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# Microstructure and Thermally Stimulated Luminescence of $\beta$-$Ga_2O_3$ Thin Films

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Thermally stimulated luminescence of X-ray irradiated $\beta$-$Ga_2O_3$ thin films was investigated. An analysis of the form of the elementary contours making the thermally stimulated luminescence curves shows that recombination processes at the thermally stimulated luminescence peaks with maxima at 77, 135, 178, and 235 K in thin films of $\beta$-$Ga_2O_3$ are described in terms of linear kinetics. The spectral composition of the thermally stimulated luminescence of the thin films was studied. Some methods are employed to determine the activation energies and frequency factors corresponding to the thermally stimulated luminescence peaks. It is established that the recombination processes occurring upon release of the trapping centers in thin films $\beta$-$Ga_2O_3$ are conditioned by diffusion-controlled tunneling recombination due to thermally-stimulated migration of $V_k$-centers.

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## 1. Introduction

Recent studies have revealed a number of interesting properties of $\beta$-$Ga_2O_3$ films obtained by various methods. Therefore, the films based on $\beta$-$Ga_2O_3$ are widely used as thin film materials for field effect transistors (FET) [1], gas sensors [2] and electrodes, transparent in the UV region [3]. Depending on the method of obtaining and the dopant, such films are used as photoluminophors [4, 5], cathodoluminophors and electroluminophors [6, 7]. In general, the optical and electrical properties of $\beta$-$Ga_2O_3$ thin films are determined by the methods they were obtained, the regimes of deposition, and subsequent technological methods that determine local centers whose energy levels are located in the band gap. One of the most sensitive methods for studying local centers and the features of their manifestation in optical and electronic processes is thermally stimulated luminescence (TSL). Therefore, TSL curves and spectra of $\beta$-$Ga_2O_3$ thin films, obtained by radio-frequency (RF) ion-plasma sputtering are investigated in this article. The application of this method leads to the deposition of the most homogeneous semiconductor and dielectric films [8].

## 2. Experimental details

Thin films of $\beta$-$Ga_2O_3$ with a thickness 0.2–0.8 $\mu$m were obtained by RF ion-plasma sputtering on substrates of $\upsilon$-$SiO_2$ amorphous fused quartz. The films were deposited in a spray-type atmosphere of argon. After deposition, the heat treatment of films was carried out in oxygen at 1000–1100 °C. X-ray diffraction studies showed the presence of a polycrystalline structure of films with a predominant orientation in the (400), (002), (111), and (512) planes. The diffraction patterns for $\beta$-$Ga_2O_3$ films were described by us recently [9] in more detail.

The morphology of the films' surface was investigated using an atomic force microscope (AFM) Solver P47 PRO. The processing of experimental data and the computation of the parameters of surface morphology were carried out using the software package Image Analysis 2.

To investigate TSL, the samples were placed in a vacuum cryostat where the temperature varied from 50 to 400 K. Irradiation was accomplished by X-ray Cu $K_\alpha$ radiation (URS-55 A unit, 40 kV, 10 mA) at 50 K. The radiation dose was measured by an IDMD-1 dosimeter. The light intensity of the TSL was recorded by an FEU-51 photomultiplier and an U1-7 electronic amplifier, whose output signal was fed through an analog-digital converter to an IBM/PC computer for recording curves and the luminescence spectrum. The TSL spectra were recorded through the MDR-12 monochromator. Linearity of heating was provided by a RIF-101 temperature controller. The heating rate was $\beta = 0.150 \pm 0.005$ K/s, which with good luminosity ensured sufficient resolution of the method.

## 3. Results and discussion

Figure 1 shows the microphotographs of $\beta$-$Ga_2O_3$ films' surface obtained by AFM. The grain diameter on the surface of the film without heat treatment on the average is 30 nm (Fig. 1a), the average roughness of the film is about 7 nm (Fig. 1b). Processing in oxygen atmosphere leads to an increase in the grains' sizes due to their growth and sintering processes, subsequently their average diameter increases to 45 nm (Fig. 1c). After annealing the surface roughness of the films increases by more than twice, on the average to 15 nm (Fig. 1d). In general, it was found that annealing of thin films at high temperatures leads to an increase in the size of the grains and the appearance of a new, rougher relief of the films surface.

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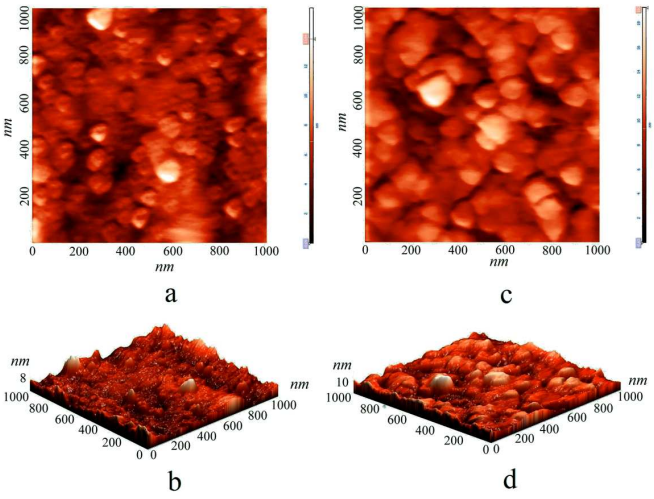


Fig. 1. AFM micrographs of $\beta$-$Ga_2O_3$ film's surface without annealing (a, b) and after annealing in atmosphere of oxygen at 1000 °C (c, d). Images (a) and (c) — two-dimensional, (b) and (d) — three-dimensional.

Films without thermal annealing have TSL of very low intensity and its detailed investigation is difficult. Figure 2 presents TSL curves of the thin films of $\beta$-$Ga_2O_3$, annealed in oxygen. It could be seen that a band with a maximum in the region at 77 K and the overlapping of bands' group in 100–260 K region are singled out in the studied temperature range.

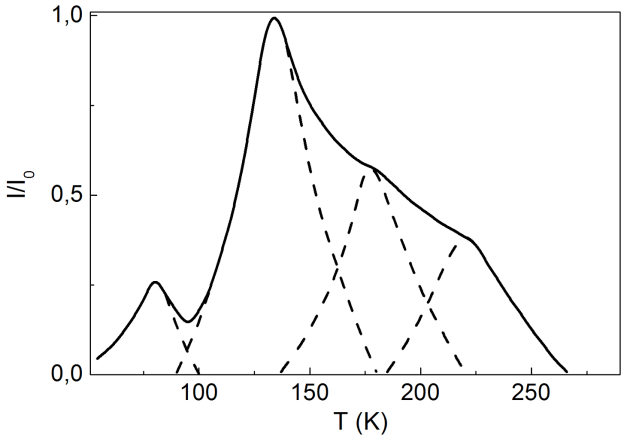


Fig. 2. TSL curves of X-ray-irradiated thin films of $\beta$-$Ga_2O_3$ samples ($D$ = 1.5 C/kg, $T$ = 50 K). Dashed lines are the elemental components.

The Alentsev–Fok method [10] was used to separate TSL curves into individual components. We applied the partially heating method and derived spectroscopy method [11] in order to check experimentally the decomposition performed. Since the low-temperature part of a TSL peak in the case of linear kinetics of luminescence, is of a larger extent as compared to its high-temperature part [12], it has been established that recombination processes at the indicated TSL peaks are described by linear kinetics.

The obtained results are close to the studies of TSL in $\alpha$-$Al_2O_3$. In particular, $\alpha$-$Al_2O_3$ single crystals in this temperature region also exhibit four TSL bands with maxima at 60, 100, 220, and 250 K [13].

An analysis of the emission spectra of TSL shows that for the TS investigated in the thin films of $\beta$-$Ga_2O_3$ samples recombination is observed in the range 2.2–4.5 eV (275–560 nm) (Fig. 3). The experimental spectrum is well modeled by two independent Gaussian (linear electron–phonon coupling model) with peaks at 2.95 eV (420 nm) and 3.15 eV (395 nm). Analysis of the TSL emission spectra shows that radiative recombination on liberation of trapping centers occurs through the same centers as in the regime of stationary photoluminescence [14].

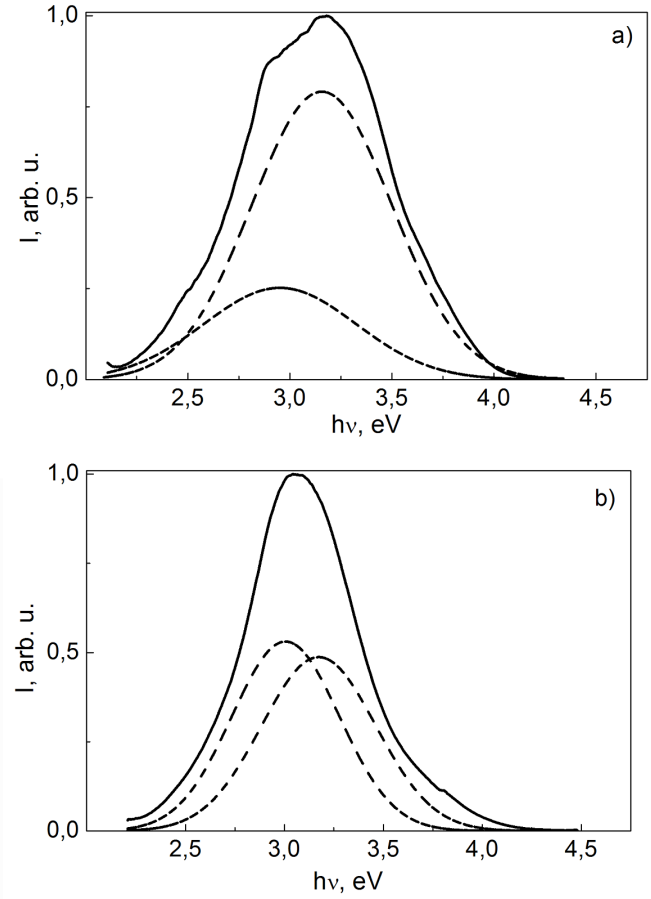


Fig. 3. TSL spectra of thin films of $\beta$-$Ga_2O_3$ for the band with $T_m$ = 77 K (a) and $T_m$ = 135 K (b). Dashed lines are the elemental components.

There is the energy of their thermal activation $E_T$ among the main parameters of the trapping centers. To calculate the latter in the investigated samples we used

different methods: the Antonov-Romanovskii method of superposition of theoretical and experimental TSL curves [15], a Lushchik method based on measuring a half-width of the investigated TSL peaks [16], and the Garlick–Gibson method of the initial luminescence build-up [17], where the depth of occurrence is determined as $E_T = d \ln I / \mathrm{d}(kT)^{-1}$.

Another important characteristic of trapping centers is the frequency factor $p_0$ characterizing the rate of effective collisions capable of realizing localized charges. For the indicated peaks, $p_0$ was determined by the formula

$$E_T = \left( \ln \frac{p_0 T_m}{\beta} - \ln \ln \frac{p_0 T_m}{\beta} \right) kT_m,$$

obtained in [18] for the case of linear kinetics, which is also typical for thin films $\beta$-$Ga_2O_3$, as mentioned above.

The results of processing of the TSL curves by various methods are presented in Table I. The obtained values of $E_T$ are close to the results of investigations of TSL in $\alpha$-$Al_2O_3$ single crystals. For the two low-temperature bands of TSL the thermal activation energies are very close to the results obtained by us and are 0.17 and 0.22 eV. The two high-temperature TSL bands in $\alpha$-$Al_2O_3$ have a somewhat larger value $E_T$, which is equal to 0.56 and 0.73 eV. Considering that the method of [15] possesses an error due to theoretical simplifications, the error in the method of the initial luminescence build-up is 2–3%, while in calculations by the peak half-width method the error is 7–15% [19]. It can be concluded that $E_T$ values obtained by the different methods for the TSL peaks virtually coincide. This allows us to contend that the investigated TSL peaks for the thin films of $\beta$-$Ga_2O_3$ with their maxima at 77, 135, 178, and 235 K are caused by individual traps which are not overlapped energetically with other traps.

TABLE I

Thermal activation energy and frequency factor of trap centers in thin films of $\beta$-$Ga_2O_3$

| $T_m$ [K] | $E_T$ [eV] | | | $p_0$ [$s^{-1}$] |
|---|---|---|---|---|
| | Antonov-Romanovskii method | Lushchick method | Initial luminescence build-up | |
| 77 | 0.16 | 0.15 | 0.13 | $6.6 \times 10^6$ |
| 135 | 0.28 | 0.19 | 0.18 | $3.2 \times 10^6$ |
| 178 | 0.38 | 0.28 | 0.32 | $4.8 \times 10^6$ |
| 235 | 0.51 | 0.51 | 0.50 | $1.2 \times 10^{10}$ |

Figure 4 depicts temperature dependence of the $E_T$ values of the investigated samples obtained by the method of the initial luminescence build-up, which has the lowest error and by the method based on measuring a half-width of the investigated TSL peaks. A considerable deviation of $E_T$ $(T)$ from linearity testifies to the presence of a remote tunneling mechanism of luminescence. By analogy with the related $Al_2O_3$ [20], $Y_2O_3$, and $Sc_2O_3$ [21] systems, in which the thermally-stimulated migration $V_k$-centers (are relaxed holes) is proved, it can be considered that the diffusion-controlled tunneling recombination observed in the thin films of $\beta$-$Ga_2O_3$ is also caused by thermally-stimulated migration of $V_k$-centers. The diffusion character of migration of electronic excitations with their possible intermediate localization is confirmed by low values of the frequency factor $p_0$ of relaxation processes. As seen from Table I, the frequency factor of the relaxation process in the thin films of $\beta$-$Ga_2O_3$ is lower by several orders of magnitude than that of trapping sites ($\approx 10^{-12}$ $s^{-1}$).

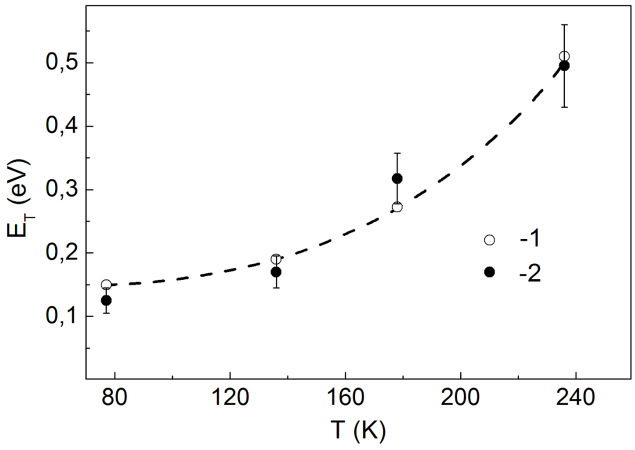


Fig. 4. Temperature-dependent $E_T$ in the thin films of $\beta$-$Ga_2O_3$ determined by the method of initial luminescence build-up (1) and by the peak half-width method (2).

## 4. Conclusion

It was established that the investigated TSL peaks for thin films of $\beta$-$Ga_2O_3$ with their maxima at 77, 135, 178, and 235 K are caused by individual traps which are not overlapped energetically with other traps. The results obtained indicate that the recombination processes upon trap centers in the thin films of $\beta$-$Ga_2O_3$ are caused by diffusion-controlled tunneling recombination due, most probably, to the thermally-stimulated migration of $V_k$-centers.

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