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XRD studies of surface layers in sapphire substrates of <10$\bar{1}$2> crystalloghaphic orientation

V.F.Tkachenko, O.A.Lukienko, A.T.Budnikov, E.A.Vovk, S.I.Krivonogov, A.Ya.Dan'ko

Institute for Single Crystals, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

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The structure perfection of surface layers has been studied by high resolution triple-crystal X-ray diffractometry (TXRD) in sapphire substrates with <10$\bar{1}$2> crystallographic orientation mechanically polished with ASM 28/20 diamond paste as well as during the layer-by-layer eliminaion of distorted surface layer by chemical-mechanical polishing (CMP) in suspension of X-ray amorphous silicon dioxide followed by annealing of this sample for 4 h at 1250°C. As the structure-sensitive parameters being measured by TXRD, the following were selected: the diffraction reflection curve shape (DRCS), the rocking curve half-width, β, the width at 10 % of RCS maximum intensity, β′, the integral reflection power, R_B. The β(h), β′(h), $\overline{R}_{exp}(h)$ dependences have been obtained at the layer-by-layer eliminaionof the h thick distorted layer by CMP. It has been shown that at CMP removal of h ~ 2.5 μm distorted layer the surface roughness R_d ~ 0.2 nm, however, the layers with increased dislocation density are found.

Методом трехкристальной рентгеновской дифрактометрии (ТРД) высокого разрешения исследовано совершенство структуры приповерхностных слоев подложек из сапфира с кристаллографической ориентацией после механической полировки алмазной пастой АСМ 28/20, а также при поэтапном снятии искаженного приповерхностного слоя химико-механической полировкой (ХМП) в суспензии рентгеноаморфного кремнезема SiO_2 и последующем отжиге этого образца при температуре 1250°C в течение 4 часов. Структурно-чувствительными параметрами, измеряемыми методами ТРД, были: форма кривой дифракционного отражения, полуширина кривой качания КДО β, ширина на высоте 10 % от интенсивности в максимуме КДО — β′, интегральная мощность отражения R_B. Получена зависимость параметров β(h), β′(h), $\overline{R}_{exp}(h)$ при послойном снятии ХМП искаженного слоя толщиной h. Показано, что при снятии ХМП искаженного приповерхностного слоя толщиной h ~ 2,5 мкм шероховатость поверхности R_a ~ 0,2 нм, однако установлено наличие слоев с повышенной плотностью дислокаций.

1. Introduction

The sapphire single crystals find a wide application as substrates for preparation of epitaxial films used widely in microelectronics and optics, in production of integrated circuits based on "silicon-on-sapphire" structures (SOS structures) and for deposition of gallium nitride and indium nitride films in light diode production. In preparation of SOS structures the sapphire substrates with <10$\bar{1}$2> surface crystallographic orientation while in light diode production, those with <0001> one. The rather high characteristics are demanded to structure perfection of sapphire crystals: the absence of "mosaicity", low dislocation density, the absence of foreign inclusions, low residual thermoelastic stresses, the

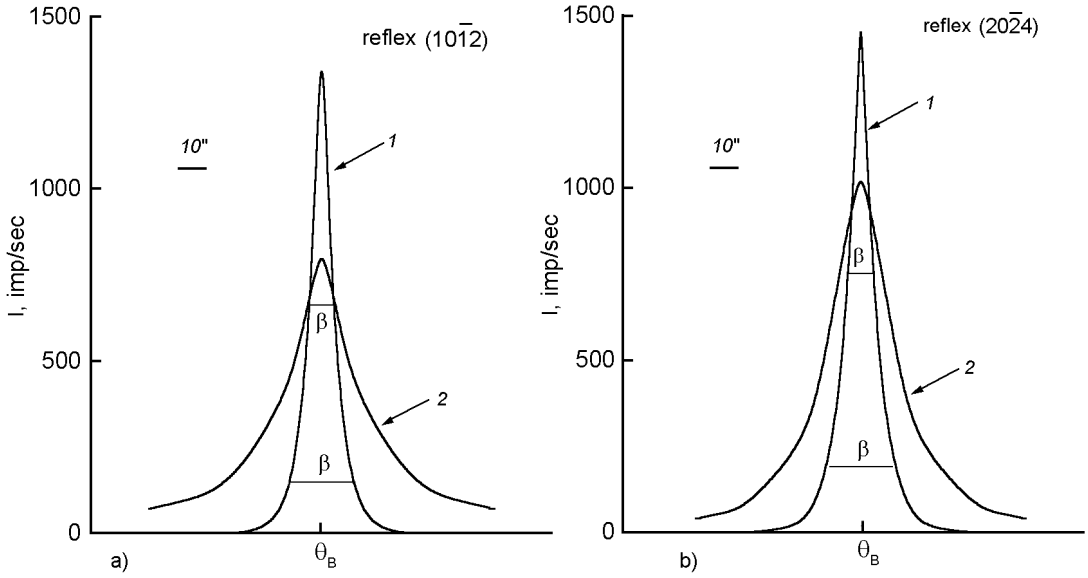

Fig. 1. Diffraction reflection curves (TXRD, Cu $K_{\alpha 1}$ emission for <10$\bar{1}$2> sapphire with crystallographical orientation after chemicomechanical (*1*) and mechanical (*2*) polishing.

specified crystallographical orientation and "basic" cut not exceeding 10 angular minutes at the ingot diameter of 200 mm. The technology of sapphire crystal growth by horizontal directional crystallization (HDC) in protecting gaseous media mets all those requirements [1].

Additional specifications to substrate surfaces include absence of defect surface layer; the dislocation density cannot exceed that in bulk crystal; the working surface roughness level should be R_a<0.3 nm; planeness L<5 μm; the working surface should be mirror-polished with optical purity 20/10 according to USA MIL-0-13830.

As the finish processing of sapphire surface, the chemical-mechanical polishing in aqueous solution of X-ray-amorphous silicon dioxide suspension [2, 3] is used widely that provides the substrates according to appropriate specifications. To elaborate the polishing technology of the crystal surfaces, the development of nondestructive control methods for substrate surface quality and studies of the surface layer structure perfection. Such methods may include the TXRD [4, 5]. Our investigations in structure perfection of substrates with basal orientation <0001> using TXRD methods have shown their high informativity and reliability [5].

This work is aimed at the study of possibility to use the TXRD to study the structure of crystals at <10$\bar{1}$2> crystallographic orientation and of substrate made from those used in SOS structure preparation.

2. Experimental

The sapphire samples studied of 70 mm in diameter and 4.5 mm in thickness were cut out of 220×220×30 mm^3 size crystal with <10$\bar{1}$2> orientation grown using the HDC technology. The <10$\bar{1}$2> surface of the sample was oriented along [11$\bar{2}$0] and [10$\bar{1}$4] to within 10 angular minutes. Then the mechanical polishing (MP) using ASM 28/20 diamond paste followed by the layer-by-layer chemical-mechanical polishing (CMP) in suspension of X-ray amorphous silicon dioxide (aerosil A-380). To quantitative determination of the surface layer thickness, h, removed by CMP the sample mass loss was measured using an Axis ANG 200 C analytical balance, the calculation was performed using the formula $h = \frac{4\Delta m}{\pi d^2 \rho}$ where Δm is the mass loss; ρ, sapphire density 3.98 g/cm^3; d, the sample diameter. To increase the mass loss determination, at the weighing, every time not the absolute sample mass prior to and polishing was determined, but the mass difference between the sample under study and reference one. The measuring error Δm was ±0.1 mg, resulting in h ~ 6 nm error for the sample ∅ 70 mm.

The optical purity and roughness of the sample was studied using a MII-4 optical microscope and a Solver P47H PRO atomic force one (Russia). The structure defect characteristics in surface layer were studied also using a DRON-3M double-crystal diffractometer in Co K_α emission in θ–2θ re-

cord mode with 2 mm slit at the counter. The thickness of distorted surface layer after the MP was estimated according to [6]. To estimate the growth dislocation density, the mirror cleaves of the samples perpendicular and parallel to <10$\bar{1}$2> plane of the crystals grown at the surface orientation <10$\bar{1}$2>, using the integral reflection power R_B: $R_B = \frac{E\omega}{I_0}$, where E is the integral reflection intensity of the corresponding reflection with subtracted background intensity; ω, the angular rotation speed of the sample; I_0, intensity of monochromatic beam incident the sample under study. The sample after CMP prior to and after additional anneal at 1250°C for 4 h was examined in the same manner.

3. Results and discussion

After the MP, a large number of scratches (about $8.6 \cdot 10^6$ per cm length) is observed on the surface microphoto and profilogram of sapphire with R_a ~ 7.7 nm and R_{max} ~ 35 nm. The estimation of the distorted surface layer using the method [6] for <10$\bar{1}$2>, <20$\bar{2}$4>, <30$\bar{3}$6>, <40$\bar{4}$8> reflections taken in TXRD in Cu $K_{\alpha 1}$ emission gives the value about 2 μm.

The more illustrative and informative data are obtained when recording DRC and registering DRCS, integral reflection power R_B, and intensity I in the reflection maximum. In Fig. 1, it is seen the substantial difference in DRCS taken for <10$\bar{1}$2> and <20$\bar{2}$4> relections of the sample processed by the CMP (curve *1*) and MP (curve *2*). For the MP processed samples, an essential DRC broadening, intensity decrease in the maxima of <10$\bar{1}$2>, <20$\bar{2}$4>, increase of the rocking curve β and the β′ width at 10 % of I_{max} as compared to DRC taken form the mirror cleave or after CMP. The main cause of the DRCS changes after the MP is the presence of a fissured layer with a little rotation of crystallites on the processed sample surface. β′ is about 120 angular seconds being essentiall less than in [7] where the crystallite misalignments after MP can approach several grades. To reveal the post-MP textured polycrystal layer, the XRD pattern were taken using a double-crystal diffractometer with a pyrolytic graphite monochromator that provides the incident X-ray beam intensity exceeding by three orders of magnitude that from TXRD and beam divergence of the order of one grade; however, the pattern taken in θ–2θ

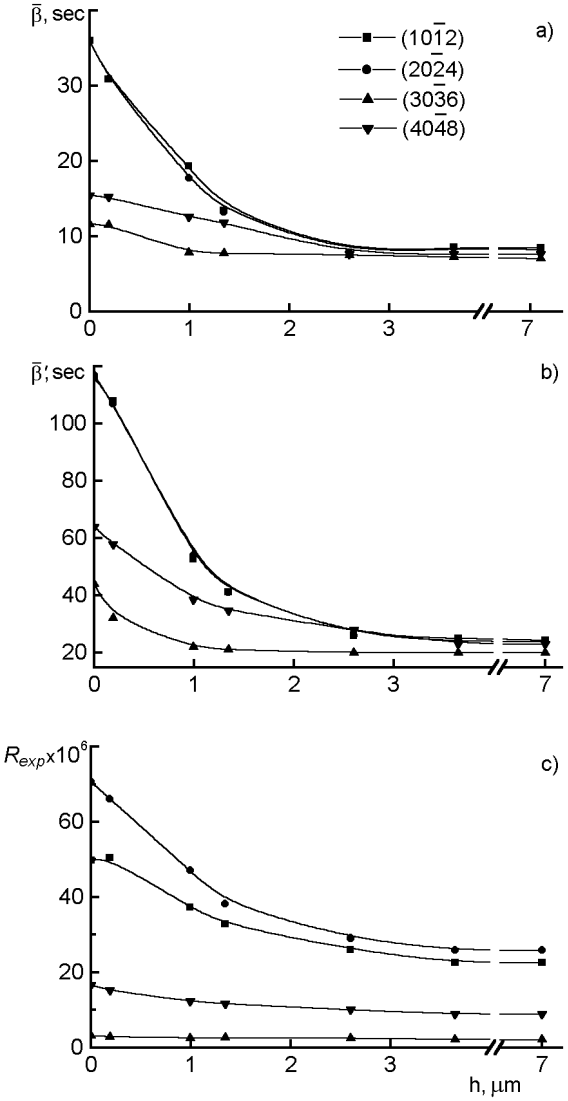

Fig. 2. Variation character of $\bar{\beta}$ (a), $\bar{\beta}'$ (b), R_{exp} (c) at layer-by-layer removal of the h thick distorted surface layer by CMP.

mode at the counter slit of 2 mm did not shown any reflections besides of those from <10$\bar{1}$2> planes. To estimate the dislocation density ρ_d in the sapphire crystal, the mirror <10$\bar{1}$2> cleaves of the crystals were used having no distorted surface layer using the integral reflection power R_B and its dependence on ρ_d [8]. In advance, R_B were calculated for Cu $K_{\alpha 1}$ emission for <10$\bar{1}$2>, <20$\bar{2}$4>, <30$\bar{3}$6>, <40$\bar{4}$8> reflections under dynamic (R_{dyn}) and kinematic (R_{kin}) approximations for the X-ray beam diffraction by sapphire crystal in Bragg reflection geometry [9] as well as the reflection angles, θ, (see Table).

The cross-section of monochromatic beam on the sample under study for different re-

flection orders S when working in TXRD. It is seen from the Table that the calculated R_{dyn} and R_{kin} values differ substantially for two first reflection orders, $<10\bar{1}2>$ and $<20\bar{2}4>$, and the R_{kin}/R_{dyn} is 3.48 and 5.67, thus providing reliable estimation of the dislocation density in the crystals being studied. Thus, the values such as DRCS, the rocking curve halfwidth β, the width β′ at 10 % of I_{max}, the integral reflection power R_{exp} and the R_{exp}/R_{dyn} ratio are sufficient to characterize the post processed structure perfection of grown crystals bulk and surface layers. To enhance the reliability of experimental measurements, the rocking curves were recorded at the sample rotation from smaller Θ_B angles to larger ones and vice versa as well as at the scanning of the sample with respect to the incident beam with the scanning pitch L = 1.5 mm according to at least 5 measurements which were averaged, their values are given in Table and in Fig. 2. The error of β, β′, R_{exp} was reduced to 2 %. To determine the defectness characteristics of distorted surface layer and its thickness h, the β, β′, R_{exp} walues were measured after each stage of layer removal by CMP and the thickness of the removed layer was determined from the sample mass loss. The $\bar{\beta}(h)$, $\bar{\beta}'(h)$, $\bar{R}_{exp}(h)$ dependences for four reflection orders from the crystallographical plane $<10\bar{1}2>$ are presented in Fig. 2. The strongest distortions in the surface layer are observed in the thickness smaller than 1.0 μm, what is evidenced by the steep curve slope for all the three characteristics in this plot sections. For those thickness, the maximum material removal rate by CMP is observed exceeding by 2–2.5 times that at the subsequent polishing.

The initial dislocation density was determined from the $R_{exp}(\rho_d)$ dependence according to the procedure [8]. It is established to be $\rho_d \sim 1 \cdot 10^4$ cm^{-2} for the mirror $<10\bar{1}2>$ cleave cleaved in parallel to the sapphire crystal surface. The dislocation density at the sapphire $<10\bar{1}2>$ surface after the CMP is $\rho_d \sim 2 \cdot 10^4$ cm^{-2}. The difference in the dislocation density in the mirror cleave free of the surface layer as compared to the sample subjected to CMP seems to be connected with the sample location within the grown crystal volume. This is confirmed by the R_{exp} measurements for a cleave perpendicular to the grown crystal surface. For the $<20\bar{2}4>$ reflection, R_{exp} was $43.12 \cdot 10^{-6}$, exceeding considerably the values for the sample post-CMP surface.

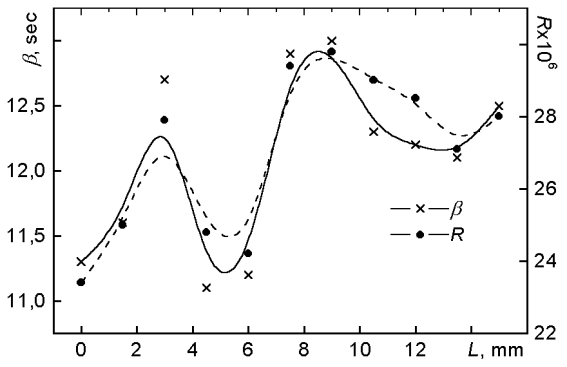

Fig. 3. β(L) and R(L) dependences at L scanning of the post-CMP sample. Reflection $<20\bar{2}4>$, Cu $K_{\alpha 1}$ emission.

After the distorted 2–2.5 μm thick surface layer is removed by CMP, the roughness is 0.2 to 0.25 nm; however, a decrease of R_{exp} down to $h \sim 3.5$ μm is still observed in $R_{exp}(h)$ dependence (Fig. 2, c) what is more clearly seen in the $R_{exp}(h)$ change character for the $<10\bar{1}2>$ and $<20\bar{2}4>$ reflections. This is seems to associated with the presence of a layer with the increased dislocation density formed due to the processing. After the CMP, the samples were annealed in air at 1250°C for 4 h. This is resulted in decreased integral reflection power R_{exp} for all the reflection orders, see

Table. Structure perfection characteristics of the sapphire with crystallographical orientation $<10\bar{1}2>$

<hkil> Reflection	θ, grad	S, μm	Calculated value, R_B			Mechanical polishing			Chemical-mechanical polishing			Chemical-mechanical polishing, annealing (1250 °C, 4 h)			Cleared facet (parallel to the surface of the sample)		
			$R_d \cdot 10^6$	$R_k \cdot 10^6$	R_k/I_d	$\bar{\beta}$, s	$\bar{\beta}'$, s	$\bar{R}_{exp} \cdot 10^6$	$\bar{\beta}$, s	$\bar{\beta}'$, s	$\bar{R}_{exp} \cdot 10^6$	$\bar{\beta}$, s	$\bar{\beta}'$, s	$\bar{R}_{exp} \cdot 10^6$	$\bar{\beta}$, s	$\bar{\beta}'$, s	$\bar{R}_{exp} \cdot 10^6$
$<10\bar{1}2>$	12.79	226	19.9	69.2	3.48	36.0	115.7	49.73	8.4	24.4	24.84	16.8	32.1	22.53	10.0	9.0	21.82
$<20\bar{2}4>$	26.28	113	21.1	119.6	5.67	36.0	117.0	70.69	8.2	23.8	29.10	17.5	34.7	24.80	11.6	8.8	27.43
$<30\bar{3}6>$	41.62	75	1.34	2.52	1.88	11.6	43.7	3.07	6.7	16.1	2.73	15.7	32.1	2.26	6.9	8.0	2.38
$<40\bar{4}8>$	62.33	56	6.28	9.99	1.59	15.4	57.9	16.57	10.3	21.9	10.87	16.9	36.0	8.64	10.8	6.7	9.84

Table, that is associated, in first turn, with the decrease in chaotic dislocation density and formation of the polygonized dislocation boundaries resulting in the DRC splitting and broadening as well as in R_a increase up to 0.7 nm. To analyze the post-CMP sample structure perfection inhomogeneity, the sample was scanned at a pitch of $L = 1.5$ mm in the crystal growth $[11\bar{2}0]$ direction with respect to the incident X-ray beam at the DRCS registration and determination of β and R_{exp} in each point. From the experimental $\beta(L)$ and $R_{exp}(L)$ (Fig. 3), this inhomogeneity is seen to attach about 18 %.

The DRCS analysis during the sample scanning evidenced also in some locations of the ordered dislocation boundaries resulting in DRC splitting at the rotation angles up to 5 angular seconds.

4. Conclusions

Thus, the TXRD methods provide a sufficient information on the structure perfection of surface layers in sapphire substrates of <10$\bar{1}$2> after MP by ASM-28/20 diamond paste followed by CMP. It if found the absence of polycrystalline layer after MP and the presence of fissured layer with small angles of the crystallite rotation ($\beta' \sim 120''$). After the finish CMP and achievement of the surface roughness ~0.2–0.25 nm, the layers with an increased dislocation density are observed in the near-surface area. The revealed structure nonuniformity over the cross-section of the sample is due mainly by the crystal growth technology. A post-CMP isothermal anneal in air at 1250°C for 4 h is found to be a very efficient technique for decrease the dislocation density in the near-surface layer of the sample. After that anneal, $R_{exp} = 24.8 \cdot 10^{-6}$, being close to the $R_{dyn} = 21.1 \cdot 10^{-6}$ value for the dispersion of X-rays by a perfect crystal calculated under dynamic approximation.

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Рентгендифрактометричні дослідження приповерхневих шарів підкладок з сапфіру з кристалографічною орієнтацією <1012>

В.Ф.Ткаченко, О.О.Лукієнко, О.Т.Будніков, О.О.Вовк, С.І.Кривоногов, О.Я.Данько

Методом трикристальної рентгенівської дифрактометрії (ТРД) високого розділення досліджено досконалість структури приповерхневих шарів підкладок з сапфіру з кристалографічною орієнтацією <1012> після механічного полірування алмазною пастою АСМ 28/20, а також при поетапному зніманні спотвореного приповерхневого шару хіміко-механічним поліруванням (ХМП) у суспензії рентгеноаморфного кремнезему SiO_2 та наступному відпалі цього зразку при температурі 1250°C протягом 4 годин. Структурно-чутливими параметрами, що вимірюються методами ТРД, були: форма кривої дифракційного відбиття, напівширина кривої хитання КДВ β, ширина на висоті 10 % від інтенсивності у максимумі КДВ — β', інтегральна потужність відбиття R_B. Отримано залежність параметрів $\beta(h)$, $\beta'(h)$, $R_{exp}(h)$ при пошаровому зніманні ХМП спотвореного шару товщиною h. Показано, що при знятті ХМП спотвореного приповерхневого шару товщиною $h \sim 2{,}5$ мкм шорсткість поверхі $R_a \sim 0{,}2$ нм, однак встановлено наявність шарів з підвищеною щільністю дислокацій.