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Effect of Activator Concentration on the Morphology of Thin Films of Y_2O_3:Eu Obtained by Radio-Frequency Sputtering

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Thin Y_2O_3:Eu films with activator concentrations of 1, 2.5, and 5 mol.% are obtained by radio-frequency (RF) ion–plasma sputtering. A study of the surface morphology of thin films by atomic force microscopy (AFM) show that, with an increase in the activator concentration, the average size of the crystalline grains forming the films increases. Based on the analysis of the results of grain-size distribution, it is found that, at activator concentrations of 1 and 5 mol.%, monomodal distributions are observed, and, at an activator concentration of 2.5 mol.%, a bimodal distribution is observed due to the growth of secondary grains. An analysis of the lognormal dependence is carried out that is used to describe the size distribution of crystalline grains.

Методою високочастотного (ВЧ) йонно-плазмового розпорошення одержано тонкі плівки Y_2O_3:Eu з концентрацією активатора у 1, 2,5 і 5 мол.%. Дослідження морфології поверхні тонких плівок методою атомно-силової мікроскопії (АСМ) показали, що із зростанням концентрації активатора зростає середній розмір кристалічних зерен, які формують плівки. На основі аналізи результатів розподілу розмірів зерен встановлено, що за концентрацій активатора у 1 і 5 мол.% спостерігаються мономодальні розподіли, а за концентрації активатора у 2.5 мол.% спостерігається бімодальний розподіл за рахунок зростання вторинних зерен. Проведено аналізу логнормальної залежности, яку використано для опису розподілу розмірів кристалічних зерен.

Key words: yttrium oxide, thin film, nanocrystallite, lognormal distribution.

Ключові слова: оксид ітрію, тонка плівка, нанокристаліт, логнормальний розподіл.

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1. INTRODUCTION

Today, interest in thin films of metal oxide materials is due to the wide possibilities of their use in optoelectronics and instrument engineering. Among them, a special place is occupied by materials doped with rare-earth ions (REI), one of the most used among which is europium Eu^{3+}. In particular, Y_2O_3:Eu^{3+} is the most efficient phosphor that emits in the red region of the spectrum [1–3]. Considering the linear dependence of the luminance of the glow on the current density and excitation energy, well-known manufacturers use only Y_2O_3:Eu^{3+} as the red component of projection televisions, as well as when creating flat full-colour vacuum fluorescence displays (VFD) and displays with field emission (DFE). The combination of small sizes of crystalline particles and the presence of a dopant, a luminescent centre, and a Eu^{3+} ion provide a uniform screen coating during the deposition of thin Y_2O_3:Eu^{3+} films consisting of nanocrystalline grains. This improves the efficiency and stability of luminescence and the expansion of potential applications [4–6]. Taking into account that the luminescence efficiency in thin Y_2O_3:Eu^{3+} films is determined by the size, morphological, and structural characteristics of nanoparticles, we studied the effect of the concentration of the Eu^{3+} activator on these characteristics. The films were obtained by the method of radio-frequency (RF) ion-plasma sputtering, which is considered optimal for applying semiconductor and dielectric films and allows you to control the structure and stoichiometry of the resulting films [7]. Among the high-precision methods for determining the size and morphology of nanoparticles, there is atomic force microscopy (AFM), which was used in this work.

2. EXPERIMENTAL TECHNIQUE

Thin films of Y_2O_3:Eu^{3+} with a thickness of 0.2–1.0 μm obtained by RF ion-plasma sputtering and discrete evaporation in vacuum on fused υ-SiO_2 quartz substrates. RF sputtering was carried out in an argon atmosphere in a system using the magnetic field of external solenoids for compression and additional ionization of the plasma column. The feedstock was Y_2O_3 grade 'ИтО-И' and Eu_2O_3 with grade 'ос.ч'. The activator concentration was 1, 2.5 and 5 mol.%. After the deposition of the films, they were heat-treated in air at a temperature of 950–1000°C.

Using the x-ray diffraction analysis (Shimadzu XDR-600), the structure and phase composition of the films were studied. X-ray diffraction studies showed the presence of a polycrystalline structure with a predominant orientation in the (222) plane. The form of the obtained diffraction patterns is almost analogous to the diffraction patterns of pure Y_2O_3 films, which we presented in [8]. All diffraction maxima are identified according to the selection rules and belong to the space group $T_h^7 = Ia^3$, which indicates the cubic structure of the obtained films.

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

3. RESULTS AND DISCUSSION

Microphotographs of the surface of $Y_2O_3:Eu^{3+}$ films obtained by the RF sputtering with different activator concentrations are shown in Fig. 1.

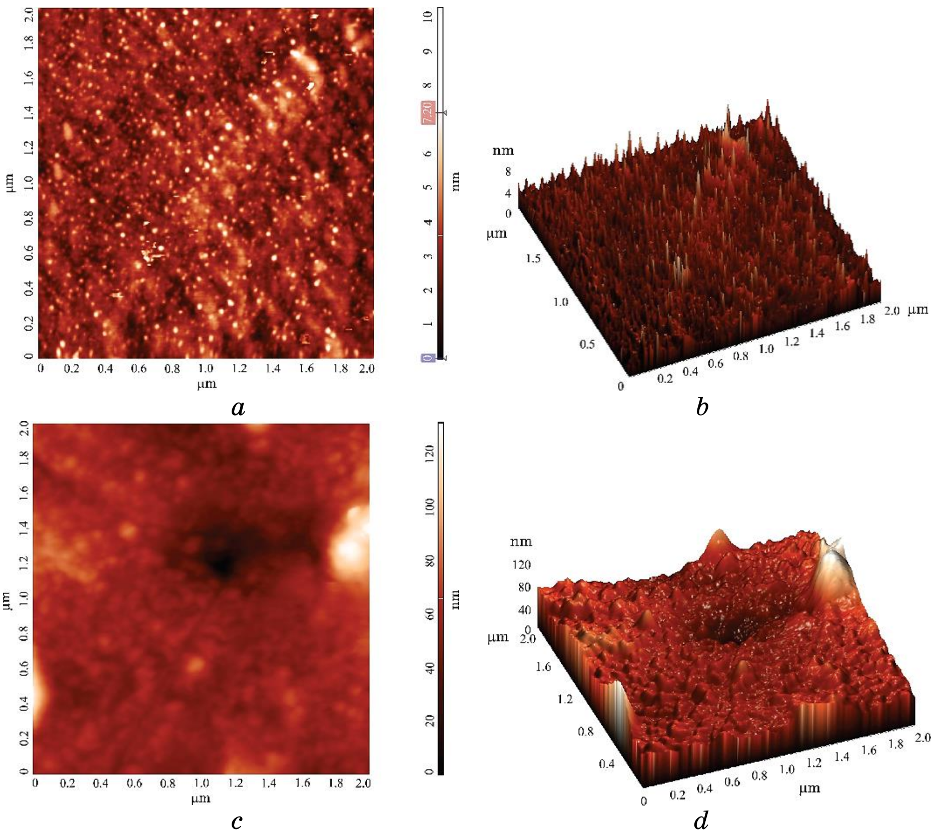
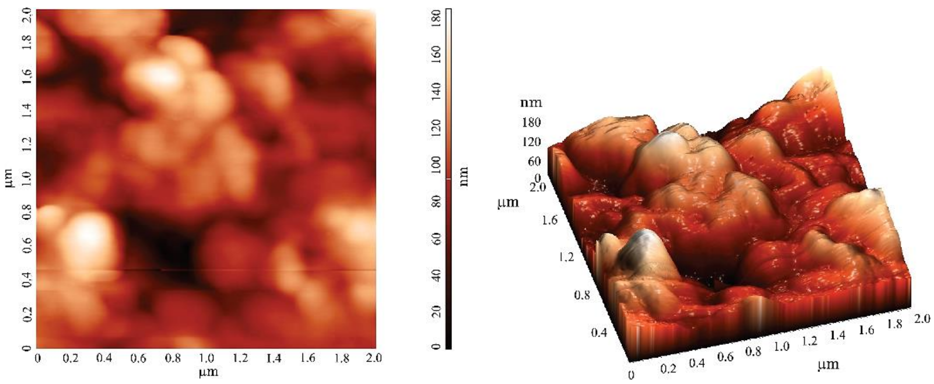


Fig. 1. Image of the surface morphology of thin Y_2O_3:Eu films obtained by RF sputtering in an argon atmosphere at activator concentrations of 1.0 mol.% (*a*, *b*), 2.5 mol.% (*c*, *d*) and 5 mol.% (*e*, *f*). Images *a*, *c*, *e* are two-dimensional; *b*, *d*, *f* are three-dimensional.



e *f*

Continuation **Fig. 1.**

TABLE 1. Parameters of crystalline grains of thin Y_2O_3:Eu films.

Parameter	Eu^{3+} activator concentration		
	1.0 mol.%	2.5 mol.%	5.0 mol.%
Root mean grain diameter, nm	15.7	63.1	196.0
Root mean square roughness, nm	0.7	5.7	34.1
Max height grains, nm	6.1	48.4	213.6

The topography of the samples was quantitatively characterized by standard parameters: root mean square roughness, maximum grain height with diameter and grain height, which were calculated according to AFM data for sections of the same size (2000×2000 nm). The characteristic parameters of thin Y_2O_3 films with different activator concentrations are given in Table 1. As can be seen from the results obtained, the activator concentration has a significant effect on the size of crystalline grains and the surface roughness of the films.

An analysis of AFM images (Fig. 1) and parameters of crystalline grains (Table 1) on the surface of Y_2O_3:Eu films shows that with an increase in the activator concentration in thin Y_2O_3:Eu films, the sizes of crystalline grains that form these films grow. Such an increase in the size of crystalline grains and, in particular, an increase in the root mean square roughness parameter indicates a complication of the surface structure.

A comparison of the histograms of the distribution of grain heights (Fig. 2) shows that an increase in the activator concentration in thin Y_2O_3:Eu films leads to the formation of sharper peaks on the film surface.

An increase in the size of crystalline grains and a simultaneous de-

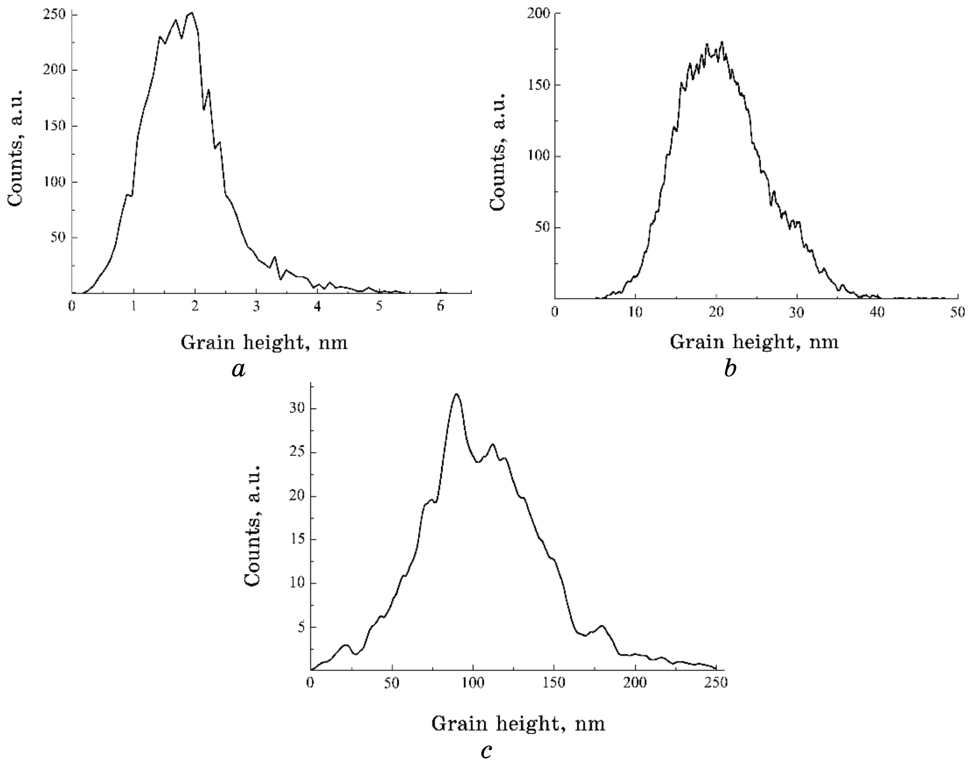


Fig. 2. Grain distribution on the AFM image of thin Y_2O_3:Eu films obtained by RF sputtering with an activator concentration of 1.0 mol.% (*a*), 2.5 mol.% (*b*) and 5.0 mol.% (*c*).

crease in the concentration of grains in thin Y_2O_3:Eu films with an increase in the activator concentration (Fig. 1) indicate the possibility of the transition of the surface of the Y_2O_3:Eu film with an increase in the activator concentration to a more nanostructured state due to crystallization of the surface layer.

The characteristic size distributions of grain diameters in thin Y_2O_3:Eu films with different activator concentrations are shown in Fig. 3.

A thorough inspection, which analysed the growth of crystalline grains and the evolution of crystalline structures [9], showed that polycrystalline thin films with a thickness of about 1 μm or less often have 2*D* similar structures, for which most grain boundaries are perpendicular to the film thickness. Most of the materials analysed in [9] have nonequilibrium grains with sizes that are smaller than the film thickness and form two-dimensional structures only after annealing. Based on numerous results in Ref. [9], it was also concluded that the for-

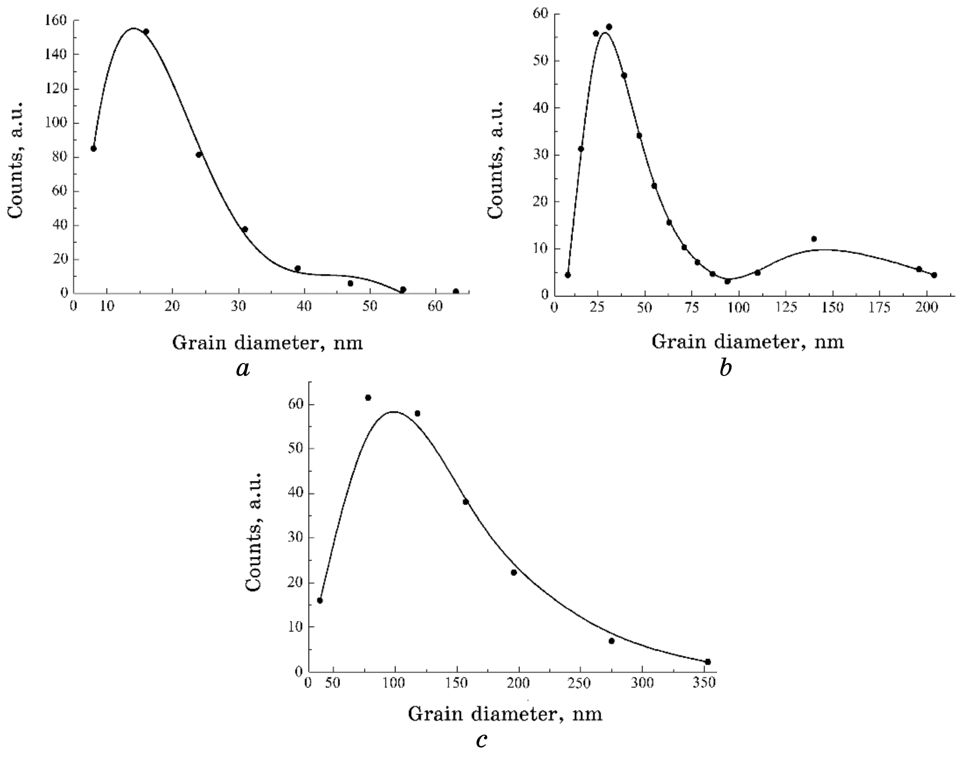


Fig. 3. Distribution of grain diameters and calculated approximation of the diameter distribution on AFM images of thin Y_2O_3:Eu films obtained by RF sputtering with an activator concentration of 1.0 mol.% (*a*), 2.5 mol.% (*b*) and 5.0 mol.% (*c*).

mation of grains in thin films is difficult to describe accurately on the basis of model concepts or analysis of experiments that are used to study foam or monolayers. In general, the grain sizes in polycrystalline films are lognormally distributed in size.

In some cases, further grain growth occurs due to the 'abnormal' or predominant growth of several grains, which usually have specific crystallographic orientation ratios relative to the plane of the substrate surface. When the number of growing grains leads to a 'matrix' of grains with static limits, a bimodal grain size distribution develops, which is called the growth of secondary grains [10]. Grains that grow abnormally often have a limited or uniform texture. Secondary grain growth in thin films usually includes evolution in the distribution of grain textures, as well as evolution in grain size distribution. Using the chi-squared χ^2 Pearson criterion, it was found that the size distribution of grain diameters in thin Y_2O_3:Eu films at different activator concentrations describes a lognormal distribution. Recall that a random variable has a lognormal distribution, if its logarithm has a normal distribution. The lognormal distribution is fully described by two parameters: μ (mathematical expectation) and σ (standard deviation) of the associated normal distribution.

To analyse the results of grain diameter size distributions in thin Y_2O_3:Eu films with a change in activator concentration, we use the lognormal distribution technique [11].

The density function of the lognormal distribution with parameters μ and σ has the form:

$$f(d) = \frac{1}{d\sigma\sqrt{2\pi}} \exp\left\{-\frac{\left(\ln(d) - \mu\right)^2}{2\sigma^2}\right\}, \quad (1)$$

The parameters μ and σ are calculated by the relations:

$$\mu = \ln\left(\bar{d}\right) - 0.5\ln\left(V^2 + 1\right), \quad (2)$$

$$\sigma = \sqrt{\ln\left(V^2 + 1\right)}, \quad (3)$$

where $\bar{d} = M(d) = \frac{1}{n}\sum_{i=1}^{n} n_i d_i$ is expected value, n is sample size, $V = S/M$ is coefficient of variation, $S = \sqrt{D}$ is standard deviation, $D = \frac{n}{n-1}\left(M\left(d^2\right) - M^2(d)\right)$ is dispersion, $M\left(d^2\right) = \frac{1}{n}\sum_{i=1}^{n} n_i d_i^2$.

Based on the calculations, it was found that at an activator concentration in thin films of Y_2O_3:Eu 1.0 mol.% and 5.0 mol.% Monomodal distributions are observed with maxima of grain diameters at 19 and 137 nm, respectively. At an activator concentration of 2.5 mol.%, a bimodal distribution is observed with maxima of about 41 and 160 nm. The characteristic parameters of the lognormal distribution of grain diameters in thin Y_2O_3:Eu films with a change in the activator concentration are given in Table 2.

Analysing the obtained values of the coefficient of variation for the distribution of the diameter sizes of low-dimensional grains, we notice

TABLE 2. Parameters of the lognormal distribution of grain sizes in thin Y_2O_3:Eu films.

Concentration of activator, mol.%	$E(d)$, nm	μ	σ	S, nm	V
1.0	19.3	2.85	0.48	9.7	0.50
2.5	40.7	3.58	0.50	21.7	0.53
	159.7	5.05	0.22	35.4	0.22
5.0	137.4	4.79	0.51	75.7	0.55

a somewhat significant scatter in the values of grain sizes, due to the asymmetry of the lognormal distribution and the presence of a 'long' right tail. Given the relationship between lognormal and normal divisions, going over to the normal distribution, it is easy to see that the data set under study is homogeneous, since, for thin films of Y_2O_3:Eu with a concentration of 1 mol.%, 2.5 mol.% and 5 mol.%, the coefficient of variation is equal to $V_n = 0.176$ and $V_n = 0.125$, respectively [11].

For the distribution of large grains in thin Y_2O_3:Eu films with an activator concentration of 2.5 mol.%, an even more uniform distribution pattern and, correspondingly, smaller mean square deviations S (the coefficient of variation for the corresponding normal distribution is equal to $V_n = 0.044$) are observed. In addition, it can be seen from the obtained results (Table 2) that, regardless of the activator concentration in thin Y_2O_3:Eu films, the lognormal distribution for describing low-dimensional grains is characterized by close values of the shape parameter $\sigma = 0.48$–0.51. Moreover, for these distributions, with an increase in the activator concentration, an increase in the scale parameter μ is observed from 2.85 to 4.79.

4. CONCLUSIONS

It has been established that during RF ion–plasma sputtering polycrystalline Y_2O_3:Eu films consisting of nanometre grains are formed. According to AFM data, it is shown that with an increase in the activator concentration from 1 to 5 mol.%, the average diameters of crystalline grains grow from 15.7 nm to 196.0 nm. Based on the analysis of grain size distribution results, it was found that at an activator concentration of 1.0 and 5.0 mol.%, monomodal distributions are observed, and, at an activator concentration of 2.5 mol.%, a bimodal distribution is observed due to the growth of secondary grains. The obtained dependences of the grain size distributions are well described by the lognormal dependence with close values of the shape parameter σ and the scale parameter μ growing with increasing activator concentration.

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