

## Thermally Stimulated Luminescence and Conductivity of $\beta$ -Ga<sub>2</sub>O<sub>3</sub> Crystals

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The paper deals with thermostimulated luminescence (TSL) and thermostimulated conductivity (TSC) of unintentionally doped (UID)  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals. The samples under study were  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals grown by the floating zone method with radiation heating and then subjected to annealing in an atmosphere of oxygen or argon. The obtained photoluminescence emission spectra are typical for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals: they contain the broad emission band of the host at 320-550 nm as well as a weak luminescence with maximum at 700 nm due to the unintentional Cr<sup>3+</sup> impurities. After exposure to X-ray radiation, the samples exhibit intense TSL at the temperature range of 85-500 K. Three low-temperature peaks at 116, 147 and 165 K are present in TSL and TSC curves of these crystals. The depths of the traps responsible for these peaks are 0.15, 0.2 and 0.3 eV, respectively. The high-temperature TSL peaks at 354 K, 385 K and 430 K with corresponding activation energies of 0.84, 1.0 and 1.1 eV were observed in samples annealed in argon or oxygen atmospheres. The TSC curves are in good agreement with the results of the TSL study. A correlation between annealing of crystals in oxidizing and inert atmospheres and intrinsic defects in single crystals  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has been established.

**Keywords:**  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals, Thermostimulated luminescence, Thermostimulated conductivity, Activation energy, Traps.

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### 1. INTRODUCTION

Gallium oxide  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is an attractive wideband (~ 4.8 eV) semiconductor material for optoelectronic devices operating at the far ultraviolet spectral region [1] and for the production of metal-semiconductor transistors (MESFETs), metal-oxide-semiconductor ones (MOSFETs) as well as Schottky diodes (SBDs) [2, 3].

Nevertheless, despite of successful use, the fundamental properties of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals are not enough studied yet. There is no consensus on the nature of intrinsic donors in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals [4-7]. Their high conductivity in earlier studies [4] was associated with shallow donors formed by oxygen vacancies, similarly to that of many other oxides. However, the theoretical computations [5] indicate that isolated oxygen vacancies should create much deeper local energy levels with a depth of more than 1.0 eV. It has been noted [5-7] that the Si impurity is the main donor in UID  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. However, some experimental data cannot be explained only by the presence of Si or other impurities. Authors of [7] consider that an impurity-vacancy complex consisting of oxygen vacancies and Si impurities also acts as a shallow donor. However, a further study is needed to confirm this hypothesis of [7]. As it has been shown in [4], it is difficult to explain why crystals grown from the same raw material with different partial oxygen pressures have different conductivity values, as well as the latter decreases after annealing in oxygen atmosphere [4, 7-9].

It is obvious that the nature of conductivity in UID gallium oxide is more complicated. It can include both impurities and intrinsic defects able to play an important role in the formation of donor and acceptor levels, and the trap and recombination centers in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

as well. The decisive role of the latter in the charge transfer processes is studied not enough. The deep trap levels created by intrinsic defects and impurities in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals are not comprehensively studied too. Despite they were discussed in a number of papers [6, 10-12], the question of the nature of some of them calls for further studies.

The goal of this study is to determine the trap levels occurring in as-grown UID  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals as well as those created after thermal treatment of them in oxidizing or inert atmospheres.

### 2. EXPERIMENTAL

The studies were carried out on UID samples of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals grown by the floating zone method with radiation heating. The raw material was gallium oxide with a purity of 99.99 %. The pressed polycrystalline rods were sintered at a temperature of 1300 °C for 10-12 h. The single crystals were grown along a crystallographic direction of [010] or [100]. The growth and rotation rates of the sintered rods were 2-4 mm per hour and 6 rpm, respectively. The growth atmosphere was the air. The  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals obtained had a length up to 30 mm and a diameter of 5-7 mm [13].

Some samples of gallium oxide crystals were annealed to determine the role of the intrinsic point defects in the trap and recombination centers creating. The  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> monocrystalline plates with the thickness of 0.2-1 mm were used for this purpose. The crystals were placed in a Pt container that was located in an evacuated closed quartz ampoule, which then filled with appropriate gas. The annealing took place at a pressure of 1 atm and a temperature of 1300 °C for 10-100 h.

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One should note that all as-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals were of blue color. The annealing of crystals in an inert atmosphere of argon did not change this color noticeably. Indeed, the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals became colorless after annealing in the atmosphere of oxygen.

The samples under study were cleaved from the grown crystals along the (100) plane. Those intended for TSC studies were of  $5 \times 2 \times 0.1$  mm<sup>3</sup> dimensions. The indium contacts on the (100) plane were applied to the surface at a distance of 3-4 mm along the *b* axis. Their current-voltage characteristics have revealed that indium forms Ohmic contacts. The TSC currents in the range from  $10^{-9}$  to  $10^{-14}$  A were measured with an electrometer.

A setup based on SF-4A quartz monochromator was used to study the X-ray luminescence and TSL. The  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> samples were placed in a cryostat and exposed to X-ray radiation during 20 min at 85 K. The X-ray excitation was provided by a microfocuss X-ray tube of URS-002 type with copper anticathode ( $U = 45$  kV and  $I = 0.3$  mA), through the beryllium window of a cryostat. The TSL curves were recorded in the linear heating mode at the temperature increase rate of 0.1 K/s. The emission wavelengths were selected by a SF-4A monochromator. All the measurements were carried out at the same conditions.

### 3. RESULTS

A broad host emission band with a maximum near 400 nm as well as the red luminescence with a maximum at 715 nm corresponding to the  ${}^4T_2-{}^4A_2$  transitions of the unintentional Cr<sup>3+</sup> impurity is present in the luminescence spectrum of the as-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals at the room temperature (Fig. 1). This broad emission band can be decomposed into three elementary bands using Gaussian fitting, in particular, the UV (380 nm), blue (430 nm) and green (520 nm) ones [14]. The host luminescence bands dominate in the as-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals. The annealing of crystals leads to a slight redistribution of emission intensity in favor of the green luminescence band and to an increase in the output of the red luminescence of the Cr<sup>3+</sup> impurity by one order of magnitude.

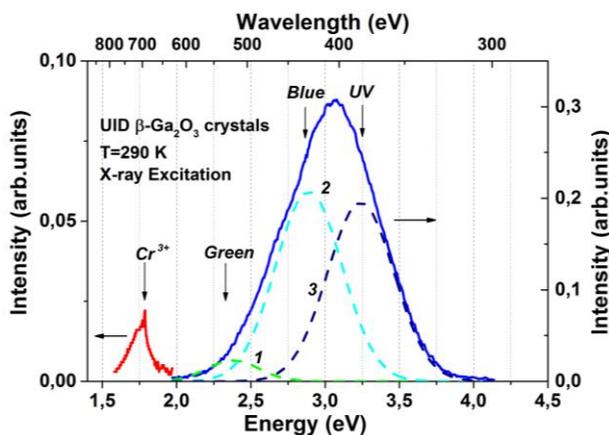


Fig. 1 – The emission spectrum of an as-grown UID  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystal obtained at X-ray excitation at room temperature

Let one note that the ultraviolet, blue, green and red emissions are found in the TSL of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals under studies. At the same time, the wavelength of TSL recording set on monochromator does not change the number and position of the peaks. The difference is only in the relative intensity of them. The luminescence of Cr<sup>3+</sup> impurity is observed over the widest temperature range from 77 K up to 550 K. In addition, the optical properties and trap levels created by Cr<sup>3+</sup> in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals are studied well. Therefore, the following TSL spectra are shown only for red luminescence range of intentional Cr<sup>3+</sup> ions.

The trap levels responsible for the TSL peaks at the temperature range of 85-450 K are revealed in the TSL curves of all the samples under study. Fig. 2a-d shows the TSL curves for the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals after X-ray excitation at a temperature of 85 K. As one can see, the TSL curves are the result of overlapping of several closely located peaks in the 85-500 K range.

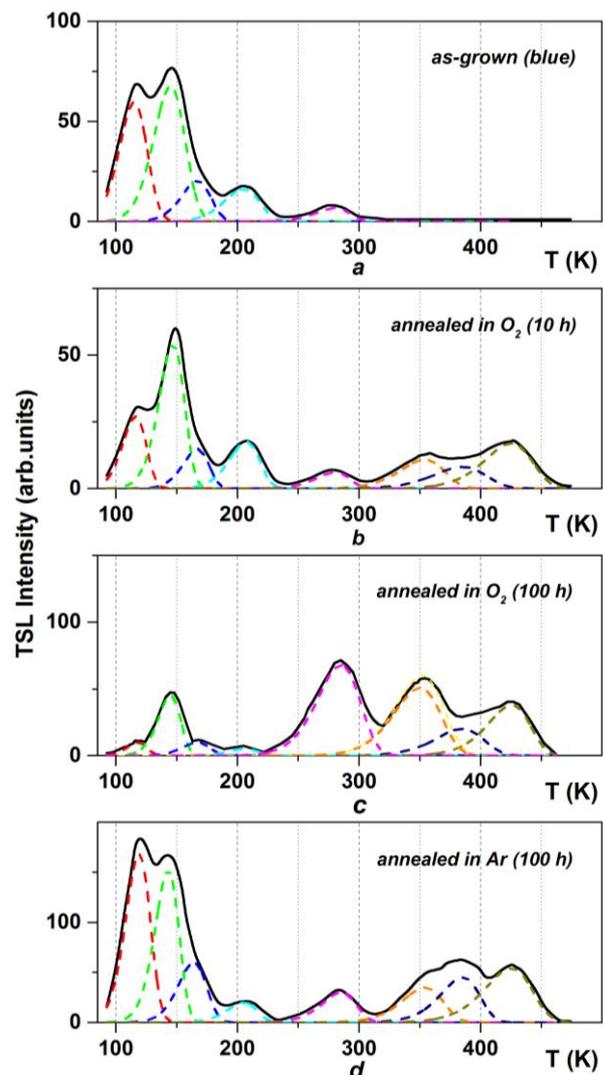


Fig. 2 – Thermostimulated luminescence curves of UID  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> single crystals of gallium oxide at the luminescence registration in the red spectral region: a – as-grown; b – annealed in an oxygen atmosphere for 10 h at 1300 °C; c – annealed in an oxygen atmosphere for 100 h at 1300 °C; d – annealed in an inert atmosphere of argon for 100 h at 1300 °C

A deconvolution of the obtained TSL curves on elementary components has been accomplished by the method of temperature cleaning (successive temperature bleaching of TL glow peaks). The sample was heated up to a temperature slightly lower than the expected peak, and then quickly cooled. The low-temperature side of the peak appears clearly after the sample heating that also makes it possible to separate elementary peaks as well as to calculate the activation energy. As follows from Fig. 2, one can select eight elementary peaks in the 85-500 K temperature range. Moreover, the experimentally deconvoluted TSL curves were also fitted theoret-

cally using the general order kinetics. As the result, the same number and positions of elementary peaks were obtained. Also it has been revealed that all peaks exhibit first order kinetics. The estimation of thermal activation energies of traps ( $E_t$ ) corresponding to separate TSL peaks was carried out by the method of initial intensity increase. In particular, the initial experimental points of elementary peaks were plotted in coordinates of  $\ln(I) = f(1/kT)$ . The slopes of the fitted lines relate to the activation energies. The positions of elementary TSL peaks maxima and their activating energies are given in Table 1.

**Table 1** – The activation energies and traps concentrations calculated based on the TSL and TSC data for  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals.

No	Temperature of maximum ( $T_m$ ), K	Activation energy of TSL ( $E$ ), eV	Activation energy of TSC ( $E$ ), eV	$N_t$ for samples annealed in O <sub>2</sub> during 10 h, cm <sup>-3</sup>	$N_t$ for samples annealed in O <sub>2</sub> during 100 h, cm <sup>-3</sup>
1	116	0.20	0.15	$\sim 3.0 \cdot 10^{15}$	$\sim 2.0 \cdot 10^{13}$
2	145	0.25	0.18	$\sim 1.9 \cdot 10^{15}$	$\sim 9.4 \cdot 10^{13}$
3	165	0.37	0.35	$\sim 2.1 \cdot 10^{15}$	$\sim 4.6 \cdot 10^{13}$
4	205	0.52	0.45	$< 10^{13}$	$< 10^{13}$
5	285	0.63	$\sim 0.5$	$\sim 1.2 \cdot 10^{16}$	$\sim 1.7 \cdot 10^{15}$
6	354	0.84	$\sim 0.6$	$\sim 1.5 \cdot 10^{17}$	$\sim 0.8 \cdot 10^{17}$
7	385	1.0	$\sim 0.8$	$\sim 1.1 \cdot 10^{17}$	$\sim 0.9 \cdot 10^{17}$
8	430	1.1	–	–	–

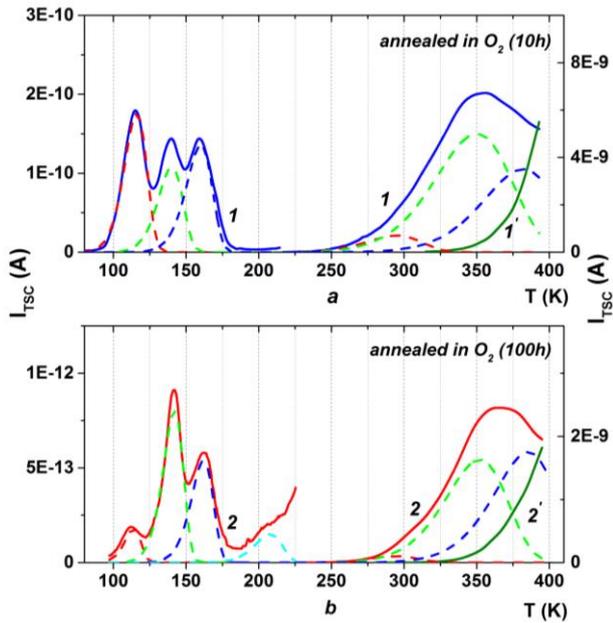
Fig. 2a presents the TSL of as-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystal. The most intense TSL peaks are present at temperatures of 116 K and 146 K. In addition, the weaker TSL peaks in the temperature range at about 165 K, 205 K and near 285 K are observed. No significant TSL peaks for as growth crystals were detected at temperatures above 300 K. A slight change in the shape of the TSL curve is observed after short-time annealing ( $\sim 10$  h) of as-grown crystals in the oxygen atmosphere (Fig. 2b). In particular, the intensity of the peak at 116 K fades by 50 % in comparison with that at 146 K. At the same time, the intensity of 165 K peak decreases only slightly, while those for the TSL peaks near 205 K and 285 K almost do not change. However, a new weak TSL peaks appear in the higher temperature range of 300-430 K. More significant changes in the shape of TSL curves are observed after prolonged annealing of the crystal in an oxygen atmosphere for 100 h (see Fig. 2c). An even stronger decrease in the amplitude of the low-temperature TSL peak at 116 K is found. Simultaneously, the amplitude of the TSL peak with a maximum near 285 K has slightly increased. On the other hand, there is an increase in the amplitude of the high-temperature TSL peaks at 354, 385 and 430 K after such annealing. The high-temperature annealing of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals in argon atmosphere (see Fig. 2d) leads to qualitatively different changes in the shape of the TSL glow curves in the low-temperature range of 85-250 K. In particular, in such a case, the relative intensity of the 116 K TSL peak increases and this peak becomes dominant on the TSL curve. The TSL peaks in the high-temperature range are similar to those for crystals after prolonged annealing in oxygen during 100 h.

The conductivity of as-grown crystals at room temperature varies within  $10^{-4} \cdot 10^{-3}$  Ohm<sup>-1</sup> cm<sup>-1</sup>, and the free electron concentration reaches  $10^{15} \cdot 10^{16}$  cm<sup>-3</sup>. To

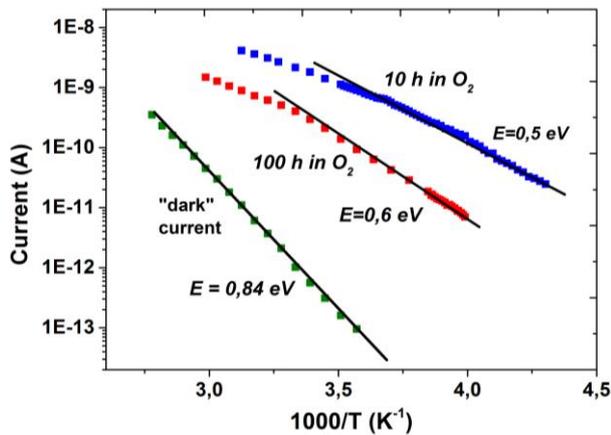
calculate the conductivity, we have used the average values of the mobility given in [6]. The conductivity is slightly changed after the annealing of as-grown  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals in an argon atmosphere. It was not possible to record weak currents of the TSC for these samples due to high background. Further TSC studies were carried out on crystals with higher resistance. Short-term annealing of as-grown crystals with a thickness of  $\sim 0.5$  mm in an atmosphere of oxygen for 10 h leads to a decrease in conductivity to  $10^{-6} \cdot 10^{-5}$  Ohm<sup>-1</sup> cm<sup>-1</sup>. At the same time, the conductivity of the crystals decreases to  $10^{-12} \cdot 10^{-10}$  Ohm<sup>-1</sup> cm<sup>-1</sup> after a more prolonged annealing of  $\sim 100$  h.

Fig. 3 shows the TSC curves of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals annealed in an oxygen atmosphere for 10 h (curve 1, blue) and 100 h (curve 2, red). The prominent maxima of the TSC are observed at about 116 K, 146 K and 165 K for both samples. In addition, there are a shoulder in the region of 205-210 K and a sharp increase in current at  $T > 250$  K for the sample annealed for 100 h in O<sub>2</sub>. By comparing the TSC curves, it is noticeable that the longer annealing in the oxygen atmosphere leads to a decrease in the total amplitude of low-temperature peaks as well as in the relative intensity of low-temperature peak at 116 K. One should note that the position of the TSC peaks correlates well with the above TSL peaks of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals.

The right part of Fig. 3 shows the wide band of TSC extending from 275 to 400 K. Green curves (1' and 2') illustrate the temperature dependence of "dark" current (without irradiation). At temperatures higher than 400 K, the "dark" current is more than that of TSC for both crystals. Therefore, the TSC curves shown in the right part of Fig. 3 are calculated as the difference between the current of the irradiated and non-irradiated samples. Therefore, the error of TSC determination



**Fig. 3** – Thermostimulated conductivity curves for  $\beta\text{-Ga}_2\text{O}_3$  crystals annealed in the oxygen atmosphere for 10 h (a) and 100 h (b) after excitation at a temperature of 85 K. Dashed lines show the decomposition of the elementary TSC peaks



**Fig. 4** – Dependence of the TSC (red and blue) and “dark” current (green) on the inverse temperature

increases in the higher-temperature range. Accordingly, the position of TSC peaks could not be exactly determined. At the same time, the wide band of the TSC correlates well with the location of the high-temperature TSL peaks. From the viewpoint of the foregoing, the broad band of the TSC in high temperature range can be also decomposed by at least three peaks, with the similar maxima at about 285 K, 354 K and 385 K. It should also be noted that an increase in the duration of annealing has always led to an increase in the relative intensity of the more high-temperature peak (for example, 385 K compared to 354 K).

The temperature dependence of the conductivity in the scale of  $\lg\sigma = f(1/T)$  is well approximated by a straight line. Taking into account that the TSC current exponentially increases in the initial part of curve with the temperature increase, one can estimate the depth of the trap, which is responsible for the TSC currents. For example, the depth of the trap levels revealed in the

TSC peak with maxima near 285 K is calculated to be 0.5 eV and that for the TSC peak at 354 K is  $\sim 0.6$  eV (see Fig. 4). At the same time, the thermal activation energy calculated from the temperature dependence of “dark” current is 0.84 eV. Table 1 shows the activation energies and traps concentrations for  $\beta\text{-Ga}_2\text{O}_3$  crystals annealed in oxygen for 10 and 100 h. The concentrations of traps were calculated using the geometric dimensions of the samples, the mobility of electrons and the integral values of the currents related to elementary TSC maxima.

#### 4. DISCUSSION

The TSL and TSC studies reveal that the defects and unintentional impurities creating the shallow and deep trap levels exist in  $\beta\text{-Ga}_2\text{O}_3$  single crystals. The intensity of the TSL and TSC peaks, and hence the concentration of the appropriate trap levels depends on the heat treatment of the samples. Since there are similar peaks in TSL and TSC curves, one can assume that these peaks are due to the thermal release of electrons from the trap levels.

Let one try to analyze how the concentration of the intrinsic point defects in  $\beta\text{-Ga}_2\text{O}_3$  may change after the heat treatment of crystals. Simple host point defects arising during the growth of  $\beta\text{-Ga}_2\text{O}_3$  crystals may be the double positively charged oxygen vacancies  $\text{V}_{\text{O}}^{2+}$ , triple negatively charged gallium vacancies  $\text{V}_{\text{Ga}}^{3-}$ , triple positively charged interstitial gallium  $\text{Ga}_i^{3+}$  and double negatively charged interstitial oxygen  $\text{O}_i^{2-}$ . Since the growth of  $\beta\text{-Ga}_2\text{O}_3$  crystals usually occurs with oxygen deficiency, the existence of interstitial oxygen  $\text{O}_i^{2-}$  in the crystals is unlikely.

A peculiarity of  $\beta\text{-Ga}_2\text{O}_3$  under heating to a high temperature in an atmosphere with a low partial pressure of oxygen is its dissociation into volatile  $\text{Ga}_2\text{O}$  and  $\text{O}_2$ . Highly volatile  $\text{Ga}_2\text{O}$  at temperatures of crystal growth sublimates and leaves the crystal. Thus, the lack of oxygen in the surrounding atmosphere leads not only to the formation of isolated oxygen vacancies  $\text{V}_{\text{O}}$ , which is also observed on other oxides, but also creates advantageous conditions for the simultaneous formation of a large number of gallium vacancies  $\text{V}_{\text{Ga}}$  and interstitial ions  $\text{Ga}_i^{3+}$ . The point defects created are mobile at high growth temperatures and can form more stable defect associates of  $(\text{V}_{\text{Ga}}\text{V}_{\text{O}})$ . Although there is no direct experimental evidence of the existence of such associates, there are indirect data indicating their existence. In particular, the photo shown in [15] obtained by using the High-Resolution Transmission Electron Microscopy (HRTEM) shows point defects, identified by the authors as vacancies of gallium and oxygen. Let one note, that these vacancies are located sufficiently close each to another. In addition, a decrease in the specific density of gallium oxide after annealing in vacuum can serve as a confirmation that the process of point defect formation proceeds with the creation of a large concentration of vacancies. Such associates are the centers of recombination luminescence [14], or components of donor-acceptor pairs of host luminescence [16], as well as manifest themselves by wide absorption and photoconductivity bands in the UV region [17]. Also, based on the analysis of the thermodynamic equilibrium of defects using quasi-

chemical equations of Kroger it has been shown [18], that the associates of  $(V_{Ga}Vo)'$  can act as the main compensating acceptors in crystals grown under small partial oxygen pressures. Accordingly, one can assume that such associates can play an important role in the reconstruction of point defects during the high temperature annealing of gallium oxide.

During the annealing of  $\beta\text{-Ga}_2\text{O}_3$  crystals at high temperatures, oxygen diffuses from the surface into the deep of crystal. Oxygen atoms can occupy sites of isolated oxygen vacancies or sites in vacancy associations  $(V_{Ga}Vo)'$ . If the oxygen atoms occupy positions of isolated oxygen vacancies, then the concentration of oxygen vacancies decreases. At the same time, if the atoms of oxygen occupy vacancies in  $(V_{Ga}Vo)'$  associations, the concentration of gallium vacancies increases. The "newly created" vacancies of gallium make deep trap levels for holes. As it follows from [8], the annealing of undoped  $\beta\text{-Ga}_2\text{O}_3$  crystals in the atmosphere of oxygen leads in the first place to the decrease of concentrations of isolated oxygen vacancies  $Vo^{**}$  on the crystal surface. In other words, the coefficient of oxygen diffusion in  $\beta\text{-Ga}_2\text{O}_3$  single crystals at high annealing temperatures  $T \sim 1200^\circ\text{C}$  is rather small. Therefore, the annealing in the atmosphere of oxygen gives mainly a surface effect. Our experimental results are well correlated with these data, since only long-term annealing at  $T \sim 1300^\circ\text{C}$  ( $\sim 100$  h) of thin crystals ( $< 1$  mm) allowed us to obtain high-resistive samples with  $\sigma \sim 10^{12}\text{-}10^{10}\text{ Ohm}^{-1}\text{ cm}^{-1}$  and to detect significant changes in the shape of TSL and TSC curves.

Also, gallium atoms may occupy isolated gallium vacancies or positions in vacancy associates  $(V_{Ga}Vo)'$  during the diffusion process. If gallium atoms occupy sites of isolated gallium vacancies, then there is a decrease in the concentration of interstitial gallium and vacancies of gallium. But if interstitial gallium occupies vacancy sites in  $(V_{Ga}Vo)'$  associations, then the concentration of interstitial gallium should decrease simultaneously with the increase in the concentration of isolated oxygen vacancies  $Vo^{**}$ .

Thus, it should be noted that after the annealing of crystals in an inert argon atmosphere, one can expect both a decrease in the concentration of the interstitial gallium and an increase in the concentration of oxygen vacancies. After the annealing of crystals in the oxygen atmosphere, the resulting concentration of oxygen vacancies will depend on the ratio between the processes of diffusion of gallium and oxygen. If the diffusion of gallium exceeds the oxygen diffusion, there should be an increase in the concentration of oxygen vacancies. Positively charged oxygen vacancies create deep trap levels for electrons. They are "acceptors" that trap electrons and ionize shallow donors remaining in the crystal ( $Ga_i^{***}$ , Si, and others). Vacancies of gallium and associates of gallium and oxygen vacancies  $(V_{Ga}Vo)'$  create deep trap levels for holes.

The TSL and TSC peak at 116 K is observed in all crystals. The depth of the trap levels responsible for this peak is  $\sim 0.15$  eV based on TSC calculations and  $\sim 0.2$  eV according to the calculations from the TSL. This value is much higher than the depth of the donor Si, Sn (0.02-0.05 eV) [6, 7], which indicates the other

nature of these trap levels. Peak at 116 K is dominant in TSL and TSC of undoped as-grown crystals. Its intensity increases after the annealing of crystals in an inert atmosphere and decreases after annealing in an atmosphere of oxygen. It is most likely that the trap levels are caused by an ionized donor. The concentration of donors is approximately equal to  $10^{17}\text{ cm}^{-3}$  in the as-grown crystals. However, donors do not appear in TSL since the Fermi level is located near the bottom of the conduction band and all levels are filled with electrons. It is necessary to ionize donors by creating deeper levels of electron traps or acceptor levels. Such deeper levels of electron traps are the positively charged oxygen vacancies. The annealing of  $\beta\text{-Ga}_2\text{O}_3$  crystals in the atmosphere of oxygen leads to a decrease in the trap concentration responsible for the peak 116 K from  $\sim 10^{17}\text{ cm}^{-3}$  for as-grown crystals to  $3 \cdot 10^{15}\text{ cm}^{-3}$  for the crystals annealed for 10 h and up to  $2.0 \cdot 10^{13}\text{ cm}^{-3}$  for crystals annealed for 100 h in an atmosphere of oxygen. Changes in 116 K peak amplitude, depending on the heat treatment atmosphere, are well consistent with the expected change in the concentration of interstitial gallium according to the above analysis. Therefore, it is logical to relate the peak 116 K to the ionized donors created by interstitial gallium. Other low-temperature TSL and TSC peaks with maxima at 146 K, 167 K and 205 K do not change significantly under the conditions of the heat treatment changing. Their intensity is practically the same in all studied crystals. Therefore, based on our results, we cannot identify their origin, and additional research is needed to identify their nature.

Deep trap levels manifesting themselves as the high-temperature TSL peaks are also sensitive to the heat treatment. The intensity of these TSL peaks in the 300-430 K range increases after the annealing of crystals. As it follows from the above analysis, the high-temperature annealing should lead to a decrease in the concentration of interstitial gallium and an increase in the concentration of oxygen vacancies. Both processes can lead to an increase in the intensity of high-temperature TSL peaks.

Similar deep trap levels in  $\beta\text{-Ga}_2\text{O}_3$  crystals were also reported by the authors of [6, 10-12, 19]. It is noted that the trap levels with a depth of 0.74 [6], 0.78 [12], 0.82 [10] and 0.8 eV [11] with a concentration at about  $10^{17}\text{ cm}^{-3}$  are present in all investigated (UID)  $\beta\text{-Ga}_2\text{O}_3$  crystals. It was established [19] that an increase in the concentration of  $Mg^{2+}$  in  $\beta\text{-Ga}_2\text{O}_3$  from 0.01 to 0.2 % leads to a 10 times increase of the intensity of TSL peaks at 354 and 385 K. Our estimates of depth and concentration of deep traps that appear at the TSL and TSP peaks at 354 K and 385 K give an energy value of  $\sim 0.84$  and 1 eV as well as a concentration of about  $10^{17}\text{ cm}^{-3}$ . These values are close to those mentioned in [6, 10-12]. The fact that such traps are found in crystals obtained from different raw materials and by various methods, further indicates that they are formed by their intrinsic defects. Investigation of the effect of thermal treatment on the TSL peaks at 354 and 385 K as well as the above analysis and the literature data on the influence of growing conditions [4, 15] and doping with  $Mg^{2+}$  ions [19] allow us to assume with high probability that these levels are formed by oxygen vacancies.

It is known, that there are three non-equivalent oxygen positions in the crystalline structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, and therefore three types of oxygen vacancies can exist. According to [20], the oxygen vacancies with four-fold coordination have the smallest formation energy. Therefore it can be assumed that the peak of the TSL at 354 K corresponds to the release of an electron from the oxygen vacancy, according to the scheme  $(V_{O}^{**} + 2e^{-}) \rightarrow (V_{O}^{**} + e^{-}) + e^{-}$ . The nearby located peak TSL at the 385 K may be due to the existence of other type oxygen vacancies. The high-temperature peak of TSL at 430 K dominates in crystals that were annealed for about 100 h in an oxidizing or inert atmosphere. However, further studies are required to establish the nature of the defects corresponding to the highest temperature TSL peak.

## 5. CONCLUSIONS

Unintentionally doped single crystals of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> grown by the floating zone technique were studied using thermostimulated luminescence and conductivity methods. The emission spectrum of the UID  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals has a broad emission band at about 400 nm attributed to the host defects as well as the luminescence of unintentional Cr<sup>3+</sup> ions at about 715 nm. The TSL curves of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals consist of several overlapping peaks at the temperature range of 85-500 K, which were deconvoluted using the method of temperature cleaning as well

as peak fit software. The kinetic parameters like the activation energy and the order of kinetic have been calculated. The behavior of point defects of gallium oxide at high-temperature annealing of crystals in atmospheres of oxygen or argon was analyzed. Observed changes in the TSL and TSC curves after the annealing of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals indicate an important role of the defects associates  $(V_{Ga}V_{O})^{\cdot}$  in the processes of diffusion and recombination of point defects. Three peaks of TSL and TSC observed in the region of low temperatures 90-200 K were registered. Their intensity changes as a result of crystals annealing. The release of non-equilibrium electrons from levels formed by ionized donors of interstitial gallium leads to TSL and TSC peak at 116 K with trap levels  $\varepsilon = 0.15$ -0.2 eV. Deep trap levels revealed in high-temperature TSL peaks at 354 and 385 K with the activation energy of 0.84-1 eV can be related with oxygen vacancies. The position of the TSC maxima coincides well with the TSL peaks of the  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals under studies. The concentration of traps was calculated using the integral values of the currents related to elementary TSC maxima.

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**Термостимульована люмінесценція і провідність кристалів  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>**

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Розглянуто термостимульовану люмінесценцію (ТСЛ) та термостимульовану провідність (ТСП) нелегованих монокристалів  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. Досліджувані зразки являли собою монокристали  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, вирошені методом оптичної зони плавки, які потім піддавали відпалу в атмосфері кисню або аргону. Отримані спектри фотолюмінесценції є типовими для монокристалів  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>: вони містять широку смугу випромінювання матриці при 320-550 нм, а також слабку люмінесценцію з максимумом при 700 нм приписану неавтономно введеної домішки Cr<sup>3+</sup>. Після опромінення X-променями зразки демонструють інтенсивну ТСЛ в діапазоні температур 85-500 К. На кривих ТСЛ і ТСП цих кристалів наявні три низькотемпературні піки при 116, 147 і 165 К. Глибини пасток, що відповідають за ці піки, становлять 0.15, 0.2 і 0.3 еВ, відповідно. Високотемпературні піки ТСЛ при 354, 385 і 430 К з відповідними енергіями активації 0.84, 1.0 і 1.1 еВ спостерігаються в зразках, відпалених в атмосферах кисню або аргону. Криві ТСП добре узгоджуються з результатами дослідження ТСЛ. Встановлена кореляція між відпалом кристалів в окислювальній та інертній атмосферах і власними дефектами в монокристалах  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

**Ключові слова:** Монокристали  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, Термостимульована люмінесценція, Термостимульована провідність, Енергія активації, Пастки.