

## STRUCTURAL CHARACTERIZATION OF BULK $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ CRYSTALS GROWN BY THE CZOCHRALSKI METHOD

A.V. Kremleva<sup>1\*</sup>, D.A. Kirilenko<sup>1</sup>, I.G. Smirnova<sup>1</sup>, V.E. Bougrov<sup>1</sup>, A.E. Romanov<sup>1,2</sup>

<sup>1</sup>ITMO University, Kronverkskiy pr. 49, St. Petersburg, 197101, Russia

<sup>2</sup>Ioffe Institute, Polytechnicheskaya 26, Saint-Petersburg, 194021, Russia

\*e-mail: avkremleva@itmo.ru

**Abstract.** Results of structural characterization of  $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$  single crystals grown from the melt with Al content  $x$  up to 0.04 are presented. Bulk  $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$  crystals were grown by exploring the Czochralski method [1]. Transmission electron microscopy (TEM) was used to investigate defect structure of the material with various composition, X-ray diffractometry was used to measure Al content  $x$ , to inspect crystallography of the growth facets and to characterize the structure quality of the samples. Possible types of defects were identified in the samples with various composition including single dislocations, cracks, and low-angle misorientation block boundaries. Measured full-width at half-maximum (FWHM) of rocking curves of 200" confirmed high quality of the grown crystals.

**Keywords:** Wide-bandgap semiconductor, monoclinic gallium oxide, defect, dislocation, stacking fault, crack

### 1. Introduction

Wide-bandgap semiconductors are of a great demand in many applications, including fabrication of highly efficient solid-state lighting sources, power electronics for smart grids, solar-blind photodetectors, sensors. One of the wide-bandgap semiconductors, which currently attracts a lot of interest, is monoclinic gallium oxide ( $\text{Ga}_2\text{O}_3$ ) with the bandgap value of  $\sim 4.9$  eV at room temperature [2]. Nowadays, the scientific community dealing with  $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$  compounds is mainly focused on studying thin epitaxial layers of the material [3]. On the other hand, bulk  $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$  crystals are the most likely candidates for fabricating components for future Smart Grid power electronics. This results from high breakdown electric field peculiar to the material – up to 10 MV/cm depending on the composition [4-5].

For achieving the above-mentioned instrument potential, the main challenge is to develop a technological processes of bulk crystals growth and production of  $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$  substrates with high crystalline quality (dislocation density less than  $1 \times 10^4 \text{ cm}^{-2}$  and stacking faults density less than  $10^2 \text{ cm}^{-1}$ ) and purity (background impurity concentration less than  $2 \times 10^{17} \text{ cm}^{-3}$ ). Similarly, to aluminum oxide liquid-phase growth, the liquid-phase growth is a low-cost approach for mass production of bulk crystals of  $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ . For the resolving of further described issues related to higher growth temperatures, however, more resilient solution is required. There are 3 main techniques for growth of bulk gallium oxide and  $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$  crystals: Edge-Defined Film-Fed Growth (EFG) [6-9], identified as Stepanov's technique in Russian literature, Czochralski method, and Bridgman method. It was determined that the Bridgman method is highly productive, but it suits only for producing crystals with low structural quality. Furthermore, the Czochralski method is basically

considered as growth method with low defect density. However, in this method, for large-size bulk  $(Al_xGa_{1-x})_2O_3$  growth, it is essential to increase oxygen content up to 100% in the growth atmosphere to maintain the oxygen balance above the melt. That is why even iridium (Ir) crucibles, where growth takes place, fade.

Operation of crucibles and tools, marked by high melting temperature, is of essential complexity for development of  $(Al_xGa_{1-x})_2O_3$  crystal growth technology. However commonly used Ir crucibles are unreliable and raise the cost of technology due to iridium fragility. Furthermore, a high oxygen level in growth atmosphere causes crucibles burning off.

Consequently, mass production is constrained by usage of expensive Ir crucibles, that actually used as consumable materials.  $(Al_xGa_{1-x})_2O_3$  with low content of Al is the most attractive material in terms of described applications. It is possible to grow  $(Al_xGa_{1-x})_2O_3$  crystals in cheap and user-friendly sapphire ( $Al_2O_3$ ) crucibles. However, sapphire crucible growth technology is still lacking in the world practice. It is due to the fact that Ga-Al-O melt partly dissolves sapphire crucible walls. However, affordable sapphire crucibles, used as consumable material, have insignificant influence on overall process cost.

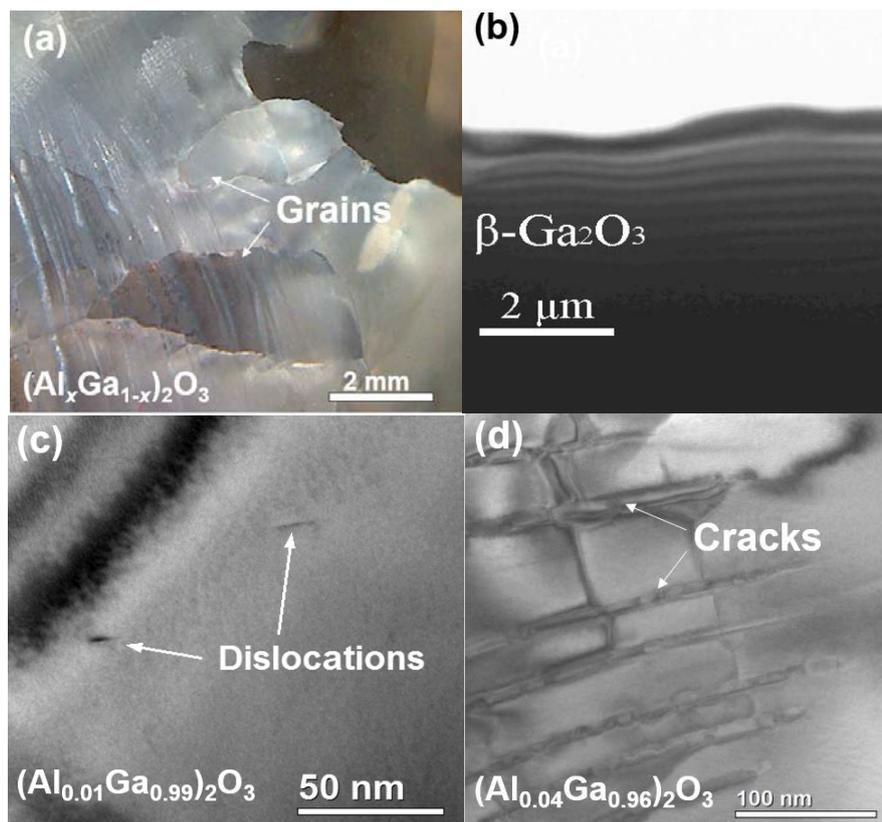
## 2. Experimental details

$(Al_xGa_{1-x})_2O_3$  bulk crystals were grown from the melt by exploring Czochralski method via pulling the molten material out on a rotating sapphire seed [10]. The seeding and the growth of our ingots were proceeded directly in the Ir or sapphire crucibles. Necessary conditions for formation of the seed and for following growth of the crystal were achieved by setting temperature gradients at every growth stage. The advantage of this approach is possibility to produce commercial-size sapphire crystals [8], if our technique would be eventually adapted for the growth of large gallium oxide crystals.

The structure of  $(Al_xGa_{1-x})_2O_3$  was analyzed by TEM. For this purpose, cross-sectional TEM specimens were prepared by a conventional procedure comprising face-to-face gluing of the wafer pieces, mechanical grinding and polishing down to the thickness of about 10-20  $\mu m$  and subsequent ion milling using  $Ar^+$  beam at 4 keV. Areas of the specimen which were sufficiently transparent for high-energy electrons (i.e. less than about 100 nm in thickness), were studied and defect structure of the epitaxial layers was analyzed using Jeol JEM-2100F transmission electron microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm). Conventional selected area electron diffraction (SAED) technique was used for analysis of the crystal structure and orientational relationships.

## 3. Results and Discussion

We studied four types of  $(Al_xGa_{1-x})_2O_3$  bulk crystals (Fig. 1). With increasing Al content, a significant number of different types of defects appears. That was observed using TEM and X-ray diffractometry. When preparing experimental samples, we used the ability of single-crystalline  $(Al_xGa_{1-x})_2O_3$  to be easily cleaved along strong cleavage planes (100) or (001) under mechanical treatment. This allowed us to fabricate samples in a form of platelets with given crystallographic orientation. Also, using mechanical cutting, we fabricated samples in a form of grains (blocks) with faces corresponding to various crystallographic planes in  $(Al_xGa_{1-x})_2O_3$  lattice. The dimensions of obtained  $(Al_xGa_{1-x})_2O_3$  bulk platelets with various Al content fabricated by cleaving were  $\sim 0.2 \times 1 \times 7$  mm. To study the uniformity of properties of the grown material, experimental samples were cut from various parts of the ingots.

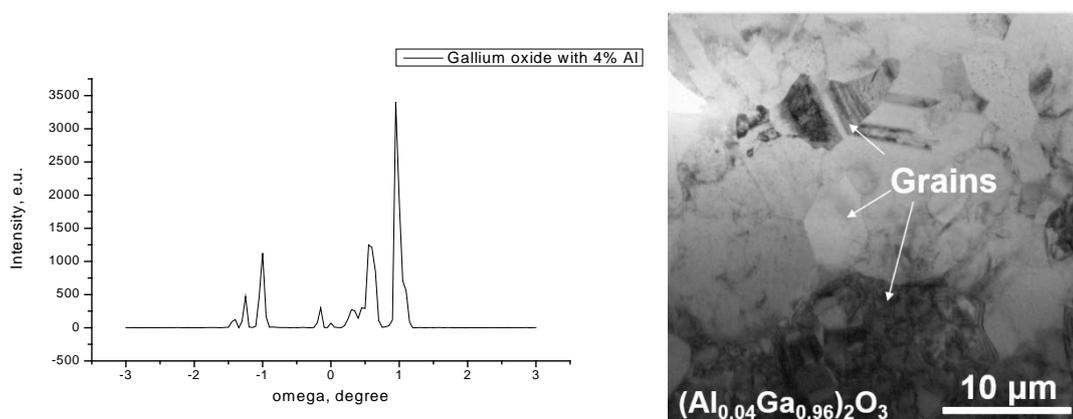


**Fig. 1.**  $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$  bulk crystals with various Al content. (a) Optical microscope image of  $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$  bulk crystal. (b) TEM image was obtained in plane (001), which shows a structure without dislocations in  $\beta\text{-Ga}_2\text{O}_3$ . (c) TEM image was obtained in plane (001), which shows dislocations in the crystal with 1% Al content. (d) TEM image was obtained in plane (001), which shows cracks in the samples with 4% Al content in the sapphire crucible

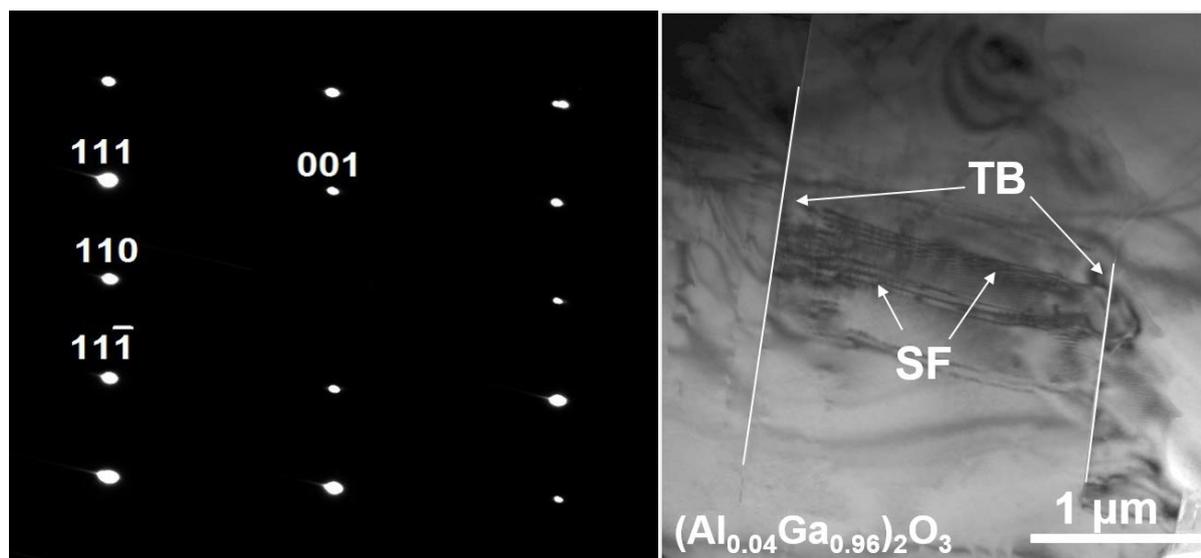
Crystallographic orientation of crystal faces and structural quality of the samples were studied using X-ray diffraction. X-ray diffraction patterns were recorded in  $(\omega)$ - and  $(\omega, 2\theta)$ -scanning modes. Dislocation-free 6H-SiC (0001) single-crystal grown with the Lely method was used as a monochromator. Figure 2 shows typical XRD patterns for samples obtained with cleaving along natural cleavage planes. As shown in Fig. 2a, the presence of two reflection peaks in  $(\omega)$ -scanning results from imperfection of the cleaved surface of the sample, namely, to the presence of (100)-oriented steps. In this case, we observe diffraction both from the surface and from a region beneath it, as both these regions appear in the scanned area. The asymmetry of the peaks indicates presence of micro-blocks with low misorientation in [100] direction (Fig. 2b). Low values of the FWHM of the recorded curves, which were limited to  $200''$  as determined by the fitting of the experimental curves with Gaussians, shows high perfection of the crystalline phase of the studied  $(\text{Al}_{0.04}\text{Ga}_{0.96})_2\text{O}_3$  in the sapphire crucible.

In addition to dislocations and cracks, we also observed stacking faults (SFs) on (001) plane of these structures (Fig. 3). SFs provide specific contrast in a bright-field image (e.g., Fig. 3b), if the scalar product of their fault vector  $\mathbf{R}$  with the diffraction vector  $\mathbf{g}$  used for this image is non-zero or non-integer. The presented dependence of the SF visibility on diffraction vector allows us to suppose the fault vector  $\mathbf{R}$  lays in the SF plane. Thus, the SF can appear due to mechanical stress. In order to determine the SF plane more precisely, we tilted the specimen to another zone axis and found that the SF visible as narrow lines when [010] direction is parallel to the electron beam. That is due to their plane is perpendicular to the

image plane in this case. It is remarkable, that SF continuously extends through the (100) twins in the grain, and its zig-zag shape (Fig. 3b) corresponds to the different orientation of (001) planes in the twins.



**Fig. 2.** Grains in  $(Al_{0.04}Ga_{0.96})_2O_3$  bulk crystals. (a)  $\omega$ -scan X-ray diffraction peaks obtained using (001) plane for  $(Al_{0.04}Ga_{0.96})_2O_3$  bulk. (b) TEM image was obtained in plane (001), which shows micro-blocks with low mis-orientation in [100] direction



**Fig. 3.** SF in  $(Al_{0.04}Ga_{0.96})_2O_3$  bulk crystals. (a) Electron diffraction pattern, used diffraction spots are marked. (b) TEM image was obtained in spot (001). The SF are clearly visible. The zigzag shape of the SF is caused by its propagation through a set of twins on (100) plane, so that the direction of the SF plane changes inside twinned part of the crystal lattice

#### 4. Conclusions

For the first time  $(Al_xGa_{1-x})_2O_3$  crystals with Al content up to 4% were fabricated from the melt by Czochralski method and were characterized by TEM and X-Ray diffraction techniques. We compared crystals grown in iridium and sapphire crucibles,  $(Al_xGa_{1-x})_2O_3$  crystals in both cases were of the same quality. We can conclude that sapphire crucibles can be used for mass production of bulk crystals of  $(Al_xGa_{1-x})_2O_3$  due to low price. We found out defect structure including twin boundaries and SFs in the plane (001) in  $(Al_xGa_{1-x})_2O_3$  with Al content up to 1.5% is of the same quality as defect structure of  $Ga_2O_3$ . Wider bandgap and

bigger breakdown electric field of (Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> bulk crystals as compared to Ga<sub>2</sub>O<sub>3</sub> make them perspective for fabrication of power electronic devices.

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