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Growth of gallium oxide crystals by free-casting in a cold crucible

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The paper studies the possibility of obtaining gallium oxide crystals by free crystallization in a cold crucible. It presents information about the features of gallium oxide garnishing melting. The first single crystals were obtained, and their characteristics were studied.

Keywords: gallium oxide, crystal growth, cold crucible, free crystallization.

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Gallium oxide, β-Ga_2O_3, is a promising ultra-wide-band semiconductor ($E_g = 4.8$ eV) [1,2]. In terms of application, it is treated as a crystal for high-voltage diodes and transistors with high breakdown voltage (8 MV/cm). Its substantial advantage over other wide-band semiconductor crystals is in that it can be grown from melt at near-atmospheric pressure. However, a high melting temperature ($\sim 1800\,^\circ$C) and high reactivity of the Ga_2O_3 melt limit the choice of crucible materials to expensive iridium and platinum-rhodium alloy. Whereas the Pt$-$30 % Rh crucible, whose melting temperature ($T_m \sim 1850\,^\circ$C) is a little higher than that of gallium oxide, requires extreme caution when approaching charge melting. Commercial crystals are generally grown in an iridium mold, they are mainly pulled from the melt using the Stepanov (EFG) or Czochralski process [3–5], in oxygen-containing atmosphere. It is pointed out that iridium in oxygen atmosphere, on the one hand, forms volatile oxides at high temperatures, while, on the other hand, there are gallium oxide dissociation and partial reduction of metallic gallium to form an intermetallic compound, IrGa. All these processes lead to apparent loss of iridium mass during growth of β-Ga_2O_3 crystals [6,7] and considerably increase the cost of grown crystals. Iridium consumption becomes most noticeable in attempts to increase the sizes of crystals to those used in the semiconductor industry (diameter of 4 inches and larger), for which oxygen concentration in the growth vessel shall be increased, sometimes to 100 % [7].

Crucibleless crystal growth processes are an alternative approach to Ga_2O_3 melting. A cold crucible process is believed to be the most promising among them [8]. A group of Japanese researchers [9] have recently conducted successful experiments for seeded pulling of β-Ga_2O_3 single crystals via the Czochralski process from the melt in a cold crucible in standard air. At the same time it should be pointed out that, having solved the crucible issue, the authors of [9] haven't made any progress in the Czochralski crystallization method. As before, they faced the problem of crystal transfer to spiral growth mode as the crystal diameter increased (proliferation).

In recent years, interest has been observed in simple and powerful crystal growth techniques such as free unseeded melt crystallization. This β-Ga_2O_3 crystal growth option was called the casting method [6], where the melt is crystallized in shallow containers with large diameters (up to 6 inches) [10]. The method is based on the fact that a mirror-smooth surface of solidified gallium oxide melt can be easily obtained on a large area (almost all over the crucible). Mirror surface corresponds to the (100) lattice plane of gallium oxide. Only an iridium crucible has been used for this method until now, which didn't solve the problem of loss of noble metals during gallium oxide crystal growth.

In this work, this is the first time when formation of a β-Ga_2O_3 ingot via the free cold-crucible crystallization technique is reported.

Gallium oxide was melted in air on the equipment provided by the Department of Electrotechnological and Converter Equipment of the St. Petersburg State Electrotechnical University „LETI" in a crucible from copper tubes cooled with running water and enveloped by a water-cooled inductor [8], using a 1.76 MHz, 100 kW vacuum-tube generator. High-purity (99.99 %) gallium oxide powder and ground crystalline scrap consisting of crystals grown via the Czochralski method in our experiments were used as initial charge. The charge was compacted directly in the crucible. Since the compacted material has no noticeable conductivity at room temperature and almost until melting, conducting pieces of graphite placed on top of the charge were used for heating and reaching the melting temperature. These pieces burnt out in air and provided heating of the charge until the gallium oxide melt appeared.

The crystallized material was analyzed using the Phenom PRO X scanning electron microscope (SEM) with a microanalysis module, the DRON-8 X-ray diffractometer and SPECORD UV-VIS spectrophotometer.

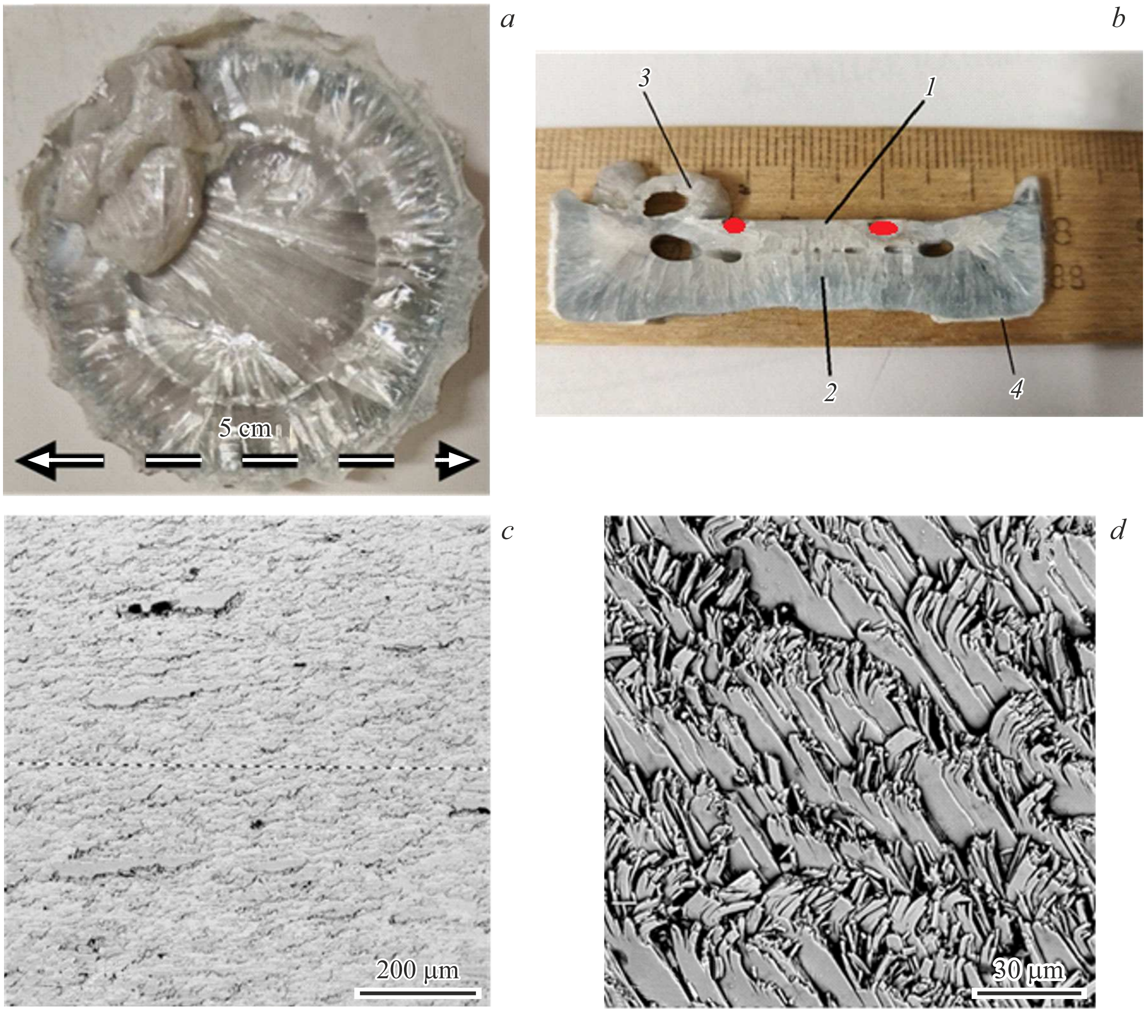

Figure 1. Free cold-crucible crystallization of gallium oxide. *a* — plan view of the crystallized material after separation from the crucible tubes; *b* — ingot cross-section (ingot areas discussed in the text are marked with numbers); *c* and *d* — SEM images of the ingot surface in the crystallized melt region (with a dashed line of elemental analysis) and skull, respectively.

A sample$\sim$ 50 mm in diameter prepared experimentally in the cold crucible is shown in Figure 1, *a*. Figure 1, *b* shows cross-section of the sample cut by a diamond saw. Several regions can be distinguished: crystallized β-Ga_2O_3 melt (ingot) (*1*) separated by a localized cavity zone from the caked gallium oxide crystallized in the solid state (*2*), molten gallium oxide lap above the melt level (*3*), thin border layer (*4*) immediately adjacent to the cold crucible consisting of finely dispersed caked powder.

SEM image of the melt crystallization region *1* (Figure 1, *c*) shows a plate-like structure typical of the β-Ga_2O_3 crystals, crystallites are facetted by two perfect cleavage planes: (100) and (001). Elemental analysis (see the table) hasn't detected any impurities in this region within the method sensitivity, i. e. less than 0.5 at.%. A crust is formed in the skull region *2* (Figure 1, *d*) to hold the melt. Crust structure consists of multiple small needle-shaped gallium oxide crystals directed from the crucible to the melt. There is a small amount of carbon impurity in this zone (up to 2.5 at.%) (see the table), which is probably caused by the fact that carbon diffused into a less dense region than the melt crystallization zone.

Sufficiently large crystals with a dimension up to 6 m (Figure 2), which were separated from the total mass of the solidified melt, were detected on the melt zone edges (highlighted in red in Figure 1, *b* in the electronic version). Figure 3, *a* shows X-ray diffraction from the major face of the grown crystal, demonstrating a series of reflections corresponding to the (100) plane of β-Ga_2O_3. Figure 3, *b* shows optical transmission spectra of a crystal grown in a

Elemental analysis data

Test region	Oxygen		Gallium		Carbon	
	at.%	wt.%	at.%	wt.%	at.%	wt.%
Melting zone	60.87	26.31	39.13	73.69	–	–
Skull	57.21	24.35	40.36	74.87	2.44	0.78

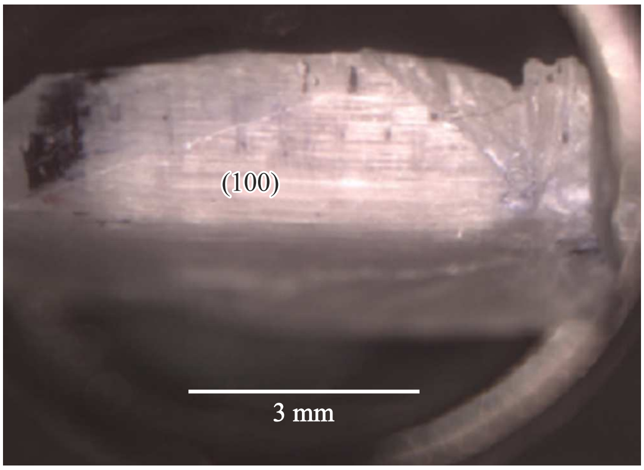

Figure 2. Gallium oxide single crystal formed from the melt in a cold crucible, partially separated from the melt.

cold crucible, and of a single crystal grown by the Czochralski method in an iridium crucible for comparison. The edge of the optical absorption zone of the crystal grown by the Czochralski method closely meets β-Ga_2O_3, and a lower quality crystal from a cold crucible has a more smeared absorption edge. Arrow in Figure 3, *b* marks a typical step on optical transmission curves, which is presence in both crystals. It is linked to one of the deep levels near the band gap edge, which were studied in more detail and described in studies investigating electronic properties of our crystals grown by the Czochralski method [11]. Optical band gap determined by the Tauc method (inset in Figure 3, *b*) taking into account the shoulder peak from the deep level [12] was almost equal for both crystals (~ 4.60 eV for the crystal from a cold crucible and 4.59 eV for the crystal grown by the Czochralski method).

The experiments show the prospects of growth of large gallium oxide crystals from the proprietary melt without a traditional precious metal mold. The quality of crystals can be improved by making an optimum heating unit using heat-insulating materials.

Conflict of interest

The authors declare no conflict of interest.

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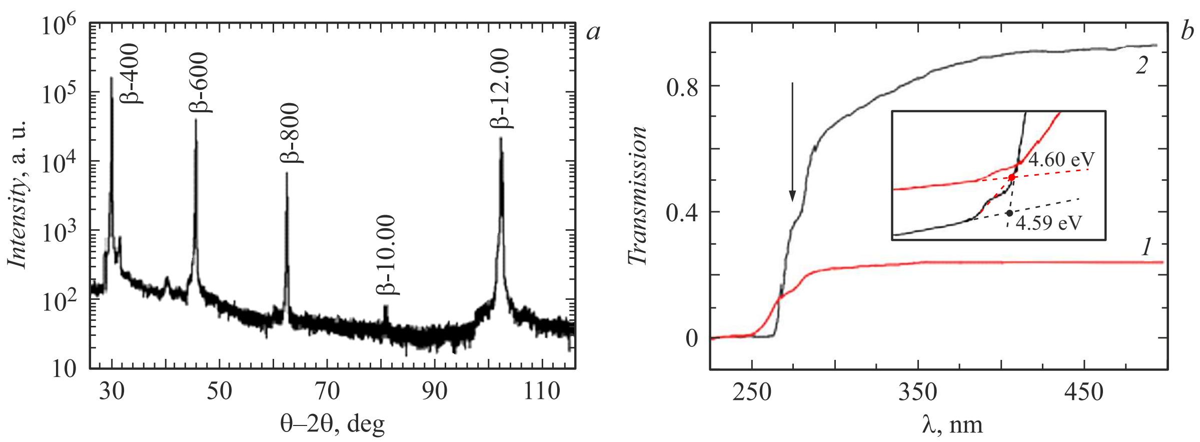

Figure 3. *a* — X-ray pattern of $\theta - 2\theta$-scanning, reflection from the (100) crystal surface. *b* — optical transmission spectra: *1* — crystal grown in a cold crucible, *2* — crystal grown from the melt via the Czochralski method. A step induced by an n-type impurity is marked by an arrow. The inset shows the optical band gap determined using the Tauc plot.

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