Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2022, т. 20, № 3, сс. 639–645

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ім. Г. В. Курдюмова НАН України)
Надруковано в Україні.

PACS numbers: 61.72.J-, 68.55.Ln, 72.20.Jv, 78.60.Hk, 81.15.Cd, 81.15.Jj, 82.80.Yc

Deposition of Thin Y_2O_3:Eu Films by Radio-Frequency Sputtering

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The dependence of the deposition rate of thin Y_2O_3:Eu films during RF sputtering on the pressure and composition of the working gas is studied. The presence of the optimal pressure of the working gas, at which the deposition rate is maximal, is established. The influence of the Eu^{3+}-activator concentration on the deposition rate of thin films and the brightness of cathodoluminescence of thin Y_2O_3:Eu films is studied. The explanation of the obtained results is carried out within the limits of backscattering and back-diffusion effects, and special attention is paid to the resonant charge-exchange mechanism.

Досліджено залежність швидкости нанесення тонких плівок Y_2O_3:Eu за ВЧ-розпорошення від тиску та складу робочого газу. Встановлено наявність оптимального тиску робочого газу, за якого швидкість нанесення є максимальною. Досліджено вплив концентрації активатора Eu^{3+} на швидкість нанесення тонких плівок і яскравість катодолюмінесценції тонких плівок Y_2O_3:Eu. Пояснення одержаних результатів проводиться в межах ефектів зворотнього розсіяння, зворотньої дифузії, а особлива увага приділяється механізму резонансної перезарядки.

Key words: yttrium oxide, thin films, radio-frequency sputtering, cathodoluminescence.

Ключові слова: оксид Ітрію, тонкі плівки, високочастотне розпорошення, катодолюмінесценція.

(Received 1 August, 2022)

1. INTRODUCTION

Among a large number of materials for optoelectronics, luminescent materials are of particular importance, which are used in the creation of displays, scintillators, and means for recording and visualizing information. In a number of materials that are promising for use in the creation of display screens, phosphors based on Y_2O_3:Eu deserve special attention, which make it possible to obtain thin-film coatings with a red luminescence [1–3]. The combination of nanosize crystalline particles and the presence of a dopant, luminescent Eu^{3+} centres, ensures the high efficiency and stability of the luminescence of this material, which contributes to the expansion of potential areas of its application [4–7].

Note that a number of methods are used to obtain thin films based on Y_2O_3:Eu [8–10]. Because of different perfection, such films obtained by different methods differ in their optical and luminescent properties. The requirements of high uniformity over the film area and preservation of the chemical composition of the film at high melting temperatures of the material led us to use the method of radio-frequency (RF) ion-plasma sputtering as a method leading to the deposition of the most uniform semiconductor and dielectric films [11, 12].

This paper presents the results of studies of the RF ion-plasma synthesis of thin Y_2O_3:Eu films depending on the pressure of the working gas in the spray system and the effect of the chemical composition of the spray atmosphere on the rate of film deposition.

2. EXPERIMENTAL TECHNIQUE

Thin Y_2O_3:Eu films with a thickness of 0.2–1.0 μm were obtained by RF ion-plasma sputtering in an atmosphere of variable composition from a mixture of argon and oxygen. For compression and additional ionization of the plasma column, the magnetic field of external solenoids was used. The films were deposited on fused quartz ν-SiO_2 substrates. The feedstock was Y_2O_3 'ИтО-И' brand and Eu_2O_3 'ос. ч.' brand. The concentration of the activator was 2.5–10.0 mol.%. 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 practically similar to the diffraction patterns of pure Y_2O_3 films, which we presented in [13].

Depending on the annealing atmosphere, the crystallite sizes changed slightly and were within $d = 5.5–7.0$ nm [14]. The use of high-temperature annealing due to the processes of growth and sintering led to an increase in the size of crystallites. In particular, at an annealing temperature of 1000°C, the sizes of crystallites increase to $d = 28.0–32.0$ nm [14].

3. RESULTS AND DISCUSSION

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

The dependence of the rate of deposition of thin Y_2O_3:Eu films on the pressure of the working gas Ar is shown in Fig. 1. As can be seen in Fig. 1, 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, estimated from the rate of deposition of a substance on a quartz substrate, with increasing pressure can be explained by back diffusion and backscattering. During back diffusion, there is a diffuse return of sputtered atoms, which have an average kinetic energy E_a approximately equal to the average kinetic energy of inert gas atoms E_g ($E_a \approx E_g$) incident on the target. During back reflection, the return of sputtered atoms to the target is observed because of their scattering on atoms of the working gas.

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

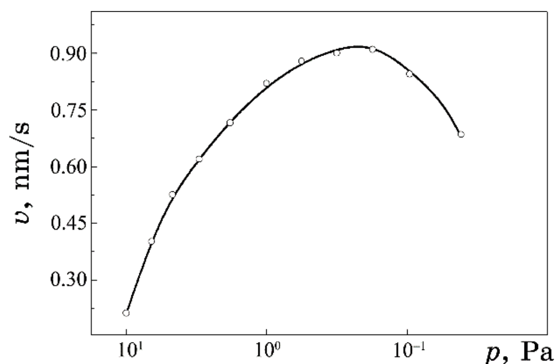


Fig. 1. Dependence of the deposition rate of thin Y_2O_3:Eu films during RF sputtering on the pressure of the working gas (Ar, 100%).

According to the obtained experimental dependence (Fig. 1), the optimal pressure of the working argon gas turned out to be 0.89 Pa during the deposition of thin Y_2O_3:Eu films. Note that this value will change with a change in the geometric parameters of the spray system and a change in the composition of the working gas.

The dependence of the rate of deposition of thin Y_2O_3:Eu films in the presence of the working gas, the $Ar + O_2$ mixture, on the density of the bombarding ions is shown in Fig. 2. As can be seen from the obtained results, an increase in the partial pressure of oxygen in the working gas mixture leads to a decrease in the deposition rate.

The dependence of the rate of deposition of thin Y_2O_3:Eu films on quartz substrates during RF sputtering in an atmosphere of $Ar + O_2$ gas mixtures of different percentage compositions is shown in Fig. 3.

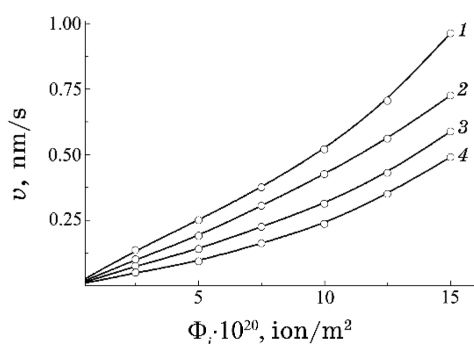


Fig. 2. Dependence of the rate of deposition of thin Y_2O_3:Eu films during RF sputtering on the density of bombarding ions at a partial oxygen pressure of 0% (*1*), 20% (*2*), 40% (*3*), 60% (*4*).

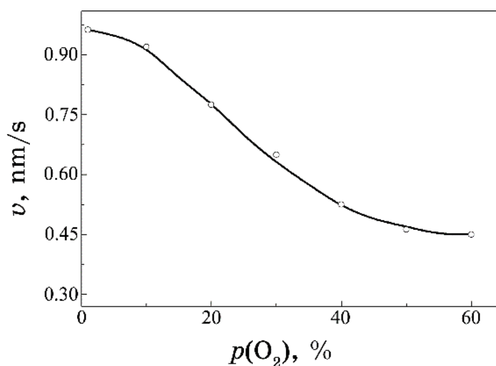


Fig. 3. Dependence of the deposition rate of thin Y_2O_3:Eu films during RF sputtering on the partial oxygen content in the $Ar + O_2$ working atmosphere.

According to the results obtained, it can be seen that an increase in the partial composition of oxygen in the $Ar + O_2$ sputtering atmosphere mixture leads to a decrease in the sputtering 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 an $Ar + O_2$ mixture, the deposition rate changes slightly with a change in the partial composition of oxygen, and such an atmosphere can be used for the rapid deposition of thin Y_2O_3:Eu films.

In addition to the studies described above, we studied the effect of the activator concentration on the structure of Y_2O_3:Eu films. It was found that, when the concentration of the activator varies from 0 to 10.0 mol.%, structure of the films was determined by the predominant orientation in the plane [222]. It should be noted that at an activator concentration of 7.5 mol.%, the less intense diffraction reflection from the [440] plane had the highest intensity among the films under study. Characteristically, thin Y_2O_3:Eu films with such an activator concentration exhibit intense cathodoluminescence (CL). The characteristic results obtained by us are given in Table.

It was found that the deposition rate of Y_2O_3:Eu films remained almost constant when the concentration of the activator changed from 0 to 10 mol.% at the steady-state parameters of the RF installation.

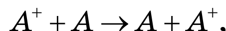
To analyse the results obtained in this work, it should be assumed that the thin Y_2O_3:Eu films under study were deposited in RF glow-discharge plasma. Such plasma is characterized by the processes of ion–atom and ion–ion charge exchange, because of which a number of effects are observed, such as backscattering and back diffusion. In addition to these processes, the results obtained in this work can be explained on the basis of one more factor—resonant charge exchange. It affects the dependence of the target-sputtering coefficient on the pressure of the working gas and the energy of the bombarding ions.

During deposition, resonant recharging proceeds according to a

TABLE. Influence of activator concentration on cathodoluminescence brightness in thin Y_2O_3:Eu films.

No.	Gas environment in the chamber		Concentration of Eu_2O_3, mol.%	CL brightness relative to the powder standard, %
	composition	pressure, Pa		
1	Ar 100 %	0.9	2.5	91
2	Ar 100 %	0.9	5	103
3	Ar 100 %	0.9	7.5	135
4	Ar 100 %	0.9	10	102

typical scheme [15]:



$$A^+ + A \to A + A^+,$$

where A^+ and A are the ion and atom of the working gas, respectively.

For a given distance R between the nuclei, the electron-transition frequency $\nu(R)$ from an atom to an ion of the working gas used is determined by the overlap of the wave functions of the electron [16]

$$\nu(R) \propto \exp(-jR),$$

where $j = \sqrt{J}$, J is the ionization potential of the atom.

On the other hand, sputtering of the target material is possible when the working gas ions reach a kinetic energy greater than a certain threshold value E_0.

As the distance between the interacting atom and ion decreases, the probability of resonant charge exchange increases. This leads to a decrease in the energy of the bombarding ions and, consequently, to a decrease in the target sputtering coefficient.

An increase in the speed of the bombarding ions with an increase in their energy leads to a decrease in the contact time. This leads to a decrease in resonant charge exchange and to an increase in the target sputtering efficiency.

Based on two mechanisms, one can explain the decrease in the target-sputtering coefficient with an increase in the pressure of the working gas. In this case, a decrease in the distance between the interacting atom and ion increases the probability of resonant charge exchange, which leads to a decrease in the energy of the bombarding ions due to an increase in the interaction time.

Therefore, to reduce the effect of resonant charge exchange on the film deposition process, it is necessary to work in the region of low pressure of the working gas at high ion energies.

4. CONCLUSIONS

The conducted studies show that the rate of deposition of thin Y_2O_3:Eu films during RF sputtering is determined by the pressure of the working gas, and this dependence is characterized by an optimal, extreme value. This optimal value is determined by the parameters of the RF installation. It has been found that an increase in the partial pressure of oxygen in the sputtering atmosphere $(Ar + O_2)$ leads to a decrease in the sputtering rate. It has been shown that the deposition rate of Y_2O_3:Eu films is practically inde-

pendent of the activator concentration in the range from 0 to 10.0 mol.%, and films with an activator concentration of 7.5 mol.% have high cathodoluminescence brightness. The explanation of the results obtained is based on the consideration of the effects of backscattering, back diffusion, and the resonant charge exchange mechanism.

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