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Structure perfection of sapphire single crystals grown by HOC method in reducing atmosphere

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The method of three-crystal X-ray diffractometry was used to investigate the structure perfection of sapphire crystals with the crystallographic orientations on the crystal surface (0001) and $(10\bar{1}2)$ grown by the method of horizontal oriented crystallization in protective gaseous atmosphere. The structure perfection was estimated for four crystallographic orientations of the surface of the samples cut out of different parts of the crystal. The dislocation density ρ determined from the dependence of the integral reflection power R_{exp} on the dislocation density for different crystallographic planes was found to differ in the range $\rho = 3\cdot10^3$–$1\cdot10^4$ cm^{-2}. For the plane $(10\bar{1}2)$ parallel to the crystal surface the change of dislocation density was more essential ($\rho = 4\cdot10^3$–$1\cdot10^5$ cm^{-2}) in comparison with the one for the plane perpendicular to the crystal surface. At densities exceeding 10^4 cm^{-2} the dislocations were mainly located in low-angle dislocation boundaries.

Методом трехкристальной рентгеновской дифрактометрии исследовано совершенство структуры кристаллов сапфира с кристаллографической ориентацией на поверхности кристалла — (0001) и $(10\bar{1}2)$, выращенных методом направленной горизонтальной кристаллизации в защитной газовой среде. Оценка совершенства структуры проводилась для четырех кристаллографических ориентаций поверхности образца, вырезанных из различных участков кристалла. Плотность дислокаций ρ, определяемая по зависимости интегральной мощности отражения R_{exp} от плотности дислокаций, для различных кристаллографических плоскостей изменялась в пределах $\rho = 3\cdot10^3$–$1\cdot10^4$ cm^{-2}. Более существенное изменение $\rho = 4\cdot10^3$–$1\cdot10^5$ cm^{-2} установлено для скола $(10\bar{1}2)$, параллельного поверхности кристалла, по сравнению со сколом, перпендикулярным ей. При плотности дислокаций в кристалле выше 10^4 см$^{-2}$ дислокации в основном располагаются в малоугловых дислокационных границах.

1. Introduction

Due to their unique physical, mechanical and chemical properties, sapphire single crystals and articles made from them have found wide use in different fields of science and technology [1]. Demand for sapphire, especially for large-size crystals of high optical quality and structure perfection, rises from year to year. One of promising methods for the growth of such crystals is horizontal oriented crystallization (HOC) in reducing gaseous media developed at the Institute for Single Crystals, NAS of Ukraine (Kharkiv) [2].

As a rule, previous studies of the structure perfection of sapphire crystals were performed for certain crystallographic orientations and planes of the samples obtained by different growth methods [1, 3].

The goal of the present work was to obtain more detailed data on the defect structure in the bulk of the crystal of a preset growth orientation. For this purpose, the structure perfection of the crystal planes with different crystallographic orientation of the surface, was investigated.

2. Experimental

The HOC method was used to grow $220\times230\times30$ mm^3 crystal samples with the crystallographic orientations of the surface (0001) and $(10\bar{1}2)$ — type 1 and type 2 crystals, respectively. From type 1 crystals there were cut out $15\times15\times1$ mm^3 samples with the orientation of the investigated surface (0001), $(10\bar{1}0)$, $(11\bar{2}0)$, $(10\bar{1}2)$ and the deviation of the cutting tool from the preset crystallographic plane up to 10 angular minutes. They were mechanically polished by a loose abrasive ASM 28/20 and then subjected to chemico-mechanical polishing (CMP) in aqueous suspension of silicon dioxide (aerosil 380). The thickness of the damaged surface-adjacent layer of the sample removed at CMP made up to 3 μm. The optical purity and surface roughness of the samples were studied using an optical microscope MP-4 and atomic-force microscope of Solver P47H RRO type (Russia). The surface of the samples subjected to CMP did not contain distorted surface-adjacent layer, its roughness was 0.2–0.3 nm [5]. Other samples were obtained from type 2 crystals as a result of cracking along the plane $(10\bar{1}2)$ due to high residual thermoelastic stresses perpendicular and parallel to the surface of the grown crystal. The spall surface of such samples did not contain distorted surface-adjacent layer formed as a result of crystal surface treatment. The spall area was approximately 80 cm^2. The side faces of the investigated samples were oriented to an accuracy of 0.5° with respect to the given crystallographic plane. For the sample with the orientation (0001) obtained from type 1 crystals the side faces of the sample were $(10\bar{1}0)$, $(11\bar{2}0)$ for the sample with $(10\bar{1}0)$ orientation the side faces were (0001), $(11\bar{2}0)$ for the crystal with the surface orientation $(11\bar{2}0)$ the side faces had the orientations (0001), $(10\bar{1}0)$ for the samples with the surface orientation $(10\bar{1}2)$ the side faces had the orientations $(10\bar{1}4)$ and $(11\bar{2}0)$. For type 2 crystals the surface orientation was $(10\bar{1}2)$ and the side faces had the orientations $(10\bar{1}4)$, $(11\bar{2}0)$.

In general, X-ray diffractometric study was realized in the Bragg geometry, but in some cases there was used the Bragg-Laue geometry. The measurements were carried out on a three-crystal X-ray diffractometer (TXD) in Cu $K\alpha_1$ radiation [4]. In the capacity of the first two monochromators we applied high-perfection germanium crystals with the dislocation density $\rho\le10^2$ cm^{-2}, the reflection (333), the Bragg angle θ equal to 45°, the scheme (n, n). For the reflection angles $\theta\approx45°$ monochromatic X-ray beam incident on the investigated crystal according to the scheme $(n, n, -m)$ is almost completely polarized (the share of the parallel polarization component is less than 0.5 %). The reflection from the two monochromators in the position (n, n) creates monochromatic beam Cu $K\alpha_1$ with an angular divergence of 0.1–0.05$''$, the spectral resolution being 10^{-4}–10^{-5} Å. Under the conditions of this approximation, the rocking curves (RC) for the investigated crystal do not require correction for instrumental broadening within the whole region of the reflection angles. Therefore, the experimental DRC can be compared with the ones calculated in the dynamic and kinematic approximation of X-ray scattering [6]. The parameters of the deviation of the experimental RC from the calculated values are bound up with disturbances of the structure of the investigated crystal. It should be noted that the TXD [4] has a sufficiently high light power $I_0\sim2\cdot10^4$ pulse/s for ~50 μ wide incident monochromatic beam and 8 mm vertical slit located after the monochromators. Thereat, the fluctuation of the intensity I_0 does not exceed 0.5 %, the error of determination of the integrated intensity E_{imp},

the full width at half maximum (FWHM) $\bar{\beta}$ of RC can be reduced to ±1 %. To eliminate the errors connected with the turn of the sample at a low angular velocity ω, the RC record was realized from smaller to larger θ angles and vice versa. The measurement results were averaged. The goniometric head made it possible to change the position of the sample in the equatorial plane of the goniometer with respect to the incident beam. By moving the examined sample with respect to the incident X-ray beam at the scanning step L = 0.1875–15 mm one can obtain the RC characteristics, $\beta(L)$ and $R(L)$ (integral reflection power) $R = E\cdot\omega/I_0$), where ω is the angular velocity of the sample turn, which characterize the degree of structure perfection of the studied sample adequately and reliably. The widely used methods of chemical polish-

ing and etching the crystal surface for establishing the dislocation density have the determination error ρ = 20–30 % [1].

3. Results and discussion

For reliable characterization of the degree of structure perfection for crystals grown by any method at a preset growth orientation, it is necessary to determine defect structure parameters for different crystallographic planes. For obtaining the true characteristic of the surface structure perfection, the distorted surface-adjacent layer formed in the process of sample preparation must be absent. As seen from Fig. 1, the presence of ~2 μm thick defect layer formed in the process of mechanical treatment using a free abrasive of ASM 28/20 type (curve *2*) results in the broadening of the RC, the change of the intensity at the reflection maximum I_{max}, the rise of the integrated reflection intensity E_{pulse} in comparison with that of the spall plane or of the sample after CMP (curve *1*). As shown in [5], CMP allows to remove the distorted surface-adjacent layer of the investigated sample, thereat the surface roughness $R_a <$ 0.3 nm. Survey of the studied samples in the Laue geometry leads to further minimization of the contribution of the surface-adjacent layer and makes it possible to increase the quantity of the registered reflections for the samples with a thickness less than 1 mm. Thus, one can obtain more complete data on the structure perfection in the crystal bulk.

The dynamical and kinematic approximation of X-ray scattering for perfect and mosaic single crystals in the Bragg geometry taking into account the absorption was used

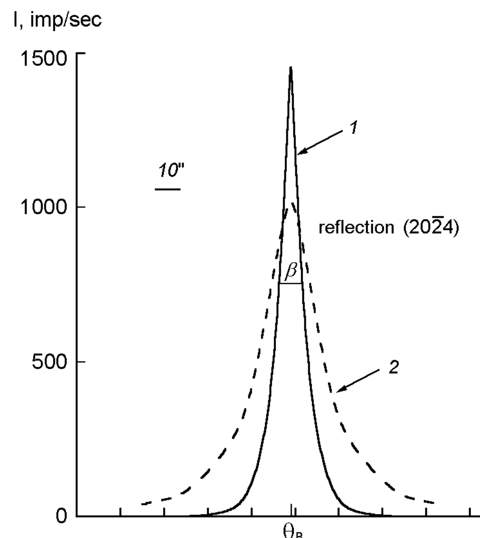

Fig. 1. Diffraction reflection curves (TXD, Cu $K\alpha_1$ radiation) for *R* (10$\bar{1}$2) sapphire with crystallographic orientation after chemical-mechanical polishing (*1*) and mechanical polishing ASM 28/20 (*2*).

to calculate the integral reflection powers and their ratios for the reflections (0006), (00012), (30$\bar{3}$0), (10$\bar{2}$0), (22$\bar{4}$0), (33$\bar{6}$0), (10$\bar{1}$2), (20$\bar{2}$4), (30$\bar{3}$6), (40$\bar{4}$8) (Table). For these reflections there were calculated the Bragg angles θ and the irradiated area of the investigated sample for the case of 2 mm wide vertical slit and 50 μm wide monochromatic beam.

As seen from the Table, for the above-mentioned reflections $1.07 < R_k/R_d <$ 10.68. The dependence $R_{exp}(\log\rho)$ was built using the reflections from the crystallographic axes characterized by the maximal

Table. Characteristics of perfect structure of sapphire

Reflection	θ, grad	*S*, mm^2	Calculated value $R\cdot10^6$				Chemical-mechanical polishing			Mechanical polishing ASM 28/20			Cleavage perpendicular to the crystal surface			Cleavage parallel to the crystal surface		
			R_d	R_k	R_d/R_k	R_k/R_d	R_{exp}	R_{exp}/R_k	β, sec	R_{exp}	R_{exp}/R_k	β, sec	R_{exp}	R_{exp}/R_k	β, sec	R_{exp}	R_{exp}/R_k	β, sec
(0006)	20.84	1.120	2.78	29.68	0.094	10.676	4.82	0.1624	6.7	5.40	0.1819	14.1	–	–	–	–	–	–
(00012)	45.33	0.560	8.11	55.84	0.145	6.885	13.11	0.2348	6.5	22.54	0.4037	12.6	–	–	–	–	–	–
(30$\bar{3}$0)	34.10	0.712	25.46	212.20	0.120	8.335	30.66	0.1445	7.6	77.62	0.3658	25.4	–	–	–	–	–	–
(11$\bar{2}$0)	18.89	1.232	14.72	83.20	0.177	5.652	29.59	0.3556	7.6	37.82	0.4546	13.9	–	–	–	–	–	–
(22$\bar{4}$0)	40.36	0.616	15.65	26.97	0.580	1.723	12.31	0.4564	6.6	19.29	0.7152	23.4	–	–	–	–	–	–
(33$\bar{6}$0)	76.25	0.408	14.79	76.10	0.194	5.145	35.11	0.4614	18.8	69.40	0.9120	46.80	–	–	–	–	–	–
(10$\bar{1}$2)	12.79	1.808	15.20	72.85	0.209	4.793	24.84	0.3410	8.4	49.70	0.6822	36.0	34.12	0.4684	15.5	21.82	0.2995	12.0
(20$\bar{2}$4)	26.28	0.904	18.83	133.70	0.141	7.100	29.10	0.2177	8.2	70.02	0.5237	35.8	43.14	0.3227	16.1	27.43	0.2052	11.6
(30$\bar{3}$6)	41.62	0.600	2.35	2.52	0.932	1.072	2.43	0.9643	6.7	3.01	1.1984	11.8	2.59	1.0277	8.9	2.39	0.9444	9.0
(40$\bar{4}$8)	62.32	0.448	9.71	35.05	0.277	3.610	10.87	0.3101	10.2	16.58	0.4730	15.5	12.80	0.3652	10.8	9.84	0.2807	9.8

R_k/R_d ratio. The study was performed on the samples with different dislocation density ρ employed in [7], as well as on new ones which underwent CMP or chemical polishing at selective etching for the determination of ρ according to the method [1]. The dependences R_{exp}(logρ) for the reflections (00012), (30$\bar{3}$0), (11$\bar{2}$0), (20$\bar{2}$4) are presented in Fig. 2. The comparison shows that the values of dislocation density obtained from X-ray topographic measurements are in satisfactory agreement with the values determined by the method of chemical etching for the same samples of sapphire crystals [8]. As seen from Fig. 2, with the growth of dislocation density in the crystal the experimental value of the integral reflection power essentially rises. At low dislocation densities in the crystal the sensitivity of R_{exp}(logρ) dependence is relatively low, and only at $\rho > 10^3$ cm^{-2} there is observed a considerable rise of this curve. The sensitivity of this method also depends on the crystallographic orientation of the studied sample, due to different values of the structure amplitude $F(hkl)$ [6]. Since the error of the experimental determination of the RC parameters R_{exp}, β is ±1 %, these characteristics define the structure perfection of the grown crystal reliably enough. In the sapphire crystals grown by the method of HOC, there is established dynamic X-ray beam scattering (the Bormann effect) [9]. This testifies that the structure perfection of the crystals is high, and permits to raise the sensitivity of X-ray diffraction analysis methods to low dislocation densities and other crystal lattice distortions [9]. The examined crystal (type 1) has the optimal spatial orientation (the exterior surface (0001), the growth direction [10$\bar{1}$0], the side surface orientation (11$\bar{2}$0) which allows to avoid the study of the structure defects of the seed. Thereat, new dislocations formed in the process of relaxation of thermoelastic stresses behind the crystallization front make an angle close to 90° with the direction [10$\bar{1}$0], and their inheritance coefficient tends to zero [8, 10]. One must also take into account the fact that the dislocation structure of the crystal undergoes an essential evolution in the process of growth-annealing in gradient high-temperature fields of the growth unit during a long period of time (~100 hours). The values of R_{exp} for different crystallographic planes (see Table) show that the dislocation density (determined from Fig. 2) is

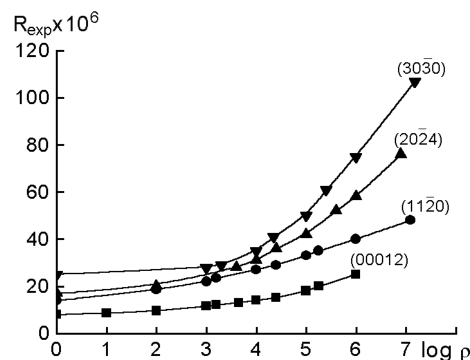

Fig. 2. Variation character of the integral reflection power R_{exp} on the dislocation density ρ for different reflections (*hkil*).

$4\cdot10^3$ cm^{-2} for the reflex (00012), $8\cdot10^3$ cm^{-2} for (30$\bar{3}$0), $8\cdot10^3$ cm^{-2} for (11$\bar{2}$0), $1\cdot10^4$ cm^{-2} for (20$\bar{2}$4). Different crystallographic planes of type 1 crystals are characterized by chaotic dislocation density which varies within the range $\rho \approx 4\cdot10^3$–$1\cdot10^4$ cm^{-2}. It should be noted that the character of the distribution of dislocation structures in the bulk of the grown crystal has the regularities similar to those observed in the case of high-temperature plastic deformation of crystalline samples [11, 12]. As shown in [13], the most probable for sapphire is the basal slip along the second-order symmetry axis (0001) in the crystallographic direction 1/3 [11$\bar{2}$0] and (0001) in the direction [1$\bar{1}$00] with the Burgers vector b = 4.758 Å and b = 8.220 Å. The analysis of the RC measured for different (*hkil*) reflections in different crystallographic directions shows not only broadening, but also splitting of the DRC caused by the presence of ordered dislocation structures, polygonal boundaries with low turn angles Δθ = 1–5 s. The distance l between the dislocations in the boundary is easily estimated from the known value b and Δθ taking into account that $l = b/\Delta\theta$. After calculating the irradiated surface of the sample (see Table) and the quantity of RC peaks one can estimate the distance between the polygonal dislocation boundaries and determine ρ in the boundaries. At dislocation densities $>10^4$ cm^{-2} the dislocations are mainly located in the low-angle boundaries. The presence of low-angle dislocation boundaries with Δθ = 1–5 sec and chaotic dislocation density $\rho \leq 10^4$ cm^{-2} have no essential influence on the optical transmission, radiation strength and homogeneity of sapphire products [1, 2]. At the same time, the presence of low-angle boundaries with

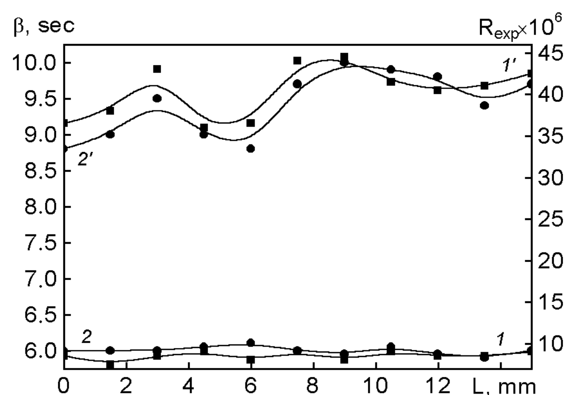

Fig. 3. Variation character of rocking curve FWHM β for reflection (00012) (*1*) and reflection (20$\bar{2}$4) (1$'$) and the integral reflection power R_{exp} for reflection (00012) (*2*), reflection (20$\bar{2}$4) (2$'$) for L-scanning study the sample.

$\Delta\theta \geq 10$ s disorientation leads to distortions of forms and color gamut of the conoscopic pattern [5]. As a rule, such low-angle twist boundaries are observed in the crystal bulk where $\rho \geq 1\cdot10^5$ cm^{-2}, and have a length of 4–6 mm. The performed study of the structure perfection of the type 2 crystal shows an essential rise of the dislocation density $\rho = 1\cdot10^5$ cm^{-2} for the crystallographic plane (10$\bar{1}$2) cleaved perpendicularly to the crystal surface. For the cleaved facet parallel to the crystal surface the dislocation density is much lower: $\rho = 4\cdot10^3$ cm^{-2}, that leads to changes in R_{exp} and β (see Table).

To estimate the uniformity of the distribution of structure defects over the cross-section of the crystal, there were measured $R_{exp}(L)$ values (Fig. 3, curve *1* for the reflex (00012) and 1$'$ for (20$\bar{2}$4) and β(L) (Fig. 3, curve *2* for the reflex (00012) and 2$'$ for (20$\bar{2}$4) at L-scanning of the investigated sample with respect to incident X-ray beam in the direction [10$\bar{1}$0] with the step L = 1.5 mm. As seen from Fig. 3 (curves *1*, *2*), for the samples with a low dislocation density ρ~10^3 cm^{-2} and the orientation of the reflecting plane (00012), β(L) and $R(L)$ do not show essential changes at scanning in the direction [10$\bar{1}$0]. At the same time, for the sample in which the dislocation density ρ 10^5 cm^{-2}, there are observed changes in β(L) and $R(L)$ by 12 % and 20 %, respectively. The structure perfection worsens in the process of crystal growth (curves *1*$'$ and *2*$'$) even for the investigated 15 mm long crystal section.

4.Conclusions

Thus, the experimental characteristics — RC, β, R — measured on TXD characterize the degree of crystal structure perfection accurately and correctly enough. More detailed description of the structure perfection can be obtained using the data on RC(L), β(L) and $R_{exp}(L)$ for different crystallographic planes. It is shown that the dislocation density for the crystal grown in the direction [10$\bar{1}$0] with the orientation of the surface (0001) for different (*hkil*) may differ by an order. The location of the crystallographic plane (10$\bar{1}$2) in the investigated samples with respect to the crystal growth surface (parallel or perpendicular) is of a great importance, since the dislocation density of such samples essentially differs (ρ = $4\cdot10^3$–$1\cdot10^5$ cm^{-2}).

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Досконалість структури монокристалів сапфіру, вирощених методом ГНК у відновлювальних умовах

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Методом трикристальної рентгенівської дифрактометрії, досліджено досконалість структури кристалів сапфіру, які вирощувалися в захисних газових середовищах методом направленої горизонтальної кристалізації з кристалографічною орієнтацією поверхні — (0001) і ($10\bar{1}2$). Оцінка досконалості структури проводилася для чотирьох кристалографічних орієнтацій поверхні зразків, які вирізані з різних областей вирощеного кристала. Щільність дислокацій, яка була визначена із графіка залежності інтегральної потужності відбиття від щільності дислокацій, змінювалася в інтервалі $\rho = 3{\cdot}10^3–1{\cdot}10^4$ cm^{-2}. Ще більш суттєві зміні $\rho = 4{\cdot}10^3–1{\cdot}10^5$ cm^{-2} встановлено для дзеркального відколу ($10\bar{1}2$) паралельно поверхні вирощеного кристала порівняно зі сколом, перпендикулярним поверхні. При щільності дислокацій в вирощеному кристалі $\rho > 10^4$ см$^{-2}$ дислокації переважно розташовуються в малокутових дислокаційних межах.