Layer, island and dendrite crystallizations of amorphous films as analogs of Frank-van der Merwe, Volmer-Weber and Stranski-Krastanov growth modes

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Electron-microscope investigations "in situ", concerning the crystallization of amorphous films, are systematized. Based on the analysis of the structure and morphology of crystals growing in amorphous films as a result of electron beam influence, a quantitative interpretation of layer polymorphic crystallization (LPC), island polymorphic crystallization (IPC) and dendrite polymorphic crystallization (DPC) is given. For each crystallization mode the parameter of dimensionless relative length $\delta_0$, equal to the ratio of the characteristic length to the value, characterizing the size of the unit cell of the crystal, was respectively assigned. Based on the video recording of the process, the kinetic curves of LPC, IPC and DPC are constructed. LPC ($Cr_2O_3, V_2O_3, Sb_2S_3, Se$ and others) is regarded as morphological analog of Frank-van der Merwe (FM) growth mode of a crystal from the vapor phase. In the case of LPC in the zone of observation in amorphous film grows a single flat crystal. By analogy with FM growth mode an energy criterion of the LPC can be written as $\sigma_a \geq \sigma_c + \sigma_{ac} + \epsilon_0$, where $\sigma_a$ is the free energy of the amorphous phase-vacuum interface, $\sigma_c$ is the free energy of the crystalline phase-vacuum interface, $\sigma_{ac}$ is the free energy of the amorphous-crystalline phase interface, and $\epsilon_0$ is the energy of deformation of the growing crystalline layer. For FPS the quadratic dependence of the rate of the crystalline phase $x$ on time $t$ takes place and $\delta_0$ = 2500–4700. IPC ($Al_2O_3, ZrO_2, Ni, Re$ and others) is regarded as morphological analog of Volmer-Weber growth mode of a crystal from the vapor phase. In the case of IPC in the zone of observation in amorphous film grows a lot of small disoriented crystals. By analogy with VW growth mode an energy criterion of the IPC can be written as $\sigma_a \leq \sigma_c + \sigma_{ac} + \epsilon_0$. For IFS the exponential dependence of $x(t)$ takes place and $\delta_0$ = 100–900. DPC (films of Fe-C, HfO$_2$) is regarded as morphological analog of Stranski-Krastanov growth mode of a crystal from the vapor phase. A characteristic sign of DPC is the formation of dendrite branches along the sides of a flat single crystal. For DPC the quadratic dependence of $x(t)$ takes place and $\delta_0$ = 3900.

Keywords: kinetic of crystallization, growth modes, in situ TEM, relative length, video recording.
Шаровая, остритцева и дендритная кристаллизация аморфных плююк как аналоги механизмов роста Франка-ван дер-Мерве, Фольмера-Вебера и Странского-Крастанова. О.Г.Багмут.
Систематизировано электролитическое диссольбирование "in situ", что способствует кристаллизации аморфных плююк. Группируются на анализ структуры и морфологии кристаллов, что ростом в аморфных плююках у результату влиянию электролитичного промена, дачо кихляние трекания шарово плюиюной кристаллизации (ШПК), остритцевой полиморфной кристаллизации (ОПК) и дендритной полиморфной кристаллизации (ДПК). Для козного типу кристаллизации можно определить амфий анома во дозвонные дозвои, данный, отличаемое влияние характеристики дозвонного амфий, амфий ванада кинетический правил ШПК, ОПК и ДПК. ШПК и ОПК (Cs₂O₃, V₃O₈, Sb₂S₃, Se и др.) рассматриваются как морфологический аналог механизма роста Франка-ван дер-Мерве при росте кристаллов из плююжей фазы. По аналогии с механизмом роста ФМ энергетический критерий ОПК может быть записан как \( \sigma_a = \sigma + \sigma_{ac} + \gamma_{d} \), где \( \sigma_a \) — свободная энергия границы раздела аморфной фазы — вакуум, \( \sigma_{ac} \) — энергия деформации зерен кристаллической фазы. Для ОПК в зоне наблюдений в аморфной плююке ростет множество мелких разориентированных кристаллов. Для ПК выполняется экспоненциальная зависимость \( y(t) \) и \( \delta_0 = 100-900 \). ДПК (плююк Fe–C, H₂O₂) рассматривается как морфологический аналог механизма роста Оганского-Крастанова при росте кристаллов из плююжей фазы. Характерным признаком ДПК является образование дендритных ветвей на сторонах плююжевой фазы. Для ДПК выполняется квадратичная зависимость \( y(t) \) и \( \delta_0 = 900 \).

1. Introduction
The classical scheme of the formation of a crystalline layer upon condensation of a vapor stream on a substrate (transformation vapor — crystal) suggests the following growth mode of a film [1]. The Frank-van der Merwe (FM) growth mode (layer-by-layer growth). According to Bauer’s criterion [2], this mode is realized when the inequality \( \gamma_s \geq \gamma_f + \gamma_{sf} \) is satisfied. Here \( \gamma_s \), \( \gamma_f \), \( \gamma_{sf} \) are the surface energy of substrate, film, and interphase energy between the film and substrate, respectively. The Volmer-Weber (VW) growth mode (island growth). This mode is realized when the opposite inequality \( \gamma_s \leq \gamma_f + \gamma_{sf} \) is satisfied. The Stranski-Krastanov (SK) growth mode (layer-plus-island growth). This mode is realized initially when \( \gamma_s \geq \gamma_f + \gamma_{sf} \), then, after critical thickness, \( \gamma_s \geq \gamma_f + \gamma_{sf} \). (Table). The above is valid
Table. Comparison of phase transformations vapor-crystal at films growth and amorphous phase — crystal at films crystallization

<table>
<thead>
<tr>
<th>Transformation vapor – crystal</th>
<th>Transformation amorphous phase – crystal</th>
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<tbody>
<tr>
<td>Growth mode [1, 2]</td>
<td>Mechanism</td>
</tr>
<tr>
<td>FM</td>
<td>$\gamma_s \geq \gamma_f + \gamma_d$</td>
</tr>
<tr>
<td>VW</td>
<td>Initially $\gamma_s \geq \gamma_f$</td>
</tr>
<tr>
<td>SK</td>
<td>Initially $\gamma_s \leq \gamma_f + \varepsilon_d$</td>
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$FM$ is the Frank-van der Merwe growth mode, VW is the Volmer-Weber growth mode, SK is the Stranski-Krastanov growth mode. LPC is the layer polymorphous crystallization, IPC is the island polymorphous crystallization, DPC is the dendrite polymorphous crystallization. $\gamma_s$, $\gamma_f$, $\gamma_d$ are the surface energy of substrate, film and interphase energy between film and substrate, respectively. $\sigma_d$, $\sigma_c$, $\sigma_{ac}$ are the surface energy of amorphous phase-vacuum interface, surface energy of the crystalline phase-vacuum interface and surface energy of the amorphous-crystalline phase interface, respectively. $\varepsilon_d$ is the energy of deformation of a crystal, when $\sigma_d \leq \sigma_c + \sigma_{ac} + \varepsilon_d$ (Table 1).

A sufficiently complete analysis and comparison of the morphological community of transformations vapor — crystal at films growth and amorphous phase — crystal at films crystallization are not available now. So, the aim of this work was to give an overview of the main types of crystallization of amorphous films with an emphasis on electron-beam crystallization "in situ" of oxides, obtained predominantly by laser evaporation.

2. Experimental

Amorphous films were prepared by the thermal deposition of material in vacuum, pulsed laser deposition in an oxygen atmosphere and by ion-plasma deposition in argon-oxygen atmosphere on substrates at room temperature. KCl crystals, cleaved in air along the (001) planes, served as substrates. After deposition and depressurization of the chamber, the films were separated from the substrates in distilled water and transferred to the object grids for the electron microscopic studies. Structural analysis was performed by electron diffractometry and transmission electron microscopy on EM-100L and PEP-100-01 electron mi-
croscopcs operated at an accelerating voltage of 100 kV. The thickness of the films varied in the range from 25 to 30 nm. The crystallization of a film was initiated by electron beam irradiation in the column of a transmission electron microscope. The crystallization of the local area of the amorphous film was initiated and maintained all the time by an electron beam at a beam current of ~20 µA. It was not a consequence of the appearance of a crystal nucleus, since it did not continue on its own (as is the case, for example, in supercooled liquids) after the termination of the electron-beam action. The crystallization rate was set by varying the electron current density $j$ through the sample, which was 1.1–6.5 A mm$^{-2}$, depending on the beam focusing. The film crystallization process was recorded from the screen of an electron microscope on a Canon Power Shot G15 camera in the video record mode at a frame rate of 30 s$^{-1}$. The experimental details are presented in [7].

Quantification of the crystallization type (LPC or IPC) was carried out on the basis of the value of relative length $\delta_0$, defined as

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

in the case of LPC, and as

$$\delta_0 = \frac{D_0}{\Omega a}$$

in the case of IPC. Characteristic unit length $D_0$ is the crystal size at time $t_0$, after which the volume of the amorphous phase decreases by a factor of $e^{-2.718}$. $a_0$ in expression (1) is a cell parameter of a growing crystal. $\Omega$ in expression (2) is the volume of the unit cell of a growing crystal. The difference in the determination of $\delta_0$ 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 a polycrystalline film whose grains have different orientations [8, 9].

3. Results and discussion

3.1. Layer polymorphous crystallization as morphological analog of the Frank-van der Merve growth mode

In the case of a LPC crystalline phase is initially formed in a thin near surface layer and its composition coincides with that of the initial amorphous phase. The velocity of propagation of the crystallization front in the tangential direction ($v_T$) significantly exceeds the velocity of crystallization front propagation along the normal to the film surface ($v_N$). The crystalline layer appears as “spreading” over the film surface.

The LPC type is inherent to a considerable extent in semiconductors (Se, Te, Sb [10, 11], Sb$_2$S$_3$ [12], etc.) and oxides (ReO$_3$ [12], Cr$_2$O$_3$ [13], V$_2$O$_3$ [14], Fe$_2$O$_3$ [15], etc.). In amorphous Cr$_2$O$_3$ films the main morphological forms (disk-shaped, sickle-shaped and needle-shaped crystals) of layer polymorphous crystallization are observed [9, 16]. In this work, the main morphological forms of LPC in Cr$_2$O$_3$ are shown in Fig. 1. This is disk-shaped (a), sickle-shaped (b) and needle-shaped (c) crystals. Each of these forms has its own kinetics of the development.

Disk-shaped crystals grow with a constant speed $v$ and unchanged morphology (Fig. 2a, 2b, 2c). The dependence of the ra-
radius $R$ of the crystal and of the area $S$ of the crystalline phase on time $t$ are shown in Fig. 2d and 2e respectively. According to these kinetic curves, the speed of displacement of the crystallization front $v = R_t = 0.173 \, \mu\text{m} \cdot \text{s}^{-1}$. There is a quadratic dependence $S(t)$ (and consequently of the fraction of the crystallized region $x(t)$): $S(t) = 0.0878 \cdot t^2 \, (\mu\text{m}^2)$. The area of the analyzed sample $S_0 = 2.9 \, \mu\text{m}^2$. So, characteristic time (after which $x = 0.632$) $t_0 = 4.58 \, \text{s}$ and characteristic length $D_0 = 1.58 \, \mu\text{m}$. For a crystal of Cr$_2$O$_3$ with the [001] zone axis (Fig. 1a), the projection of the unit cell on the plane of the film is a rhomb with a side $a_0 = 0.496 \, \text{nm}$ and apex angle of 120°. In this case, according to (1), the relative length $\delta_0 = 3185$. It is comparable to the values $\delta_0 \sim 4300$–4700 for the layer polymorphic crystallization of amorphous $V_2O_3$ films obtained by laser evaporation [8].

Sickle-shaped crystals grow with a variable rate $v$ and with a changeable morphology (Fig. 3a, 3b, 3c). Fig. 3d shows the $R(t)$ curve for sickle-shaped (in the initial stages) crystal of Cr$_2$O$_3$ during electron beam crystallization of the film. According to this, at the initial stages (stages of the sickle and of the ring), there is a parabolic dependence $R(t) \sim t^2$. At the final stage of growth (stage of the disk), there is a linear dependence $R(t) \sim t$. At this stage the growth of the crystal occurs with a velocity $v_f = 0.075 \, \mu\text{m} \cdot \text{s}^{-1}$. The kinetic curve $S(t)$ is shown in Fig. 3e. In part 1 (the sickle-shaped stage) and in part 3 (disk stage) $S(t) \sim t^2$ (in $S$ $t^2$ coordinates the experimental data are placed on straight lines). In part 2 (ring-shaped stage) the dependence $S(t)$ is more complex.

Needle-shaped crystals some time grow with a constant speed $v$ and with unchanged morphology (Fig. 4a, 4b). But during growth process on the lateral surface of a needle-shaped crystal is possible the formation of outgrowths (Fig. 4c). Fig. 4d shows the dependence of a crystal length $L$ and length of lateral outgrowths $h_1$ and $h_2$ on...
Fig. 3. Kinetic of growth of a sickle-shaped crystal in amorphous film of Cr$_2$O$_3$ (LPC). Electron microphotographs correspond to the time moments $t$, which have passed from the beginning of the recording of the crystallization process: (a) $t = 2.10$ s; (b) $t = 2.60$ s; (c) $t = 3.07$ s. (d) The dependence of the arc radius $R$ of the crystallization front at time $t$. Region 1 — the sickle and ring stages, region 2 — the stage of the disk. (e) The dependence of the area $S$ of the crystalline phase on time $t$. Region 1 — the stage of the sickle, 2 — the stage of the ring, 3 — the stage of the disk.

time $t$. When outgrowth occurs on the lateral surface of the needle-shape crystal, the rate of the increasing of in $L$ decreases. The straight section of $L$ corresponds to the growth rate of a crystal length $v_L = 1.746 \mu m s^{-1}$, that is commensurate with the rate of growth of the lateral outgrowth $v_{hL} = 1.604 \mu m s^{-1}$ and $v_{hZ} = 1.453 \mu m s^{-1}$. The dependence $S(t)$ is shown in Fig. 4e. A straight line (in coordinates $S(t) - t^2$) indicates that $S(t) \sim G_t t^2$ with the coefficient $G_S = 0.105 \mu m^2 s^{-2}$. When outgrowth occurs on the lateral surface of the needle-shape crystal, the rate of increasing of $S$ increases and the linear dependence than is not satisfied.

3.2. Island polymorphous crystallization as morphological analog of the Volmer-Weber growth mode

In the case of IPC crystalline phase formed in a thin near surface layer and its composition coincides with that of the amorphous phase. The final stage of the process leads to the formation of a polycrystalline film (Fig. 5). Crystalline phase does not tend to eliminate the free surface of amorphous phase ("no wetting" condition). This type of reaction is inherent in the crystallization of some amorphous metals and oxides (Ni, Re [12], Al$_2$O$_3$ [5], ZrO$_2$ [7], etc.).

Fig. 6 illustrates the kinetics of IPC of amorphous film of ZrO$_2$. Electron micrographs corresponds to the time moments $t$, which have passed from the beginning of the recording of the crystallization process: (a) $t = 28.63$ s; (b) $t = 127.00$ s; (c) $t = 194.87$ s. The dependences of average diameter $D(t)$ of crystals are shown in Fig. 6d. The straight line was plotted by the data of $D$ measurements using the least-squares technique. The average growth rate of crystals (that was determined from the slope of the line to abscissa) $v = 0.002 \mu m s^{-1}$. 

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The dependence $S(t)$ is shown in Fig. 6e. The fact, that the crystallization curve in coordinates $\ln[-\ln(1 - S/S_0)] - \ln t$ are straight line, indicates that occurs the Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation $S - S_0[1 - \exp(-nt^\beta)]$, where $k$ and $n$ are the kinetic parameters of crystallization [17]. According to [7] for $v = 0.002$ μm$^{-1}$s$^{-1}$ kinetic parameter $k = 1.3$ and $n = 0.001$. So, characteristic time $t_0 = n^{-1/k} = 203$ s and characteristic length $D_0 = v_0 = 0.41$ μm. The volume of ZrO$_2$ cubic cell $\Omega = 1.32 \times 10^{-10}$ μm$^3$. In this case, according to (2), the relative length $\delta_0 = 805$. It is comparable to the values $\delta_0 \approx 1000$ for the special case of IPC in amorphous film of V$_2$O$_3$ [8]. The smaller the grain size of the crystallized film, the smaller the dimensionless parameter $\delta_0$.

Thus, electron-beam crystallization of amorphous ZrO$_2$ films, deposited by ion-plasma sputtering (Fig. 5b), results to the formation of a highly disperse polycrystalline structure with $\delta_0 = 100$ [7]. The charge and energy of ions in condensed on a substrate stream during ion-plasma and laser sputtering are different. Ion-plasma deposition creates a large density of defects (for example, color centers) in the surface layer of KCl, which leads to a higher density of hidden crystallization centers in an amorphous ZrO$_2$ film.

3.3. Dendrite polyhedral crystallization as morphological analog of the Stranski-Krstanov growth mode

DPC was observed in amorphous films of Fe–C [18], V–O and HfO$_2$ [12]. Phase transformation amorphous phase-dendrite HfO$_2$ of a monoclinic modification accompanied by the formation of outgrowths (dendrite branches of the second and third order) on the lateral surface of the dendrite branches of the first order (Fig. 7). It should be considered as morphological analogue of SK growth mode of a crystal from the vapor
Fig. 5. Island polymorphous crystallization (IPC) of amorphous films. Electron microscopic images of crystallizing films of Al₂O₃ (a) (laser evaporation), of ZrO₂ (b) (ion-plasma evaporation), of ZrO₂ (c) (laser evaporation). SAED patterns are shown in the upper left corner of the micrographs.

Fig. 6. Kinetic of crystals growth in amorphous film of ZrO₂ (IPC). Electron microphotographs corresponds to the time moments t, which have passed from the beginning of the recording of the crystallization process: (a) t = 28.63 s; (b) t = 127.00 s; (c) t = 194.87 s. (d) The dependence of the average diameter D of crystals on time t. (e) The dependence of the area S of the crystalline phase on time t.

The crystalline phase of HfO₂ is denser than of amorphous one. Therefore a crystal, growing in amorphous film, is in the field of tensile stresses, which can initiate the growth of new crystals on the lateral surface of the already existing one.

Kinetic of dendrite growth in amorphous film of HfO₂ are shown in Fig. 8. Electron microphotographs corresponds to the time moments t, which have passed from the beginning of the recording of the crystallization process: (a) t = 5.03 s; (b) t =

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Fig. 7. Dendrite polymorphous crystallization (DPC) of amorphous film of HfO₂. (a) Electron microscope image of dendrite in amorphous film. (b) Geometric selection in a growing aggregate of HfO₂ crystals. (c) SAED pattern from the dendrite branch of the first order. Numbers 1, 2, 3 marks the branches of the dendrite of the first, second and third order, respectively.

Fig. 8. Kinetic of dendrite growth in amorphous film of HfO₂ (DPC). Electron microphotographs corresponds to the time moments t, which have passed from the beginning of the recording of the crystallization process: (a) t = 5.03 s; (b) t = 10.77 s; (c) t = 15.67 s. (d) The dependence of the dendrite branches length h₁, h₂, h₃ on time t. (e) The dependence of the area S of the crystalline phase on time t.

10.77 s; (c) t = 15.67 s. The dependence of the length of the dendrite branch of the first order h₁ and of the second order h₂ and h₃ on time t is shown in Fig. 8d. The increase of h₁, h₂ and h₃ occurs at a constant rate ν₁ = 0.064 µs⁻¹, ν₂ = 0.041 µs⁻¹, ν₃ = 0.040 µs⁻¹, respectively. The ratio ν₁ > ν₂ > ν₃ shows, that the dendrite branches of...
the first order grow faster than all. The later the branch appeared, the more slowly it grows.

Fig. 8e shows the quadratic dependence of the area $S$ of the crystalline phase on time: $S(t) = 0.007 t^2$ ($\mu m^2$). The area of the analyzed sample $S_0 = 2.65 \mu m^2$. So, characteristic time $t_0 = 15.5 \text{s}$ and characteristic length $d_0 = 2 \sqrt{t_0} = 2.0 \mu m$. Various branches of dendrites of $\text{HfO}_2$ have different crystallographic orientations. Therefore, the relative length of crystallization $\delta_0$ should be defined as (2), where the volume of the unit cell of the monoclinic modification of $\text{HfO}_2 \Omega = 1.3828 \times 10^{-10} \mu m^3$. According (2) for dendrite polymorphous crystallization of $\text{HfO}_2$ the relative length $\delta_0 = 3868$.

4. Conclusions

The generality of the processes of crystal growth from the vapor phase and from the amorphous state is that in both cases a disorder-order transition takes place. This predetermines the structural and morphological analogy (Table) between the main forms of crystal growth on substrates (FM, VW and SK growth mode) and the main types of crystallization of amorphous films (LPC, IPC and DPC).

Frank-van der Merwe growth mode corresponds to the type of layer polymorphous crystallization, since in both cases a single-crystal layer is formed. In the case of LPC of $\text{Cr}_2\text{O}_3$ under the action of an electron beam, crystals with different morphologies (disk-shaped, sickle-shaped and needle-shaped crystals) can originate in amorphous film, each of which has its kinetics of development. At a fixed density of the electron beam through the film disk-shaped crystals grow with a constant speed, unchanged morphology for with $x(t) \sim t^2$ and $d_0 \sim 3200$. Sickle-shaped crystals grow with a variable rate and with a changeable morphology: with increasing of the crystalline fraction $x$, the sickle-shaped crystal takes the form of a ring and further the form of a disk. After it crystal grows with constant speed and unchanged morphology. Before the appearance of lateral branches, the needle-shaped crystal grows with a constant speed and with unchanged morphology before it.

Volmer-Weber growth mode corresponds to the type of island polymorphous crystallization, since in both cases a polycrystalline layer is formed. In the case of IPC of $\text{ZrO}_2$ average diameter of crystals $<D> \sim t$, $x(t)$ is described by the exponential relation and $\delta_0 = 800$.

Implementation of Stranski-Krastanov growth mode somewhat analogous to the type of dendrite polymorphous crystallization, since in both cases the surface of a single-crystal layer serves as the site for the formation of branches with a different shape and orientation. In the case of DPC of $\text{HfO}_2$ single crystals in the form of dendrite branches of the first order are the place of formation of branches of the second and third order. Branches are formed from a number of randomly oriented crystals in the process of geometric selection [19, 20]. The length of the dendrite branches $h \sim t$, the fraction of the crystalline phase $x \sim t^2$ and the relative length $\delta_0 \sim 3900$. It should also be considered as a manifestation of SK growth mode the formation of lateral branches at growth of needle-shaped crystals in amorphous films of $\text{Cr}_2\text{O}_3$.

References