# Features of Deposition and Formation of the Structure of Y$_2$O$_3$:Eu Thin Films Obtained by Radio-Frequency Sputtering

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The structure, surface morphology, and features of deposition of thin Y$_2$O$_3$: Eu films with radio-frequency ion-plasma sputtering are studied. The presence of the optimal working-gas pressure, at which the deposition rate of films is maximum, is revealed. Its value is determined by the gas composition and geometrical parameters. The working-gas composition influence on the deposition rate of Y$_2$O$_3$:Eu films is investigated.

Досліджено структуру, морфологію поверхні й особливості нанесення тонких плівок Y$_2$O$_3$:Eu при високочастотному йонно-плазмовому розпорошенні. Встановлено наявність оптимального тиску робочого газу, величина якого визначається складом газу і геометричними параметрами та за якого швидкість нанесення плівок є максимальною. Досліджено вплив складу робочого газу на швидкість нанесення плівок Y$_2$O$_3$:Eu.

Исследованы структура, морфология поверхности и особенности нанесения тонких плёнок Y$_2$O$_3$:Eu при высокочастотном ионно-плазменном распылении. Установлено наличие оптимального давления рабочего газа, величина которого определяется составом газа и геометрическими параметрами и при котором скорость нанесения плёнок является максимальной. Исследовано влияние состава рабочего газа на скорость нанесения плёнок Y$_2$O$_3$:Eu.

**Key words:** yttrium oxide, thin films, crystallites.

**Ключові слова:** оксид ітрію, тонкі плівки, кристаліти.

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## 1. INTRODUCTION

Recently, the metal oxide materials are attracting much attention through wide possibilities of their use in modern optoelectronics and instrument engineering. The large band gap as well as the high values of dielectric permeability make them promising in the development of full-colour screens, scintillators, reflective coatings, and UV detectors. The cubic yttrium oxide is one of widespread crystalline matrixes of phosphors, which are 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 disadvantage of this material is the unsatisfactory morphology of the particles that does not provide the smooth and uniform coating of screens and high resolution. This situation leads to the active study of various nanostructured objects based on $Y_2O_3$: Eu [4–7]. The combination of small sizes of crystalline particles and the presence of a $Eu^{3+}$ ion dopant as the luminescent centre ensures uniform screen coverage during the deposition of $Y_2O_3$:Eu thin films, which consist of nanocrystalline grains, improves the efficiency and stability of the luminescence and promotes the expansion of potential application ranges. Thus, the investigation of the structure and conditions of fabrication of $Y_2O_3$:Eu thin films, which are formed from nanocrystalline grains, is important for their further application in various fields of science and technology. In this work, such studies are carried out for $Y_2O_3$:Eu thin films obtained by radio-frequency ion-plasma sputtering; the use of this method leads to the deposition of the most homogeneous semiconductor and dielectric films [8].

## 2. MATERIALS AND METHODS

$Y_2O_3$:Eu thin films obtained by radio-frequency ion-plasma sputtering in an atmosphere of a mixture of argon and oxygen from 100% atmosphere of oxygen to 100% atmosphere of argon in the system using the external magnetic-field solenoids for compression and for additional ionization of the plasma column on fused quartz $\upsilon$-$SiO_2$ substrates. The thickness of films is 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 'ос.ч'. The activator concentration was 2.5 ml.%. After deposition of films, the heat treatment in air at 950–1050°C was held.

The study of the structure of the obtained films was carried out on a DRON-3 X-ray diffractometer and an HZG-4A automated diffractometer for the investigation of polycrystalline substances. The

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

## 3. RESULTS AND DISCUSSION

A detailed study of the diffraction patterns of $Y_2O_3$:Eu thin films deposited by RF sputtering on substrates without heating (without additional annealing in air atmosphere) reveals a relatively wide band in the $2\Theta \approx 28-31°$ region (Fig. 1, *a*), which is due to the reflection from 222 plane. For the ordered structure of $Y_2O_3$, the value 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 $2\Theta$ 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 composition of the sputtering target. In the presence of oxygen in the spray atmosphere, determining for the formation of films, there is a creation of defects, which include excess oxygen, because of the interaction of oxygen 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
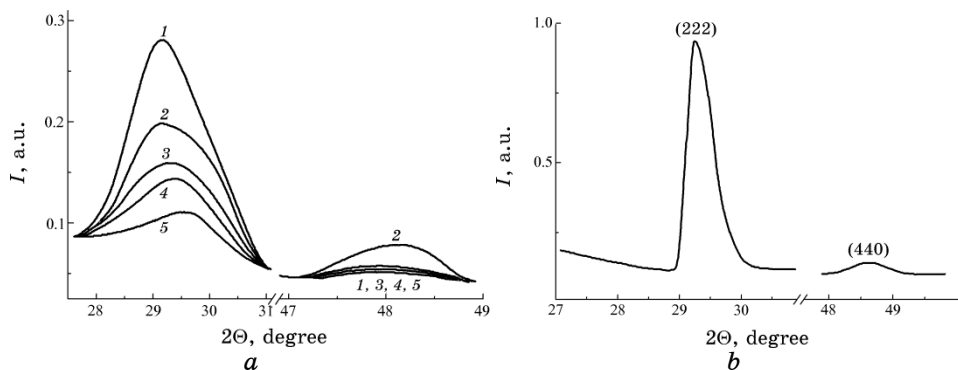


**Fig. 1.** X-ray diffraction patterns of (*a*) $Y_2O_3$:Eu thin films obtained by RF sputtering (without annealing) and deposition in an atmospheres of 100% Ar (*1*), 75% Ar + 25% $O_2$ (*2*), 50% Ar + 50% $O_2$ (*3*) 25% Ar + 75% $O_2$ (*4*), 100% $O_2$ (*5*) and (*b*) the film of annealed at 1000°C in air atmosphere and obtained in argon atmosphere.

$Y_2O_3$: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 [9].

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 [10], the material of target is sputtered because of direct impulse transfer from the bumping ion and the obtaining energy by a surface atom, and 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 [11]. Most experimental studies, especially under sputtering of dielectrics and refractory materials, demonstrate 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 [12]. At the increasing 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 physical-chemical processes involving oxygen.

Thus, the sputtering of an yttrium oxide target occurs as a result of knocking out the surface atoms due to the direct transfer of momentum from the bombarding ion, and in the case of relatively high concentrations of oxygen in the sputtering atmosphere, as a result of the emission of surface atoms [13] due to the release of energy in the surface zone of the target. As a result, the appearance of a change in the sputtering mechanism and the intensive bombardment of film surface with negative oxygen ions leads to a change in the structure of $Y_2O_3$:Eu films, the creation of a larger number of defects, which include excess oxygen, and it manifests itself in X-ray diffraction patterns (Fig. 1, *a*). After high-temperature annealing, the intensity of the diffraction maxima increases sharply, and their width significantly decreases (Fig. 1, *b*). The obtained results indicate that, at annealing in the temperature range of 950–1050°C, the ordering structure of the cubic modification of $Y_2O_3$ occurs.

As known, the width of the diffraction maxima depends on the size of the coherent scattering regions (the size of the crystallites). In this case, the crystallite sizes $d$ are determined from the well-known Debye–Scherrer equation [14] by the expansion of X-ray diffraction bands: $d = 0.94\lambda/(\beta\cos\Theta)$, where $\lambda = 0.15418$ nm is wavelength of Cu$K_\alpha$-radiation, $\beta$ is the width of the diffraction band at
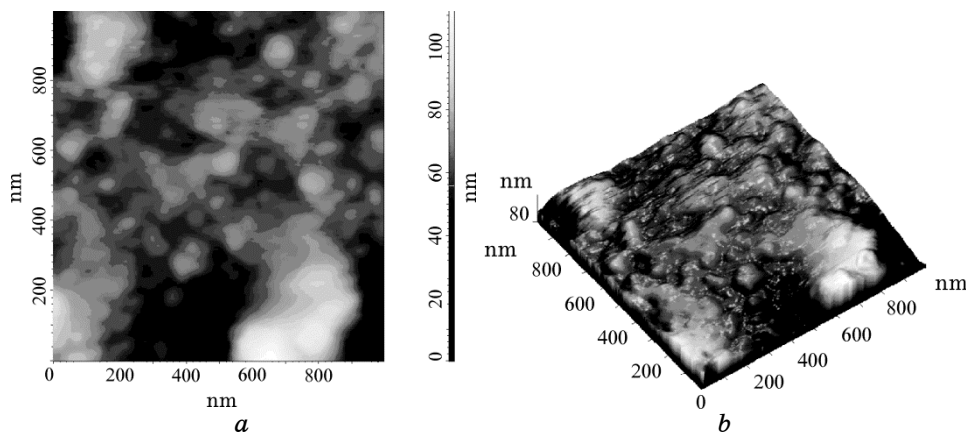
**Fig. 2.** The image of the surface morphology of annealed $Y_2O_3$:Eu thin films obtained by the method of radio-frequency ion-plasma sputtering in argon atmosphere at the activator concentration of 2.5 mol.% (*a*, *b*). Image (*a*) is two-dimensional, and image (*b*) is three-dimensional.

half height, and $\Theta$ is diffraction angle. Based on the obtained results, the sizes of crystallites, from which $Y_2O_3$:Eu thin films are formed, depending on the preparation conditions, are estimated. In particular, as found, at RF sputtering in argon atmosphere, the crystallite size is $d = 5.5-6.0$ nm, and at sputtering in oxygen, $d = 6.5-7.0$ nm. The use of annealing leads to increase in the size of crystallites due to their growth and sintering. For example, at annealing temperature of 1000°C, the crystallite sizes reach $d = 28.0-32.0$ nm.

Micrographs of the surface of annealed $Y_2O_3$:Eu films obtained using AFM are shown in Fig. 2. The diameters of grains on the film surface are on average of 43.0 nm (Fig. 2, *a*), the average square roughness of surface is about 17.5 nm. The obtained values of grain sizes, which form the surface of film, are rather close to the values obtained by the Debye−Scherrer equation for the expansion of X-ray diffraction bands.

Our studies show a significant effect of the pressure and composition of the gas, in which thin films are deposited, on the deposition rate of $Y_2O_3$:Eu thin films.

The dependence of the deposition rate of $Y_2O_3$:Eu thin films on the pressure of the working gas of Ar is shown in Fig. 3. As seen in Fig. 3, this dependence has the maximum value of the deposition rate at a certain value of the pressure of the working gas. The decrease in the sputtering coefficient, which is estimated by the deposition rate of the substance on the quartz substrate, at increasing pressure, can be explained by reverse diffusion and backscattering.

At reverse diffusion, there is a diffusion return of sputtered atoms with an average kinetic energy $E_a$ approximately equal to the average kinetic energy of inert gas on the target, $E_g$ ($E_a \approx E_g$). In the case of backscattering, a return of sputtered atoms to the target is observed as a result of their scattering by the atoms of the working gas.

A strong decrease in the sputtering coefficient for target in the region of 10 Pa can be associated with an increase in the flux density of bombarding ions, which increase the local temperature of the target.
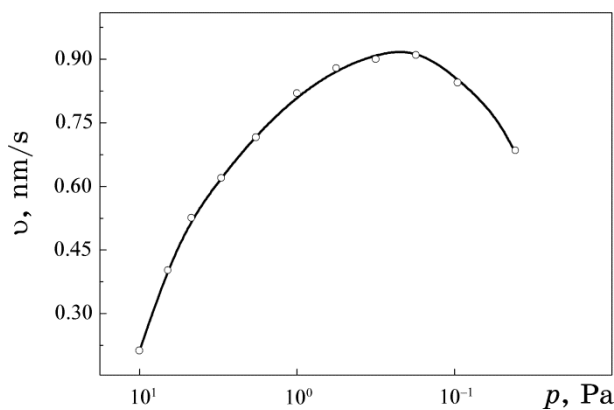


**Fig. 3.** Dependence of the deposition rate of $Y_2O_3$:Eu thin films at RF sputtering on the pressure of the working gas (Ar, 100%).
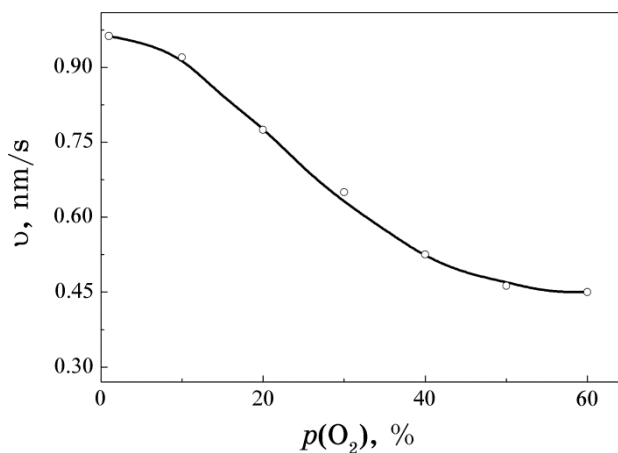


**Fig. 4.** Dependence of the deposition rate of $Y_2O_3$:Eu thin films at RF sputtering on the partial content of oxygen in the working atmosphere of Ar + $O_2$.

According to the experimental dependence (Fig. 3), the optimal pressure of the working gas of argon was equal to 0.89 Pa at sputtering of Y$_2$O$_3$:Eu thin films. Note that this value will change with a change of the geometrical parameters of the sputtering system and with a change in the composition of the working gas.

The dependence of the deposition rate of Y$_2$O$_3$:Eu thin films on quartz substrates at RF sputtering in the atmosphere of a mixture of Ar + O$_2$ gases with different composition by percentage is shown in Fig. 4.

According to the obtained results, an increase in the partial composition of oxygen in the mixture of the sputtering atmosphere of Ar + O$_2$ leads to a decrease in the deposition rate. This dependence can be explained by a decrease in the total kinetic energy of the ions bombarding the target, since $m_{Ar} > m_{O_2}$. In the region of 0–10% O$_2$ in the Ar + O$_2$ mixture, the deposition rate weakly changes at the change in the partial composition of oxygen, and such atmosphere can be used for the fastest deposition of Y$_2$O$_3$:Eu thin films.

## 4. CONCLUSIONS

The carried out studies show that, at the RF ion-plasma sputtering in an atmosphere of a mixture of argon and oxygen of different composition by percentage, the Y$_2$O$_3$:Eu thin films with crystallite sizes of 5.5–7.0 nm are obtained. Annealing in air leads to both the ordering of the cubic structure of films and the increasing of the crystallite size to 28.0–32.0 nm. The presence of an optimal pressure of the working gas at the deposition of films, which is determined by both the gas composition and the geometrical parameters of the sputtering system, is established. As shown, an increase in the partial pressure of oxygen in the mixture of the working Ar + O$_2$ gas leads to a decrease in the deposition rate of Y$_2$O$_3$:Eu thin films.

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