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Effect of high-temperature annealing on the internal friction and optical transmittance of single crystal gallium oxide

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ABSTRACT
The effect of high-temperature annealing on the structure and properties of single crystal β-phase gallium oxide is reported in this work. The investigated sample obtained by cleaving from a bulk β-Ga_2O_3 ingot grown by the edge-defined film-fed growth method. Some of the samples were annealed in an oxygen-containing atmosphere at temperatures up to T = 1673 K. The temperature dependences of internal friction and dynamic modulus of elasticity were obtained by the composite oscillator method at a frequency of 100 kHz. Optical absorption spectra were investigated in the wavelength range from 200 nm to 2 μm. It was found that annealing and redistribution of gallium vacancies in beta-phase gallium oxide crystals is accompanied by simultaneous changes in the internal friction in the temperature region around 290 K and in the optical spectrum in the infrared region.

KEYWORDS
Young's modulus • internal friction • optical transmittance • vacancies • single crystal • gallium oxide

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Introduction

The design of new devices for power electronics and energy converters is essential for improving the energy efficiency of production and maintaining ecological balance. In modern devices, efficiency improvements are provided by technologies based on wide bandgap semiconductors such as silicon carbide and gallium nitride. The use of ultrawide bandgap semiconductors such as gallium oxide, aluminum nitride, and diamond should lead to the next round of technological development due to their unique electrical characteristics and high temperature stability. Various applications of these materials in power electronics [1], ultraviolet [2] and X-ray detectors [3] have been predicted. The availability of methods to produce single crystals of beta-phase gallium oxide (β-Ga_2O_3) from melt [4] allows the creation of bulk elements and substrates for homoepitaxy, which provides a technological advantage in the use of this semiconductor [5]. High-temperature growth and prevention of thermal decomposition of other Ga_2O_3 polymorphs are possible only for epitaxial layers [6] and small particles.

Gallium oxide is an ultrawide bandgap semiconductor with an optical band edge near 250 nm (~4.9 eV) [2,4,5]. Most of β-Ga_2O_3 crystals available today are n-type due to the unintentional doping by silicon. At the same time, varying the dopant content during growth implies achieving and controlling the desired crystal properties [7]. The mechanisms of the influence of oxygen and gallium vacancies on the electrical conductivity and other characteristics of gallium oxide are also still not studied in detail. Studies of different types of vacancies are important to clarify the redistribution of charge carriers localized near the corresponding sites of the crystal lattice. Variations of different types of vacancies should apparently change the number of stable hole centers and anisotropic electrical properties in the β-Ga_2O_3 [8,9]. In the same way, the electrical properties of β-Ga_2O_3 are related to the migration energy of vacancies. Relevant questions in view of the complexity of organizing direct experiments and interpreting indirect measurements were solved earlier mostly numerically by density functional theory (DFT) calculations [10–16] with some rare exceptions [8,9,17–19]. Structure-dependent mechanical properties were determined previously on epitaxial layers and single crystals of β-Ga_2O_3 by nanoindentation [20], which is important from the point of view of their application. However, such measurements did not allow us to draw conclusions about the fine effects associated with impurities in this material.

In this work, we study the internal friction, dynamic modulus of elasticity (Young's modulus) and optical transmittance of gallium oxide single crystals before and after high-temperature annealing in an oxygen atmosphere.

Materials and Methods

Gallium oxide single crystal samples were obtained from a melt using edge-defined film-fed growth (Stepanov) method similar to reported in [4].

To exclude defects introduced by processing, the investigated sample plates with thickness about 1 mm were prepared by cleaving along the (100) crystallographic plane. The procedure for preparing samples by this method is described in detail in [21]. The length of the studied specimens was about 33 mm, their dimensions in rectangular cross-section did not exceed 3 mm. For strain amplitudes in the range of $10^{-8} \leqslant \varepsilon \leqslant 10^{-3}$ considered in this paper, the use of the dislocation theory of anisotropic internal friction is appropriate. In the framework of this theory, the deformation of a crystal under the action of elastic waves is composed of the deformation of the ideal crystal lattice and additional deformation due to the motion of dislocations. The main contribution to the internal friction comes from the motion of dislocations distributed on slip systems in the sample volume. In this case, the role of surface topology is less significant than the possible influence of the disturbed layer during processing, since later correlates with the stress distribution in the standing ultrasonic wave. Also due to the straightforward delamination and absence of a disturbed surface layer, these samples were used to evaluate the crystalline quality using X-ray. The area of measurement of optical characteristics and maximum mechanical stress during ultrasonic vibrations was located at the geometric center of the plate (100). X-ray diffraction of this region was obtained to confirm the crystalline quality of the samples. The rocking curve were obtained by two-crystal X-ray diffractometry under condition of symmetric 800 (Cu$K\alpha_1$) reflection. Analysis of Bragg peaks and determination of the exact lattice parameter were carried out with the high precision three-crystal X-ray spectrometer.

The samples were annealed in a muffle furnace with air atmosphere at 1673 K. The annealing time was 9 h. After annealing, the temperature was slowly reduced to room conditions for 20 h. We chose the annealing mode based on the high migration energy of gallium and oxygen atoms inside the bulk sample in the corresponding vacancy positions [22,23].

To determine the internal friction and dynamic modulus of elasticity (effective Young's modulus), we used the method of composite piezoelectric oscillator with an excitation frequency about of 100 kHz. This method, first presented by Quimby [24], is based on the transfer of elastic vibration energy between the quartz crystal and the cemented sample. To measure the vibration damping, a second quartz crystal is also used, thus forming a three-component oscillator which vibrates as a single body [25]. Effective Young's modulus E was calculated according to the first longitudinal mode of standing waves condition as:

$$E = 4\rho l^2 {f_s}^2, \quad (1)$$

where ρ is the density of the material under study, l is the length of the sample, f_s is the frequency of oscillations in the sample. The oscillation attenuation in the sample δ_s corresponds to internal friction (IF). This value δ_s and the oscillation frequency f_s are determined according to the equations of motion and constants [25,26]. Previously, we have shown the possibility of using this method to study microplasticity and structure-dependent internal friction in gallium oxide [27].

Optical transmittance studies were performed on a LAMBDA 1050 (PerkinElmer) with a 2D detector module. The same samples before and after annealing, obtained by chipping of the crystal along the cleavage plane (100) without further processing, were used. Relative change of transmittance ΔT was determined according to equation:

$$\Delta T = \frac{T_a - T_0}{T_0}, \quad (2)$$

where T_0 is the absorption before annealing and T_a is the absorption after annealing.

Results and Discussion

The full width at half-maximum of rocking curves was no more than 50" for all the samples studied. A shift in the parameter a from 12.2255 to 12.2272 Å was observed in the samples before and after annealing, correspondingly.

The temperature dependences of effective Young's modulus and internal friction for β-Ga_2O_3 were obtained by composite oscillator studies. In Fig. 1, it can be seen that the internal friction both before and after annealing decreases with decreasing temperature while Young's modulus increases. Measurements of E and IF of samples after annealing in a wider temperature range were hampered by the peculiarities of equipment operation. The Young's modulus of Ga_2O_3 on the pre-annealed samples increased by 20 GPa (or 4 %) from 257 GPa at room temperature to 267 GPa at 120 K. An increase in the E values from 264 GPa at room temperature to 275 GPa at 120 K was observed on the samples after annealing. The steepness of the E curve is generally preserved, and insignificant changes are explained by the peculiarity of the measurement method itself.

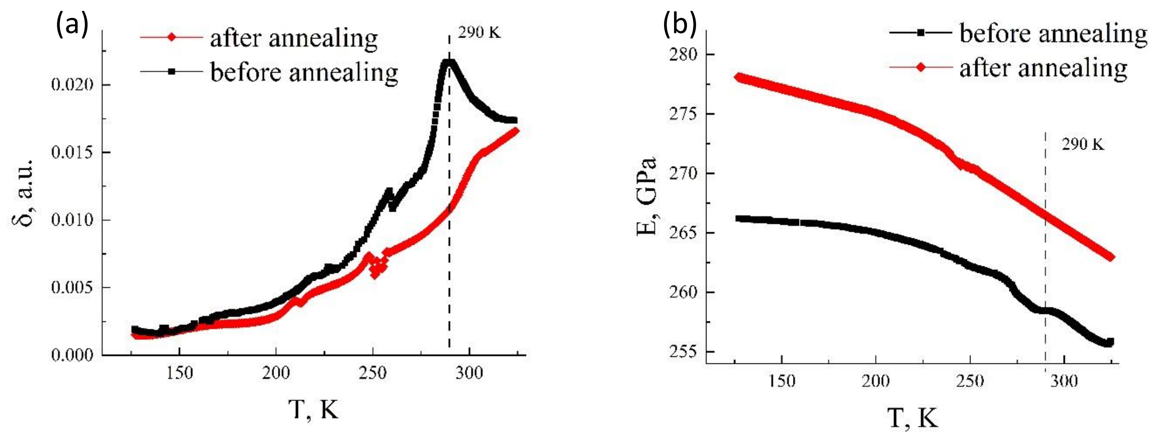

Fig. 1. Temperature dependences of (a) internal friction δ and (b) Young's modulus E of beta-phase Ga_2O_3 samples before and after annealing. The dotted line shows the temperature at which relaxation occurs

The increase in internal friction and decrease in E with temperature in semiconductor materials is primarily due to the larger amplitude of vibrations of atoms in the lattice and greater scattering of phonons (elastic waves) on them. After annealing, there was an increase in Young's modulus and a decrease in internal friction associated with the relaxation of residual stresses in the crystal lattice due to a decrease in the density of defects (vacancies) and their redistribution.

At a temperature of about 290 K one can observe a relaxation peak of internal friction marked in Fig. 1(b) by a dashed line. This peak corresponds to a bend in the Young's modulus curve. This relaxation peak in gallium oxide seems to be associated with point defects such as vacancies. The energetically most suitable mechanism for this process is the Hashiguchi relaxation, which is associated with the interaction of dislocations (kinks) with intrinsic defects: vacancies and their complexes.

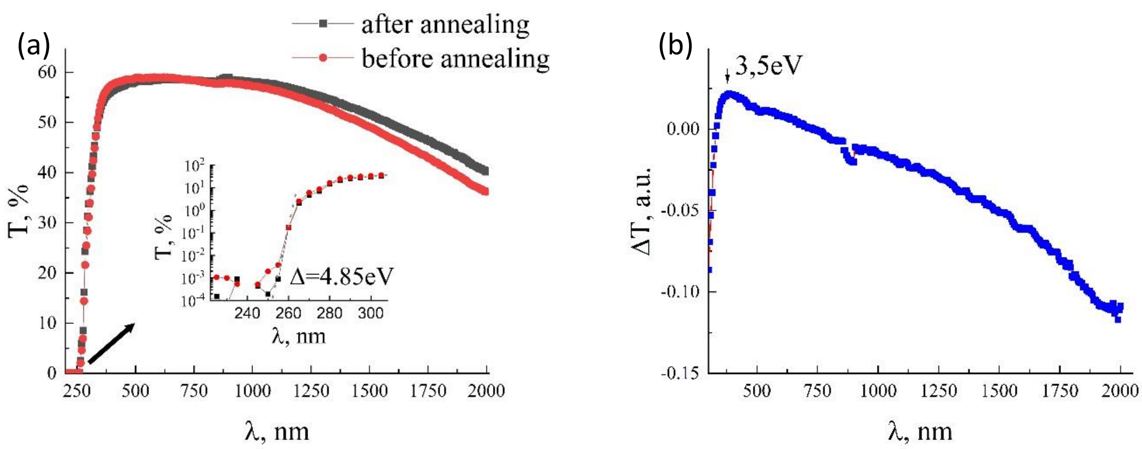

Fig. 2. The optical absorption spectra (a) and optical band edge – inset, the relative change in its value (b) for samples of single crystal gallium oxide before and after annealing for 12 h at 1673 K

The optical transmission edge is located around 269 nm, which corresponds to a band gap energy of about 4.85 eV (Fig. 2(a) – inset). The smooth decrease in transmission with increasing wavelength (Fig. 2) is associated with absorption by free electrons [9,28]. Additional absorption in the high-energy region around 3.5 eV (Fig. 2(b)) can be caused by defects like gallium vacancies [29]. Thus, the decrease of transmittance in the high-energy part and its simultaneous increase in the long-wave part can be related to the redistribution of gallium vacancies of different types. At the same time, the change of energy in the longwave region may be intrinsically correspond to various transitions from the valence bands to the conduction band caused by residual strain and impurities [30].

Conclusions

In this paper, the effect of high-temperature annealing on the structure and properties of single-crystalline beta-phase gallium oxide is investigated. Data on internal friction and optical absorption are presented. It is found that annealing is accompanied by simultaneous changes in the internal friction in the temperature region around 290 K and in the optical spectrum in the infrared region, which is associated with the redistribution of gallium vacancies of different types with a general decrease in their number. This is consistent with the hypothesis of the effect of high-temperature annealing on gallium vacancies, which leads to an increase in the crystalline quality of the material. The presented results are also in agreement with known experimental [17,28–30] and theoretical [9,12] works.

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