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Crystallization of phosphorus-doped amorphous silicon films prepared by glow discharge decomposition of silane

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Résumé. — La cristallisation dans le silicium amorphe dopé au phosphore, et obtenu par décomposition de silane, a été observée en utilisant les mesures de conductivité électrique. Ceci nous a permis d'obtenir l'énergie d'activation E_v de la vitesse de croissance V_g en fonction de la concentration du dopage C_p (variant de 0,05 à 5 %). On trouve une énergie E_v égale à 3 eV pour $C_p \leq 0,5$ %. Cette énergie augmente pour des concentrations de dopage supérieures. Ces résultats sont comparés avec ceux obtenus par Csepregi *et al.* en utilisant la méthode de canalisation. Ils obtiennent une énergie E_v indépendante du dopage et égale à 2,4 eV.

Abstract. — Crystallization kinetic of phosphorus-doped amorphous silicon films prepared by glow discharge of silane is observed by using conductivity measurements. The activation energy E_v of the growth rate V_g is deduced as a function of doping level C_p (ranging from 0.05 to 5 %). E_v has a constant value equal to 3 eV for $C_p \leq 0.5$ % and increases for higher values of C_p . We compare these results with Csepregi *et al.*'s ones, obtained by channeling. They obtain E_v equal to 2.4 eV in the whole doping level range.

1. **Introduction.** — Crystallization in amorphous material occurs through nucleation and the growth of the crystallites formed during the nucleation process [1]. The growth rate V_g is the rate at which the crystalline to amorphous interface moves. The nucleation rate n is the number of stable crystallites which appear per unit time in an untransformed volume of unity. Experimentally V_g (as well as n) appears to be thermally activated :

$$V_g = V_{g0} \exp(-E_v/K_B T)$$

V_{g0} is independent of temperature T , K_B is the Boltzmann constant, and E_v is the activation energy of V_g .

The crystallized fraction $x(t)$ is defined as $x(t) = V(t)/V_0$ where $V(t)$ is the total crystallized volume at time t , and V_0 is the total volume of the sample. The crystallized fraction $x(t)$ can be obtained from the conductivity of the layer at time t , $\sigma m(t)$,

when the conductivities σa and σx of the amorphous and crystalline materials are known through [2] :

$$\ln\left(\frac{1}{1-x(t)}\right) = \ln \cdot \left[1 - \frac{\left(\frac{1 - \frac{\sigma m(t)}{\sigma a}}{1 + 2 \frac{\sigma m(t)}{\sigma a}} \right)}{\left(\frac{\frac{\sigma x}{\sigma a} - \frac{\sigma m(t)}{\sigma a}}{\frac{\sigma x}{\sigma a} + 2 \frac{\sigma m(t)}{\sigma a}} \right)} \right] \quad (1)$$

We have shown [3, 4] that V_g is generally obtained in the case of surface-induced crystallization (SIC) and n is obtained from the bulk-induced crystallization (BIC), when V_g is known. In the case of BIC, we have shown that

$$\ln \frac{1}{1-x}$$

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varies roughly as t^r with $1 < r \leq 3$. We have observed that when $n = 0$, $\ln \{ 1/(1 - x) \}$ varies roughly as t^2 and in the case of $n \neq 0$ it varies as t^3 .

Csepregi *et al.* [5] compared the growth rate (V_g) obtained on undoped and doped (with electrically active impurities B, P, As) implanted a-Si films. They found that after implanting the ^{31}P impurity at concentrations ranging from 0.9 to $2.8 \times 10^{20} \text{ cm}^{-3}$, the activation energy (E_v) of V_g stays constant, and the pre-exponential factor V_{g0} is multiplied by a factor of 6. They report that for concentrations higher than $2 \times 10^{20} \text{ cm}^{-3}$ ($\approx 5 \times 10^{-3}$ atomic per cent), the growth rate does not appear to be strongly dependent on the dopant concentration.

Reilly and Spear [6] have studied the crystallization in undoped and doped specimens of amorphous silicon prepared by glow discharge decomposition of silane. They found a temperature of crystallization T_c equal to 620°C for undoped specimens. They found that phosphorus doping can reduce T_c appreciably, and observed a decrease of 110°C for a vapour doping level of 2.4×10^{-3} atomic per cent. This can be associated with an increase in the growth rate and/or the nucleation rate.

The aim of this paper is to study V_g as a function of temperature and doping level, for phosphorus doped and undoped amorphous silicon films prepared by glow discharge decomposition of silane, the phosphorus doping concentration ranging from 0.5×10^{-4} to 5×10^{-2} (atomic concentration).

2. Experimental results. — **2.1 SAMPLE PREPARATION.** — Phosphorus doped and undoped amorphous silicon films have been prepared by glow discharge decomposition of silane, most of them deposited on sintered alumina substrate, some being deposited on quartz substrate. The doping is realized by addition of

phosphine with silane in the gas phase during glow discharge decomposition. The phosphorus doping concentration C_P is defined as :

$$C_P = \frac{[\text{PH}_3]}{[\text{SiH}_4]}$$

where $[\text{PH}_3]$ is the phosphine concentration and $[\text{SiH}_4]$ is the silane concentration. The preparation conditions detailed in [7] are summarized in table I.

Thickness measurements were made with a Talystep ($\pm 0.02 \mu\text{m}$). Substrates are degassed for 60 min. at 700°C prior to the deposition. The amorphous layers are exposed to the atmosphere between the deposition and the crystallization process.

Prior to crystallization, samples are annealed at a temperature of about 500°C for 15 hours in order to exodiffuse hydrogen. This will be discussed under Discussion and Conclusions.

2.2 RESULTS. — Electrical conductivity measurements (σ) were made using two kinds of apparatus. The low conductivity measurements were made using a Keithley 610C electrometer with a relative error less than 10 %. In the case of high conductivity measurements, we used an AOIP Keithley Multimeter Efficace MNK 179.

We used a planar configuration contact electrode made by pressing with platinum foil. The annealing was made in an oven under argon atmosphere (stabilized at $\pm 1^\circ\text{C}$). We observed no change when annealing was made in vacuum with a residual pressure of 10^{-6} torr.

In figures 1 to 3 we present examples of the variation of the electrical resistance $R(t)$ versus time during isothermal runs at various temperatures for samples of series 1 to 6.

Table I. — *Experimental conditions for sample deposition.*

Series	1	2	3	4	5	6
Dimensions (mm^2)	4×4	4×4	4×4	4×1.5	4×1.5	4×4
$C_P = \frac{[\text{PH}_3]}{[\text{SiH}_4]}$	0.05	0.1	0.5	1	5	0
Substrate temperature of deposition ($^\circ\text{C}$)	400	400	400	300	400	420
Thickness (μm)	0.5	0.5	0.5	0.55	0.6	0.6
Rate of deposition ($\text{\AA}/\text{min.}$)	200	200	200	200	200	150
Residual pressure (torr) ($\times 10^{-2}$)	2.2	2	2	2	2.2	1.6
RF power (W)	70	70	70	70	70	80
Sample voltage (V)	+ 35	+ 35	+ 35	+ 35	+ 35	0
Target voltage (V)	− 500	− 500	− 500	− 500	− 500	− 450
Values of $\frac{R_a}{R_c} = \frac{\sigma_C}{\sigma_a}$	21	35	210	370	18	10

Fig. 1. — Variation of the electrical resistance *versus* time in phosphorus-doped (0.05%) amorphous silicon layers for various temperatures. □ 560 °C; + 580 °C; ○ 600 °C; ● 620 °C; × 640 °C.

Fig. 2. — Variation of the electrical resistance *versus* time in phosphorus-doped (5%) amorphous silicon layers for various temperatures. ○ 600 °C; ● 620 °C; × 640 °C.

As observed in the case of crystallization of evaporated amorphous Ge and Si [3, 4], initiation times exist, mainly for low annealing temperatures. These

Fig. 3. — Variation of the electrical resistance *versus* time in undoped amorphous silicon layers for various temperatures. □ 630 °C; × 640 °C; ○ 650 °C; ● 660 °C; + 670 °C.

initiation times are not presented in figures 1 to 3. The lowest annealing temperature here is 560 °C, which corresponds to an initiation time $t'' \approx 12$ hours.

3. DISCUSSION AND CONCLUSIONS. — In crystallization occurring through nucleation and growth, the observed initiation time is generally interpreted as a time during which the nucleation rate increases from zero to its steady state value [1].

In our case, it can also be due to the presence of H atoms inhibiting the crystallization process. But we shall show that the hydrogen effect is negligible in the present study.

In previous hydrogen exodiffusion studies on undoped [8] and heavily phosphorus doped [9] films, we showed (by nuclear reaction measurements) that a non zero residual hydrogen concentration exists, and stays constant even after crystallization. This residual concentration C_{resid} is about 0.25 % for undoped films and 0.16 % for phosphorus doped layers. Roughly similar kinetics of H exodiffusion are observed for both cases.

Apart from this residual H concentration, it has been shown that [8, 10] :

(1) A weakly bound H whose concentration C_{10} ($C_{10} \approx 0.08$ at. concentration) leave the sample by diffusion with a diffusion coefficient D for $T < 500$ °C, so an annealing at 500 °C during $t = 15$ hours reduces the concentration of weakly bound H by a factor :

$$\exp\left(-\frac{D\pi^2}{4e^2}t\right) \approx 10^{-20},$$

with $D(500 \text{ °C}) = 8.9 \times 10^{-13} \text{ cm}^2/\text{s}$;

(2) A tightly bound H, occupying isolated Si-H bonds, whose concentration C_{20} ($C_{20} = 0.02$ at concentrations), leave their sites for $T \geq 500$ °C following a first order law with a kinetic coefficient K_2 . So the same annealing (500 °C, $t = 15$ h) reduces the concentration of tightly bound H by a factor of

$$\exp[-K_2(500\text{ °C}) \times t] \simeq 10^{-1},$$

with $K_2(500\text{ °C}) = 3.6 \times 10^{-6} \text{ s}^{-1}$.

This implies that this above annealing removes the whole weakly bound H and only a part of the tightly bound H. But we shall show that the remaining tightly bound H will leave the sample just at the beginning of the initiation time even at the lowest crystallization temperature (560 °C).

Doing the same calculation as in (2) and using $K_2(560\text{ °C}) = 1.1 \times 10^{-4} \text{ s}^{-1}$, we show easily that the necessary time to decrease the tightly bound H concentration from C_{20} to C_{resid} is about $t' \simeq 40$ min., much lower than the initiation time ($t'' \simeq 12$ h).

For each annealing temperature, the electrical resistance varies from an initial value $R(t=0) = R_a$, which corresponds to the amorphous phase, to a final constant value which is assumed to correspond to the crystalline phase. This will be discussed later. Thus for each isothermal run, we can calculate :

$$\frac{R_a}{R_x} = \frac{\sigma x}{\sigma a}.$$

The values of $\sigma x/\sigma a$ are given in table I for each series.

Fig. 4. — Variations of $\ln(1/(1-x))$ versus σ_m/σ_a for the following values of $\sigma x/\sigma a$: curve 1, $\underline{21}$; curve 5, $\underline{18}$; curve 6, $\underline{10}$.

Fig. 5. — Variation of $\log_{10} [\ln(1/(1-x))]$ versus $\log_{10} t$ for samples of series 1 annealed at various temperatures : $\square$ 560 °C; $\times$ 580 °C; $+$ 600 °C; $\circ$ 620 °C; $\bullet$ 640 °C.

Fig. 6. — Variation of $\log_{10} [\ln(1/(1-x))]$ versus $\log_{10} t$ for samples of series 5 annealed at various temperatures : $\times$ 580 °C; $+$ 600 °C; $\circ$ 620 °C; $\bullet$ 640 °C.

Fig. 7. — Variation of $\log_{10} [\ln(1/(1-x))]$ versus $\log_{10} t$ for samples of series 6 annealed at various temperatures : Δ 620 °C; $+$ 630 °C; $\circ$ 640 °C; $*$ 650 °C; $\bullet$ 660 °C; $\times$ 670 °C.

Using equation (1), we obtain the variations of $\ln \{1/(1-x)\}$ versus $\sigma m/\sigma a$ for each series (see figure 4 for example). We then deduce the variations of $\ln \{1/(1-x)\}$ versus time. These variations are presented in figures 5 to 7.

From these figures we observe that $\ln \{1/(1-x)\}$ varies roughly as t^α . At the beginning of the annealing time, $\alpha \simeq 1$, during a short time, then over most of the annealing time we see that α is much larger than 1, smaller than 3, and about 2.

We have shown that such crystallization kinetics correspond to a BIC (Bulk Induced Crystallization) without homogeneous nucleation ($n = 0$) in good agreement with electron-microscopy results [3]. Therefore :

$$\ln \frac{1}{1-x} = P \frac{\Pi}{S} \times (a_0 + V_g t)^2 \quad (2)$$

where P is the number of crystallites present at time $t = 0$ and a_0 their initial size, S is the area of the sample. Barna *et al.* [11], using electron microscopy, have shown that exposure of amorphous germanium samples to the atmosphere can avoid homogeneous nucleation. As mentioned above, our samples were exposed to the atmosphere before crystallization, so we can reasonably use equation (2). In our case, figures 5 to 7 show that the predominant variation of $\ln \{1/(1-x)\}$ is as t^2 , so we can take the simplified equation :

$$\ln \frac{1}{1-x} \simeq P \frac{\Pi}{S} V_g^2 t^2. \quad (3)$$

A comparison of each curve of figures 5 to 7 with equation (3) allows us to obtain a value of the quantity

$$\sqrt{P \frac{\Pi}{S}} \times V_g$$

for each annealing temperature and for various doping levels. It was not possible to determine here P/S but we can reasonably assume that it has a constant value for each series (i.e. for each doping level). The variation of

$$\sqrt{P \frac{\Pi}{S}} \times V_g \text{ versus } T$$

provides E_v for a given value of C_p . We present in figure 8 the variation of E_v versus C_p . For comparison we also show in this figure the variation of E_v versus C_p obtained by Csepregi *et al.* [5] on phosphorus-doped implanted amorphous silicon films.

The following observations may be made from an examination of figure 8. The activation energy E_v obtained by the channelling method [5] does not depend on C_p over the entire level range investigated.

Table II. — Variations of E_v versus C_p .

C_p (%)	0	0.05	0.1	0.5	1	5
E_v (eV)	3	2.6	3	3	3.4	4.3

Fig. 8. — Variation of the activation energy of the growth rate E_v as a function of the phosphorus concentration C_p : + present study; ● Csepregi's results [5].

On the other hand, for our experimental results obtained by conductivity measurements, the activation energy of V_g stays constant for $0 \leq C_p \leq 0.5$ % and then increases for $C_p > 0.5$ % (this will be investigated later).

In this method we assume that the final state observed on $R(t)$ ($\lim_{t \rightarrow \infty} R(t) = R_x$) for isothermal runs at each annealing T , and particularly at 560 °C, is a crystalline state. This has been verified by Reilly and Spear [6], who observe crystallization of such a doped material at a temperature as low as 510 °C, by characterizing and identifying the final state by using electronic transport measurements.

On the other hand, adopting this assumption we have been able to determine :

- the growth rate V_g as well as the nucleation rate n for evaporated amorphous Ge; these results are in excellent agreement with Barna *et al.* [11] whose results were obtained by using electron microscopy,

- V_g for evaporated amorphous Si in agreement with the results of Mayer *et al.* [12] by using channeling measurements.

In conclusion, it appears from this study that for doping levels $C_p \leq 0.5$ %, we observe a similar behaviour of V_g for two different kinds of amorphous silicon film obtained in different ways : one prepared by glow discharge decomposition of silane, and other obtained by the implantation method.

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