

The effect of high-temperature annealing on the properties of bulk β -Ga₂O₃ obtained in different growth atmospheres

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ABSTRACT

The work presents the results of the experiments on annealing in air of bulk crystals of gallium oxide grown in Ar+O₂ and CO₂ atmospheres at a temperature of 1400 °C. The annealing time was 5 hours; the time to reach the temperature was 3.5 hours; the cooling time was 20 hours. Annealed samples show increasing of transmission in infrared area of electromagnetic spectrum and decreasing of width of X-ray rocking curve which means the reduction of the number of defects in crystals. Full width at half maximum of rocking curve for annealed samples was almost the same for both atmospheres: FWHM_a = 84 arcsec for sample grown in Ar+O₂ atmosphere and FWHM_a = 80 arcsec for sample grown in CO₂, which means that after annealing, the quality of the samples became comparable, despite the initial difference.

KEYWORDS

β -Ga₂O₃ • bulk crystal • annealing • optical spectroscopy • XRD

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Introduction

Recently, the theme of ultra-wide bandgap (UWBG) semiconductors has been gaining big attention [1–4]. The term UWBG is commonly used to denote semiconductors with a larger band gap E_g than traditional wide bandgap semiconductors such as silicon carbide ($E_g=3.2\text{eV}$ [5]) and gallium nitride ($E_g=3.4\text{ eV}$ [6]). Usually, compounds III-V (BN, AlN, AlGaIn), diamond and compounds based on gallium oxide are considered as UWBG. The bulk crystal of gallium oxide (β -Ga₂O₃) is a semiconductor with a band gap of about 4.8 eV [7,8], with excellent electrical characteristics, such as large breakdown electric field of about 8 MV/cm theoretically [9] and about 3.8 MV/cm in the device [10], high radiation resistance [11] and relatively high electron mobility (up to 200 cm²V⁻¹s⁻¹ [12]). One of the main advantages of gallium oxide over other UWBG semiconductors is the possibility of fabricating bulk crystals by liquid phase growth methods such as the Czochralski method [13–19] and the edge-defined film-fed growth (EFG) method [20–25] used in the industry.

Experiments on the annealing of bulk β -Ga₂O₃ crystals have shown that annealing in an oxygen-containing atmosphere leads to an increase in optical transmission in the IR region and a drop in the concentration of charge carriers [26–28]. During annealing without oxygen, for example in nitrogen [28] or in vacuum [29], the reverse processes occur – the concentration of carriers increases, transmission decreases.

Previous experiments have shown that increasing the oxygen concentration in the growth atmosphere improves the quality of crystals [30,31], as well as high-temperature annealing in an oxygen-containing atmosphere [26–28,31–33]. In addition, experiments have shown that the properties of the crystal after annealing change significantly at an annealing temperature of 1200 °C and above [31,33]. In this paper, the effect of annealing on gallium oxide crystals grown in different growth atmospheres is evaluated.

Experimental setup and methodology

For this study bulk single crystals of gallium oxide were grown in the industrial facility “Nika-3” (production of EZAN, Russia) using the Czochralski method as described in our previous work [30]. An iridium crucible was used to form the melt. β -Ga₂O₃ crystals were used as seeds. Ga₂O₃ powder with a purity of 99.999 % (5N) was used as a starting material for the formation of the melt. The growths were conducted in an argon atmosphere with the addition of 5 vol. % of oxygen and in CO₂ atmosphere at a pressure of 1.4 bar.

For the studies plane-parallel plates with thicknesses of 1 mm were cut from crystal boule along the cleavage plane (100).

Annealing was conducted in a shaft furnace at a temperature of 1400 °C for 5 hours (the time to reach the temperature was 3.5 hours, the cooling time was 20 hours) in air. Sample for annealing was placed on sapphire substrate in corundum crucible.

Results and Discussion

The main difficulties in obtaining gallium oxide from the melt are the high melting point (1795–1820 °C [16,34]) and melt decomposition into volatile forms during growth in an atmosphere with oxygen deficiency [16]. The decomposition of the gallium oxide melt can be described by the following reactions:



With crystal growth, decomposition leads to a lack of oxygen in the melt, which in turn leads to a violation of stoichiometry in the grown crystal and the formation of oxygen vacancies in crystal. Vacancies in β -Ga₂O₃ lead, for example, to an increase in optical absorption in the IR region of the spectrum [35].

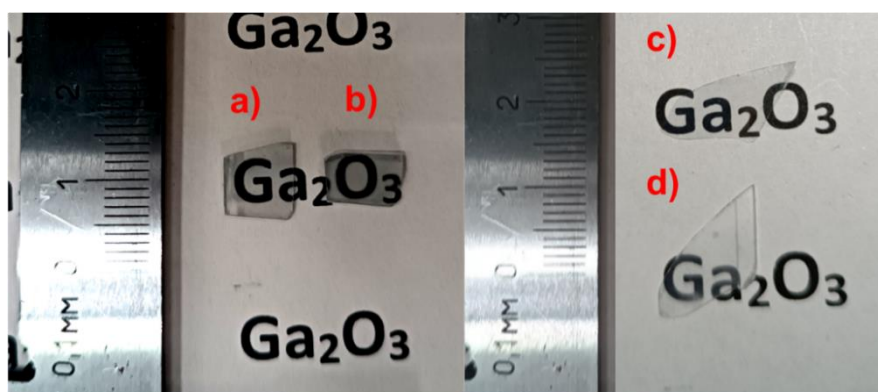


Fig. 1. Photo of the samples of β -Ga₂O₃: a) sample grown in CO₂ atmosphere; b) annealed sample grown in CO₂ atmosphere; c) sample grown in Ar+O₂ atmosphere; d) annealed sample grown in Ar+O₂ atmosphere

After annealing, the sample became visually cloudy (Fig. 1), which indicates a change in the morphology of its top surface, presumably due to diffusion processes. For further experiments, a rough surface layer 0.1 mm thick was exfoliated from each annealed sample and the measurements were carried out on the remaining part of the samples.

Figure 2 shows the normalized transmission spectra of samples. The graph shows that annealing led to an increase in transmission in the IR region of the spectrum, which means a decrease in the number of absorbing centers that can be oxygen vacancies [35]. There is also a strong difference between samples grown in Ar+O₂ and in CO₂ atmosphere, due to the almost five times higher [31] oxygen concentration in the growth atmosphere, which reduces the volatilization of oxygen from the melt [16].

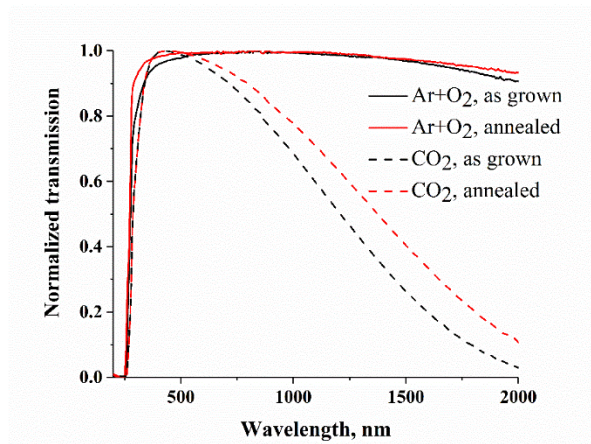


Fig. 2. Normalized transmission spectra of samples of β -Ga₂O₃.

Solid line – samples grown in Ar+O₂ atmosphere, dashed line – samples grown in CO₂ atmosphere

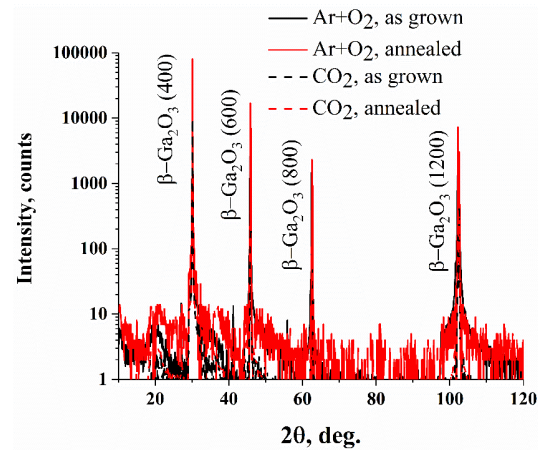


Fig. 3. XRD 2 θ -spectra of annealed and non-annealed samples of β -Ga₂O₃.

Solid line – samples grown in Ar+O₂ atmosphere, dashed line – samples grown in CO₂ atmosphere

XRD spectra (Fig. 3) showed the presence of peaks corresponding to the (100) plane of the β -Ga₂O₃ and showed no phase changes between samples. Figures 4 and 5 present normalized rocking curves of samples for peak (400). For sample grown in the Ar+O₂ atmosphere we can see significant reduction in the full width at half maximum (FWHM) of the rocking curve (RC) from FWHM_{na} = 208 arcsec for the non-annealed sample to FWHM_a = 84 arcsec for the annealed one.

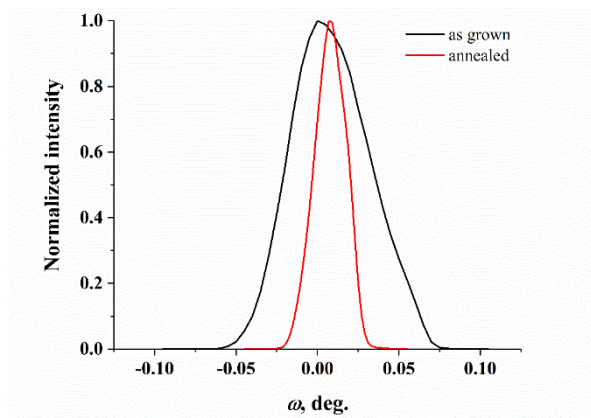


Fig. 4. Rocking curve ω for the peak (400) of annealed and non-annealed samples of β -Ga₂O₃ grown in Ar+O₂ atmosphere. FWHM_{na}=208 arcsec, FWHM_a= 84 arcsec

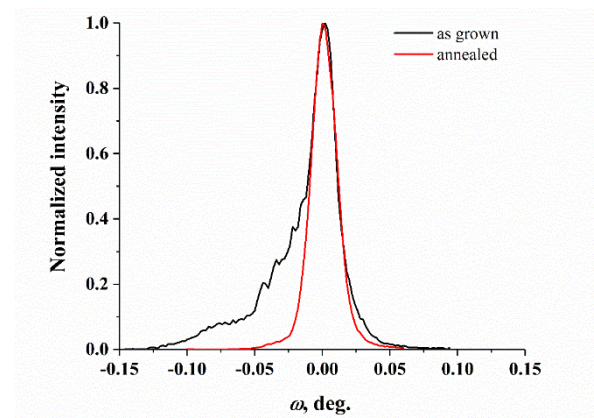


Fig. 5. Rocking curve ω for the peak (400) of annealed and non-annealed samples of β -Ga₂O₃ grown in CO₂. FWHM_{na}=82 arcsec, FWHM_a= 80 arcsec

Together with the visible change in the morphology of the sample surface after annealing, we can say about the movement of defects on to the surface and an increase in the bulk crystalline quality.

For the sample grown in CO_2 before annealing, a wide tail is observed on the RC, which indicates the presence of defect blocks in the crystal. The RC of the non-annealed sample can be decomposed by gaussians to the three peaks (see Fig. 6), similar to how it was done in [36], which means the presence of multiple disoriented blocks. After annealing, this tail disappears, which shows a decrease in the number of defects i.e., an improvement in crystal quality. The FWHM of RC after annealing correspond to the FWHM of strongest peak at the RC of the non-annealed sample.

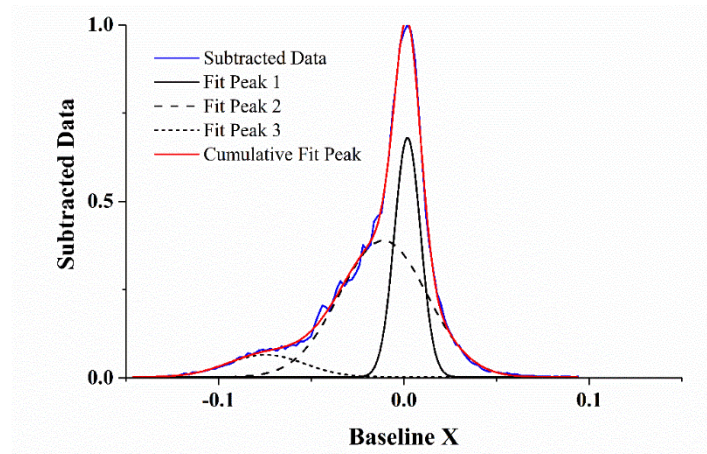


Fig. 6. Decomposition of rocking curve ω for the peak (400) of non-annealed sample $\beta\text{-Ga}_2\text{O}_3$ grown in CO_2 atmosphere by gaussians

Conclusions

The work showed that annealing of $\beta\text{-Ga}_2\text{O}_3$ bulk crystals in air at 1400 °C for 5 hours leads to an increase in transmission in the infrared region of the electromagnetic spectrum and a decrease in the width of the rocking curve, which indicates a decrease in the number of defects in crystal. As has been shown in [35] oxygen vacancies can serve as absorption centers in a gallium oxide. Thus, the increase in transmittance in the IR region can be explained by a decrease in the concentration of oxygen vacancies during annealing in an oxygen-containing atmosphere (in air). RC shows that after annealing FWHM is almost same for samples grown in CO_2 and $\text{Ar}+\text{O}_2$ (95:5 vol. %) atmosphere, which means that after annealing, the quality of the sample obtained in the atmosphere of CO_2 , which was initially lower, became comparable to the quality of the sample obtained in the atmosphere of $\text{Ar}+\text{O}_2$. In general, it can be concluded that annealing leads to a significant improvement in the quality of the samples regardless of the growth atmosphere, although the sample grown in CO_2 still shows higher absorbance in IR range of electromagnetic spectrum.

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