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RESEARCH ARTICLE

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Crystal growth modes and crystallization kinetics of amorphous films according to transmission electron microscopy “in situ”

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ABSTRACT

The generality of the processes of crystal growth from the vapor phase on substrate and from the amorphous state in films is that in both cases a disorder-order transition takes place. This predetermines the structural and morphological analogy between the main forms of crystal growth on substrates and the main types of crystallization of amorphous films. Based on the analysis of the structure and morphology of crystals growing in amorphous films at electron beam influence, a quantitative interpretation of layer polymorphous crystallization (analog of Frank-van der Merwe growth mode), island polymorphous crystallization (analog of Volmer–Weber growth mode) and dendrite polymorphous crystallization (analog of Stranski–Krastanov growth mode) where given. For each crystallization mode the parameter of dimensionless relative length δ_0, equal to the ratio of the characteristic length to the value, characterizing the size of the unit cell of the crystal, were assigned and crystallization curves were built.

1. INTRODUCTION

Physical disturbance on the amorphous film can initiate its crystallization. If this is the disturbance of an electron beam, then we are talking about electron-beam crystallization, which can be performed in a transmission electron microscope column, using the so-called "in situ" method [1]. The phenomenological scheme of the transformations amorphous-crystal film suggests the following modes [2, 3]. 1. Layer polymorphous crystallization (LPC), when the inequality $\sigma_a \geq \sigma_c+\sigma_{ac}+\varepsilon_d$ is satisfied. Here σ_a, σ_c, σ_{ac} are the surface energy of amorphous phase-vacuum interface, of the crystalline phase-vacuum interface and surface energy of the amorphous-crystalline phase interface respectively. ε_d is the energy of deformation of the growing crystalline layer. 2. Island polymorphous crystallization (IPC), when the opposite inequality $\sigma_a \leq \sigma_c+\sigma_{ac}+\varepsilon_d$ is satisfied. 3. Dendrite polymorphous crystallization (DPC), when initially $\sigma_a \geq \sigma_c+\sigma_{ac}+\varepsilon_d$, and after critical dimension of a crystal, when $\sigma_a \leq \sigma_c+\sigma_{ac}+\varepsilon_d$.

The aim of this work was to give an overview of kinetics and types of crystallization of amorphous films, obtained predominantly by laser evaporation.

2. EXPERIMENTAL

Laser erosion plasma was deposited on substrates of KCl (001) at room temperature. Sputtering of a target (Cr, V, Zr, Hf) was carried out in an oxygen atmosphere ($P(O_2)$ ~ 0.13 Pa) with the use of a radiation from an LTI-PCh-5 laser operating in the Q-switched mode. The thickness of the films varied in the range from 20 to 35 nm. Crystallization of films was initiated by electron beam irradiation in the column of a transmission electron microscope at a beam current of ~ 20 μA. The rate of crystallization was controlled by varying the density *j* of the electron current through the sample, which was varied in the range from 1.1 to 6.5 A·mm^{-2} depending on the electron beam focusing.

The structural analysis was carried out by the methods of electron diffraction and transmission electron microscopy on EM-100L and PEM-100-01 electron microscopes operating at an accelerating voltage of 100 kV. The process of crystallization of a film was recorded from the screen of an electron microscope with a Canon Power Shot G15 camera in the video recording mode at a frame rate of 30 s^{-1}. Data on the kinetics of the crystallization process were obtained from the analysis of individual frames of the video recorded "in situ" at a fixed electron current density.

Quantification of the crystallization type (LPC, IPC ore DPC) was carried out on the basis of the value of relative length δ_0, defined as

$$\delta_0 = \frac{D_0}{a_0} \tag{1}$$

in the case of LPC, and as

$$\delta_0 = \frac{D_0}{\sqrt[3]{\Omega}} \tag{2}$$

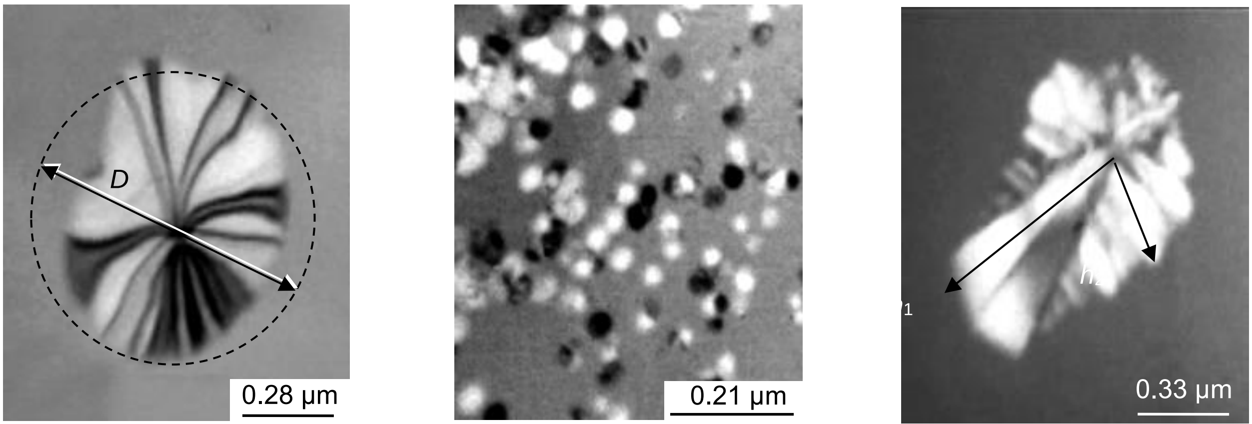
in the case of IPC and DPC. Characteristic unit of length D_0 is average crystal size at a moment of characteristic unit of time t_0, after which the volume of the amorphous phase decreases by a factor of e = 2.718 [4,5]:

$$D_0 = vt_0. \tag{3}$$

In expression (1) a_0 is a cell parameter of a growing crystal. In expression (2) Ω is the volume of the unit cell of a growing crystal. In expression (3) v is the crystal growth rate. The difference in the determination of δ_0 is due to the fact, that in the case of LPC a single crystal (with a cell parameter a_0) is formed in the investigated region, and in the case of IPC and DPC a polycrystalline film whose grains have different orientations [3, 6].

3. RESULTS AND DISCUSSION

Fig. 1a shows the mode of LPC of amorphous film of Cr_2O_3. A contrast extinction contour indicates to a dome-like bend of a crystal due to the tensile action of amorphous matrix. The dependence of the disk diameter *D*(*t*) of the crystal and of the fraction of the crystalline phase *x*(*t*) on time *t* are shown in Fig. 2a and 2b respectively. According to Fig. 2a the crystal growth rate $v = D'_t \approx 1.434$ μm·s^{-1}. There is a quadratic dependence $x(t) = 1.276\, t^2$. So, characteristic unit of time t_0 = 0.704 s. According to (3) characteristic unit of length $D_0 = v \cdot t_0$= 1.01 μm. For the (001) Cr_2O_3 orientation the projection of the unit cell on the plane of the film is a rhomb with a side a_0 = 0.496 nm. In this case, according to (1), the relative length $\delta_0 = D_0/a_0 \approx 2036$.



(a) (b) (c)

Figure 1. Crystal growth modes at electron beam effects on amorphous film. a - layer polymorphous crystallization of Cr_2O_3. b - island polymorphous crystallization of ZrO_2. c - dendrite polymorphous crystallization of HfO_2.

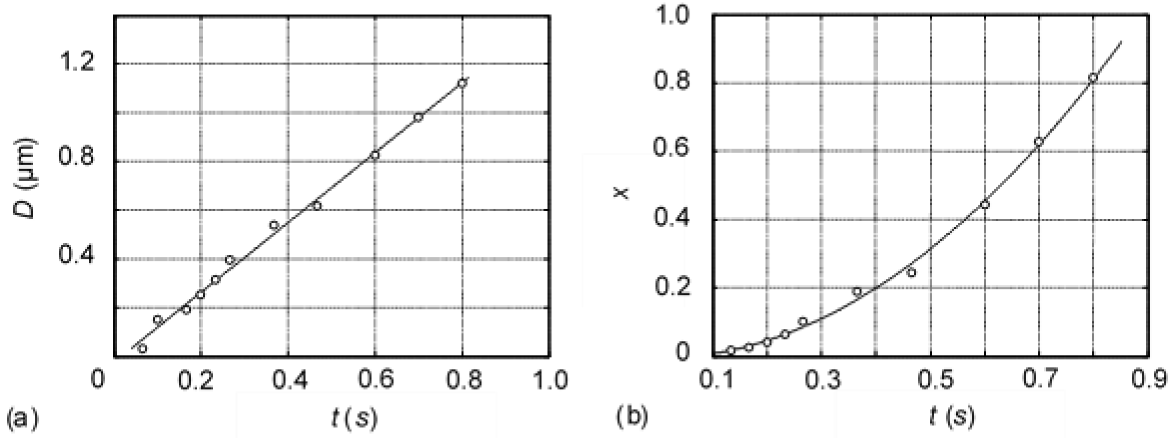


Figure 2. Kinetics of layer polymorphous crystallization of Cr_2O_3. a - The dependence of the diameter of the crystal *D*(t). b - The dependence of the fraction of the crystalline phase *x*(*t*).

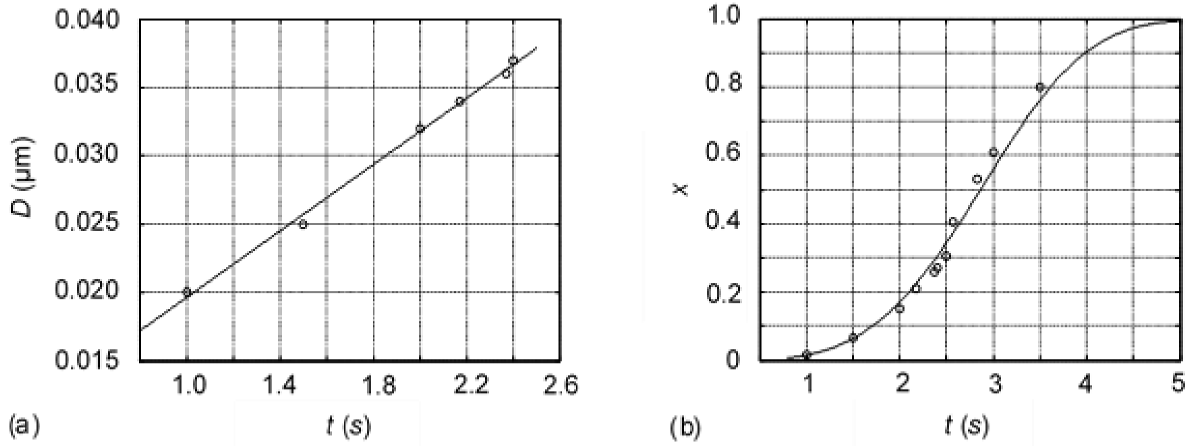


Figure 3. Kinetics of island polymorphous crystallization of ZrO_2. a - The dependence of the average iameter of the crystal *D*(t). b - The dependence of the fraction of the crystalline phase *x*(*t*).

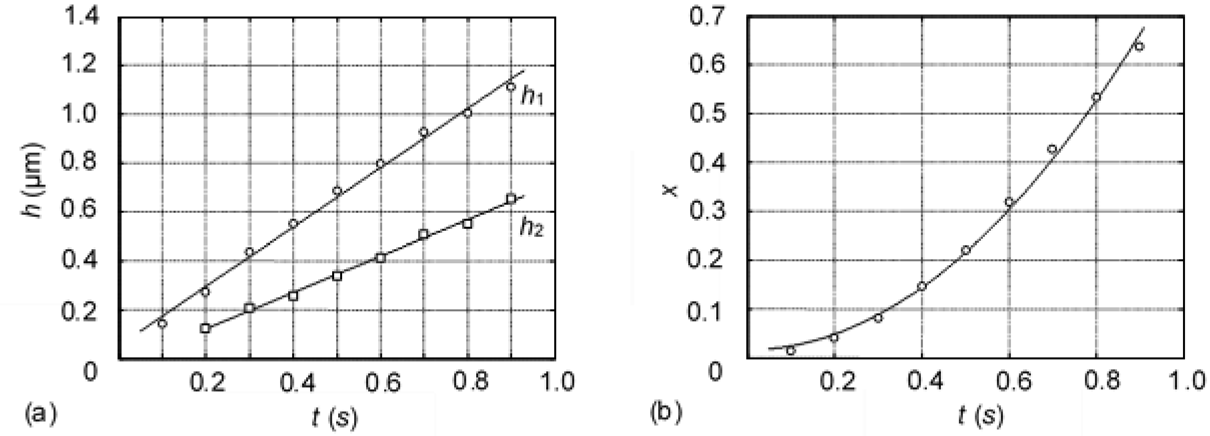


Figure 4. Kinetics of dendrite polymorphous crystallization of HfO_2. a - The dependence of the dendrite branches length h_1 and h_2 on time *t*. b - The dependence of the fraction of the crystalline phase *x*(*t*).

Fig. 1b shows the mode of IPC of amorphous film of ZrO_2. The dependence of the average diameter $D(t)$ of the crystals and of the fraction of the crystalline phase $x(t)$ on time t are shown in Fig. 3a and 3b respectively. According to Fig. 3a, the growth rate of the average diameter of the crystals $v = D'_t \approx 0.012$ μm·s^{-1}. There is exponential dependence $x(t)=1\text{-}\exp(-0.015t^{3.6})$. So, characteristic time t_0=3.211 s and characteristic length $D_0=v\cdot t_0$=0.039μm. The volume of ZrO_2 cubic sell $\Omega=1.32\cdot10^{-10}$μm^3. In this case, according to (2) the relative length $\delta_0=D_0/\Omega^{1/3} \approx 77$. The smaller the grain size of the crystallized film, the smaller the relative length δ_0.

Fig. 1c shows the mode of DPC of amorphous film of HfO_2. The dependence of the dendrite branches length h_1 and h_2 on time t is shown in Fig. 4a. According to Fig. 4a the growth rate of the dendrites branches of the first order $v_1 = (h_1)'_t \approx$ 1.215 μm·s^{-1} and of the second order $v_2 = (h_2)'_t \approx$ 0.744 μm·s^{-1}. The smaller the dendrite branch order, the smaller its growth rate. According to Fig. 4b takes place a quadratic dependence $x(t) = 0.799\,t^2$. So, characteristic time t_0 = 0.889 s and characteristic length $D_0 \approx 2v_1t_0 \approx 2.160$ μm. The volume of HfO_2 monoclinic sell $\Omega=1.38\cdot10^{-10}$μm^3. In this case, according to [2], the relative length $\delta_0=D_0/\Omega^{1/3} \approx 4180$.

4. CONCLUSION

Data of this work and of the literature [6, 7] show, that typical value of δ_0 are several thousand for LPC and DPC, and several hundreds for IPC. The dependence $x(t)$ is quadratic for layer and dendrite polymorphic crystallization, and exponential one for island polymorphic crystallization.

The generality of the processes of crystal growth from amorphous state and from the vapor state is that in both cases a disorder-order transition takes place. It is natural to compare the formation of a single crystal layer in amorphous film (mode of LPC) to the formation of a single crystal layer on substrate during vapor condensation (layer-by-layer growth), that corresponds to Frank-van der Merwe growth mode [8]. According to Bauer's criterion [8], this mode is realized when the inequality $\gamma_s \geq \gamma_f+\gamma_{sf}$ is satisfied. Here γ_s, γ_f, γ_{sf} are the surface energy of substrate, film, and interphase energy between the film and substrate, respectively. Formation of a polycrystalline layer in amorphous film (mode of IPC) correspond to formation of a polycrystalline layer on substrate during vapor condensation (island growth), that corresponds to Volmer-Weber growth mode. This mode is realized when reverse inequality $\gamma_s \leq \gamma_f+\gamma_{sf}$ is satisfied.

Formation of a single-crystal branch of the first order in an amorphous film and growth of the second order branches on their lateral surface (mode of DPC) correspond to Stranski-Krastanov growth mode (layer-plus-island growth). This mode is realized initially when $\gamma_s \geq \gamma_f+\gamma_{sf}$. Then, after critical thickness, when $\gamma_s \leq \gamma_f+\gamma_{sf}$.

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