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Synthesis and Structure of Y_2O_3:Eu Thin Films

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The Y_2O_3:Eu thin films were obtained by radio frequency (RF) ion-plasma sputtering in different atmospheres. The phase composition of the obtained films was investigated based on x-ray phase analysis and various causes of diffraction stripes expansion were considered. It is shown that an increase in the O_2 sputtering atmosphere of Ar leads to a decrease in the size of the nanocrystallites forming the Y_2O_3:Eu film from 5.9 to 5.0 nm and a decrease in the structural perfection of the films and an increase in their mechanical stresses.

Методом високочастотного (ВЧ) йонно-плазмового розпорошення в різних атмосферах одержано тонкі плівки Y_2O_3:Eu. На основі рентґенофазової аналізи досліджено фазовий склад одержаних плівок і розглянуто різні причини розширення дифракційних смуг. Показано, що збільшення у розпорошувальній атмосфері Ar вмісту O_2 приводить до зменшення розмірів нанокристалітів, які формують плівку Y_2O_3:Eu, від 5,9 до 5,0 нм і зменшення структурної досконалости плівок та збільшення в них механічних напружень.

Методом высокочастотного (ВЧ) ионно-плазменного распыления в различных атмосферах получены тонкие плёнки Y_2O_3:Eu. На основе рентгенофазового анализа исследован фазовый состав полученных плёнок и рассмотрены различные причины уширения дифракционных полос. Показано, что увеличение в распылительной атмосфере Ar содержания O_2 приводит к уменьшению размеров нанокристаллитов, формирующих плёнку Y_2O_3:Eu, от 5,9 до 5,0 нм, уменьшению структурного совершенства плёнок и увеличению в них механических напряжений.

Key words: yttrium oxide, thin films, nanocrystallite.

Ключові слова: оксид ітрію, тонкі плівки, нанокристаліти.

Ключевые слова: оксид иттрия, тонкие плёнки, нанокристаллиты.

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1. INTRODUCTION

Among the materials for optoelectronics, luminescent materials used in the creation of displays, scintillators, devices for recording and visualization of information occupy a special place. The cubic yttrium oxide is one widespread the crystalline matrix of phosphors, which activated by rare earth ions [1–3]. Among them, the most investigated phosphor of micron dispersion is the Y_2O_3:Eu phosphor with red colour of emission. The results of the study of this material can be used as basic information to analyse the characteristics and mechanism of luminescence in the study of the effect of dimensional effects on the radiation efficiency of submicron phosphors [4]. In recent years, studies on Y_2O_3 nanoparticles activated by rare earth metals have been actively pursued in this area [5, 6]. Such systems have unique spectroscopic properties, such as anti-Stokes luminescence, quantum firing and prolonged afterglow, due to the presence of rare earth metals [7]. The combination of small sizes of crystalline particles and the presence of alloying impurities—luminescent centres—of rare earth metal ions ensures the high efficiency and stability of the luminescence of such materials, which contributes to the expansion of potential applications. This led to structural studies of thin Y_2O_3: Eu films obtained by radio frequency (RF) ion-plasma sputtering, depending on the composition of the sputtering atmosphere. This method is optimal for the production of homogeneous semiconductor and dielectric films.

2. EXPERIMENTAL TECHNIQUE

Y_2O_3:Eu thin films 0.2–1.0 μm thick obtained by RF ion-plasma sputtering on fused quartz υ-SiO_2 substrates. RF sputtering was carried out in an atmosphere of argon, oxygen or a mixture of these gases in the system using the magnetic field of external solenoids for compression and additional ionization of the plasma column. As the raw material were used Y_2O_3 grade ИтО-И and Eu_2O_3 with grade ‘ос.ч’. The activator concentration was 1 ml.%.

The method of x-ray diffraction analysis (Shimadzu XDR-600) for the structure and phase composition of the obtained films was investigated. X-ray diffraction studies have shown the presence of a polycrystalline structure with a predominant orientation in the plane (222). However, in the Y_2O_3:Eu films obtained in an argon atmosphere, the reflex from the plane (440) has a somewhat higher intensity. All diffraction peaks 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 films obtained.

3. RESULTS AND DISCUSSION

X-ray phase analysis is one of the most reliable ways of determining the composition and structure of a test substance. Figure 1 shows that x-ray diffraction patterns of thin films of Y_2O_3:Eu obtained by RF ion-plasma sputtering in different atmospheres. A detailed examination of the diffraction patterns of Y_2O_3:Eu films deposited on a non-heated substrate (without additional annealing in air) shows that they contain a relatively wide band in the region $2\Theta \approx 28–31°$, which is caused by the reflection from the plane (222) in Y_2O_3 cubic modification. For the ordered structure of Y_2O_3, the value of maximum is $2\Theta \approx 29.18°$. At the same time, we found that with an increase in the oxygen content in the composition of the sputtering atmosphere (Fig. 1, curves *1–5*), the reflection maximum is shifted towards larger values of the 2Θ angle and its asymmetry increases. The reason for this shift may be a partial decrease in the interplanar spacing in Y_2O_3:Eu. Using RF sputtering, the structure of the obtained films depends on such factors as the substrate temperature, the energy and composition of the bombarding ions, and the

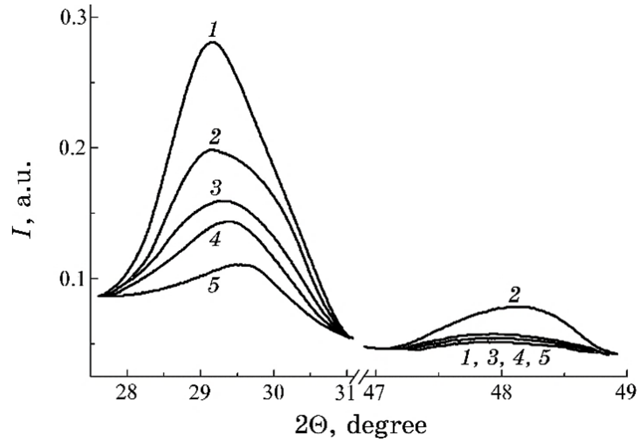

Fig. 1. X-ray diffraction patterns of Y_2O_3:Eu thin films obtained by RF sputtering (without annealing), deposited in an atmospheres of 100% Ar (*1*), 75% Ar + 25% O_2 (*2*), 50% Ar + 50% O_2 (*3*) 25% Ar + 75% O_2 (*4*), 100% O_2 (*5*).

composition of the sputtering target. In the presence of oxygen in the sputtering atmosphere, determining for the formation of films is the creation of defects, which include excess oxygen, because of the interaction of oxygen that contained in the plasma with the created of Y_2O_3:Eu film. In particular, our studies have shown that under the same conditions of sputtering of the target, the temperature of the Y_2O_3:Eu films are approximately 1.5 times higher at sputtering in an oxygen atmosphere than at sputtering in an argon atmosphere. Most likely, the observed increase in temperature is caused by an increase in the intensity of the bombardment by O ions of the created film [8].

Another reason the high sensitivity of the structure of Y_2O_3:Eu films to the content of oxygen in the sputtering atmosphere can be a change in the properties of the target itself at reactive deposition. As shown in [9], the material of target is sputtered as a result of direct impulse transfer from the ion that is bumping and the obtaining energy by a surface atom, and also due to the process of energy release in the surface zone of the target, when elastic collisions of internal atoms are sufficient to knock out surface particles [10]. Most experimental studies, especially when sputtering dielectrics and refractory materials, vindicate on the benefit of the mechanism of the first type. However, in the reactive environment, the second mechanism can also have a significant influence on the process of sputter [11]. At the increase of the partial pressure of oxygen in the sputtering atmosphere, the darkening of the surface of the yttrium oxide target was observed. This indicates a change in the composition and structure of the target surface due to the release of energy in the surface zone of the target because of the occurrence of physic-chemical processes involving oxygen.

As known, the width of the diffraction bands depends on the presence in the sample of defects, mechanical stresses and on the size of the regions of coherent scattering (the size of the nanocrystallites). Thus, the data on the widths of diffraction bands on diffraction patterns can be used to determine the size of the particles forming the sample and the mechanical stresses in them [12]. According to Debye and Scherrer, the relationship between bandwidth and crystallite size d (nm) is given by the equation

$$d = 0.94\lambda/\beta\cos\theta, \quad (1)$$

where λ is the wavelength equal to 0.15418 nm (CuK_α-radiation), β is the width of the band at half height, θ is diffraction angle.

The second reason for the expansion of the bands on the diffraction patterns may be the defects and imperfections in the structure of the crystallites, which cause the stresses in the crystals. Expanding of bands associated with stresses described by the relation

$$\varepsilon = \beta/4\mathrm{tg}\theta\,, \qquad (2)$$

where ε is the average value of the crystal-lattice stresses.

In the second case, for the characteristic bands on the diffraction pattern, the ratios $\beta/(4\mathrm{tg}\theta)$ will be close in magnitude. If, however, the band expansion is due to the presence of very small particles in the sample, then the values of $\beta\cos\theta$ will be close for the characteristic bands. Table shows the results of calculations of the crystallite sizes d and the average values of the crystal-lattice stresses ε in Y_2O_3:Eu films, depending on the composition of the RF sputtering atmosphere, performed for the main characteristic band—29.2° from the plane (222).

A graphical representation of the obtained results is shown in

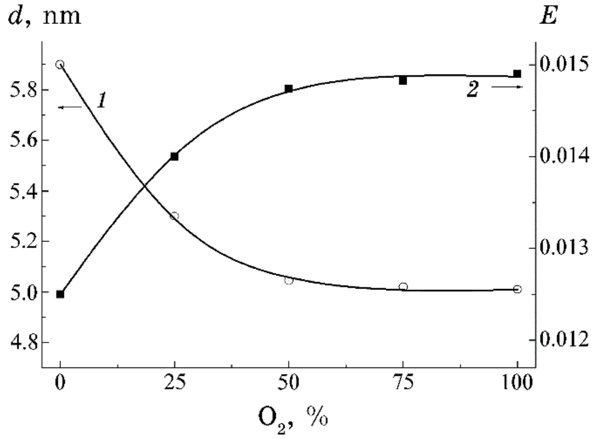

Fig. 2. The dependence of the nanocrystallite sizes (*1*) and the average stresses of the crystal lattice (*2*) in Y_2O_3:Eu thin films on the O_2 content in the sputtering atmosphere Ar.

TABLE. Analysis of diffraction band extensions from the plane (222) in thin films Y_2O_3:Eu, depending on the composition of the atmosphere of the RF-sputtering.

Sputtering atmosphere	Angle 2θ, degree	β	*d*, nm	ε
100% Ar	29.2	0.0279	5.9	0.0125
75% Ar + 25% O_2	29.2	0.0314	5.3	0.0140
50% Ar + 50% O_2	29.3	0.0332	5.0	0.0148
25% Ar + 75% O_2	29.4	0.0332	5.0	0.0147
100% O_2	29.6	0.0332	5.0	0.0146

Fig. 2. The analysis of the results in Table and Fig. 2 indicates that for films deposited in a sputtering atmosphere containing 50% or more O_2, defects in nanocrystallites that cause mechanical stresses are the main reason for the expansion of diffraction bands. This indicates that the addition of O_2 to the sputtering atmosphere reduces the structural perfection of Y_2O_3:Eu thin films and results in a reduction in the size of nanocrystallites forming a film from 5.9 to 5.0 nm, respectively.

4. CONCLUSIONS

Based on x-ray analysis data, it is established that Y_2O_3:Eu films obtained by the RF sputtering are formed in cubic modification of Y_2O_3, and the composition and type of formed modification are independent of the content in the sputtering atmosphere of Ar and O_2 gases. Analysis of the diffraction band expansion based on the estimation of the magnitude of the crystal lattice stresses and the size of the coherent-scattering regions showed that the increase O_2 in the sputtering atmosphere of the Ar results in a decrease in the size of the nanocrystallites forming the film Y_2O_3:Eu from 5.9 to 5.0 nm and a decrease in the structural thickness and increase their mechanical stresses.

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