Functional Materials 14, No.4 (2007)

Structure perfection of bulk and near-surface layers in sapphire single crystals

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Received October 24, 2007

Triple-crystal X-ray diffractometry has been used to study the structure perfection in bulk and surface layer of basal-oriented sapphire single crystals grown using horizontal directional crystallization (HDC) in reducing atmosphere by the Czochralski technique and machined and annealed in various manners.

Методами трехкристальной рентгеновской дифрактометрии исследовано совершенство структуры монокристаллов, приповерхностного слоя сапфира базисной ориентации, выращенных методом горизонтальной направленной кристаллизации (ГНК) в восстановительной среде и методом Чохральского, прошедших различные виды механической обработки и отжига.

High structure perfection sapphire single crystals of basal crystallographic orientation {0001} are used widely as deposition substrates to provide articles for optics, microelectronics and quantum engineering, in particular, epitaxial gallium nitride films in LED production. The substrate surface should met rather hard requirements, namely, the roughness $R_a \leq 0.3$ nm, optical purity class P 0-10, shape accuracy on 2 inch diameter (wedge μm, sag μm) [1]. However, there are very scarce literature data on the structure perfection in the near-surface layer of finished crystal. The rocking curve half-width β obtained using a double-crystal X-ray diffractometer in copper emission for {0006} reflection after chemical finishing is reported to be 10 to 12 angular seconds [2]. The same β value is reported in as measured using a diffractometer with fourfold reflection from a Ge, {220} monochromator.

Those parameter values are attainable in sapphire single crystals grown using horizontal directional crystallization (HDC) in reducing atmosphere [3] Czochralski and Kyropoulos [4] techniques and finished using polishing colloidal silicon dioxide suspension made of Aerosil 380 (the SiO_2 particle size 380 Å). Such a chemical treatment provides the removal of distorted surface layer formed due to machining by diamond abrasive materials. However, there are no literature data concerning the distorted surface layer thickness, defectness in that layer as well as the structure perfection of the surface layer after chemical finishing and thermal annealing. The main characteristics of the substrate surface are now obtained by the roughness measurements using an atomic force microscope [1].

We have used the triple-crystal X-ray diffractometry (TXD) [6, 7] to study the structure perfection of single crystals grown using HDC, Czochralski and Kyropoulos techniques and the surface layers of the crystals after mechanical treatment (MT) using ASM 28/20 abrasive, chemical finishing (CF) using Aerosil 380, and high-temperature annealing.

The structure perfection degree of the grown crystals and the treated surface layer

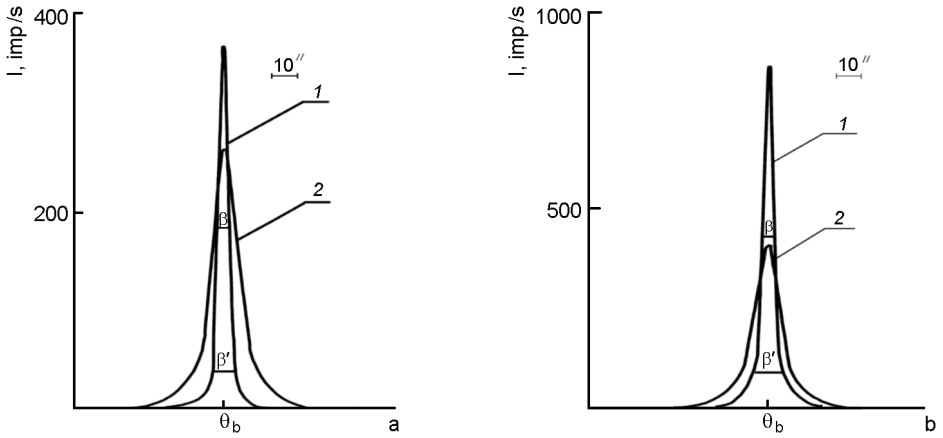

Fig. 1. Diffraction reflection curve (TXD, Cu $K_{\alpha 1}$ emission). {0006} (a) and {00012} (b) reflections after chemical (curves 1) and mechanical (2) finishing.

was characterized by the diffraction rocking curve shape (RCS), the full width of half maximum (FWHM) (β), the curve width at height corresponding to 10 % of I_{max} (β′), and the integral reflaction power I^R. Those parameters were measured by TXD in Cu Kα emission for different reflection orders (0006), (00012) in the Bragg reflection geometry and $\{30\bar{3}0\}$, $\{11\bar{2}0\}$, $\{22\bar{4}0\}$ in the Bragg-Laue geometry at transmission through the bulk of the sample under study, the DRCS being recorded for the Laue and anomalous transmitted (Bohrman) reflection. The sample was scanned at 1.5 mm scan step with respect to the incident X-ray beam, thus making it possible to judge the structure perfection of the crystal bulk and surface. From large ($220\times220\times30$ mm^3) sapphire crystals grown using HDC [3] and (∅200 mm, h = 300 mm) ones grown by Czochralski, 0.5 and 1 mm thick discs of ∅50.8 mm and ∅77.2 mm were cut out oriented in the crystallographic plane {0001} to within 10′ and the side cut oriented in $\{10\bar{1}0\}$ to within 20′. The cut discs were machined and mechanically finished using ASM 28/20 abrasive, then finished chemically using colloidal silicon dioxide polishing suspension. The distorted surface layer formed due to mechanical finish was removed in step-by-step manner. To monitor the removed layer and the removal rate, the sample under treatment was weighed to within 0.2 mg. This method provides the removed layer thickness monitoring at an error of ±24.8 nm and ±10.8 nm for ∅50.8 mm and ∅77.2 mm discs, respectively.

The removal rate at the CF was somewhat higher at the initial stage and then attained a constant value of about $1\cdot10^{-3}$ mg/min per 1 cm^2 surface. It is to note that such a removal rate is typical of the treated surface oriented in {0001} plane to within 10′. When the deviation attained several degrees, the removal rate of the distorted surface layer increased by a factor of 3 to 5.

After mechanical finishing with ASM 28/20 abrasive, a diamond background is remained at the sample surface, the disc becomes curved as well as a distorted surface layer is present resulting in broadened the full width of half maximum β and increased integral reflection power I^R (Fig. 1, Table 1). Using the method described in [7], the distorted layer has been estimated to be about 2 μm thick textured polycrystalline layer. The errors in the determined intensity of the incident X-ray beam, intensity in the Bragg reflection maximum, integral reflection power, diffraction reflection curve, taking into account the dynamical scattering effects in perfect sapphire crystals, hinder the correct measurements of the distorted layer thickness of ≥1 μm using the method [7]. The RCS, the rocking curve half-width β width at 10 % of I_{max} β′, integral reflection power $\overline{I^R}$ for different reflections and different measurement geometry have been found to be more sensitive parameters that characterize the distorted surface layer. In Fig. 1, presented are diffraction rocking curves for (0006) and (00012) sapphire reflections measured by TXD in the (n, n, $-m$) mode in $Cu_{K\alpha1}$ emission for a sample mechanically finished using ASM 28/20 and then finished chemically in colloidal silica solu-

Table 1. Parameters of crystals.

No.	Sample characteristic	Bragg eflection geometry						Laue geometry		Bohrmann geometry		Dislocation density, cm^{-2}
		Reflection (0006)			Reflection (00012)			Reflection $\{30\bar{3}0\}$	Reflection $\{10\bar{2}0\}$	Reflection $\{30\bar{3}0\}$	Reflection $\{11\bar{2}0\}$	
		$\bar{\beta}$, s	$\bar{\beta}'$, s	$\bar{I}^R \cdot 10^6$rad	$\bar{\beta}$, s	$\bar{\beta}'$, s	$\bar{I}^R \cdot 10^6$rad	$\bar{\beta}$, s	$\bar{\beta}$, s	$\bar{\beta}$, s	$\bar{\beta}$, s	
1	MF, ASM 28/20	14.1	44.2	5.40	12.6	35.1	22.54	–	–	–	–	$3 \cdot 10^6$
2	MF, ASM 28/20 + annealing (1100°C, 10 h)	8.4	22.1	5.32	7.8	21.9	16.59	–	–	–	–	$8 \cdot 10^4$
3	MF, ASM 28/20 + annealing (2000°C, 10 h)	14.2	31.1	5.33	13.9	35.4	19.4	–	–	–	–	$2 \cdot 10^3$
4	CF (at Inst. Single Cryst., Kharkiv)	6.7	16.1	4.83	6.5	14.7	13.09	6.9	6.9	6.7	6.8	$2 \cdot 10^5$
5	CF (at Inst. Superhard Mater., Kyiv)	7.3	18.6	5.22	7.2	20.5	16.06	7.5	7.6	7.4	7.4	$3 \cdot 10^4$
6	CF (a Chochralski cryst., Russia)	6.0	12.4	4.00	6.0	12.6	11.14	6.0	6.2	6.1	6.0	$4 \cdot 10^3$
7	CF (USA)	6.4	13.5	3.88	6.3	13.5	10.51	6.4	6.5	6.3	6.4	$2 \cdot 10^3$
8	Chemical polishing ($\rho \approx 0$)	5.6	12.3	3.32	5.4	12.1	8.62	5.4	5.5	5.2	5.3	0
9	CF + annealing (1100°C, 2 h; at Inst. Single Cryst., Kharkiv)	6.9	16.8	4.70	6.7	14.4	12.75	6.8	6.9	6.6	6.8	$2 \cdot 10^4$

MF, mechanical finishing; CF, chemical finishing

tion with the removal of an about 2 μm surface layer (curve 1).

It is seen from Fig. 1 that, in spite of mechanical finishing, the samples show a considerable change in DRCS, the intensity in DRC maximum, β and β′ as well as in I^R. A similar dependence is observed also for {0006} reflection (see Fig. 1a and Table 1), though the monochromatic beam cross-section at the sample is increased twice and the Bragg angles of incidence for the second crystal monochromator ($\theta_M = 45.3°$) and the sample ($\theta = 20.7°$) are quite different. The comparable β and RCS values for the (0006) and (00012) reflections become attainable due to the developed TXD design [5] and the selected experimental geometry (n, n, $-m$). For double-crystal diffractometers, and even when four reflections from the monochromator, the experimental rock half-widths exceed twice our results, that is due to a considerable contribution form the instrumental DRC blurring factor [2].

The studied samples mechanically finished with ASM 28/20 abrasive and exhibiting the distorted surface layer, diamond background, surface curvature, the roughness R_a, and P 0-40 optical treatment class were then subjected to step-by-step chemical finishing. After each chemical treatment step, the TXD patterns of DRC for (0006) and (00012) were recorded in 10 points, the samples were scanned at 1.5 mm steps. Then, the averaged parameters β, β′ and $\overline{I^R}$ were plotted as functions of the removed distorted layer thickness Δt (Fig. 2a, b, c). No changes in the dependences plotted are seen after an about 1.2 μm thick layer is removed. All the chemical removal steps were carried out for the same sample with a certain density of growth dislocations, the sample being scanned along the growth direction [10$\bar{1}$0]. It is to note that the RCS parameters $\beta(\Delta t)$, $\beta'(\Delta t)$, and $\overline{I^R}(\Delta t)$ characterize the structure perfection not only of the surface layer but also of the crystal bulk. However, the behavior character of $\beta(\Delta t)$, $\beta'(\Delta t)$, and $\overline{I^R}(\Delta t)$ is remained at the chemical treatment of sapphire crystals grown t different initial dislocation densities (see Table 1), that is, after the mechanical treatment with ASM 28/20 abrasive, it is sufficient to remove the about 1.5 μm thick distorted surface layer to attain the structure perfection typical of the grown crystal bulk.

The absence of the distorted surface layer after removal of $\Delta t \sim 1.5$ μm by the chemical finishing is confirmed directly by

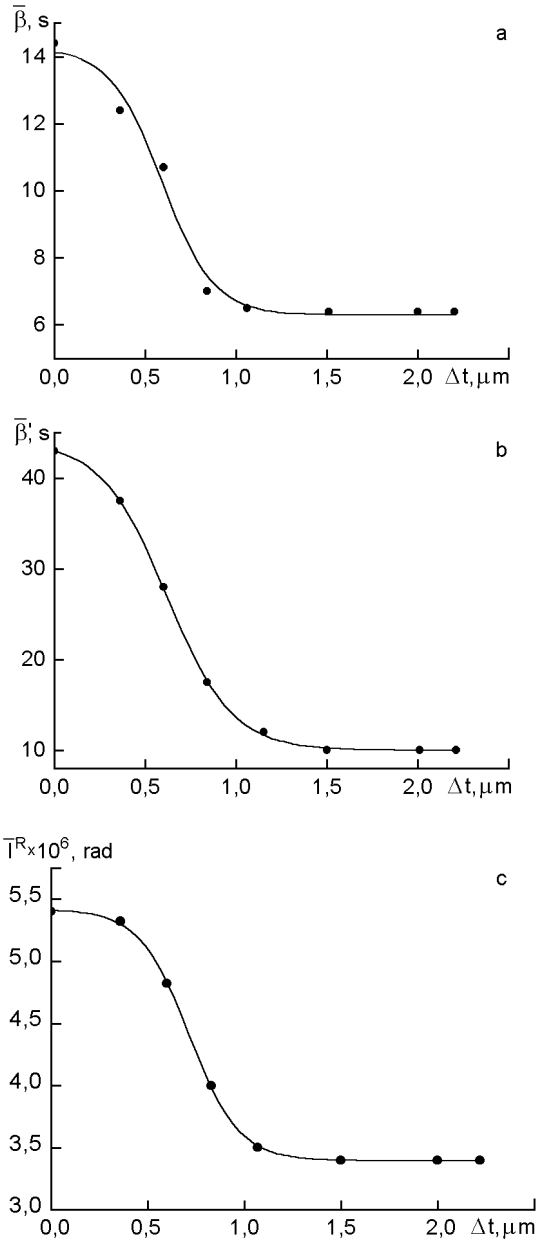

Fig. 2. $\overline{\beta}$ (a), $\overline{\beta'}$ (b) and $\overline{I^R}$ (c) changes at layer-by-layer chemical removal of the distorted surface layer (Δt thick) for (0006) reflection.

the DRCS parameters $\overline{\beta}$, $\overline{\beta'}$ and $\overline{I^R}$ measured in the Laue and Bohrmann geometries for {30$\bar{3}$0} and {11$\bar{2}$0} reflections and for (0006) and (00012) ones in the reflection Bragg geometry as well as by the data obtained at a dislocation-free area of the crystal with the distorted layer removed by chemical polishing in $KHSO_4$ melt at 725°C (see Table). It is to note that it is just basal orientation sapphire of 1 and 0.5 mm thickness that is used as the substrate; in those cases, μt

values are 12.47 and 6.23, respectively (μ is the normal photoelectric absorption coefficient) in Cu $_{K\alpha 1}$ emission. That thickness values are optimal to study the bulk structure perfection in the presence of X-ray dynamic scattering (the Bohrmann effect). The anomalous transmission itself evidences a high structure perfection of the crystals studied having the dislocation density $\rho \leq 10^4$ cm^{-2}. The similarity of β values obtained in the Bragg reflection geometry and in the Laue and Bohrmann transmission geometries for chemicall finished samples evidences the absence of distortions in the crystal surface layer (Table 1). An additional annealing (at 1100°C in air for 10 h) of samples finished with ASM 28/20 abrasive results in removal of the disc curvature and the dislocation density reduction in the surface layer that is evidences by reduction of $\beta(\Delta t)$, $\beta'(\Delta t)$, and $\overline{I^R}(\Delta t)$. The annealing of those samples at about 2000°C in a reducing atmosphere for 10 h results in thermal etching of the crystal surface and formation of ordered dislocation structures causing the small-angle rotations and the DRC blurring. No anomalous X-ray transmission has been observed for the samples finished mechanically and then annealed at 1100°C and 2000°C.

Thus, the crystals grown using HDC [3] and Chochralski technique, finished mechanically and then treated with Aerosil-380 resulting in removal of about 1.2 to 1.5 μm surface layer show the same structure perfection in the surface layer as in the bulk. An additional annealing of the optimally chemically treated samples in air at 1100°C for 2 h does not result in the surface structure deterioration of substrate made of basal orientation sapphire. The TXD methods are very effective in determination of the surface layer and bulk structure perfection of sapphire crystals.

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Досконалість структури об'єму та приповерхневих шарів монокристалів сапфіру

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Методами трикристальної рентгенівської дифрактометрії досліджено досконалість структури об'єму та приповерхневого шару монокристалів сапфіру базисної орієнтації, вирощених методом горизонтально-направленої кристалізації (ГНК) у відновлювальному середовищі та методом Чохральського, підданих різним видам механічної обробки та відпалу.