the Silane based VHF-Glow Discharged (VHF-GD) method which is a novel high rate deposition method recently developed at IMT [9]. This method increases the deposition rate without any degradation of the material quality. The deposition parameters are listed in ref. [10].

The substrates were first annealed at 200 °C in UHV (p<1.E-8 torr) for 30 min. and then cooled down for one hour, a treatment which is not expected to modify the H-concentration. Without breaking the UHV a 4000 to 5000 Å thick Cu-layer was then deposited by evaporation on top of the Si substrate. No subsequent Si-diffusion through Cu grain joints has been observed (Type C diffusion [11]). Then the samples were transferred into the RBS chamber (p<5.E-7 torr) were they were fixed on a Ag backing that could be heated by IR radiation. The temperature variations could be performed within less than 50 s. and the temperature could be kept constant within ± 2 °C during the annealing. After each heat treatment, the samples were exposed to the MeV alpha-beam, 0.5 mm in dia., produced by our Van de Graaff accelerator. Backwards (150 °) elastically scattered alphas were detected by a surface barrier Si detector (RBS spectra). The data were analysed with our own "RBSERA" computer code.

3. Results

The RBS spectra of Fig. 1 show clearly the formation of Cu_4Si: spectrum 1 comes from the unannealed Cu/a-Si:H sample, spectra 1 and 2 from the annealed sample at 185 °C for 11 and 30 min. resp. The step on the right part of these last two spectra is due to the silicide. In fig. 2 the thickness x of Cu_4Si plotted versus the square root of the annealing time t at different temperatures, shows a linear behaviour : $x = (k(T)\cdot t)^{1/2}$ where k(T) is the rate of formation. This result indicates that this process is controlled by diffusion [1]. The temperature thres-

hold for Cu_4Si formation is found to be around 150° C. From the Arrhenius plot of $k(T) = ko \cdot exp(-E_a/kT)$ (k = Bolzmann constant) shown in fig. 3, we obtain a value of 1.9 eV for the activation energy E_a. On can expect E_a to be dependent on the H concentration and the structure of the Si layer (a-Si:H, nc-Si:H). The investigation of these problems and of the H affinity of the diffusing metal is in progress.

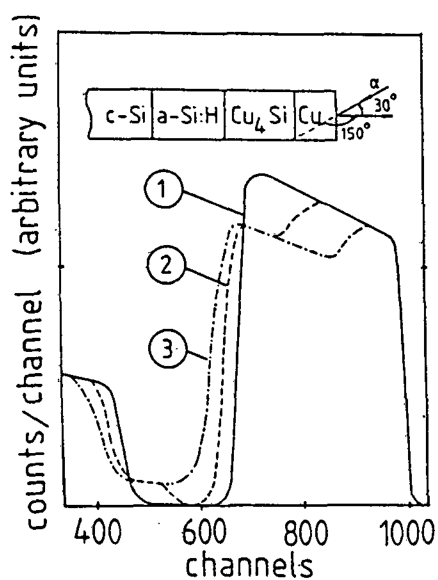


Fig. 1 : see text

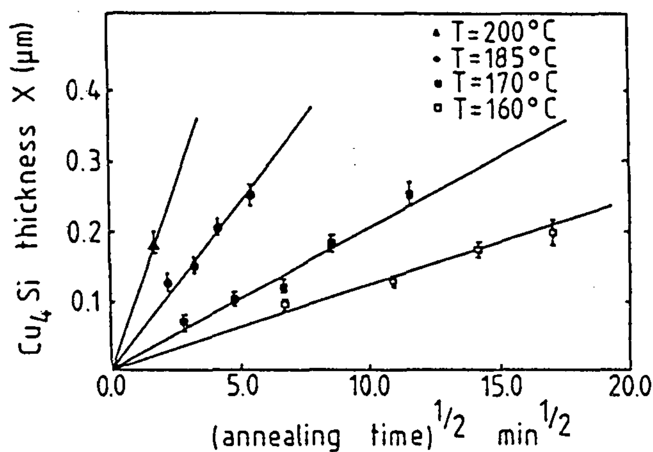


Fig. 2 : see text

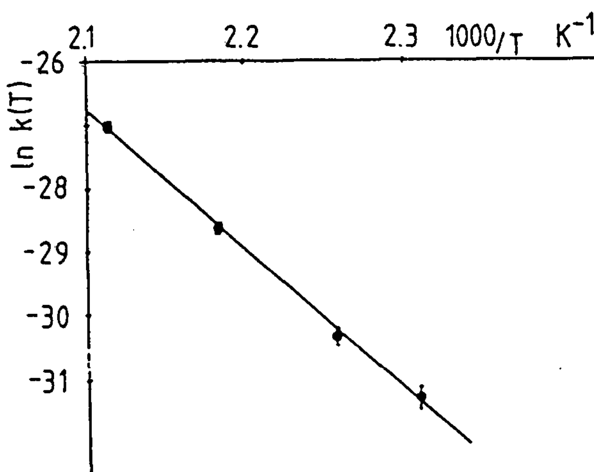


Fig. 3 : see text

4. References

[1] Marc-A. Nicolet and S.S. Lau in "VLSI Electronics : micro-structure science" vol. 6, chap. 6.

[2] G. Winterling and G. Müller, Physica Scripta T13, 45 (1986).

[3] J.M. Poate, D.C. Jacobson, J.S. Williams, R.G. Elliman and D.O. Boerma, Nucl. Inst. Meth. in Phys. Res. B19/20, 480 (1987).

[4] G. Elliman, J.M. Gibson, D.C. Jacobson, J.M. Poate and J.S. Williams, Appl. Phys. Lett. 46, 478 (1985).

[5] R.J. Nemanich, C.C. Tsai and T.W. Sigmon, Phys. Rev. B23, 6828 (1981).

[6] Pr. M. Vanecek, Inst. of Phys., Academy of Sciences, Prague, Tchek., private communication.

[7] J. C. Oberlin, A.C. Chami, E. Ligeon and C. Prunier, Nucl. Inst. Meth. in Phys. Res. B19/20, 462 (1987).

[8] W.-K. Chu, J.W. Mayer and M.-A. Nicolet, Rutherford Back-scattering Spectrometry, Academic Press 1978.
J. Weber, Swiss User Group "Surfaces and Interfaces", 4th Meeting, Fribourg 1988, p.12.

[9] H. Curtins, N. Wyrsch and A. V. Shah, Elect. Lett. 23, 228 (1987).

[10] M. Favre, H. Curtins and A. V. Shah, J. Non-Cryst. Sol. 97/98, 731 (1987).

[11] J.C. Fischer, J. Appl. Phys. 22, 74 (1951).
R.T.P. Whipple, Philos. Mag. 45, 1225 (1954).

Les articles suivant font partie intégrante de cette thèse:

(1). X.-M.Tang, J.Weber, F.Finger and V.Viret "ERA-measurement of the H-concentration in a-Si:H as a function the annealing temperature" Helv. Phys. Acta. 63 (1990) 499

(2). X.-M.Tang, J.Weber, Y.Baer and F.Finger "Hydrogen diffusion in a-Si:H" Solid State Commun. 74 (1990) 171

(3). X.-M.Tang, J.Weber, Y.Baer and F.Finger "Dispersive diffusion of Hydrogen in a-Si:H: Influence of the film deposition temperature" Phys.Rev. B42 (1990) 7945

(4). X.-M.Tang, J.Weber, Y.Baer and F.Finger "Annealing-temperature influence on the dispersive diffusion of Hydrogen in undoped a-Si:H" Phys.Rev. B43 (1990) 7277

(5). X.-M.Tang, J.Weber, Y.Baer and F.Finger "The Dispersive diffusion of Hydrogen in undoped a-Si:H" Physica B.170 (1990) 146

(6). X.-M.Tang, J.Weber, Y.Baer and M.Favre "Silicide formation for Cu on a-Si:H" Helv. Phys. Acta. 62 (1990) 253

Le text complet de la thèse est déposé à l'Institut de Physique, Université de Neuchâtel.