

# Structural and morphological features of crystallization reactions of amorphous films according to the electron microscopy data

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The possibility of classifying the crystallization reactions of amorphous films according to a number of structural and morphological features was revealed by electron-microscopic investigation "in situ". Layered polymorphic crystallization, islands polymorphic crystallization, dendrite polymorphic crystallization and fluid-phase crystallization were distinguished. The first three types of crystallization reactions occur without changes in chemical composition corresponding to amorphous film. In the case of fluid-phase crystallization the separation of the medium to crystalline and gas phases takes place. It is noted, that the layered polymorphic crystallization can be regarded as a "coherent" crystallization occurring in the accordance to the optical Huygens principle.

Рассмотрена возможность классификации реакций кристаллизации аморфных пленок по ряду структурно-морфологических признаков, выявляемых при электронно-микроскопическом исследовании "in situ". Выделены слоевая полиморфная кристаллизация, островковая полиморфная кристаллизация, дендритная полиморфная кристаллизация и жидкофазная кристаллизация. Первые три типа реакций кристаллизации происходят без изменения химического состава, соответствующего аморфной пленке. В случае жидкофазной кристаллизации имеет место расслоение среды на кристаллическую и газовую фазы. Отмечено, что слоевая полиморфная кристаллизация может рассматриваться как "когерентная" кристаллизация, проходящая в соответствии с оптическим принципом Гюйгенса.

## **1. Introduction**

Today materials in amorphous thin-film state attract considerable attention due to their wide application in various technological areas. In one case, the efficient functioning of electronic devices based on amorphous materials requires the stability of the amorphous state (for instance, photovoltaic devices), and in the other one, numerous phase transformations like "amorphous phase-crystal-amorphous phase" occurred in local film area have a great impact on device working characteristics (optical registration systems). In the both cases the character of transformations from amorphous to crystalline state as well as systematization

of crystallization reactions on the based features should be investigated.

The films in amorphous state can crystallize spontaneously or under an influence of physical factors providing transformation from metastable non-crystalline solid state (NSS) into a stable crystalline state. According to [1], in case of amorphous alloys (metallic glasses), crystallization took place through the following reactions: 1. Polymorphic crystallization, whereas amorphous substance transforms into crystalline without change in composition. Polymorphic crystallization is typical both for pure elements and for stoichiometric chemical compounds. 2. Preferred crystallization of one of the phases during the first process stage

and the following crystallization of matrix on the second stage. 3. Eutectic crystallization in which an almost spontaneous formation of two crystalline phases takes place. The crystallization reaction type is a function of free energy of various phases on concentration of chemical elements.

In [2] it was shown that NSS formation in Ge–Sb–Te and As–In–Sb–Te crystalline compounds used as optical registration devices was accomplished by liquid phase alloying induced by local melting of substance exposed to pulsed laser irradiation. It was found that transformation rate of NSS area into crystalline is determined both by crystal growth rate and by crystallization center formation rate. Dependent on dominated process two types of crystallization is possible: the growth crystallization and the crystal nucleation one.

In the case of amorphous substance in thin-film state the crystallization process is well revealed by using *in-situ* transmission electron microscopy. In this case, the crystallization process can be initiated either by local heating of selected area of the film under electron beam irradiation or by heating the total film surface inside a specialized adapter. The aim of the present activity is the study and systematization of crystallization reactions of amorphous films basing on their structural-morphological features.

## 2. Experimental

The amorphous films were prepared by vacuum condensation as well as by pulsed laser sputtering of metallic and semiconductor targets in vacuum and in oxygen medium. The substance was deposited on the surface of KCl crystal chip (001) at room temperature. The obtained films were separated from the substrates in distilled water for the following electron microscopic investigations.

The films of 20–100 nm in thickness transparent for an electron beam were investigated. The film thickness was defined on a number of impulses of the laser irradiation influencing the sprayed target. Additional local control of  $t$  was carried out after the film crystallization taking into consideration the distance between interferential images of extinction contours in a dark field according to [3]. The film structure was investigated by electronographic methods and transmission electron microscopy. The phase transformations were initiated either by local radiating influence of

the electron beam on an amorphous film, or by means of integrated thermal heating of overall film surface in a specialized adapter in a column of electron microscope. In the second case, the samples temperature was measured on changing the electric current capacity of the adapter's resistance furnace used for heating. In the both methods of physical influence on a substance the structural-morphological features of crystallization reactions were almost identical.

## 3. Results and discussion

Basing on our own researches and taking into consideration the literature data the following classification of crystallization types of amorphous films by their structural-morphological features is offered.

### 3.1. Layer polymorphic crystallization (coherent crystallization)

In the case of layer polymorphic crystallization (LPC), the crystalline phase (the primary single crystal  $cf$  in Fig. 1a) is formed in thin subsurface layer in film area exposed to electronic beam (arrow "e" in Fig. 1a). The crystalline phase composition corresponds to the amorphous phase structure (af). (The amorphous phase — vacuum interface as the crystalline phase incipient place was experimentally proven in [4], when investigating  $Ge_2Sb_2Te_5$  amorphous films). Crystallization front rate  $v_\tau$  in a tangential direction (parallel to the film surface) considerably exceeds crystallization front rate  $v_n$  normal to the film surface.

The crystalline layer looks like spreading over on the film surface. The movement of crystallization front may be described as the moving of line at  $v_\tau$  velocity, which corresponded to interaction of amorphous phase, crystalline phase and vacuum (solid line  $g-g'$  in Fig. 1a). During single crystal growth  $g-g'$  line (crystallization line) is moved like light wave front in accordance with Huygens-Fresnel principle [5]. Each point of crystallization line generates secondary flat crystallization centers. Such secondary centers have similar orientation with those of the primary crystal (coherent with each other). Intergrowing for the time  $\Delta t$  they provide transition of every point of crystallization line over a length of  $v_\tau \Delta t$ . New position of the crystallization line (dotted line in Fig. 1a) corresponds to envelope of secondary crystallization centers. Therefore, formation of single-crystalline nucleus and its following growth according to LPC mechanism may be

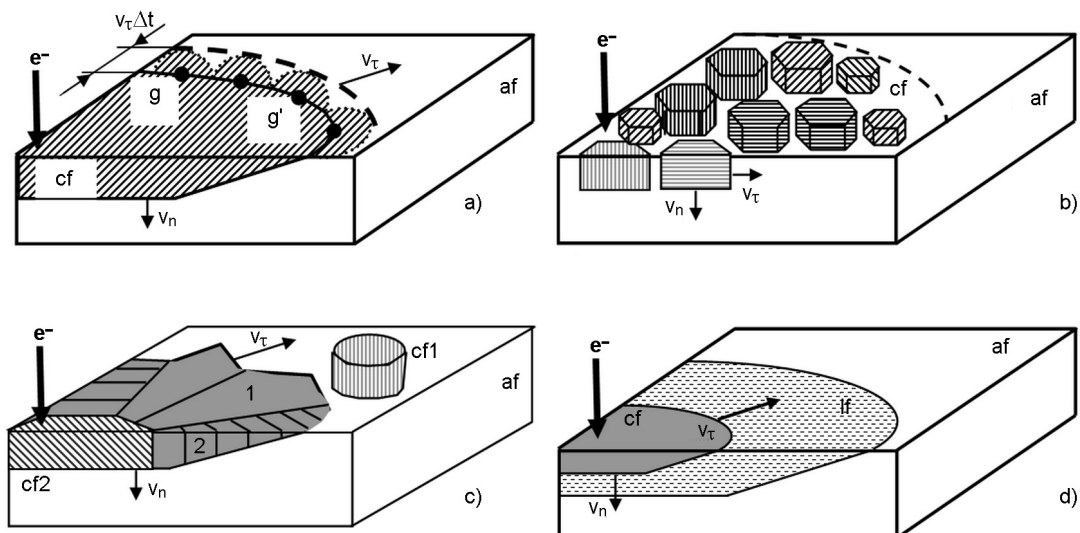


Fig. 1. Scheme of crystallization variants of amorphous films: (a) layer polymorphic crystallization; (b) island polymorphic crystallization; (c) dendrite polymorphic crystallization; (d) fluid phase crystallization. af — Amorphous phase, cf — crystalline phase, lf — liquid phase. Arrow  $e^-$  points to the place of electronic beam irradiation.

considered as a type of coherent crystallization of the amorphous film.

Layer growth according to Frank and Van-der-Merve mechanism is similar to LPC growth mechanism in the case of film growth from vapor phase on a substrate [6]. According to [7] the energy criterion of LPC mechanism can be described as:

$$\sigma_a \geq \sigma_c + \sigma_{ac} + \varepsilon_d, \quad (1)$$

where  $\sigma_a$  is free surface energy of amorphous phase-vacuum interface,  $\sigma_c$  — free surface energy of crystalline phase-vacuum interface,  $\sigma_{ac}$  — free surface energy of amorphous-crystalline phase interface,  $\varepsilon_d$  — strain energy of growing crystalline layer. The crystalline phase is tent to eliminate the free surface of amorphous film with high value of  $\sigma_a$  ("wetting" condition).

LPC mechanism is more inherent to Se, Sb,  $Sb_2S_3$ ,  $Sb_2Se_3$  semiconductors and  $Cr_2O_3$ ,  $V_2O_3$ ,  $Fe_2O_3$  oxides. An example of the LPC, as a result of local electron beam heating of  $Cr_2O_3$  amorphous film obtained by Cr laser sputtering in oxygen medium is shown in Fig. 2a. The film thickness is 21.7 nm. Only single  $Cr_2O_3$  flat crystal is nucleated and grow on a surface of amorphous film at  $v_\tau \approx 1.2 \mu\text{m}\cdot\text{c}^{-1}$  in a spot exposed to electron beam. Similar growth rate and LPC mechanism took place during amorphous film annealing in vacuum at  $T_0 = 930$  K. When growing, the crystal is bent due to stretch

tensions, and TEM image revealed extinction contours. Zone-axis images are formed in places where extinction contours are crossed (Fig. 2a) (Zone-axis oriented along  $[001]$   $Cr_2O_3$ ), and Fig. 2b.

As a rule, crystalline phase density is higher then amorphous phase one. Therefore, during growth the single crystal undergoes stretch tensions, and splits into band blocks. On a final growth stage the single crystal transforms into spherulite [8]. The band blocks are separated between each other by low angle dislocation boundaries. Dislocations are formed on the crystallization line, and introduced into the bulk during the crystal growth. Fig. 2c shows an example of such a low angle dislocation boundary which separates 1 and 2 bound blocks in  $Sb_2S_3$  film. The image was taken in high resolution mode for (020) type crystalline planes with  $d = 0.565$  nm.

In Se,  $Sb_2Se_3$ ,  $Fe_2O_3$  and  $Cr_2O_3$  amorphous films a so-called "transrotational structures" may be formed at distinct stage of LPC. Such crystals have strong inner crystalline lattice bending [9–11].

Decrease of free surface energy of the amorphous film may be originated as a result of decreasing the surface roughness during crystallization in accordance with LPC mechanism.

This thesis was proven by atomic force microscopy investigations on  $Fe_2O_3$  films carried out by V.Y.Kolosov in [9, 12]. Fig. 2d shows micro relief image of  $Fe_2O_3$  amorphous film surface (zone 1), obtained by

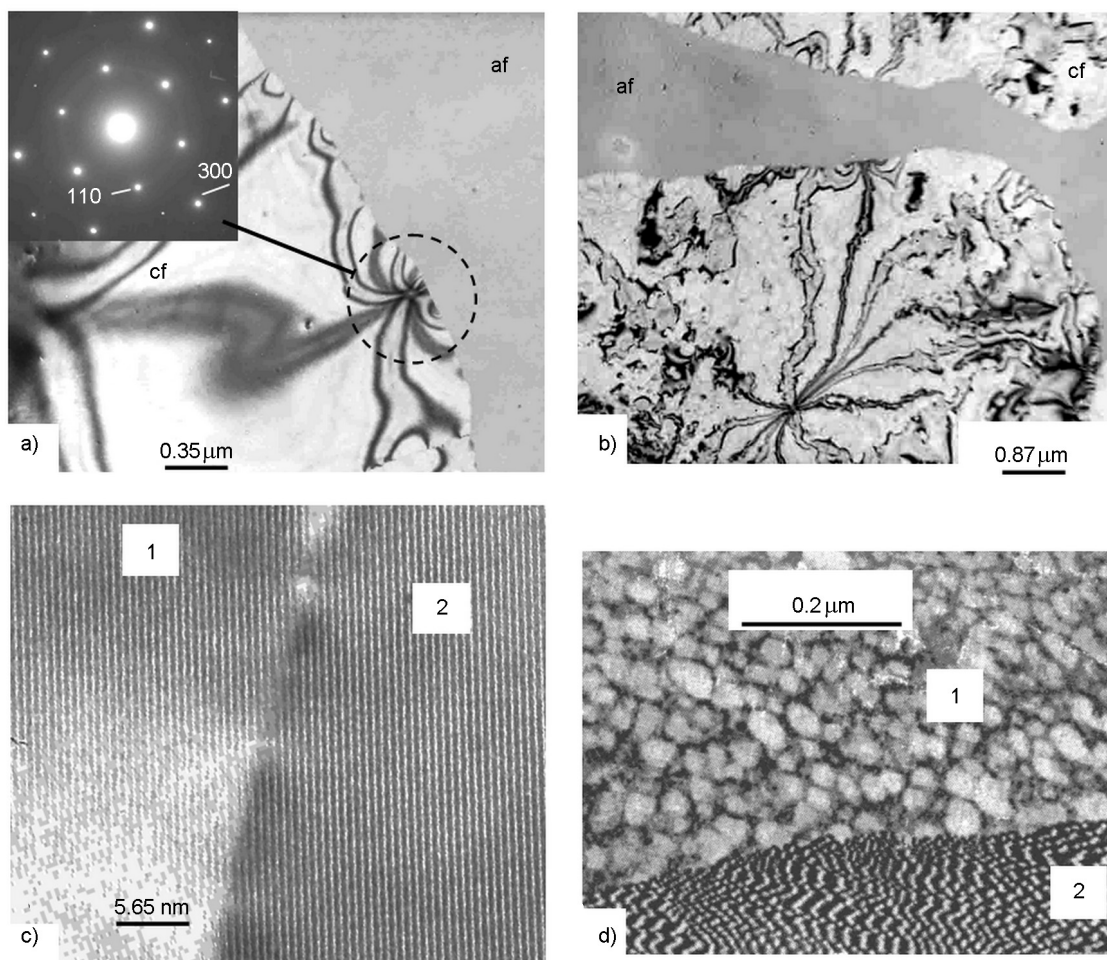


Fig. 2. Layer polymorphic crystallization of amorphous films:  $\text{Cr}_2\text{O}_3$  crystalline phase formation initiated by local influence of electron beam (a);  $\text{Cr}_2\text{O}_3$  crystalline phase formation as a result of thermal annealing of the film (b); low angle dislocation boundary image, separating spherulite band blocks under direct resolution of (020)  $\text{Sb}_2\text{S}_3$  crystalline planes (c); atomic-force microscopy image of  $\text{Fe}_2\text{O}_3$  amorphous and crystalline films surface area [12] (d).

$\text{Fe}(\text{CO})_5$  thermal oxidation on NaCl substrate. The film surface relief becomes rough due to formation of 0.01–0.05  $\mu\text{m}$   $\text{Fe}_2\text{O}_3$  amorphous globules. The crystallized surface of the film after electron beam heating was smooth due to elimination of globular structure (crystal 2 at lower image part).

Distinct relationship between the surface relief change and crystallization phenomenon is given in [13], where the decrease of surface roughness accompanied with crystallization of branches of Sb fractal clusters deposited onto graphite was described. When the deformation energy accumulated in clusters branches increases critical value, the transition  $3\text{D} \rightarrow 2\text{D}$  took place.

In the case when the amorphous film composition differs from a stoichiometric one, LPC mechanism starts after segrega-

tion of crystals of exceeded elements in amorphous matrix. Fig. 3a depicts primary segregation of Sb microcrystals in amorphous matrix (marked with arrows) and the following  $\text{Sb}_2\text{S}_3$  layer crystallization initiated by electron beam heating in a column of electron microscope. It should be noticed, that the presence of Sb islands in amorphous layer didn't affect on the structure and morphology of  $\text{Sb}_2\text{S}_3$  growing crystals.

### 3.2. Island polymorphic crystallization ("non coherent" crystallization)

During island polymorphic crystallization (IPC) the crystalline phase is formed in a subsurface layer (Fig. 1b) having the same amorphous composition like in the case of LPC. However in consequence of high formation rate of disoriented (non coherent) crystallization centers and due to

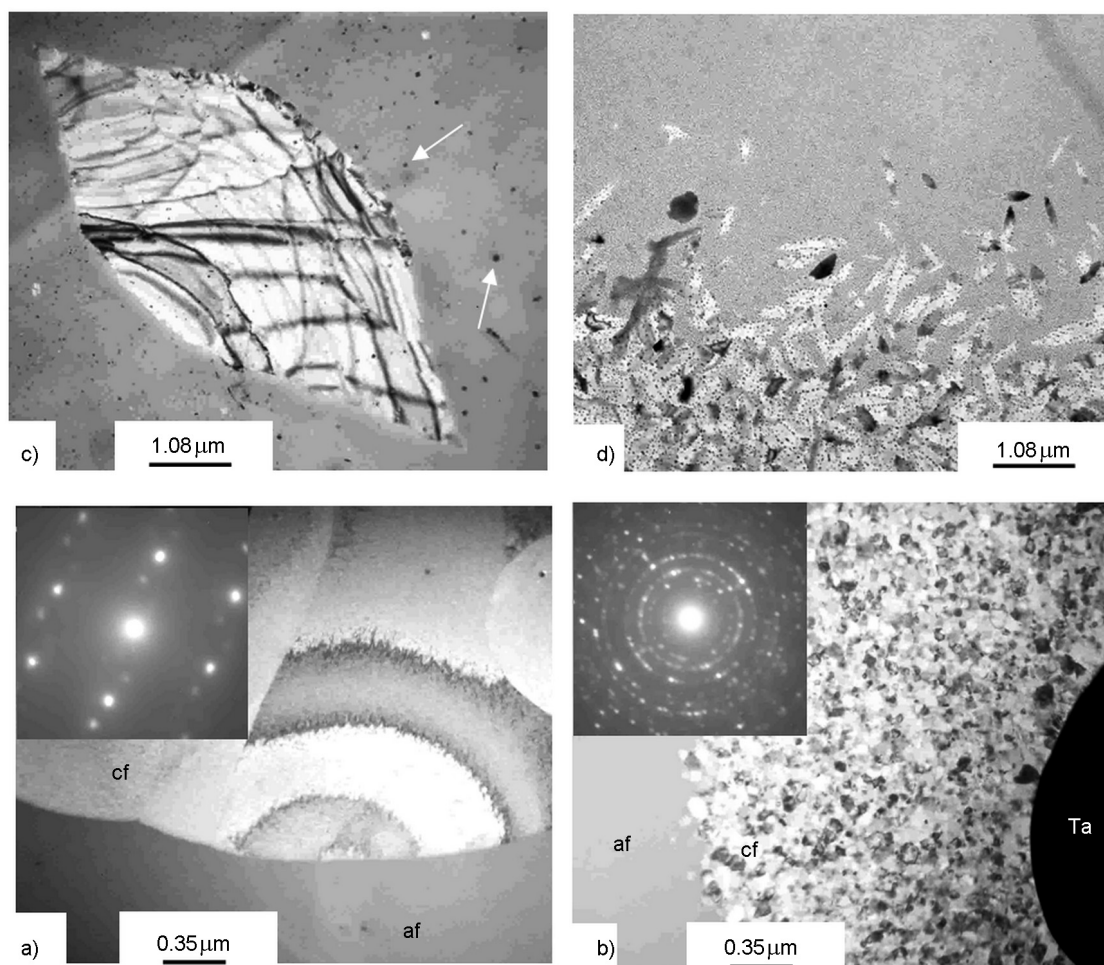


Fig. 3. Transition from layer to island polymorphic crystallization in  $\text{Sb}_2\text{S}_3$  (a, b) and  $\text{Ta}_2\text{O}_5$  amorphous films (c, d). The primary precipitation of microcrystal of Sb in amorphous matrix of  $\text{Sb}_2\text{S}_3$  are marked with arrows.

the fact that  $v_\tau \approx v_n$ , the fine-polycrystalline layer is formed on a final stage ("non coherent" crystallization of amorphous film). The IPC growth mechanism from vapor phase is analogous to Folmer-Weber island growth [6, 7]. Energy criterion of IPC mechanism is the following relationship:

$$\sigma_a < \sigma_c + \sigma_{ac} + \varepsilon_d. \quad (2)$$

As  $\sigma_a$  is low, the crystalline phase is not tent to eliminate the free surface of amorphous film ("nonwetting condition").

The mechanism of IPC is inherent to some amorphous metals and oxides (Ni, Re,  $\text{Al}_2\text{O}_3$  etc.) during crystallization. An example of IPC after electronic beam influence on  $\text{Al}_2\text{O}_3$  amorphous film obtained by laser sputtering of Al in oxygen medium is shown in Fig. 4a. Fine crystallites (cf) correspond to  $\gamma\text{-Al}_2\text{O}_3$  cubic modification. The similar

structure is formed in the case of uniform film heating in vacuum at  $T_0 = 1220$  K.

The presence of active substance on the surface of amorphous layer can change the crystallization mechanism. For instance, the layer mechanism is distinctly appears during crystallization of  $\text{Sb}_2\text{S}_3$  amorphous films (Fig. 3a). The islands of Au, revealed on  $\text{Sb}_2\text{S}_3$  amorphous film surface, slow down the motion of crystallization line. LPC mechanism is changed into IPC one leading to the formation of  $\text{Sb}_2\text{S}_3$  highly dispersed polycrystalline structure (Fig. 3b).

The local electron beam irradiation and integral thermal heating in vacuum of  $\text{Ta}_2\text{O}_5$  amorphous films obtained by Ta laser sputtering in oxygen medium initiate their crystallization according to LPC mechanism (Fig. 3c). The origination rate of non-coherent crystallization centers is increased due to intensive heat release on the local film area. In this case IPC mechanism is real-

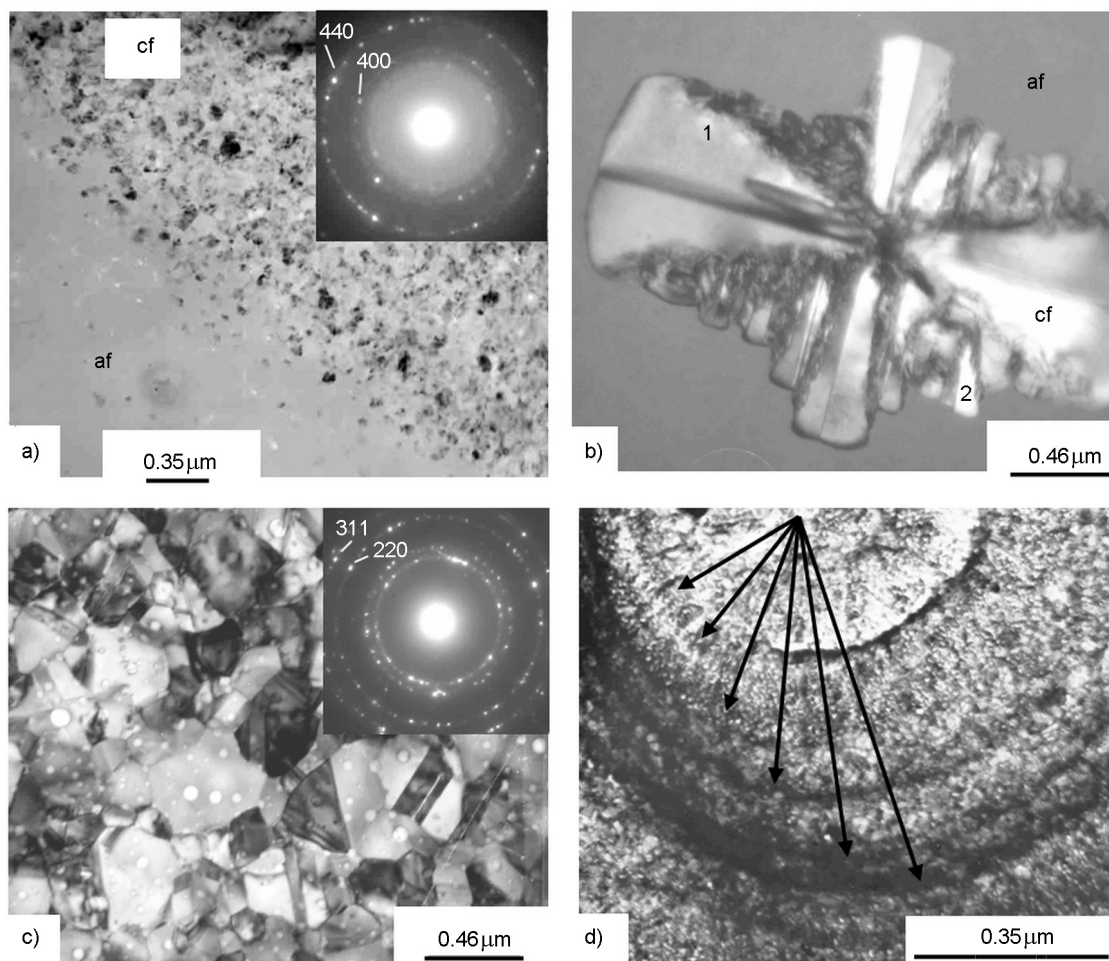


Fig. 4. Crystallization of amorphous films under electronic beam heating:  $\text{Al}_2\text{O}_3$  island polymorphic crystallization (a);  $\text{HfO}_2$  dendrite polymorphic crystallization (b); Au-O fluid phase crystallization of amorphous gas-saturated film (c, d).

ized. Fig. 3d shows an example of IPC for  $\text{Ta}_2\text{O}_5$  amorphous film after heat release during cooling of Ta liquid micro-bubble which was incorporated into the film from laser sputtered target (so-called "spray effect").

According to [4] intensive electron beam heating of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  crystallized film changes LPC mechanism into IPC one.

### 3.3. Dendrite polymorphic crystallization

In the case of dendrite polymorphic crystallization (DPC) the dendrite crystals are formed in subsurface layer of the amorphous film with composition similar to the amorphous phase. The main morphological features are the presence of branches of the first and second orders. The progress of DPC can proceed in two ways. In the first case, a single-crystalline nucleus (cf 1 in Fig. 1c) of one of the polymorphic modifications of presented substance is formed in

amorphous matrix. During growth process as a result of the size factor effect the nucleus is split in blocks with another type of the crystalline lattice (cf 2 in Fig. 1c), which are the growth centers of dendrite branches of the first order. Next, the dendrite branches of the second order are formed on them. Hereinafter, dominant growth of dendrite branches of the first order can be considered as layer polymorphic crystallization. In the second case, DPC follows without change of the crystalline lattice type of the growing nucleus. Fig. 4b shows an example of DPC of  $\text{HfO}_2$  amorphous film after electronic beam irradiation which was obtained by Hf laser sputtering in oxygen medium. When growing,  $\text{HfO}_2$  crystal with the monoclinic lattice turns to dendrite structure in a spot exposed to the electronic beam. In Fig. 4b the 1 and 2 numbers depict dendrite branches of the first and second orders, respectively. An intensive

crystallization of  $\text{HfO}_2$  takes place during thermal annealing of the films in vacuum at  $T_o = 830$  K. Some features of dendrite structure formation during explosive crystallization in Co and Co-Pd nano-crystalline films were investigated in [14].

### 3.4. Fluid-phase crystallization

In the case of fluid-phase crystallizations (FPC) occurred in the amorphous layer being in non-equilibrium state, the liquid is formed which is practically instantly crystallizes (lf and cf on Fig. 1d). The type of FPC is inherent to gas-saturated condensates obtained by laser ablation of noble metals in gaseous medium [15, 16]. Fig. 4c demonstrates an example of FPC for oxygen-containing Au film ( $t \approx 90$  nm) due to an electron beam initiation. The image depicts the central area of a so-called explosive crystallization of the amorphous film at  $v_\tau \approx 20 \mu\text{m}\cdot\text{c}^{-1}$ . The oxygen which is not dissolved neither in liquid nor in crystalline Au is precipitated in a form of babbles in the formed liquid. Next, the babbles turned out to be incorporated inside the grains of crystallized Au. According to the electric resistance data of the film crystallization of the amorphous Au-O layer takes place at  $T_o = 362$  K. The presence of spherical babbles and voids in the crystalline grains are structural-morphological features of FPC of amorphous gas-saturated films. In the case of crystallization of amorphous gas-saturated films according to layer-phase crystallization, for instance Se-O amorphous films, the spherical shape of gas-contained babbles is no longer preserved after moving the crystallization front [17].

Other structural-morphological features of impact fluid-phase crystallization of amorphous gas-saturated films are radial crystal growth from the center of the electron beam localization and the presence of concentric joints occurred by periodical slowdown of crystallization front due to gas babbles (Fig. 4d).

## 4. Conclusions

Basing on the structural-morphological features of nucleation and growth of crystalline phase, the following classification of the variety of crystallization reactions forms of amorphous films is proposed [18].

1. Layer polymorphic crystallization (coherent crystallization). This type of crystallization is similar to layer film growth on substrate from vapor phase (Frank and Vander-Merve growth). The main structural-

morphological features are as follows: low density of crystallization centers, nucleation of flat crystals on amorphous film surface, and their following oriented growth parallel to the film surface. Due to phase transformations the crystalline film is formed in which the diameters of flat grains oversized the film thickness.

2. Island polymorphic crystallization (non-coherent crystallization). This type of crystallization is similar to island film growth from vapor phase (Folmer-Weber growth). The main structural-morphological features are following: high density of crystallization centers; nucleation of equiaxed disoriented crystals on film surface, and their following growth into the bulk. As a result of phase transformations, fine-dispersed polycrystalline film is formed.

3. Dendrite polymorphic crystallization. In the case of dendrite polymorphic crystallization (DPC) the dendrite crystals are formed in subsurface layer of the amorphous film with composition similar to amorphous phase. The main morphological features are the presence of branches of the first and second orders.

4. Fluid-phase crystallization in amorphous gas-saturated films. Structural-morphological features of impact fluid-phase crystallization of amorphous gas-saturated films are radial crystal growth from the center of the electron beam localization and the presence of concentric joints occurred by periodical slowdown of crystallization front due to gas babbles. After FPC transition, the crystalline grains of the central film area contained spherical babbles and pores occurred as a result of gassing in liquid phase.

The first three types of crystallization reactions took place without change in chemical composition corresponding to the amorphous film. In the case of fluid-phase crystallization, the bipartition into crystalline and gas phases occurred.

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## **Структурно-морфологічні ознаки реакцій кристалізації аморфних плівок згідно з даними електронної мікроскопії**

**О.Г.Багмут**

Розглянуто можливість класифікації реакцій кристалізації аморфних плівок за рядом структурно-морфологічних ознак, що виявляються під час електронно-мікроскопічного дослідження "in situ". Відокремлено шарову поліморфну кристалізацію, острівцеву поліморфну кристалізацію, дендритну поліморфну кристалізацію та рідкофазну кристалізацію. Перші три типи реакцій кристалізації проходять без зміни хімічного складу, який відповідає аморфній плівці. У разі рідкофазної кристалізації відбувається розшарування середовища на кристалічну та газову фази. Зазначено, що шарова поліморфна кристалізація може розглядатися як "когерентна" кристалізація, яка здійснюється згідно з оптичним принципом Гюйгенса.