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CRYSTALLIZATION OF AMORPHOUS Se FILMS

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Abstract - Crystallization in amorphous Se films produced by flash evaporation technic has been studied from conductivity measurements on the temperature range 313 to 353K. The experimental results show an heterogenous nucleation and that the crystallization depends upon thickness ; they allow us to determine the parameters which characterise this phenomenon : Growth and nucleation rates, concentration and mean size of the crystallites in good agreement with microscopy studies, as well as the growth rate activation energy.

Introduction - Crystallization in amorphous materials involves electron diffraction and microscopy [1][2], differential thermal analysis [3][4], photoemission and optical absorption [5][6]. Recently Germain et al [7][8] have shown that conductivity measurements can be applied to study crystallization processes. This method can provide both the determination of the crystallization type as well as the parameters which govern and characterise the crystallization and has been used for materials such as Ge and Si. For these materials the ratio from crystalline to amorphous conductivities is about 20 whereas for Se, it is up to 10^5 , which leads to an ajustement of the model. This paper deals with an attempt to apply this model to Se films and to give the values of the corresponding parameters.

Theoretical - The model developped by Germain et al is based on the existence of two types of crystallites: one due to homogenous nucleation (crystallites being created and growing all along the crystallization takes place), the other due to heterogenous nucleation (the crystallites being present at the initial time), both growing in two ways, first in a three-dimensionnal (spherical) way as long as their diameter is smaller than the thickness e of the layer, then in a two-dimensionnal (cylindrical) way and interfering in two crystallization modes : bulk induced crystallization (B.I.C) and surface induced crystallization (S.I.C).

Bulk induced crystallization - Starting from Avrami relation, which gives the crystallization volume $V(t)$, for homogenous nucleation :

$$V(t) = \int_0^t \eta Y_1 Y_2 Y_3 V_I (t-t') dt$$

(where η is a shape factor, Y_i the growth rate of the crystallites in the i direction and V_I the nucleation rate)

and assuming an isotropic growth rate, the authors have established the crystallization kinetic equations :

$$(1) \quad \ln \frac{1}{1-x} = P \frac{\pi}{S} (a_0 + v_g t)^2 + \frac{1}{3} n' v_g^2 (t^3 - \tau^3) + \frac{1}{3} \frac{n'}{e} v_g^3 t^4 \quad \text{for } t > \tau$$

$$(2) \quad \ln \frac{1}{1-x} = P \frac{\pi}{S} (a_0 + v_g t)^2 + \frac{1}{3} \pi \frac{n'}{e} v_g^3 t^4 \quad \text{for } t < \tau$$

(τ being a critical time for the growth of a crystallite to switch from a spherical to a cylindrical mode, v_g the growth rate, P the number and a_0 the mean size of the initial crystallites and n' the nucleation rate).

Surface induced crystallization - In case of S.I.C they also calculated both the variation with time of the conductance of the layer :

$$\frac{\Sigma(t)}{\Sigma(a)} = 1 + \left(\frac{\sigma_c}{\sigma_a} - 1 \right) \frac{v_g t}{e}$$

(where $\frac{\sigma_c}{\sigma_a}$ is the ratio of the crystalline to the amorphous conductivities) and the crystalline fraction

$$x = P \pi a^2 \frac{v_g}{v_\infty} t \quad \text{for } t < \tau$$

$$\ln \frac{1}{1-x} = \frac{P \pi}{S} (a_0 + v_g t)^2 \quad \text{for } t > \tau$$

Then using the Landauer equation,

$$\ln \left(\frac{1}{1-x} \right) = \ln \left| 1 - \left(\frac{\sigma_a^{-\sigma}}{\sigma_a + 2\sigma} \right) \left(\frac{\sigma_c^{-\sigma}}{\sigma_c + 2\sigma} \right)^{-1} \right|$$

which gives for spherical shaped crystallites the relation between the crystalline fraction x versus the conductivity of the layer, it is possible as far as $\frac{\sigma_c}{\sigma_a}$ is known, to obtain the crystallization type as well as the values of the parameters.

Experimental - The samples having a thickness ranging from 5000Å to 1µm have been prepared by flash evaporation technic [9] Fig. 1 exhibits a typical crystallization curve $\frac{\Sigma(t)}{\Sigma(a)}$ versus time (ab) increase

of the conductivity with the temperature, (bc) stabilisation and (cd) real isothermic crystallization. The isothermic crystallization has been studied for two series of samples: 1µm thick (S.1) and 5000Å thick (S.2), the corresponding curves $\ln \frac{1}{1-x} = f(t)$ and

$\ln \ln \left(\frac{1}{1-x} \right) = \ln(t)$ have been plotted on figures 2 and 3 (S.1), 4 and 5 (S.2).

Equations (1) and (2) being reduced

to $L \left(\frac{1}{1-x} \right) \approx \lambda t^r$, we can see that the behavior of the samples depends upon thickness ; they exhibit a $r=1, 2$ and 4 behavior for the highest thickness (S.1) and $r=1, 2$ and 3 behavior for the lowest (S.2), which indicates in both kind first an heterogenous crystallization at the beginning of the phenomenon and then an homogenous crystallization in the bulk.

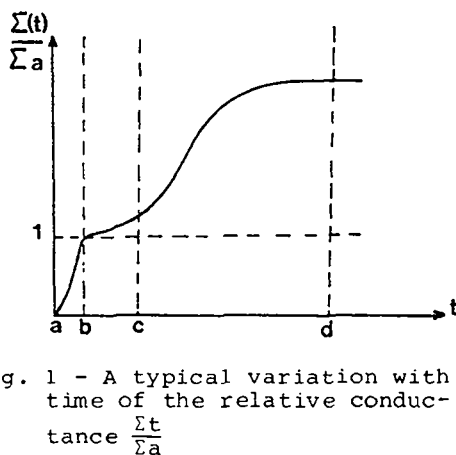


Fig. 1 - A typical variation with time of the relative conductance $\frac{\Sigma(t)}{\Sigma(a)}$

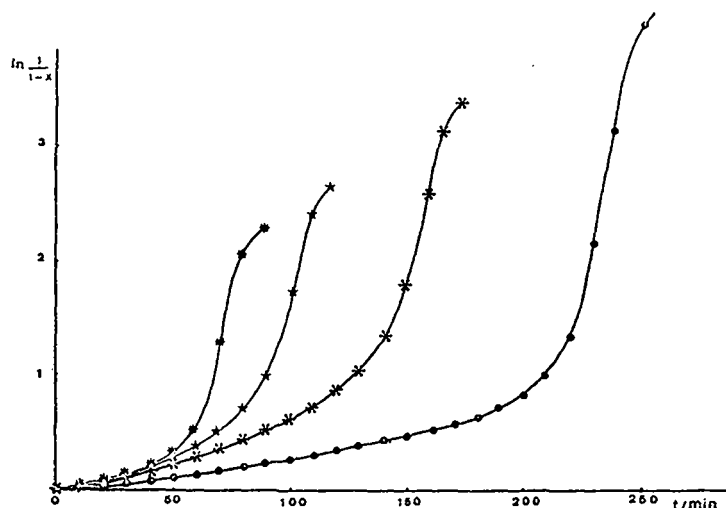


Fig.2 - Thickness $e=1\mu\text{m}$; $\text{Ln } \frac{1}{1-x} = f(t)$ with temperature as parameter : \bullet 351K, \times 246K, $*$ 340K, \bullet 337K

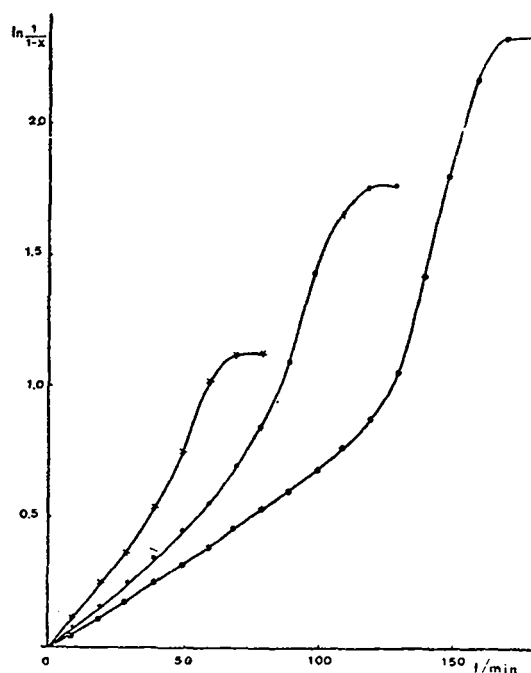
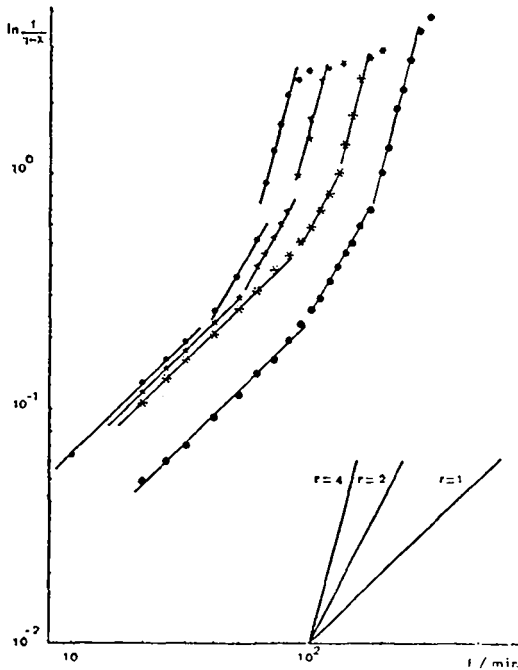


Fig.3 - Thickness $e=5000\text{\AA}$, $\text{Ln } \frac{1}{1-x} = f(t)$ with temperature as parameter : \times 346K, \bullet 341K, \bullet 338K

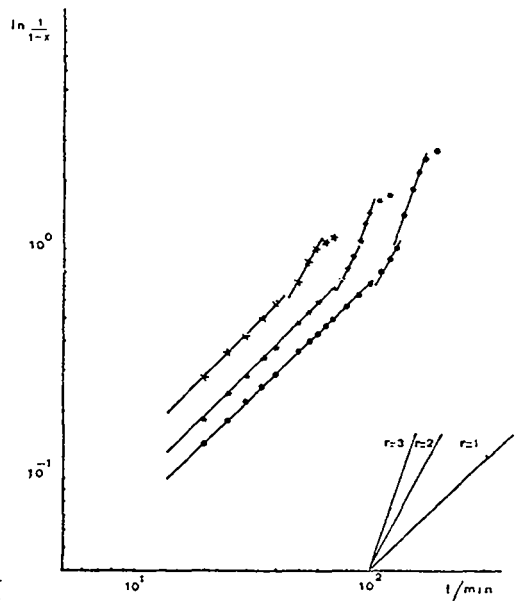
The values of the parameters have been calculated for each series : the growth rate v_g increases with the temperature $|0.6$ to 2.3\AA s^{-1} for a temperature range 334 to 351K (S.1) and 0.6 to 1.8\AA s^{-1} for temperature range 338 to 346K (S.2) and appears to be rather independent of the thickness while the nucleation rate n' increases from 1 to $3 \cdot 10^8 \text{ cm}^{-3} \text{ s}^{-1}$ (S.1) and from 1 to $1.5 \cdot 10^9 \text{ cm}^{-3} \text{ s}^{-1}$ (S.2) in the same temperature ranges. The other

parameters have been found constant both with temperature and thickness: $0.2\mu\text{m}$ for the mean size of the crystallites, in good agreement with microscopy measurements, and 10^{-8} cm^{-2} for their concentration per unit surface. We have also calculated the activation energy of the growth rate from the curve $v_g = f(\frac{1}{T})$ which we found approximately equal to 0.78 eV whatever the thickness.

Conclusion - The adaptation of Germain and al method to materials like selenium which ratio, crystalline to amorphous conductivities is very high, leads to a good determination of the parameters which govern the crystallization kinetics. The different results are in good agreement with those obtained by other methods : electron microscopy and differential thermal analysis.

Fig.4 - Thickness $e = 1 \mu m$

$\text{LnLn} \frac{1}{1-x} = f(\text{Ln } t)$ with temperature as parameter : * 351K, * 246K, * 340K; ● 337K

Fig.5 - Thickness $e = 5000 \text{ \AA}$

$\text{LnLn} \frac{1}{1-x} = f(\text{Ln } t)$ with temperature as parameter : * 346K ; * 341K; ● 338K

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