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The Local Trap Centres in Thin β-Ga_2O_3:Cr^{3+} Films

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The results of the investigation of thermally stimulated luminescence (TSL) of thin β-Ga_2O_3:Cr^{3+} films are presented. The depth of the trap centre (TC) responsible for the TSL band with a maximum in the region of 290 K is determined. The non-elementary nature of this TC is established, and the possibility of the realization of diffusion-controlled tunnel recombination at releasing the TC in thin β-Ga_2O_3:Cr^{3+} films is indicated. The measured TSL spectra show the presence of a wide band of emission due to ${}^4T_2 \to {}^4A_2$ transitions in Cr^{3+} ions. The *R*-lines (for the $2E \to {}^4A_2$ transitions) and their phonon repetitions in the long-wavelength region are interpreted.

Наведено результати дослідження термостимульованої люмінесценції (ТСЛ) у тонких плівках β-Ga_2O_3:Cr^{3+}. Визначено глибини центру захоплення (ЦЗ), відповідального за смугу ТСЛ з максимумом в області 290 К. Встановлено неелементарність даного ЦЗ та вказано на можливість наявности у тонких плівках β-Ga_2O_3:Cr^{3+} дифузно-контрольованої тунельної рекомбінації під час звільнення ЦЗ. Виміряні спектри ТСЛ показують наявність широкої смуги свічення, зумовленої ${}^4T_2 \to {}^4A_2$-переходами у йонах Cr^{3+}. Інтерпретовано *R*-лінії (переходи $2E \to {}^4A_2$) та їхні фононні повторення у довгохвильовій області.

Key words: gallium oxide, thin films, activator, thermally stimulated luminescence.

Ключові слова: оксид Ґалію, тонкі плівки, активатор, термостимульо-

вана люмінесценція.

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1. INTRODUCTION

In recent years, the needs of science and technology have put forward a number of practically important materials, including pure and doped gallium oxide β-Ga_2O_3 [1–4]. Among them, the β-Ga_2O_3:Cr^{3+} occupies an important place in both monocrystalline [5, 6] and thin-film or nanocrystalline [7, 8] states. In particular, the thin β-Ga_2O_3:Cr^{3+} films are promising luminophores in the red region of the spectrum at used in flat screens PDP (plasma display panel), which are actively developing [9]. The efficiency of transfer of excitation energy from the main substance to the centres of luminescence is largely determined by the presence of trap centres (TC), which are manifested in thermally stimulated luminescence (TSL). This led to the investigation of the TC of charge carriers and the determination of their parameters by thermal activation methods in thin β-Ga_2O_3:Cr^{3+} films. These thin films are obtained by radio-frequency (RF) ion-plasma sputtering. The application of this method is considered as optimal for the deposition of semiconductor and dielectric thin films [10].

2. EXPERIMENTAL TECHNIQUE

Thin films of β-Ga_2O_3:Cr^{3+} with a thickness 0.3–0.8 μm were obtained by RF ion-plasma sputtering on substrates of ν-SiO_2 fused quartz. RF sputtering was carried out in an atmosphere of argon in the system using the magnetic field of external solenoids for compression and additional ionization of the plasma column. The raw material for the manufacture of the target was β-Ga_2O_3 with grade 'ОСЧ' (the purity 99.99%). The doping impurity in form of Cr_2O_3 oxide with a concentration of 0.01–0.1 wt.% was added to the target material. After deposition of the thin films, the thermal treatment in oxygen atmosphere at 1000–1100°C was held. X-ray diffraction studies of the obtained thin films showed, as for undoped β-Ga_2O_3 films, the presence of a polycrystalline structure with a predominant orientation in the (400), (002), (111) and (512) planes. The diffraction patterns for β-Ga_2O_3 films were described by us earlier [11] in more detail.

In the investigation of thermally stimulated luminescence, the samples were placed in a vacuum cryostat, where the temperature varied between 80 and 400 K, and irradiated with x-rays of CuK_α-

radiation ('УРС-55', 40 kV, 10 mA) at 80 K. The dose of x-irradiation was measured with a dosimeter 'ИДМД-1'. The value of radiation exposure varied between 0.15 and 3.30 C/kg. The intensity of TSL luminescence was recorded by a photomultiplier 'ФЭУ-51' with a light filter 'КС-15' and an electrometric multiplier. The linearity of heating was provided by the 'РИФ-101' temperature regulator. The heating rate was $\beta = 0.150 \pm 0.005$ K/s that provided a sufficient resolution for the studied samples with a good light sum. The spectrums of thermally stimulated luminescence were investigated using a quartz spectrophotometer 'СФ-4А'. The emission spectrums were adjusted taking into account the dispersion of the monochromator and the sensitivity of the photomultiplier 'ФЭУ-51'.

3. RESULTS AND DISCUSSION

The investigation of TSLs previously excited by x-rays of thin β-Ga_2O_3:Cr^{3+} films makes it possible to determine local energy levels within the band gap, which are manifested in the capture of charge carriers. These levels occur due to doping and may be due to intrinsic defects of the crystal lattice. To establish the parameters of the trap centres of charge carriers in thin films of β-Ga_2O_3:Cr^{3+}, which arise because of doping with chromium, the TSL curves were measured through a light filter 'КС-15'. This light filter transmits emission with wavelengths over 630 nm, which corresponds to the luminescence spectrums of β-Ga_2O_3:Cr^{3+} [12–15]. In addition, the use of this light filter makes it possible to eliminate the emission of TSL due to recombination processes in the matrix - a thin film of β-Ga_2O_3. This luminescence occurs in the spectral region of 320–570 nm [16].

The typical TSL curves of thin β-Ga_2O_3:Cr^{3+} films are shown in

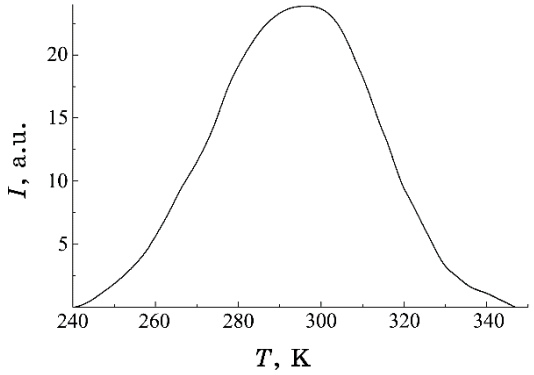

Fig. 1. The TSL curve of thin β-Ga_2O_3:Cr^{3+} films after x-ray irradiation ($D = 1.55$°C/kg, $T = 80$ K).

Fig. 1.

As can be seen, in the investigation temperature range, the characteristic band of TSL with a maximum in the region of 290 K is observed. The obtained results show that recombination processes in this band are described by linear kinetics, because in the case of linear luminescence kinetics the low-temperature part of the TSL band is longer than high-temperature, and in the case of quadratic, *vice versa* [17].

One of the main parameters of TC is the energy of their thermal activation E_T. To determine the E_T in the studied thin β-Ga_2O_3:Cr^{3+} films, the approximate Urbach ratio $E_T = 25kT$ [17], the method for superposition of theoretical and experimental TSL curves, proposed in [18], the method based on measuring the half-width of the studied TSL peaks [19] and the method of initial luminescence build-up [17], where the depth of occurrence is defined as $E_T = d(\ln I)/d(kT)^{-1}$ were used.

The second important characteristic of the TC is the frequency factor p_0, which characterizes the frequency of effective collisions that are able to release localized charges. The value of p_0 for the detected peak of TSL was determined by the formula:

$$E_T = \left(\ln \frac{p_0 T_{\max}}{\beta} - \ln \left(\ln \frac{p_0 T_{\max}}{\beta} \right) \right) kT_{\max},$$

which was obtained in [20] for the case of linear kinetics, which, as noted above, is also characteristic of thin β-Ga_2O_3:Cr^{3+} films.

The results of processing the TSL curve by different methods are given in Table.

Given that the method [17] has a certain error due to theoretical simplifications, the error of the initial luminescence build-up meth-

TABLE. The thermal activation energy and frequency factor of TC in thin films of β-Ga_2O_3:Cr^{3+}.

$T_{\max}$, K	E_T, eV				p_0, s^{-1}
	Urbach's method [17]	Antonov-Romanovskii method [18]	Lushchick method [19]	Initial luminescence build-up method [17]	
290	0.62	0.63	0.29	0.65	$7.14 \cdot 10^7$

od is 2–3%, and the error when calculating the half-width peak method 7–15% [21], we can conclude that the E_T values obtained by using most methods are almost the same. A characteristic feature is the underestimated value of E_T, calculated by the Lushchick method, which is due to the large half-width of the investigation band TSL. This situation indicates that this band of TSL is not an emission of the monoenergy centre, but contains extensions by energy. This may be due either to the overlap of two levels that are energetically close, or to the quasi-continuous energy distribution of the level of the TC. Based on the results of TSL studies of single β-Ga_2O_3:Cr^{3+} crystals [15], this situation is well explained by the presence of low-intensity curves with maxima in the region of 300 K and 320 K in TSL spectrum, which can expand the TSL band of thin β-Ga_2O_3:Cr^{3+} films.

As can be seen from Table, for thin β-Ga_2O_3:Cr^{3+} films, the frequency factor of the relaxation process was determined by the E_T method of initial luminescence build-up, which has the smallest error, is several orders of magnitude lower than the frequency factor of the trap centres ($\sim 10^{12}$ s^{-1}). A similar situation is observed in pure thin films of β-Ga_2O_3, where the possibility of diffusion-controlled tunnel recombination is shown [16]. This may indicate that, likely in pure thin β-Ga_2O_3 films, the diffusion-controlled tunnel recombination is observed in thin β-Ga_2O_3:Cr^{3+} films due to thermally stimulated migration of holes delocalized from V_k-centres.

The spectral composition of the emission of the TSL band with a maximum in the region of 290 K (Fig. 2) correlates well with the photoluminescence spectrums of single β-Ga_2O_3:Cr^{3+} crystals [12–15]. Based on the results [13–15, 22], this emission is due to electronic transitions in Cr^{3+} activator centres, which occupy octahedral positions in the β-Ga_2O_3-crystal lattice. In general, the luminescent spectrum can be caused either by the displacement of chromium

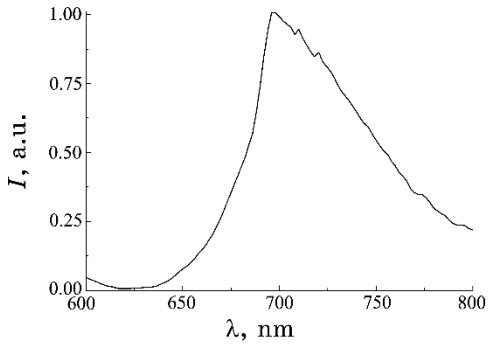

Fig. 2. The TSL spectrum of thin β-Ga_2O_3:Cr^{3+} films in the band with a maximum in the region of 290 K.

ions from the centre of inversion, or by the interaction with lattice oscillations. The luminescence spectra of β-Ga_2O_3:Cr^{3+} consist of a series of lines and bands of different intensities, which are superimposed on a wide unstructured band of emission. This wide band in the spectral region of 680–800 nm arises due to the radiation electronic transition $^4T_2 \rightarrow {}^4A_2$ [22]. According to Refs. [13–15, 22], two R-lines of different intensities are observed in the β-Ga_2O_3:Cr^{3+} spectra at 688.9 nm and 696.6 nm. The lines are observed due to electronic transitions to the $^4A_2$ ground state from two sublevels ^2E-state which is split in the crystal field ($\bar{E}$ and $2\bar{A}$) (so-called non-phonon (NPL) or zero-phonon transitions). In the long-wavelength region, as a rule, weaker lines appear due to phonon repetitions of these phonon-free transitions (oscillating or vibrating bands), which are shifted relative to non-phonon R-lines to the long-wavelength region of the spectrum (Stokes bands).

The TSL spectra of the thin β-Ga_2O_3:Cr^{3+} films obtained by us (Fig. 2) have a wide maximum in the spectral range from 693 to 696 nm. Most likely, this maximum is due to the undivided doublet of R_1 and R_2-lines, as the accuracy of the equipment used and the relative weakness of the signal did not allow separating these lines.

The typical local maximums on the luminescence spectrum of TSL of thin β-Ga_2O_3:Cr^{3+} films in the region of 710 and 721 nm are due to phonon repetitions of non-phonon R-lines. By averaging the energies of the R_1 and R_2 lines, these local maximum can be interpreted as R_1, R_2–332 cm^{-1}, and R_1, R_2–566 cm^{-1}. This interpretation is in good agreement with the results of studies of the vibrational spectra of thin β-Ga_2O_3 films [23, 24].

The obtained emission spectrums of TSL of thin β-Ga_2O_3:Cr^{3+} films show that radiative recombination upon release of the trap centre with the thermal activation energy of about 0.65 eV occurs through the same centres as in the stationary luminescence mode.

4. CONCLUSIONS

Our investigation shows that in thin β-Ga_2O_3:Cr^{3+} films obtained by RF ion-plasma sputtering, the TSL curve due to activator emission contains a band with a maximum in the region of 290 K. The depth of occurrence of the TC responsible for this TSL is about 0.65 eV. The non-elementary nature of this TC has been established. The value of the determined frequency factor p_0 indicates the possibility of existence of diffusion-controlled tunnel recombination due to thermally stimulated migration of holes delocalized from V_k-centres. In the TSL spectra of thin β-Ga_2O_3:Cr^{3+} films, the broad luminescence band with a maximum around 695 nm is observed that corresponds to the electron–vibrational transitions $^4T_2 \rightarrow {}^4A_2$ in the acti-

vator ion. The maximum of the band is associated with *R*-lines ($^2E \rightarrow {}^4A_2$ transition), and the local maximum in the long-wavelength region are associated with phonon repetitions of *R*-lines.

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