

Autoepitaxy and the main orientational relations at crystallization out of amorphous state in Cr–O and V–O films

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Studied have been the joining characteristics of crystals growing in amophous films of stoichiometric Cr_2O_3 and V_2O_3 under annealing. The films were deposited by laser sputtering of chromium and vanadium targets in oxygen atmosphere. The annealing of films was performed using electron beam in the column of an electron microscope. Using the transmission electron-diffraction and electron microscopy methods, the main morphological types of Cr_2O_3 and V_2O_3 nanocrystals were determined as well as the nanocrystal evolution in the course of growth. Orientation relations have been established for conjunction of crystals of different morphological types as a result of autoepitaxial growth out of amorphous phase as well as at a random contacts thereof.

Исследованы особенности срастания кристаллов, растущих в аморфных пленках стехиометрических составов Cr_2O_3 и V_2O_3 при отжиге. Пленки осаждали лазерным распылением мишеней хрома и ванадия в атмосфере кислорода. Отжиг пленок осуществляли электронным лучом в колонне микроскопа. Определены основные морфологические типы нанокристаллов Cr_2O_3 и V_2O_3, а также их эволюция в процессе роста. Установлены ориентационные соотношения при сопряжении кристаллов различных морфологических типов как в результате автоэпитаксиального роста из аморфной фазы, так и при их случайном контактировании.

The autoepitaxy is a kind of epitaxy, when the oriented growing of crystalline matter takes place on a single-crystal substrate of the same material. This phenomenon finds a wide application in technology of semiconductor electronics at growing of thin films of Ge, Si, GaAs and other semiconductors on single-crystal substrates made from the same materials [1]. The versions of its manifestation are studied comprehensively enough at the crystallization of a matter both from a gaseous state (condensation of vaporized matter on a substrate in vacuum), and from a liquid state (deposition of matter from liquid solutions or melts) [2]. At the same time, the information on auto-epitaxy realization variations at the crystallization out of amorphous state are rather scanty. At present, the amorphous state of matter is the most efficient precursor in the nano-structure synthesis [3]. Thus, the physical characteristics of a film (coating) after its full or partial crystallization depends not only on the crystal size, but also on orientation relations between individual nanocrystals, that defines the grain boundary structure. The grain boundaries are formed both at contacting of crystalline grains with arbitrary orientations growing in amorphous matrix, and at regular growth of one crystal on a lateral surface of other crystal, i.e. during autoepitaxy. Therefore, a comprehensive investigation of the autoepitaxy out of amorphous state and of orientation relations between contacting nanocrystals is rather actual now.

Several examples of autoepitaxy of Cr_2O_3 and V_2O_3 crystals at annealing of amorphous metal-oxygen films are mentioned in [4] and [5], respectively. In these works, studied have been the regularities of structure formation and crystallization in amorphous Cr–O and V–O films obtained by laser sputtering of chromium and vanadium in oxygen atmosphere. If the amorphous stoichiometric Cr–O film is formed, then it crystallizes under annealing under formation of Cr_2O_3 nanocrystals of with hexagonal crystal lattice. The V_2O_3 crystals growing under heating in amorphous stoichiometric V–O films have a similar structure and morphology.

At the initial transformation stage in amorphous Cr_2O_3 films, the crystals of three basic morphological types grow [6]: rounded, thread-like and crescent-like shapes. The rounded crystals are always oriented with a basic plane (001) Cr_2O_3 parallel to the film surface. The thread-like and crescent-like crystals are oriented so that the different crystal planes may be parallel to the film surface (including situation when the (001) Cr_2O_3 planes are oriented parallel to the film surface). In the electron-microscopic images of such crystals, numerous of bent extinction contours are observed that evidences a complex distortion of the crystal lattice.

The aim of this work consists in investigation of the autoepitaxy phenomenon at crystallization out of amorphous state including: (i) electron-microscopic research of evolution of main morphological types of Cr_2O_3 and V_2O_3 crystals during their growth in an amorphous matrix being crystallizing under annealing; and (ii) determination of the main orientation relations at conjunction of crystals of different morphological types.

The high purity chromium and vanadium targets were sputtered by nanosecond laser radiation pulses (AIG: Nd^{3+}, wavelength 1.06 μm) in oxygen atmosphere under 0.13 Pa pressure. The pulse repetition frequency $\nu = 25$ Hz. The products of laser erosion were condensed on substrates at room temperature. We have used both orienting substrates in the form of KCl single crystals cleaved along cleavage planes (001), and neutral substrates in the form of KCl single crystals coated with a thin (transparent for an electron beam) film of amorphous carbon. The films where separated from the substrate in distilled water and transferred onto the object grids. The phase transition

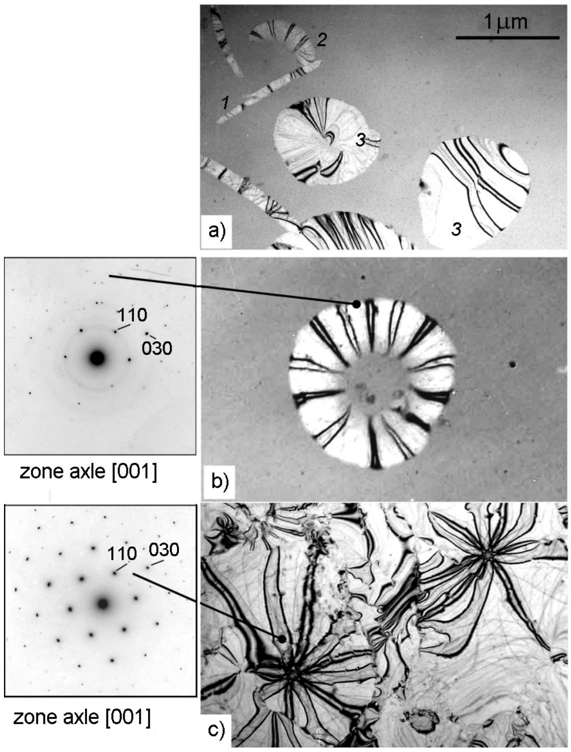

Fig. 1. The crystallization of amorphous Cr_2O_3 film. (a). The main morphological types of crystals: *1*, thread-like; *2*, crescent-like; *3*, rounded. (b). Ring-shaped crystal. (c). The final stage of film crystallisation. The bent extinction contours are distinctly see in all microphotos (a contrast streakiness). The contrast in all electron diffraction patterns is inverted.

from amorphous state into crystalline one was initiated by local heating of a selected area of an amorphous film by an electron beam in the electron microscope column ("in situ" technique).

Morphology of nanocrystals. The local heating of an amorphous film area by electron beam initiates a homogeneous nucleation of a thread-like crystals (crystal *1* in Fig. 1a). The crescent-like crystals are formed during bending of thread-like crystals (crystal 2 in Fig. 1a). If the crescent-like crystals is oriented with a basal plane (001) parallel to the film surface, then it grows and bents along a circle arc of. When the crystal tips come in a contact with one another and grow together, than the ring-shaped spherulite crystal (roll) shown in Fig. 1b will be formed. The rounded crystals may nucleate both in the free state (crystal 3 in Fig. 1a), and in bound state, heterogeneously on a lateral surface of a thread-like or crescent-like crystal.

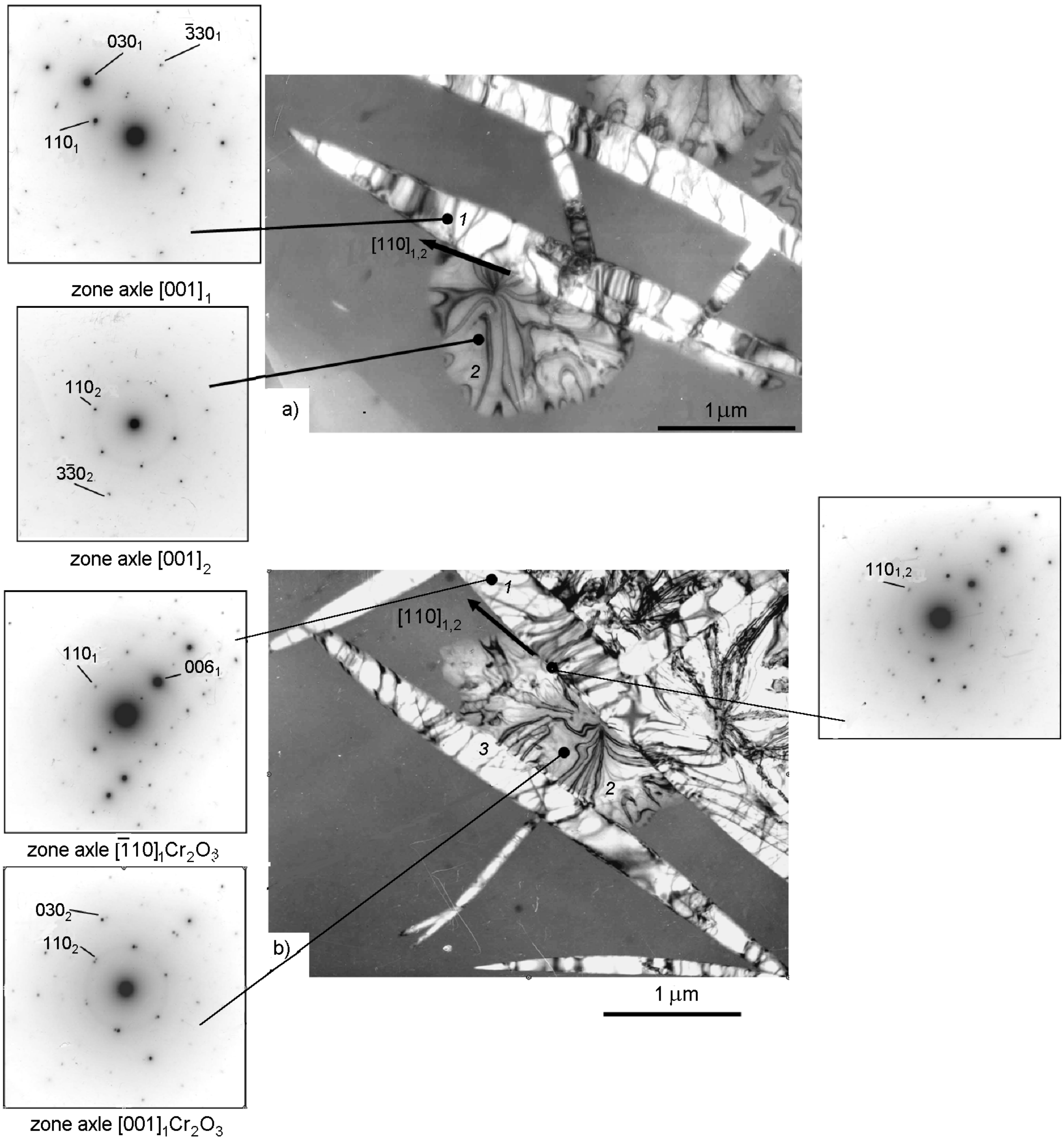

Fig. 2. Autoepitaxy at crystallization of amorphous Cr_2O_3 film. Orientation overgrowth of rounded crystal (2) along lateral surface of a thread-like crystal (1). (a). Parallel orientation relation $(001)_1[110]_1$ // $(001)_2[110]_2$ (row 1 of the Table). (b). Unparallel orientation relation $(\bar{1}10)_1[110]_1$ // $(001)_2[110]_2$ (row 2 of the Table). Joining of the crystals 2 and 3 takes place after its contacting during their growth and is not autoepitaxial.

At the final transformation stage, the main part of the film crystalline phase consists of joint crystals having originally the rounded form (Fig. 1c). In this case, the crystal/vacuum interface has the minimum energy and is represented by the (001) planes with the smallest Miller indices.

Autoepitaxy. The main conjunction versions of crystals of different morphology types being observed at the crystallization of amorphous stoichiometric Cr_2O_3 and V_2O_3 films are summarized in the Table. The Table includes both versions regular overgrowth of one crystal on the surface of other one (autoepitaxial growth), and arbitrary linking at the contacting. The criterion of regularity for crystal overgrowing is the coincidence of certain planes and directions, usually crystallographic simple ones, of the overgrowing crystal and crystal-substrate [7].

The autoepitaxial overgrowth of a rounded crystal on a lateral face of a thread-like crystal is presented in Fig. 2a

Table. Conjunction of nanocrystals at crystallization of amorphous films

No.	Crystal	Crystal morphological type					Rotation axis	Angle of rotation β(°)	Joining planes (which are normal to the film surface)	Literature
		Thread-like (1)			Rounded (2)					
		$[uvw]_{\uparrow}$	(hkl)	$[uvw]_{\leftrightarrow}$	$[uvw]_{\uparrow}$	(hkl)				
1	Cr_2O_3	[001]	(001)	[110]	[001]	(001)	$[110]_{1,2}$	0; 180	$(\bar{1}10)_1 // (\bar{1}10)_2$	–
2	Cr_2O_3	$[\bar{1}10]$	$(\bar{1}10)$	[110]	[001]	(001)	$[110]_{1,2}$	90	$(001)_1 // (\bar{1}10)_2$	–
3	Cr_2O_3	$[\bar{6}61]$	$(\bar{6}65)$	$[5\bar{5}12]$	[001]	(001)	$[5\ \bar{5}\ 12]_1$ $[001]_2$	75.2 33.8	$(110)_1 // (010)_2$	–
4	Cr_2O_3	[121]	(015)	[100]	[001]	(001)	$[100]_{1,2}$	32.3	$(01\bar{2})_1 // (010)_2$	[4]
5	V_2O_3	[212]	(1010)	$[\bar{5}43]$	[001]	(001)	$[010]_{1,2}$	17.1	$(22\bar{3})_1 // (\bar{2}10)_2$	[5]

Note: $[uvw]_{\uparrow}$ — indices of zone axis; (hkl) — indices of crystal planes, parallel to the film surface; $[uvw]_{\leftrightarrow}$ — indices of direction, parallel to the long axis of thread-like crystal. Orientation relations. Row 1 — $(001)_1[110]_1 // (001)_2[110]_2$. Row 2 — $(\bar{1}10)_1[110]_1 // (00\underline{1})_2[110]_2$. Row 3 — $(\bar{6}65)_1[5\ \bar{5}12]_1 // (001)_2[100]_2$. Row 4 — $(015)_1[100]_1 // (001)_2[100]_2$. Row 5 — $(\bar{1}20)_1[212]_1 // (\bar{1}20)_2[001]_2$.

(row 1 of the Table). A parallel alignment in this case takes place:

$$(001)_1[110]_1//(001)_2[110]_2. \qquad (1)$$

The autoepitaxial overgrowth in unparallel alignment is shown in Fig. 2b (row 2 of the Table). At a lateral area of a thread-like crystal 1, a rounded crystal 2 originates and grows deep into amorphous phase. The direct and repeated electron-microscope observations "in situ" have shown,that the tangential growth rate of thecrystal 2 increases when it reaches a lateral surface of another thread-like crystal 3. Between crystals 1 and 2, the following orientation relation takes place:

$$(\bar{1}10)_1[110]_1//(001)_2[110]_2. \qquad (2)$$

The orientation relation (2) also corresponds to coincidence of crystallographically simple planes and directions of the overgrowing crystal (crystal 2) and crystal-substrate (crystal 1). At a random, mechanical contact during the growth of thread-like crystal and rounded form crystal, the parallelism of crystallographically simple planes and directions may not be observed (for example, for crystal 3 and 2 in Fig. 2b).

A similar kind of conjunction between a thread-like crystal and rounded crystal of Cr_2O_3 is shown in Fig. 3. At a heating of a film with an electron beam, thread-like crystal 1 initially homogeneously nucleates and grows in amorphous matrix. The interpretation of a selected area diffraction pattern (with zone axle $[\bar{6}61]$) has shown, that the planes $(\bar{6}65)$ Cr_2O_3 are oriented parallel

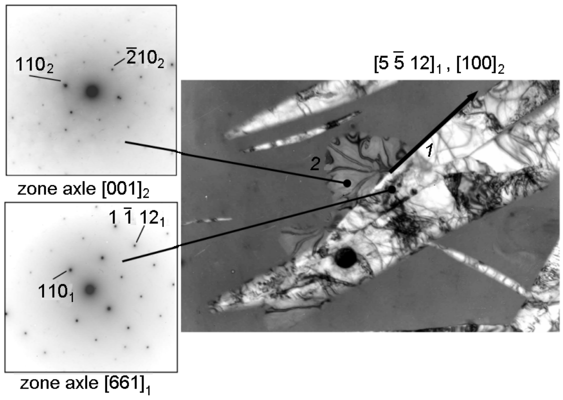

Fig. 3. Joining of the thread-like (1) and of rounded form (2) crystals of Cr_2O_3. After their contacting takes place the following orientation relationship: $(\bar{6}65)_1[5\bar{5}12]_1$ // $(001)_2[100]_2$ (row 3 of the Table).

to the film surface, and the long axis of a thread-like crystal is directed along $[5\ \bar{5}\ 12]$ (row 3 in the Table). The nucleation and growth of a rounded crystal 2 takes place near the lateral surface of the crystal 1. At the contact between crystals 1 and 2, the following orientation relation takes place:

$$(\bar{6}65)_1[5\ \bar{5}\ 12]_1 // (001)_2[100]_2. \qquad (3)$$

If the lattice orientation of the crystal 1 is taken as a basis, then the lattice orientation of the crystal 2 is obtained after realization of following operations: (1) Rotation of the crystal 1 lattice by angle $\beta_1 = 75.2°$ (β_1 is the angle between axes $[\bar{6}61]$ and [001]) around the axle $[5\ \bar{5}\ 12]_1$. (2) Further rotation by angle $\beta_2 = 33.8°$ around [001]. Thus, in the case of orientation relation (3), there is no parallelism of crystallographicallyy simple planes and directions between conjuncting crystals.

The rows 4 and 5 of the Table correspond to autoepitaxy versions observed before between the main morphological forms of Cr_2O_3 [4] and V_2O_3 [5] nanocrystals.

Thus, in the most cases at crystallization in the amorphous matrix, a homogeneous nucleation of thread-like crystals of Cr_2O_3 in arbitrary orientations occurs. The crescent-like crystals are formed during bending of thread-like crystals. At the lateral surface of a thread-like crystals and crescent-like crystals, the rounded crystals may heterogeneously nucleate. The main linking kinds of two main morphological types (thread-like crystals and rounded ones) are determined. During crystallization of amorphous films, both a regular overgrowth of one crystal at the other one (autoepitaxial growth), and arbitrary joining thereof at contacting. At the final transformation stage, the main amount of the film crystalline phase is presented by rounded crystals. In this case, the surface energy of the crystal/vacuum interface is presented with (001) planes of Cr_2O_3 with the minimum Miller indices and reaches a minimum.

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Автоепітаксія та основні орієнтаційні співвідношення при кристалізації з аморфної фази у плівках Cr–O и V–O

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Досліджено особливості зрощування кристалів, що ростуть в аморфних плівках стехіометричних Cr_2O_3 та V_2O_3 при відпалі. Плівки осаджено лазерним розпиленням мішеней хрому та ванадію в атмосфері кисню. Відпал плівок здійснювали електронним променем у колоні мікроскопа. Визначено основні морфологічні типи нанокристалів Cr_2O_3 та V_2O_3, а також їх еволюцію у процесі росту. Встановлено орієнтаційні співвідношення при спряженні кристалів різних морфологічних типів як у результаті автоепітаксіального росту з аморфної фази, так і при їхньому випадковому контактуванні.