Growth technology and characterization of bulk crystalline gallium oxide

D I Panov¹, V A Spiridonov¹, D A Zakgeim¹, A V Kremleva¹, D A Bauman¹, A E Romanov¹ and V E Bougrov¹

¹ITMO University, St. Petersburg, 197101, Russia.
²Ioffe Institute, St. Petersburg, 194021, Russia.

Abstract. In this paper, we study the process of growth from the melt by Chokhralsky method of bulk β-Ga2O3 crystals. The effect of different configurations of growth zones and ambient composition on resulting bulk crystal quality has been evaluated. It is shown that the vertical gradient has a great influence on the quality of the growing crystal and the stability of growth. The optical properties of obtained β-Ga2O3 crystals were investigated. The crystallographic orientation of crystal faces and the structural quality of the samples were studied with the use of XRD.

1. Introduction

Nowadays, there is great interest all over the world in the development of new semiconductor materials. One of such promising materials is a beta-gallium oxide (β-Ga2O3). β-Ga2O3 is already successfully used in many applications, for example, MOSFETs with a breakdown voltage above 1000 V [1], conductive transparent substrates for the epitaxy of optoelectronic structures based on III-nitrides [2]. This becomes possible due to unique Ga2O3 physical properties such as wide bandgap (~4.8 eV), high breakdown electric field (>8 MV/cm), relatively high electron mobility (~150 cm²/Vs) [3–6], and transparency in visible and UV spectral range [5,7].

In contrast to other wide bandgap semiconductors (GaN, AlN, SiC), Ga2O3 can be relatively easily obtained as a bulk crystal. The most widely used techniques for that are the Czochralski (CZ) method [7, 8] and Edge defined Film-fed Growth (EFG) [9,10].

The process of β-Ga2O3 growth from the melt is complicated by the possibility of melt chemical decomposition in the inert atmosphere. The Ga2O3 melt can decompose into divalent gallium oxide, monovalent oxide and, finally, metallic gallium (Ga2O3 → GaO → GaO2 → Ga and O2). As a result, metallic gallium can form intermetallic alloys (Ir-Ga) with elements of growth equipment (crucibles, formers, seed holders), which eventually leads to the destruction of equipment made of precious metal. Another negative consequence of the violation of the stoichiometry of the melt is the formation of defects in the growing crystal. In recent papers, much attention has been paid to the study of the influence of growth atmosphere composition on the quality and physical properties of the resulting bulk crystals [11, 12]. Among others, Galazka's research group published a series of papers on the advantages of the usage of the oxygen-containing atmosphere in the Czochralski growth process [5,7,12,13].

2. Experimental

The growth of β-Ga2O3 crystals was performed in the industrial system "NIKA-3" having inductive heating of the growth zone. Powdered 99, 99 (4N) Ga2O3 was used to produce the initial melt in the growth processes. The melting was performed in iridium (Ir) crucible with a diameter of 40 mm and a height of 25 mm, and a crystalline sapphire (Al2O3) was used as the seed. In some experiments, the possibility of using of a tungsten ring as a re-emitter concentrator (afterheater) has been investigated. In each process, the growth chamber was evacuated to the residual pressure of 10⁻² mbar and filled with a mixture of gases, argon (Ar) and carbon dioxide (CO2). Two series of experiments with different configurations of growth zones were carried out:

1) In the first series of experiments, a set of ZrO2 disks with a diameter larger than the diameter of the crucible was used as the growth zone thermal insulation. The growth was carried out in the pure Ar
atmosphere at a pressure of 1.5 Bar. A massive tungsten ring with a diameter of 95 mm and a height of 65 mm was used as an induction radiation re-emitter, screening the Ir crucible from the RF radiation of inductor. Schematics of the growth zone with a re-emitting ring is shown in figure 1a.

2) In the second series of the experiment, the re-emitting ring was removed and Ir crucible was heated directly by RF radiation. Coaxial pipes made of ZrO\(_2\) ceramics were used as a growth zone thermal insulation, the space between them was filled with ceramic powder. Schematics of this zone is shown in figure 1b. In this case, the growth atmosphere was a mixture of Ar and CO\(_2\) in various ratios (including pure CO\(_2\)), with a total pressure of 1.5 bar.

3. Results and discussion

3.1 Growth processes

In the first series of experiments, a tungsten ring was introduced into the growth zone to address several issues such as:

1) Protection of the iridium crucible by screening it from inductor RF power. Provided that the crucible may contain microcracks, corona discharges can occur in them, leading to local overheating and even local melting of the crucible.

2) Ensuring the optimal vertical temperature gradient in the growth direction.

The tungsten ring is higher than crucible and thus provides a smooth temperature transition between melt and ambient. The fact is, that sharp cooling of the crystal leads to the emergence of thermal stresses. Relaxation of the resulting stresses provokes the formation of extended structural defects and cracking of the crystal.

However, the usage of a tungsten re-emitting ring has drawbacks such as:

1) the slower temperature response of the system to changes in the power supplied to the inductor, which makes it difficult to control the growth process using a weight sensor. This, in turn, makes it impossible to stabilize the shape of the growing crystal. When using a re-emitting tungsten ring, an uncontrolled expansion of the crystallization front was observed, which led to a spiral shape of the resulting crystals (see figure 2a).

2) The usage of a re-emitting tungsten ring imposes restrictions on the composition of growth atmospheres - only an inert atmosphere, such as Ar, should be used. The presence of even a small amount of oxygen leads to intensive oxidation of the tungsten ring at the melting temperature of Ga\(_2\)O\(_3\).

At the same time, it is well known, that the growth of high-quality Ga\(_2\)O\(_3\) requires the usage of oxygen-containing atmospheres [13]. In an inert growth atmosphere, the gallium oxide melt decomposes into volatile components and metallic Ga (Ga\(_2\)O\(_3\) → GaO → Ga\(_2\)O → Ga and O\(_2\)) [14]. The appearance of free gallium leads to the formation of an intermetallic compound Ir-Ga, which in turn leads to the destruction of the crucible [15]. The formation of volatile components leads to the deposition of an amorphous Ga\(_2\)O\(_3\) on parts of the chamber and even on the growing crystal itself, (one can see the white coating on the crystal shown in figure 2a). Also, a violation of the stoichiometry of the melt leads to a deterioration of the quality of the growing crystal.

As a result, we decided to use the growth zone with direct heating of the iridium crucible by inductor RF power. This allowed us to use the oxygen-containing growth atmosphere for chemical stabilization of the Ga\(_2\)O\(_3\) melt. As a source of oxygen CO\(_2\) was used. At the gallium oxide melting temperature (about 1850°C) it partially decomposes into CO and O\(_2\) emitting up to 1 vol.% of molecular oxygen [16,17].
addition of oxygen significantly reduced the rate of decomposition of the melt, which led to the purification of the crystal surface. The removal of the re-emitting ring made it possible to significantly speed up the temperature response of the system to changes in the power supplied, which made it possible to control the size of the growing crystal using a weight sensor. However, after removing the re-emitting tungsten ring, we had to seriously upgrade the thermal insulation in the growth zone to obtain an optimal temperature gradient in a vertical direction at the melt/crystal boundary interface. As thermal insulation, coaxial pipes made of zirconium ceramics were used, the space between them was filled with ceramic powder. This configuration of thermal insulation significantly suppressed gas convection near the crucible and greatly reduced heat loss. This made it possible to achieve an optimal vertical temperature gradient, which provides precise control of the growth process (rate, weight, diameter). The cylindrically shaped β-Ga2O3 boules were reproducibly grown, as can be seen from figure 2b.

Figure 2. Examples of Czochralski grown β-Ga2O3 crystals. Samples were grown with zones shown in figure 1a and figure 1b, correspondingly.

3.2 XRD results
The quality of obtained β-Ga2O3 crystals was investigated by the XRD method. The DRON 8 X-ray diffractometer in a slit configuration with fine focus X-ray tube with a copper anode and a NaI (Tl) scintillation detector and Ni-beta filter was used in these studies. The XRD patterns were recorded in (ω)– and (ω,2θ)–scanning modes. Samples for XRD studies were prepared by means of cleaving along natural cleavage planes.

Figure 3. XRD patterns of β-Ga2O3 obtained in (ω,2θ) mode (a) and in (ω) mode (b).

Figure 3 shows typical XRD patterns for the sample shown in figure 2a (grown in Ar atmosphere). As can be seen from figure 3, the diffraction pattern obtained in (ω, 2θ)–scan contains only peaks corresponding to reflections from (400), (600) and (800) faces, which correspond to crystallographic planes in β-Ga2O3. The presence of two reflection peaks in (ω)–scanning (figure 3b) is due to the
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. The asymmetry of the peaks is indicative of the presence of micro-blocks with low misorientation in [100] direction. The value of the full-widths at half-maximum (FWHM) of the recorded curves is 50' as determined by the fitting of the experimental curves with Gaussians.

![Figure 4](image)

**Figure 4.** XRD patterns of β-Ga₂O₃ obtained in ($\omega$,2$\Theta$)-mode (a) and ($\omega$)-mode (b)

In figure 4 represents XRD patterns for the sample depicted in figure 2b (grown in CO₂ atmosphere). This sample is monocrystalline and its XRD spectrum contains peaks from β-Ga₂O₃ (400) and (600) reflections. The peak at $2\Theta \approx 45.8^\circ$ is the farthest diffraction peak from β-Ga₂O₃. Figure 4b shows the rocking curve for β-Ga₂O₃ (600) reflection, FWHM is approximately 24', which indicates a much higher crystal quality of this sample compared to the one, grown in Ar atmosphere.

### 3.2 Optical properties

The optical properties of the obtained β-Ga₂O₃ crystals were studied. The optical transmission spectrum was measured on a plane-parallel plate with a thickness of 1 mm using the "Photon RT" system. Plates were made by cleaving the crystal along the crystallization interface, which allowed us to have smooth enough samples without any additional surface treatment.

![Figure 5](image)

**Figure 5.** Spectra of optical transmission of grown β-Ga₂O₃ crystals as a function of wavelength (a) and photon energy (b).

As mentioned earlier, the melt of gallium oxide is chemically unstable and the composition of the atmosphere affects the electrical and optical properties of the resulting crystals. From the optical transmission spectra shown in Figure 5a, it can be seen that the more intense absorption in the IR region of the sample obtained in an oxygen-containing atmosphere. The melt stoichiometry violation results in the formation of defects in the crystal, which reduce the concentration of free electrons responsible for IR
absorption. This observation is supported by [7], where authors studied the influence of growth atmosphere composition on the concentration of free electrons in the resulting crystal.

From the spectral position of the edge of the fundamental absorption, we have estimated the width of the bandgap to be approximately 4.7 eV. This value is slightly smaller than the data reported by other research groups [7, 12, 14], probably, due to the presence of a certain number of defects.

4. Conclusions
In this paper, we studied the process of growing β-Ga2O3 crystals using the Czochralski method. Using various configurations of growth zone and growth atmosphere compositions, we have proved experimentally that oxygen-containing growth atmosphere results in better crystalline quality of Ga2O3 crystals. The FWHM of the XRD rocking curve decreases from 50’ for samples grown in pure Ar atmosphere to 24’ for samples grown in CO2. The oxygen-containing growth ambient imposes restrictions on the use of materials in growth processes. Only iridium, which is stable in an oxygen-containing atmosphere at a melting point of Ga2O3, can be recommended for use as a crucible and a re-emitting ring. When the crucible itself is directly heated by radiofrequency radiation, the thermal insulation of the growth zone must be carefully adjusted to ensure the necessary vertical temperature gradient. By doing this we have succeeded in the fabrication of cylindrically shaped β-Ga2O3 boules having about 2 cm in diameter. The reasonable crystal quality of obtained boules has been proven also by optical transmittance measurements. The bandgap about 4.7 eV has been estimated from the absorption edge.

Acknowledgments.
This work was supported by the Russian Science Foundation, Project No. 19-19-00686.

References.
[1] Tippins H H 1965 Phys. Rev. 137 A865–71
[2] Minami T, Shirai T, Nakatani T and Miyata T 2000 Jpn. J. Appl. Phys. 39 L524
[3] Pearton S J, Yang J, Cary P H, Ren F, Kim J, Tadjer M J and Mastro M A 2018 Applied Physics Reviews 5 011301
[4] Stepanov S I, Nikolaev V I, Bougrov V E and Romanov A E 2016 Rev.Adv.Mater.Sci. 44 63–86
[5] Galazka Z 2018 Semicond. Sci. Technol. 33 113001
[6] Chikoidze E, Fellous A, Perez-Tomas A, Sauthier G, Tchelidze T, Ton-That C, Huynh T T, Phillips M, Russell S, Jennings M R (Michael R), Berini B, Jomard F and Dumont Y 2017 Materials Today Physics 3 118–26
[7] Galazka Z, Irmscher K, Uecker R, Bertram R, Pietsch M, Kwasniewski A, Naumann M, Schulz T, Schewski R, Klimm D and Bickermann M 2014 Journal of Crystal Growth 404 184–91
[8] Butenko P N, Panov D I, Kremleva A V, Zakgeim D A, Nashchekin A V, Smirnova I G, Bauman D A, Romanov A E and Bougrov V E 2019 Materials Physics and Mechanics 42 802–7
[9] Kuramata A, Koshi K, Watanabe S, Yamaoka Y, Masui T and Yamakoshi S 2016 Jpn. J. Appl. Phys. 55 1202A2
[10] Masuya S, Sasaki K, Kuramata A, Yamakoshi S, Ueda O and Kasu M 2019 Jpn. J. Appl. Phys. 58 055501
[11] Zinkevich M and Aldinger F 2004 Journal of the American Ceramic Society 87 683–91
[12] Galazka Z, Uecker R, Irmscher K, Albrect M, Klimm D, Pietsch M, Brützam M, Bertram R, Ganschow S and Formari R 2010 Crystal Research and Technology 45 1229–36
[13] Galazka Z, Uecker R, Klimm D, Irmscher K, Naumann M, Pietsch M, Kwasniewski A, Bertram R, Ganschow S and Bickermann M 2016 ECS J. Solid State Sci. Technol. 6 Q3007
[14] Maslov V N, Nikolaev V I, Krymov V M, Bugrov V E and Romanov A E 2015 Phys. Solid State 57 1342–6
[15] Arkan N, Charifi Z, Baaziz H, Üner Ş, Ünver H and Uğur G 2015 Journal of Physics and Chemistry of Solids 77 126–32
[16] Baldini M, Galazka Z and Wagner G 2018 Materials Science in Semiconductor Processing 78 132–46
[17] Tomm Y, Reiche P, Klimm D and Fukuda T 2000 Journal of Crystal Growth 220 510–4