ELECTRON-DIFFRACTION STUDY OF THE CRYSTALLIZATION KINETICS OF AMORPHOUS ANTIMONY FILMS

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Abstract

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ELECTRON-DIFFRACTION STUDY OF THE CRYSTALLIZATION KINETICS OF AMORPHOUS ANTIMONY FILMS

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It has been established that in thin films obtained by evaporation, antimony exists in the amorphous phase (^{1}). X-ray and electron-diffraction studies have shown that the short-range order in amorphous antimony differs from the short-range order in crystalline antimony ($^{2-4}$).

A number of studies have been devoted to the crystallization of amorphous antimony. It was noted in (^{5}) that amorphous antimony can transform into crystalline antimony by way of α- and β-transformations. The α-transformation is a slow crystallization of amorphous antimony through the growth of spherulites; the β-transformation proceeds in an explosive manner and leads to mechanical destruction of the specimen. As a result of both the α- and the β-transformations, one and the same crystal lattice is formed.

In (^{6}) a diagram of the α- and β-transformations is given as a function of the condensation rate and film thickness.

It should be noted that the existing methods do not make it possible to obtain data on the crystallization kinetics of amorphous antimony. It seems to us that, for studying the kinetics of these processes, the most suitable method is the kinematic method of recording electron diffraction (^{7}), which makes it possible continuously to record the state of the film on a moving photographic plate; we used this method with an analysis of line intensities. For this purpose, from amorphous antimony films of thickness $h \sim 150$ Å, prepared by evaporation in vacuum at $p \sim 150^{-5}$ mm Hg with a rate of 5 Å/sec, we obtained isothermal kinematic electron-diffraction patterns at temperatures of 135, 150, 180, and 200°. Figure 1 shows such an electron-diffraction pattern obtained at 150°. In the photograph, the upper diffuse lines belong to amorphous antimony, the lower sharp ones to the crystalline phase of antimony; in between is the region of coexistence of both phases with a gradual strengthening of the lines of the crystalline phase. Studying the intensity of these lines of the crystalline phase at definite intervals of annealing time makes it possible to judge the amount of crystallized phase.

Indeed, as noted in (^{8}), the intensity of the lines I_{hkl} is related to the irradiated volume of crystalline substance by the relation

$$I_{hkl} = I_0 \lambda^2 \left| \frac{\Phi_{hkl}}{\Omega} \right|^2 V \, \frac{d_{hkl} \Delta}{4\pi L \lambda} \, P. \tag{1}$$

Here, with good approximation, one may take $I_{hkl} \sim V$.

Thus, by studying the intensities of the lines, one can obtain the law of crystallization of the amorphous film. To determine the line intensities, microphotograms were obtained from various sections of the kinematic electron-diffraction pattern. Such a microphotogram is shown in Fig. 2. From these microphotograms, with the aid of the blackening curve, the intensities of the lines $(11\bar{2}0)$ and $(21\bar{3}2)$ were determined, since the amorphous phase has no appreciable effect on them.

Passing from intensity to volume by normalization, we constructed crystallization isotherms (Fig. 3). Comparison of these isotherms with the analytical expression for the kinetic curves of phase transformations (^{9})

$$V_t = V_0[1 - \exp(-kt^m)]$$

shows that the best agreement is obtained for $m \approx 3$. Here

Figure 1. Kinematic electron diffraction pattern showing the crystallization of an amorphous antimony film at 150°

V_0 is the volume of the amorphous phase at the beginning of the process; V_t is the volume of the crystallized phase at time t; $k = 0.8 w_3 (k_s c)^2$, where w_3 is the rate of formation of nuclei of the new phase per unit of untransformed volume; c is the linear growth rate; k_s is the shape coefficient.

Taking into account that w_3 and c obey the Arrhenius equation, we obtain

$$\lg k = A - \frac{1}{RT}(E_3 + 2E_p),$$

i.e., the total activation energy of the process consists of two terms: $E_{\text{ob}} = E_3 + 2E_p$, where E_3 is the activation energy of nucleation, and E_p is the activation energy of crystallite growth.

From the kinetic crystallization curves we obtain the following values for k:

T, °C	135	150	180	200
$\lg k$	−15.9	−13.7	−11.3	−8.0

Fig. 2. Microphotograms from various sections of the kinetic electron diffraction pattern shown in Fig. 1. Annealing temperature 150°

The plot of the dependence of $\ln k$ on $1/T$ is linear, which gives E_{ob} a value of 38 kcal/mole. Since in the electron diffraction patterns the width of the lines of crystalline antimony is almost constant, it may be assumed that growth of the crystalline phase occurs mainly through the formation of new nuclei.

Fig. 3. Kinetic curves of crystallization of amorphous antimony films

Determining the overall crystallization rate from the tangent of the angle of inclination of the tangent to the kinetic curves, from the dependence of $\ln v$ on $1/T$ we find an activation energy equal to 19 kcal/mole, which corresponds to the activation energy of nucleation E_3. The value of E_3, also calculated from $1/\tau_0$ (10), where τ_0 is the incubation time, was likewise found to be 19 kcal/mole. The activation energy of crystallite growth E_p, determined from the relation $E_{\text{ob}} = E_3 + 2E_p$, is 9.5 kcal/mole.

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