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Surface Morphology of $ZnGa_2O_4$:Mn Thin Films Obtained by RF Ion-Plasma Sputtering on Quartz Substrates

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Thin films of $ZnGa_2O_4$:Mn are obtained by means of the radio-frequency ion-plasma sputtering in an argon atmosphere on amorphous υ-SiO_2 substrates. The study of the surface morphology of $ZnGa_2O_4$:Mn thin films by means of atomic force microscopy shows that heat treatment in an air atmosphere increases the average grain diameter from 113 nm in an unannealed film to 274 nm in an annealed sample. Additionally, the root-mean-square (RMS) roughness of the thin-film surface is increased from 3.8 nm to 6.2 nm, respectively. The analyses of the distributions of crystallites in diameter and volume are carried out, and it is shown that the process of heat treatment of thin films leads to grain growth due to the processes of growth and sintering.

Методом високочастотного йонно-плазмового розпорошення в атмосфері арґону на аморфних підкладинках υ-SiO_2 одержано тонкі плівки $ZnGa_2O_4$:Mn. Дослідження морфології поверхні тонких плівок методом атомно-силової мікроскопії показали, що термооброблення тонких плівок $ZnGa_2O_4$:Mn у атмосфері повітря приводить до зростання середніх діяметрів зерен від 113 нм для невідпаленої плівки до 274 нм для відпаленого зразка та середньоквадратичної шерсткости поверхні тонких плівок від 3,8 нм до 6,2 нм відповідно. Проведено аналізу розподілів кристалітів за діяметром і за об'ємом; показано, що процес термооброблення тонких плівок приводить до зростання зерен за рахунок процесів росту та спікання.

Key words: zinc gallate, magnesium activator, thin films, crystallites, surface morphology, atomic force microscopy, annealing of films.

Ключові слова: ґалат Цинку, маґнійовий активатор, тонкі плівки, кристаліти, морфологія поверхні, атомно-силова мікроскопія, відпал плівок.

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1. INTRODUCTION

In recent years, many scientists have been studying the properties of $ZnGa_2O_4$ thin oxide films, both pure and doped with various impurities, due to the widespread use of these compounds in instrumentation and optoelectronics. In particular, thin films based on $ZnGa_2O_4$ are used in field emission displays, gas sensors, electronic devices, and these compounds are promising for the creation of deep ultraviolet photodetectors (DUV PDs), which are potentially used in optical communications, for detecting missile threats, as well as for monitoring ozone holes, x-ray photodetectors (XPDs), which can be used in medical imaging, for quality control in the food industry, and environmental monitoring [1–10]. In addition, due to its electrical properties, $ZnGa_2O_4$ is a potentially promising material for the manufacture of transistors, voltage converters, and high-performance Schottky diodes [11].

The development and improvement of the properties of thin-film materials based on $ZnGa_2O_4$ to expand the possibilities of their use remains an important task. In general, the issue of the physical properties of thin films is complicated by the fact that their structure is often far from perfect. Obtaining the required and stable reproducible properties of polycrystalline films is limited by the presence of intergranular boundaries. The physical properties of polycrystalline thin films largely depend not only on the material characteristics but also on the energy levels that arise due to the presence of intergranular boundaries. It is clear that these levels are determined by the size of the crystallites that form the thin films. This led to the study of the surface morphology of $ZnGa_2O_4$ thin films doped with Mn using atomic force microscopy (AFM). Thin-film samples were obtained by the method of radio-frequency ion-plasma sputtering, which is optimal for obtaining homogeneous semi-conductor and dielectric films [12].

2. EXPERIMENTAL TECHNIQUE

Thin films of $ZnGa_2O_4$:Mn with a thickness of 0.6–1.0 µm were obtained by RF ion-plasma sputtering on amorphous substrates of fused quartz υ-SiO_2. The 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 starting material was a mixture of ZnO and Ga_2O_3 oxides of stoichiometric composition of the 'ОСЧ' grade (extra pure). The concentration of the Mn activator was 1 mol.%. After the films were deposited on υ-SiO_2 substrates, they were subjected to heat treatment in an air atmosphere at 1000–1100°C.

The structure and phase composition of the obtained films were studied by x-ray diffraction analysis (Shimadzu XDR-600). X-ray diffraction studies have shown the presence of a polycrystalline structure with a predominant orientation in the (022), (113), (004), and (333) planes. The characteristic diffractograms of $ZnGa_2O_4$ thin films were presented earlier in Ref. [13].

During the analysis of the obtained films, elemental analysis of the samples was performed at several points on the surface of the films using an OXFORD INCA Energy 350 energy dispersive spectrometer. The x-ray photoelectron spectroscopy (XPS) method was also used to analyse the elemental composition of the surface of the obtained thin films. The x-ray photoelectron spectroscopy (XPS, Phoibos 150, Specs) spectra were recorded using a monochromatic x-ray source AlK_α (1486.6 eV). The binding energy was calibrated from the signal from C1s at 285.0 eV.

The surface morphology of the films was studied using an INTEGRA TS-150 atomic force microscope (AFM). The image of the surface of thin films was recorded in semi-contact mode.

3. RESULTS AND DISCUSSION

Microphotographs of the surface of $ZnGa_2O_4$:Mn thin films obtained by RF ion-plasma sputtering on fused quartz υ-SiO_2 substrates without heat treatment and after heat treatment in the air atmosphere are shown in Fig. 1.

Based on the AFM images of the surface morphology of the samples under study, a number of standard parameters were calculated for areas of the same size (5000×5000 nm): root-mean-square roughness, average grain diameter, average grain area and volume, and grain height at the maximum number of grains. The characteristic parameters of $ZnGa_2O_4$:Mn thin films obtained by RF sputtering on υ-SiO_2 substrates without heat treatment and after heat treatment in the air atmosphere are given in Table. As can be seen from the obtained results, heat treatment in the air atmosphere of $ZnGa_2O_4$:Mn thin films obtained by RF sputtering on υ-SiO_2 substrates has a significant effect on the size of crystal grains and the surface roughness of the films.

The analysis of AFM images (Fig. 1) and crystal grain parameters (Table) of the surface of $ZnGa_2O_4$:Mn films shows that the size of

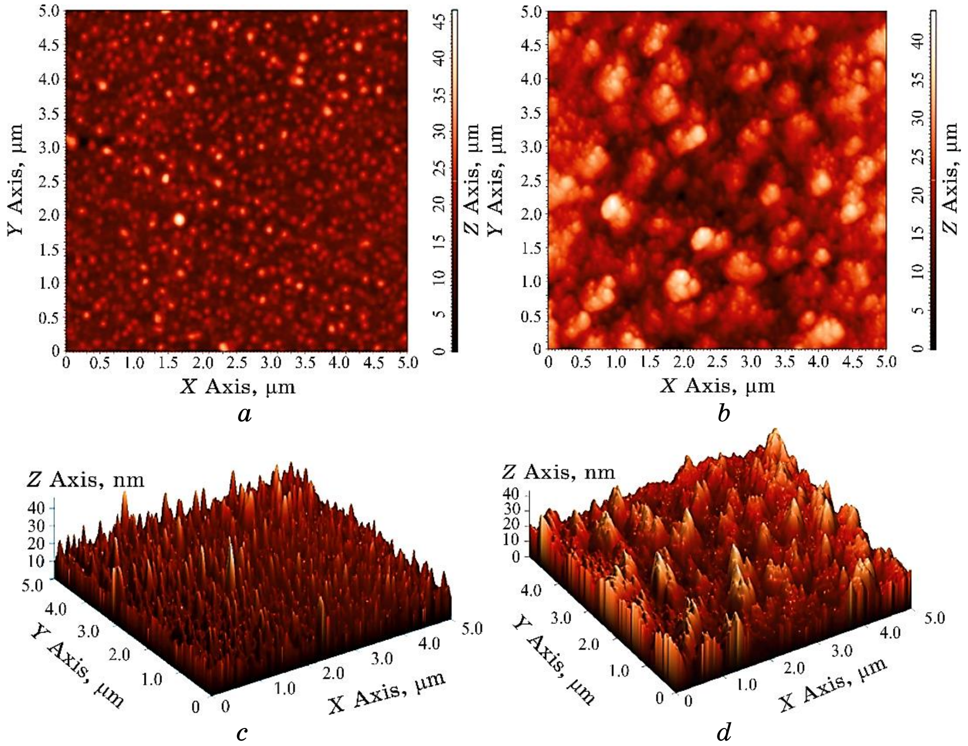

Fig. 1. Surface-morphology images of $ZnGa_2O_4$:Mn thin films obtained by RF sputtering on υ-SiO_2 substrates: (*a*, *c*) without thermal treatment and (*b*, *d*) after thermal treatment in an air atmosphere. Images (*a*) and (*b*) are two-dimensional; (*c*) and (*d*) are three-dimensional.

TABLE. Parameters of crystal grains of $ZnGa_2O_4$:Mn thin films.

Parameter	Without heat treatment	Heat treatment in the air
Average grain diameter, nm	113	274
RMS roughness, nm	3.9	6.2
Grain height with maximum number of grains, nm	13	18
Average grain area, nm^2	4730	23900
Average grain volume, nm^3	11400	65700

crystallites of $ZnGa_2O_4$:Mn thin films sputtered on a υ-SiO_2 substrate after heat treatment within the air atmosphere increases significantly compared to the sample without heat treatment.

An increase in the size of crystallite grains and, in particular, an increase in the average grain diameter and RMS roughness indicates a complication of the surface structure of thin films.

Comparison of the histograms of the distribution of grain heights (Fig. 2) shows that the heat treatment of $ZnGa_2O_4$:Mn thin films in the air atmosphere affects the increase in grain height compared to unannealed films. In particular, if we compare the RMS surface roughness of thin films, it is much higher for films deposited on quartz substrates that have been heat-treated in an air atmosphere than for films without heat treatment. Annealing films in an air atmosphere leads to an increase in this parameter by about 1.6 times compared to unannealed films.

The heat-treatment process affects the morphology of the surface of thin films, since an increase in the size of crystalline grains and a simultaneous decrease in the concentration of grains for $ZnGa_2O_4$:Mn thin films after their heat treatment are observed (Table) that indicates the possibility of transition of the film surface to a more nanostructured state due to the crystallization of the surface layer.

It is worth noting that the annealing temperature and the annealing atmosphere in which the heat treatment of thin films takes place are important, as they have different effects on the formation of the surface morphology of thin films. As noted in Ref. [14], annealing of thin films at high temperatures leads to the appearance of an additional Ga_2O_3 phase in addition to the existing $ZnGa_2O_4$ phase, since Zn atoms diffuse from the film surface at high annealing temperatures. In Ref. [15], the influence of the annealing atmosphere on the formation of surface morphology was analysed for $ZnGa_2O_4$:Cr thin films obtained by RF ion-plasma sputtering and it

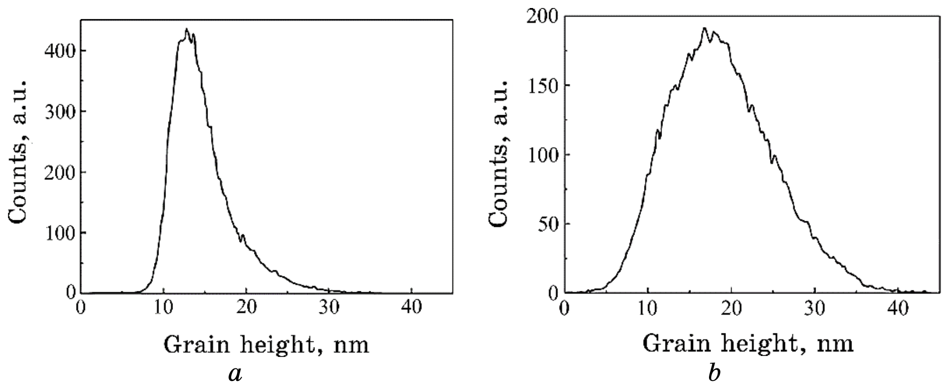

Fig. 2. The distribution of grain height in AFM images of $ZnGa_2O_4$:Mn thin films obtained by RF sputtering on υ-SiO_2 substrates: (*a*) without thermal treatment and (*b*) after thermal treatment in an air atmosphere.

was shown that the annealing atmosphere affects the size of crystallites, from which the obtained thin films are formed. The formation of the $ZnGa_2O_4$ film is also influenced by the method of obtaining thin films, as evidenced by the results obtained in Ref. [16].

The characteristic distributions of grain-diameter sizes in $ZnGa_2O_4$:Mn thin films depending on the presence of heat treatment are shown in Fig. 3.

According to a thorough review [17], polycrystalline thin films with a thickness of up to 1 μm often have 2*D*-like structures, which are typical for our $ZnGa_2O_4$:Mn films. In such structures, most grain boundaries are perpendicular to the film surface. For most of the materials analysed in Ref. [17], films are formed from nonequilibrium grains with sizes smaller than the film thickness and form two-dimensional structures only after annealing. Based on numerical results, authors of Ref. [17] also concluded that the formation of grains in thin films is difficult to describe accurately using modelling or comparison with experiments that described the study of foam or monolayers. In general, grain sizes in polycrystalline films are lognormally distributed in size. In some cases, further grain growth is observed due to 'anomalous' growth or preferential growth of several grains, which usually have specific crystallographic orientation relations relative to the surface plane of the substrate. Our results show that such a situation is most likely characteristic of the $ZnGa_2O_4$:Mn films obtained by us. When the number of growing grains leads to a 'matrix' of grains beyond the static boundaries, a bimodal grain-size distribution develops, which is called secondary-grain growth [18]. Grains that grow abnormally often have a limited or homogeneous texture. The growth of sec-

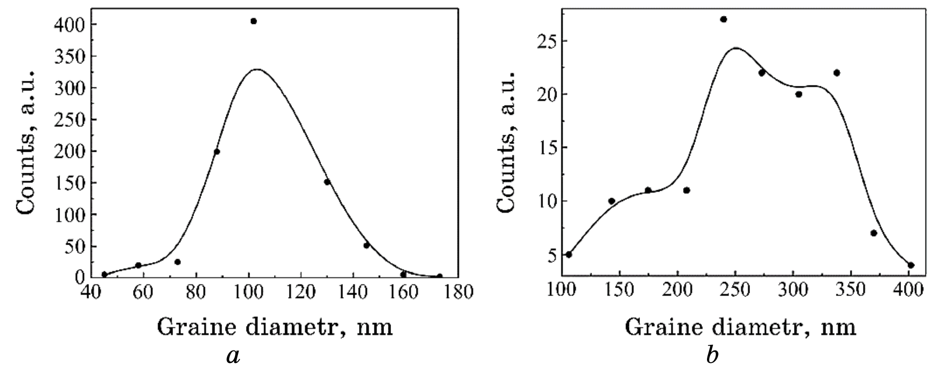

Fig. 3. The distribution of grain diameter sizes and the calculated approximate diameter distribution in AFM images of $ZnGa_2O_4$:Mn thin films obtained by RF sputtering on υ-SiO_2 substrates: (*a*) without thermal treatment and (*b*) after thermal treatment in an air atmosphere.

ondary grains in thin films typically involves an evolution in the distribution of grain textures as well as an evolution in the grain size distribution.

Our results on the distribution of grain-diameter sizes in $ZnGa_2O_4$:Mn thin films (Fig. 3, *a*) indicate that, when these films are deposited on amorphous υ-SiO_2 substrates, a unimodal distribution of diameters with a maximum in the region of 105 nm is observed. A more complex shape of the diameter distribution is formed, when thin films of $ZnGa_2O_4$:Mn are annealed in an air atmosphere (Fig. 3, *b*). For such films, the diameter distribution shows three maxima in the region of 170 nm, 250 nm, and 325 nm, indicating the appearance of a trimodal diameter distribution. The diameter distributions (Fig. 3) and the values of the average diameter sizes (Table) indicate that during the heat treatment, grain growth occurs due to the processes of growth and sintering. It should be noted that a similar situation is observed during RF deposition on υ-SiO_2 substrates and for thin films based on β-Ga_2O_3 [19, 20]. The growth of secondary and tertiary grains was observed in these films during both RF sputtering and heat treatment.

For a more detailed analysis, let us consider the distribution of grain volumes in $ZnGa_2O_4$:Mn thin films. The characteristic distributions of grain-volume sizes in $ZnGa_2O_4$:Mn thin films depending on the presence of heat treatment are shown in Fig. 4.

As can be seen from Fig. 4, when thin films of $ZnGa_2O_4$:Mn are deposited on a υ-SiO_2 substrate, the distribution of grains in volume is quite well described by a normal logarithmic law. This situation is typical for the distribution of grains by diameter in polycrystalline films [21]. For $ZnGa_2O_4$:Mn thin films on υ-SiO_2 substrates after annealing in the air atmosphere, a downward distribution is observed without local maxima that can be explained by the formation of nonequilibrium grains on the amorphous substrate, since the annealing was carried out at high temperatures.

Analysis of the XPS spectrum recorded for the unannealed $ZnGa_2O_4$:Mn thin film obtained by RF sputtering on υ-SiO_2 substrates (Fig. 5) showed the presence of peaks corresponding to Zn($2p^3$), Ga($3d^5$), and O($1s$) atoms. The peak for the Mn atom is not observed in the recorded spectrum, which can be explained by the low concentration of the dopant. The presence of the Mn dopant was observed in the recorded cathodoluminescence spectra, as evidenced by the characteristic emission peak of manganese.

In addition to the peaks corresponding to the peaks of the elemental composition of the film, the spectrum shows a peak corresponding to the C($1s$) atom at a binding energy of 285.0 eV, against which the spectrum was calibrated, and a peak corresponding to the Si($2p^3$) atom observed due to the used amorphous υ-SiO_2 substrate

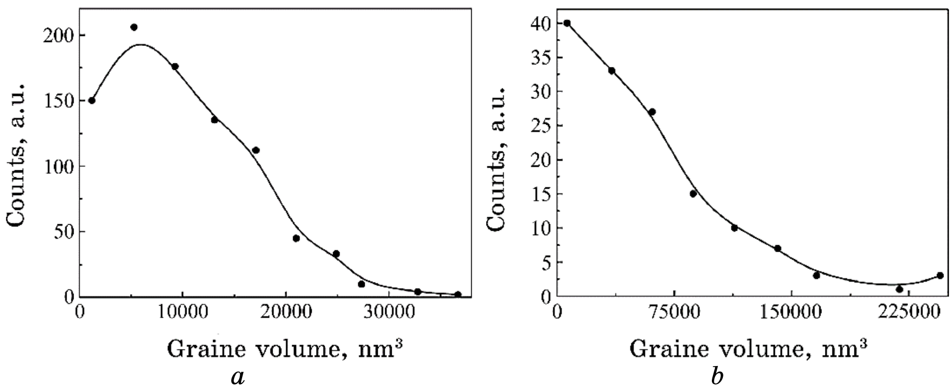

Fig. 4. The grain-size distribution and calculated approximated-volume distribution in AFM images of $ZnGa_2O_4$:Mn thin films obtained by RF sputtering on υ-SiO_2 substrates: (*a*) without thermal treatment and (*b*) after thermal treatment in an air atmosphere.

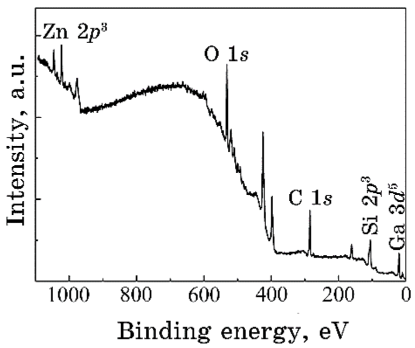

Fig. 5. XPS spectrum of an unannealed $ZnGa_2O_4$:Mn thin film obtained by RF sputtering on υ-SiO_2 substrates.

during RF sputtering of $ZnGa_2O_4$:Mn thin films.

4. CONCLUSIONS

It has been established that, during RF ion-plasma sputtering on amorphous υ-SiO_2 substrates, thin films of $ZnGa_2O_4$:Mn are formed from nanometer grains. Based on the AFM images, it is shown that the average diameters of the crystallites of unannealed $ZnGa_2O_4$:Mn films on υ-SiO_2 substrates are of 113 nm. The heat treatment of films in an air atmosphere leads to an increase in average grain diameters up to 274 nm and an increase in RMS roughness from 3.9 nm to 6.2 nm. Based on the analysis of the results of the diameter-size distribution, it is shown that, for unannealed films, a unimodal distribution with a maximum in the region of 105 nm is observed, and for annealed films within the air atmosphere, a distribution with three maxima at 170 nm, 250 nm, and 325 nm is observed. Based on the analysis of the results of the distribution of grain-diameter sizes, it is shown that the heat-treatment process of thin films leads to grain growth due to the processes of growth and sintering.

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