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Influence of Obtainment Conditions and Excitation Into Spectral and Kinetic Characteristics of Cathodoluminescence in $Y_2O_3:Eu$ Thin Films

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The spectra and kinetics of the rise and decay of the cathodoluminescence (CL) of thin films of $Y_2O_3:Eu$ obtained by RF-magnetron sputtering was investigated. Based on the shape of the CL spectra at different excitation energies, showed the possibility of creating irregular solutions of yttrium and europium oxides and the structural features of the surface and bulk layers. The time constant for the decay CL for 612 nm emission was determined and the value of which is within the range (1.8 - 4.1) ms. This value is a complex function of the type of film deposition atmosphere, the activator concentration and duration of the exciting pulses was shown. The features of the risen CL and the proposal based on the delay rise CL analyze structural perfection of $Y_2O_3:Eu$ thin films.

Key words: yttrium oxide, cathodoluminescence, thin films.

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Introduction

Among the large number of materials the luminescent materials have particular importance for using in the optoelectronics. They are used for creating displays, scintillators, for the means for recording and visualizing information. The cubic yttrium oxide the Y_2O_3 is one widespread crystalline matrix of phosphors that was activated with rare earth ions [1–4]. Among them the most investigated phosphor micron dispersion is the $Y_2O_3:Eu$ phosphor with red emission region. Results of the investigation of this material can be used as the base information for the analysis of the characteristics and mechanism of luminescence in the investigation of the impact of size effects and structural excellence on emission efficiency submicron phosphors [5]. For this purpose we used the method of local cathodoluminescence (CL), which has a number of features compared to traditional investigation optical methods [6]. This method is highly sensitive to changes in the electronic structure of the material (impurity and structural defects) as well as makes it possible to investigate the change of luminescent properties of structures and materials at a depth from 10–20 nanometers to several micrometers. Moreover, the high energy excitation of luminescence allows the investigation of optical transitions, for which the energy

of excitation is needed above 6 eV (with vacuum ultraviolet region). This method also allows investigating the processes of energy transfer between the high-energy states, the electronic structure of defects, which are channels for nonradiative recombination. All these factors determine the kinetics of the rise and decay of the luminescence, which caused her research in $Y_2O_3:Eu$ thin films.

Take note, that to obtaining films based on Y_2O_3 used a number of methods, so the films are different by optical and luminescence properties because of their different perfection. In this regard, in this paper investigates spectral and kinetic CL properties of $Y_2O_3:Eu$ thin films, obtained by radio-frequency ion-plasmas sputtering, which is optimal to obtain the most homogeneous semiconductor and dielectric films.

I. Experimental technique

Thin films of $Y_2O_3:Eu$ was obtained by radio-frequency ion-plasmas sputtering in 100% atmosphere of oxygen or in 100% atmosphere of argon in the system using the magnetic field external solenoids for compression and for additional ionization the plasma column on fused quartz $v\text{-SiO}_2$ substrates. The thickness of the films ranged between 0.2 μm and 1.0 μm . The initial components were of Y_2O_3 grade ИтО-И and Eu_2O_3 with grade “oc.ч”. The activator concentration

was 2.5 and 5.0 ml. %. After deposition of the films, the heat treatment in air at 950–1050°C was held. The X-ray diffraction investigation showed the presence of the polycrystalline structure films preferentially oriented in the plane (222). The view of the obtained diffraction pattern is nearly similar to the diffraction pattern for pure Y_2O_3 thin films, which are given by us in [7]. Herewith, the reflex from the plane (440) has a little more intensity for the $Y_2O_3:Eu$ thin films which were deposited in argon atmosphere.

The investigation of CL properties was conducted in the pulsed electron excitation mode. The luminescence spectra were recorded by installation which was mounted on the base CΦ-4A spectrophotometer by using ΦEY-79 photomultiplier. The signal from photomultiplier fed to the resonance amplifier and was recorded by ampermeter as well as the signal was transmitted through the analog-to-digital the converter of interface on the IBM/PC computer for the record the spectrum of luminescence. The scanning of the wavelength by monochromator was carried using the stepper motor. The stepper motor was driven by computer through control unit. The spectra of luminescence were investigated in the range from 200 nm to 800 nm at 295 K. The kinetics of the rise and decay were recorded using the FEU-79 photomultiplier. Next digitizing the signal from the photomultiplier, performed C1-117 electronic oscillographe, allowed to get the array of data, which was contained information about the kinetics of the rise and decay in a convenient form for further processing.

II. Results and discussion

The typical spectra of CL of the obtained $Y_2O_3:Eu$ thin films at different energies excited electrons are shown in Fig. 1. The narrow bands of emission appear in the spectra of luminescence of the thin films. These bands are caused the intrinsic central transitions between electron shells within Eu^{3+} activator. The wavelength of maximum emission is $\lambda_{max} = 612$ nm, which corresponds to red of luminescence. All the observed electronic transitions ${}^5D_{0-7}F_j$ for Eu^{3+} ions are marked in Fig. 1. They include the allowed magnetic dipole transitions ${}^5D_{0-7}F_1$ (for Eu^{3+} ions in C_2 and C_{3i} lattice sites of Y_2O_3) and the allowed electric dipole transitions ${}^5D_{0-7}F_2$ (for Eu^{3+} ions only in the sites C_2). The unit cell of the cubic Y_2O_3 has 32 of yttrium ions that can be substituted with other of rare earth ions. 8 of these ions occupy the central position (the C_{3i} symmetry), and the remaining of 24 ions have lower symmetry C_2 [8, 9]. Thus, the Eu^{3+} ions may find themselves in one of two non-equivalent positions which leads to differences in spectra of luminescence. If to take into account that the radius of Y^{3+} ions and of Eu^{3+} ions are close enough to each other and are 0.90 and 0.94 Å, respectively, therefore when we carry out activation with europium ions of the Y_2O_3 the cubic structure of the crystal lattice are almost unchanged with minor changes parameters [10].

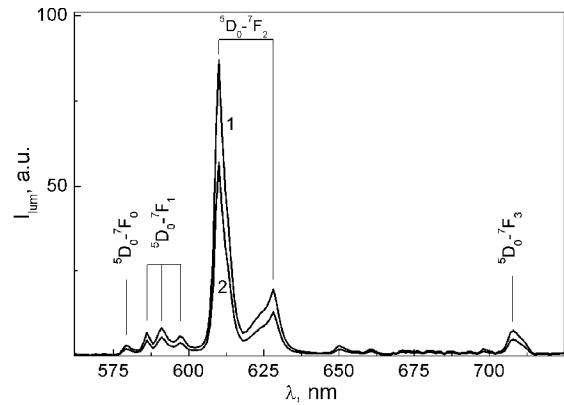


Fig. 1. The spectra of the CL of $Y_2O_3:Eu$ thin films at different energies excited electrons. The activator of concentration is 5%, the atmosphere of deposition is Ar (100%). The parameters of the pulse electron irradiation: the current density of the electron beam $j=5 \times 10^{-2}$ A/m²; the pulse duration 5×10^{-4} s; pause between pulses 0.1 s, the energy of excited electrons 5.0 keV (1) and 4.5 keV (2)

In describing the spectrum of luminescence $Y_2O_3:Eu$ is often used so-called the "asymmetrical relationship" I_{612}/I_{596} of intensity of luminescence bands in 612 nm and 596 nm regions, that corresponds to the ratio of the number Eu^{3+} cations in the respective states of local symmetry $N_{C_2} / N_{C_{3i}}$ [5, 10–13]. The luminescence at 612 nm band is determined by the electric dipole transition ${}^5D_{0-7}F_2$ that is very sensitive to the nearest environment of the radiant Eu^{3+} ion. The band with maximum at 596 nm is determined by magnetic dipole transition ${}^5D_{0-7}F_1$ which is insensitive to the immediate environment [10, 13–15]. The ratio of amplitude intensities I_{612}/I_{596} is used for estimation of the relation $N_{C_2} / N_{C_{3i}}$ [5, 12, 14, 16] and for analysis of structural perfection $Y_2O_3:Eu^{3+}$.

In the matrix Y_2O_3 for Y^{3+} ions the ratio $N_{C_2} : N_{C_{3i}}$ equal to 3:1 in equilibrium state in the ideal lattice. With a uniform substitution of Eu^{3+} ions on Y^{3+} ions we had to get a close result. However, for $Y_2O_3:Eu$ thin films this ratio has significantly more value. The value of this ratio depends on the energy of bombarding electrons. For example, at the electric current density of excitation 5×10^{-2} A/m² the increase of energy electronic excitation from 4.5 keV to 5.0 keV leads to the growth of this ratio from 10.4 to 14.0 (Fig. 1). Note that the results of amplitude ratio $I_{612}/I_{596} = (8-10)$ are close enough to obtained the results in [5] at the investigation of photoluminescence powder materials $Y_2O_3:Eu$ different dispersion, obtained by sol-gel method.

Our results show us that while increasing energy of bombarding electrons, that is increasing depth of penetration the electrons in the $Y_2O_3:Eu$ thin film, contributes to increases the relative contribution of glow Eu^{3+} ions in the sites C_2 relatively C_{3i} sites in the luminescence. Such rejection is most likely indicates the formation of irregular oxide solutions of yttrium and europium in $Y_2O_3:Eu$ thin film during its deposition. The increase energy of excited electrons and, consequently, their of the penetration depth shows that the relative

number of Eu^{3+} ions in sites C_{3i} predominates on the surface regarding depth. The increase in the relative number of Eu^{3+} ions at C_2 sites in the depth of the film, the deposited in argon atmosphere (Fig. 1), most likely caused by the decrease in the local symmetry the environment ions of europium by ions of oxygen. Inasmuch as the film annealed in air atmosphere, the local symmetry of Eu^{3+} ions was increased in the first place on the surface at the annealing process.

To investigate the mechanism of energy transfer with rare-earth activator in the films of Y_2O_3 matrix we have analyzed a number of the kinetics of the rise and decay of the CL of $\text{Y}_2\text{O}_3:\text{Eu}$ thin films for the luminescence at $\lambda_{\text{max}} = 612 \text{ nm}$. The typical kind of kinetics for various films depending on the excitation energy is shown in Fig. 2 and in Fig. 3. It was found that the kinetics of decay of luminescence the investigated of $\text{Y}_2\text{O}_3:\text{Eu}$ thin films at different energies and doses of irradiation are well approximated by mono exponential functions. The obtained results show us that the time constant of decay in the investigated films varies depending on atmosphere deposition of films, the activator concentration and the duration of the excitation bombing impulses. In particular, it was found that the $\text{Y}_2\text{O}_3:\text{Eu}$ thin films deposited in argon atmosphere and in oxygen atmosphere with a concentration of activator 5 mol% are more of the luminous than the films with a concentration of activator 2.5 mol%. The constant of decay time for the first films are larger than for the second films (Table 1). Furthermore, for all types of thin films the decay time at low excitation duration (4 ms) is greater than the decay time at high excitation duration (6–9 ms). This can be explained by the fact that the surface layers of the film are more structurally nonuniform than volume. So, most likely, after the termination of the excited electronic pulse these heterogeneity have done contribute to the kinetics of luminescence by increasing the time of decay due to the greater relative contribution at low doses irradiation.

Table 1

The dependence of the constant decay time of the CL for $\text{Y}_2\text{O}_3:\text{Eu}$ thin films deposited in argon atmosphere for the luminescence at 612 nm from the excitation time and the concentration of activator*

The concentration of activator Eu^{3+} , mol%	The time of excitation $t_{\text{ex}} \times 10^4$, s	$t \times 10^3$, s
2.5	4	3.7
2.5	6	2.2
2.5	9	2.2
5.0	4	4.1
5.0	6	3.4
5.0	9	3.3

*The density of excitation current 10^{-2} A/m^2 , the voltage 4.5 keV.

At comparing of $\text{Y}_2\text{O}_3:\text{Eu}$ films with different times of irradiation but with the same activator concentration was found that for films are irradiated with electronic pulse frequency of 100 Hz for 20 h the time constant of decay is greater than for the non-irradiated films (Table 2). This

is due to the fact that at long-times irradiation of the thin films by electrons the structural defects or inhomogeneities in the films in the region of value of the depth of the penetration of the electron beam are formed.

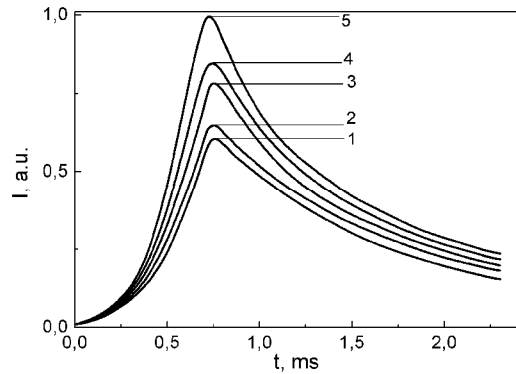


Fig. 2. The dependence the kinetics of the rise and decay of the CL from the excitation energy and the technological conditions to obtain $\text{Y}_2\text{O}_3:\text{Eu}$ thin films. The parameters the pulses of the electron excitation: the pulse duration $5 \times 10^{-4} \text{ s}$; pause between pulses 0.1 s, the current density of the electron beam $j = 1 \times 10^{-2} \text{ A/m}^2$. The activator of concentration is 2.5%, the atmosphere of deposition is Ar (100%), the energy of excited electrons 5.5 keV (1) and 6.0 keV (2). The activator of concentration is 5%, the atmosphere of deposition is O_2 (100%), the energy of excited electrons 4.0 keV (3) and 5.5 keV (4), 7.0 keV (5).

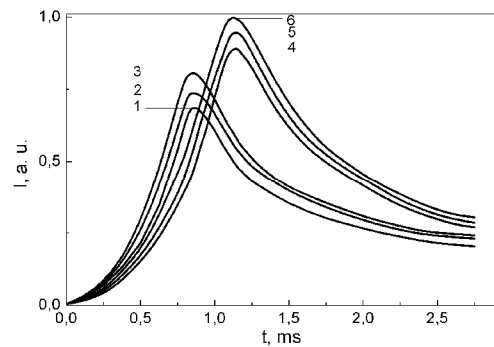


Fig. 3. The dependence the kinetics of the rise and decay of the CL from the excitation energy and the technological conditions to obtain $\text{Y}_2\text{O}_3:\text{Eu}$ thin films. The parameters the pulses of the electron excitation: the pulse duration $9 \times 10^{-4} \text{ s}$; pause between pulses 0.1 s, the current density of the electron beam $j = 1 \times 10^{-2} \text{ A/m}^2$. The activator of concentration is 2.5%, the atmosphere of deposition is Ar (100%), the energy of excited electrons 5.0 keV (1) and 6.0 keV (2), 6.5 keV (3). The activator of concentration is 5%, the atmosphere of deposition is O_2 (100%), the energy of excited electrons 5.0 keV (3) and 6.0 keV (4), 6.5 keV (5).

As shown in Table 1 and Table 2, the constant decay time of the CL for the $\text{Y}_2\text{O}_3:\text{Eu}$ thin films for the luminescence at 612 nm is in the range (1.8–4.1) ms depending on the structural perfection of films and activator concentration.

The theoretical calculations of electric dipole transitions, magnetic dipole transitions and electric quadrupole transitions for lanthanide show that these

values have the following meanings: $\tau_{el} \sim 10^{-4}$ s; $\tau_{mag} \sim 0.5 \times 10^{-2}$ s; $\tau_q \sim 2$ s [17]. Comparing the values received by us with data based on the results of the spectral composition of emission (Fig. 1) shows that we have the luminescence caused by electric dipole transitions and the emitting at 612 nm of Eu^{3+} ions are in the crystal lattice sites of Y_2O_3 with point symmetry C_2 .

Note also that the received by us the time constant of decay τ is good agreement with renowned researches the decay of luminescence in different samples of $\text{Y}_2\text{O}_3:\text{Eu}$ [18–22]. As stated in the [18] the value of the decay time of $^5\text{D}_0-^7\text{F}_2$ transition for $\text{Y}_2\text{O}_3:\text{Eu}$ ceramics with dimensions of the crystallites of 10 nm was obtained of 1.3 ms. In the investigation the constant of the decay

time of $\text{Y}_2\text{O}_3:\text{Eu}$ nanocrystals in [19] was found that the constant of the decay time is in the range from 2.0 to 3.7 ms. The research [20] show that the lifetime of $\text{Y}_2\text{O}_3:\text{Eu}$ nanophosphorus with size of 5 nm to 7 nm for the concentration of activator 2.4 mol% is 3.08 ms, and for the concentration of activator 5.2 mol% is 2.40 ms. For the microcrystals the constant of the decay time at 612 nm of luminescence is less and for the concentration of activator 3.5 mol% is $\tau = 1.07$ ms and for 5.2 mol% is $\tau = 1.02$ ms. According to [21] for $\text{Y}_2\text{O}_3:\text{Eu}$ single crystals the constant of the decay time is $\tau \approx 4$ ms, whereas in [22] for $\text{Y}_2\text{O}_3:\text{Eu}$ single crystals the constant of the decay time is defined as 1.90 ms and 1.72 ms for the concentration of the activator 3 and 8 %, respectively.

Table 2

The dependence of the constant of the decay time of the CL of $\text{Y}_2\text{O}_3:\text{Eu}$ thin films at 612 nm of luminescence from the excitation time and the previous of the irradiation*

The atmosphere of deposition films, the irradiation	The concentration of the activator, mol%	The time of exitation, $t_{ex} \times 10^4$, s	$t \times 10^3$, s
Argon 100%, nonirradiated	2.5	4	3.7
	2.5	6	2.2
	2.5	9	2.2
Argon 100% irradiated	2.5	4	4.1
	2.5	6	3.2
	2.5	9	3.0
Oxygen 100%, nonirradiated	5.0	4	2.0
	5.0	6	1.9
	5.0	9	1.8
Oxygen 100%, irradiated	5.0	4	4.0
	5.0	6	4.0
	5.0	9	3.3

*The density of excitation current 10^{-2} A/m², the voltage 4.5 keV.

Our investigation show that such differences in the constant of decay time for $\text{Y}_2\text{O}_3:\text{Eu}$ phosphor at 612 nm of the luminescence, caused $^5\text{D}_0-^7\text{F}_2$ electric dipole transition, is due to the fact that this value τ is a complex function, which is determined by the methods and conditions of obtain, the ways and doses of excitation, the size of crystallites, the perfection of structure and concentration of the activator.

In the analysis the kinetics of the rise and decay of the CL was found that the delay of the rise CL relatively decay the impulse of the electronic excitation (Fig. 3) in some cases is observed. This is brighter expressed for $\text{Y}_2\text{O}_3:\text{Eu}$ films the deposited in oxygen atmosphere and in addition this shift depends from the energy and dose irradiation. In particular, by the increasing the dose of electron irradiation (by increasing the impulse duration) is observed shift over time of the maximum of the rise of the CL relatively the decay the impulse of the electronic excitation. This effect can be explained by structural inhomogeneities, which are clearly manifested in the films deposited in oxygen atmosphere. As a result of such the inhomogeneities the ions of activator Eu^{3+} can be located in interstitial defective positions the crystal lattice of $\text{Y}_2\text{O}_3:\text{Eu}$ or carry out the transitions due to the diffusion between C_2 and C_{3i} sites of Y_2O_3 matrix. Thus based on the dependence of the rise of the CL from energy and dose of the irradiation can be analyze structural perfection of $\text{Y}_2\text{O}_3:\text{Eu}$ thin films.

Conclusions

On the basis of spectra form analysis of the CL at different energies of the excitation is shown the possibility of formation of irregular solutions of yttrium and europium oxide in $\text{Y}_2\text{O}_3:\text{Eu}$ thin films and the increasing the number of Eu^{3+} ions in a state of lowered symmetry C_2 in depth the film relatively to the surface. The obtained values the time constant of the decay of the CL are indicate that luminescence of $\text{Y}_2\text{O}_3:\text{Eu}$ at 612 nm caused by the electric dipole transitions between energy levels $^5\text{D}_0-^7\text{F}_2$. From the analysis dependence the time constant of the decay of the CL from the concentration of activator, conditions of the deposition and the time of the irradiation was shown that the surface layers have more the structural inhomogeneities than volume. The structural perfection of $\text{Y}_2\text{O}_3:\text{Eu}$ thin films can analyze on the basis dependence of the rise of the CL from the energy and dose of the irradiation was found.

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Вплив умов одержання і збудження на спектральні і кінетичні характеристики катодолюмінесценції тонких плівок $Y_2O_3:Eu$

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Досліджено спектри та кінетику розгоряння і загасання катодолюмінесценції (КЛ) тонких плівок $Y_2O_3:Eu$ отриманих методом ВЧ-магнетронного напилення. На основі форми спектрів КЛ при різних енергіях збудження показано можливість утворення нерегулярних розчинів оксиду ітрію і європію та особливості структури поверхневих і об'ємних шарів. Визначено постійну часу загасання КЛ для свічення 612 нм, величина якої перебуває в межах (1.8–4.1) мс. Показано, що дана величина є складною функцією від виду атмосфери напилення плівок, концентрації активатора і тривалості збуджуючих імпульсів. Досліджено особливості розгоряння КЛ і запропоновано на основі затримки розгоряння КЛ аналізувати структурну досконалість тонких плівок $Y_2O_3:Eu$.

Ключові слова: оксид ітрію, катодолюмінесценція, тонкі плівки.