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STRUCTURE AND MORPHOLOGY OF ZnO FILMS CO-DOPED WITH AL AND RARE EARTH DEPOSITED BY SPRAY COATING TECHNIQUE

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ABSTRACT. In this work, the influence of co-doping with Al and rare earth ions (RE= Er, Gd, Nd) on the structure and morphology of zinc oxide (ZnO) films is presented. Spray coated thin films were obtained using a mixture of nitrate substances diluted in equal quantities of distilled water and ethanol. The coated films were deposited on quartz glass and Si(100) substrates using a constant concentration of 0.15M, a temperature of 210ºC, pressure of 2 bar and 10 minutes time of deposition. After this step, the coated films were annealed at 3 different temperatures (600ºC, 800ºC and 1000ºC) for 5 minutes each. The influence of dopant and annealing treatment upon crystallographic structure of the films was analyzed by X-ray diffraction (XRD). Microstructural and surface analysis from scanning electron microscopy (SEM) and AFM measurements evidenced that the type of doping and the annealing treatment modify the surface morphology of the films.

Keywords*: spray coating technique, AZO-RE thin films, XRD, SEM, AFM.*

INTRODUCTION

Metal-oxide thin-film transistors (TFTs) have shown increasing utilization in a wide range of applications. Zinc oxide (ZnO) is one of the most interesting transparent and conducting oxide (TCO) due to its electro-optical properties, large band gap, abundance in nature and high electrochemical stability. It has an n-type

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electrical conductivity and it is transparent to visible light. These advantages are of considerable interest for practical applications such as, gas sensors [1,2], piezoelectric devices and many others. With a proper choice of dopant atoms, the luminescence properties of ZnO films can be changed. By introducing Al atoms as dopants, the defect environment is changed whether these atom substitutes the zinc atom or it occupies the interstitial site. Al doping is expected to change the optical and electrical properties of ZnO films. To improve morphological, structural, electrical and optical properties, we decided to use rare earth dopants. In accordance to literature these type of dopants can increase electrical conductivity and form more uniform structures in thin films. Furthermore, different techniques have been applied to obtain ZnO nanostructured thin films such as RF magnetron sputtering [3], chemical vapor deposition [4], pulse laser deposition [5], spray pyrolysis [6], sol-gel process [7], etc. Among these techniques, spray coating techniques is frequently used because of its inexpensive equipment, reproducibility and simplicity to deposit large area, excellent control of chemical uniformity and stoichiometry and possibility of microprocessor based spraying. In a spray pyrolysis process, reaction temperature is a basic operating variable. In addition, solution properties such as precursor composition, concentration, or the addition of a co-solvent may be crucial to achieve the desired product composition and morphology [8,9]. Spray coating has been developed as a powerful tool to synthesize various Al-doped ZnO thin films [10-13] and RE doped ZnO [14-18]. Considering the numerous studies done on aluminum and rare earth doped ZnO by spray coating technique, to our knowledge has not used this method for synthesis of ZnO films co-doped with (Al + RE).

In this research, we describe a spray coating method to obtain ZnO films co-doped with Al+RE (RE= Er, Gd, Nd) and to study the effect of processing parameters such as annealing temperature on the structure and morphology of samples.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of ZnO films co-doped with Al and RE = Er,Gd,Nd (further AZO doped with RE), deposited on quartz glass, and annealed at three different temperatures (600ºC, 800ºC, 1000ºC). The vertical lines in the image show the position of peaks for crystallographic planes with (hkl) for: ZnO –green lines, Al_2O_3-blue vertical lines, RE oxide Re_2O_3 – red vertical lines. All the marked diffraction peaks of ZnO in Fig. 1 can coincidently be indexed by the known hexagonal standard ZnO. The crystallographic phase of doped ZnO belongs to the wurtzite-type ZnO. Diffraction peaks correspond to (100), (002), (101), (102), (110), (103) and (112) planes of wurtzite ZnO, confirming that all the polycrystalline films are randomly oriented. For ZnO film codoped with Al and Er (AZO –Er doped film in fig. 1),

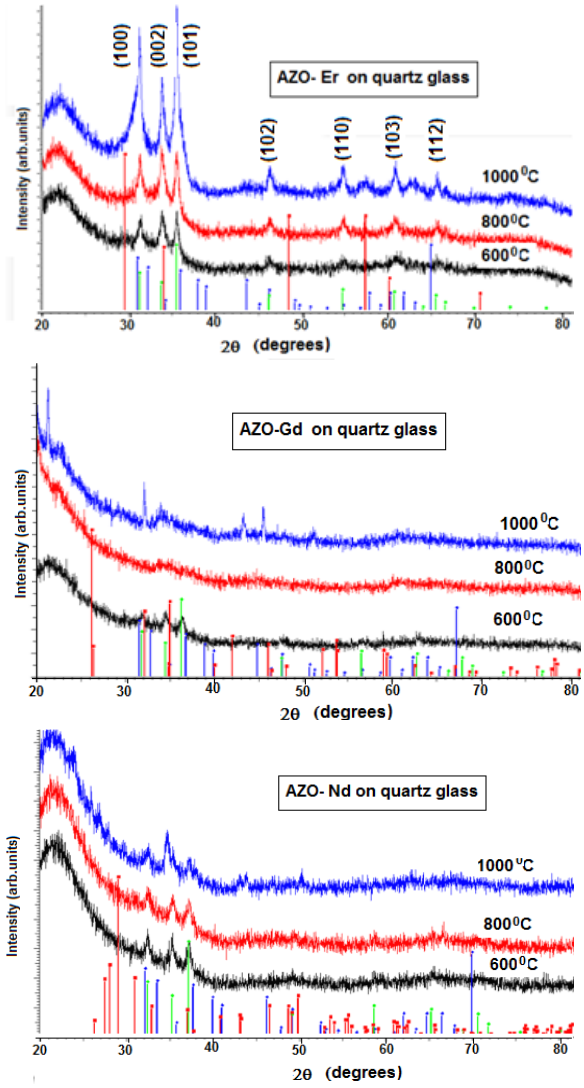

Fig. 1. XRD patterns for AZO film doped with Er,Gd,Nd, deposited on quartz glass substrates and annealed at 3 temperatures (600ºC, 800ºC ,1000ºC).

the relatively high intensity of the (101) peak is indicative of anisotropic growth and implies a preferred orientation. The peak intensities (100), (002) and (101) and the linewidth increased with increasing annealing temperature. The increase of linewidth suggests that the crystallinity of films is affected by the stresses because of the difference in ion radius size between zinc and the dopant (Al and Er) and the

segregation of dopants in grain boundaries. Furthermore, Gd-doped AZO thin films reveal a pronounced amorphous structure for the films deposited on quartz glass, XRD of the AZO-Nd doped film show an amorphous structure, but the presence of (100), (002) and (101) peak evidenced the presence of crystalline phase. For film obtained by using annealing temperature t=1000ºC, the intensity of (002) peak increases comparatively with the films obtained for t=600, 800ºC.

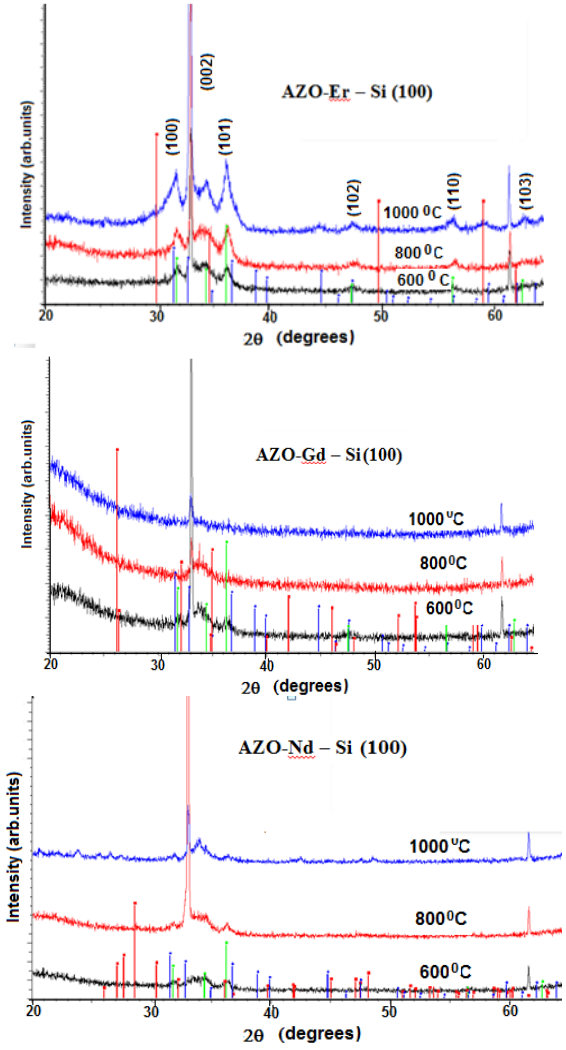

Fig. 2. XRD patterns for AZO-RE (RE=Er,Gd,Nd) thin films deposited on Si(100) substrates and annealed at three temperatures (600ºC, 800ºC, 1000ºC).

XRD results show significant differences between the films deposited on two types of substrates. Si(100) substrate and quartz glass substrate differently influenced the growth of films, and crystallographic plane orientation, respectively. Therefore, for films deposited on Si(100) substrate the intensity of (002) peak is higher and more evident than for thin films deposited on quartz glass substrates. The c-axis epitaxy is influenced by the type of RE ion and annealing temperature. For Er doped AZO film, the relatively high intensity of the (200) peak comparatively with (101) and (102), suggests the anisotropic growth with a preferred c-axis orientation. For Gd and Nd doped AZO films deposited on the Si(100) substrates the c-axis epitaxy is higher that for Er doped AZO film, and is influenced by substrate temperature. For Gd doped film, the higher intensity for (002) peak was obtained for the annealing temperature of 600ºC and for Nd-doped films for the annealing temperature of 800ºC, respectively. Nevertheless, the films show a good *c*-axis orientation, corresponding to vertical growth with respect to Si(100) substrate. This preferred orientation is due to the minimal surface energy of the (002) plane that corresponds to the dense packed plane of the ZnO hexagonal structure. The value of lattice constant, c is calculated from the XRD data and is given in *Table 1*. It is observed that the *c*-axis length is influenced by the type of RE dopant, but it does not change much with the increase of annealing temperature. It was observed that doping of AZO with RE ions lead to the *c*-axis length decreases. Responsible for the decrease in the *c*-axis length was the induced cationic vacancies created by Nd^{3+} doping in the ZnO host matrix [15]. Similar *c*-axis variations were also reported in Er doped ZnO [19] and Ce doped ZnO [20]. The influence of annealing temperature on the stress along the c-axis direction for codoped ZnO films deposited on Si(100) substrate was investigated. By using the biaxial strain model, for the hexagonal lattice of ZnO, the stress (σ) in the film can be calculated with the following formula:

$$\sigma = \frac{2c_{13}^2 - c_{33}(c_{11}+c_{12})}{2c_{13}} \times \varepsilon \quad (1)$$

where ε (c_{film}-c_{bulk})/c_{bulk}, c_{bulk} =5.200 Å is the unstrained lattice parameter (American Society for Testing and Materials) and c_{film} is measured by XRD.

By using the elastic constants c_{ij} of single-crystalline ZnO from reference [21], we obtain $\sigma_{film} = -233 \times \varepsilon$ (GPa). This compressive stress takes place during deposition process itself.

Table 1 shows that, the calculated stress in the direction of the c-axis for Er and Gd doped films, decreases with increasing annealing temperature. The positive sign of the stress is the indication of tension stress. For Nd doped films, by increasing annealing temperature, the sign of stress changes from negative to positive values,

suggesting a change from tension stress to compressive stress. The RE-ions tend to create additional stress in the lattice structure of films and along c-axis because Er^{3+}(0.89 Å), Gd^{3+}(0.935 Å) and Nd^{3+}(0.98 Å) have larger ion radius than that of Zn^{2+} ion (0.74 Å), which makes the replacement more difficult, thus distorting the ZnO lattice [22,23].

Table 1. Calculated stress and strain in the film lattice

Sample name	Annealing temperature (°C)	Lattice parameter, c (nm)	ε (%)	σ (GPa)
AZO-Er	600	5.184	-0.31	0.72
	800	5.191	-0.17	0.40
	1000	5.196	-0.08	0.18
AZO-Gd	600	5.161	-0.75	1.74
	800	5.165	-0.67	1.56
	1000	5.169	-0.59	1.39
AZO-Nd	600	5.196	-0.08	0.18
	800	5.204	0.08	-0.18
	100	5.208	0.15	-0.36

SEM images emphasize the strong influence of the type of dopant and the annealing temperature upon the structure of spray coated films. Therefore, with increasing the annealing temperature, larger cracks begin to form as shown in figures below. Even if the cracks/valleys are not very deep into the surface structure, the film is not uniform anymore, making it impossible for electrical measurements.

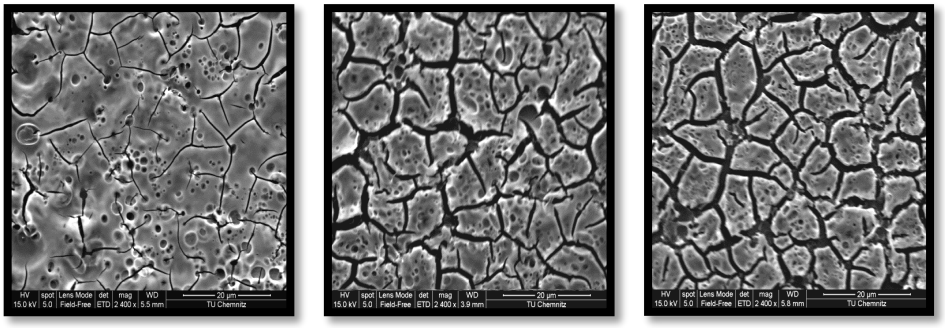

Fig. 3. AZO-Er spray coated on Si(100) and annealed at temperatures: 600ºC, 800ºC, 1000ºC (left to right).

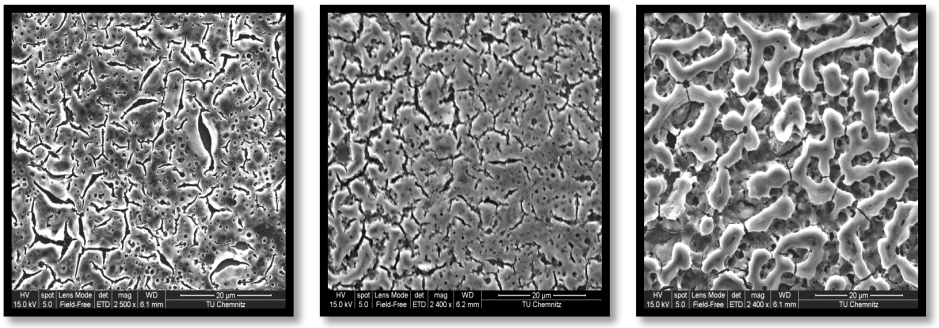

Fig. 4. AZO-Gd spray coated on Si(100) and annealed at temperatures:
600ºC, 800ºC, 1000ºC (left to right).

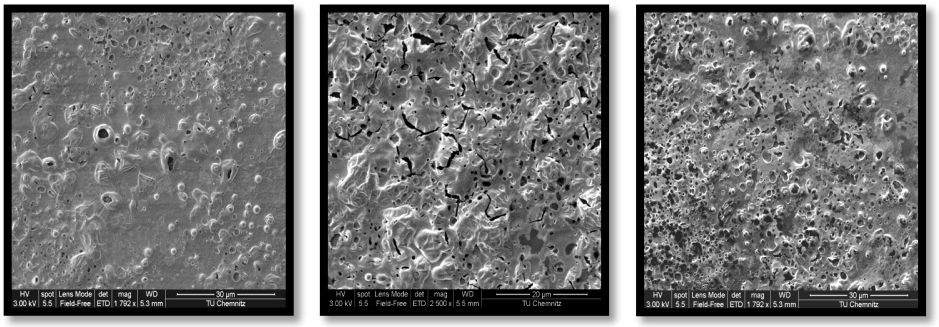

Fig. 5. AZO-Nd spray coated on Si(100) and annealed at temperatures:
600ºC, 800ºC, 1000ºC (left to right).

SEM for the the Si(100) spray coated samples provide some interesting information regarding the surface. Hence, these results accentuate the difference in sample structure with increasing the annealing temperature, resulting in the appearance of larger cracks and more defined crystallites, which could prove the intensity of the peaks from XRD.

AFM images complete the surface analysis which are in accordance with the SEM results.

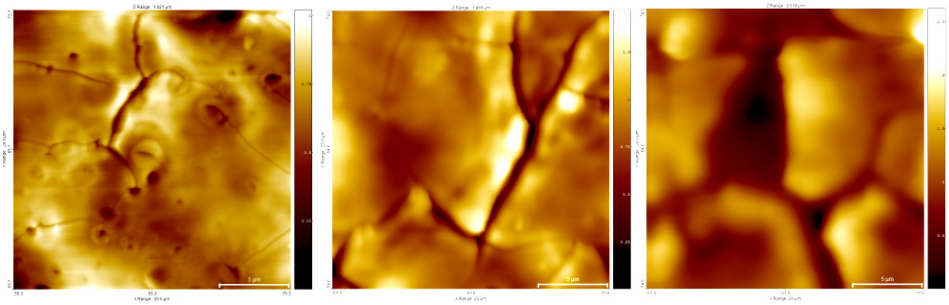

Fig. 6. AZO-Er spray coated on Si(100) and annealed at temperatures: 600ºC, 800ºC, 1000ºC (left to right).

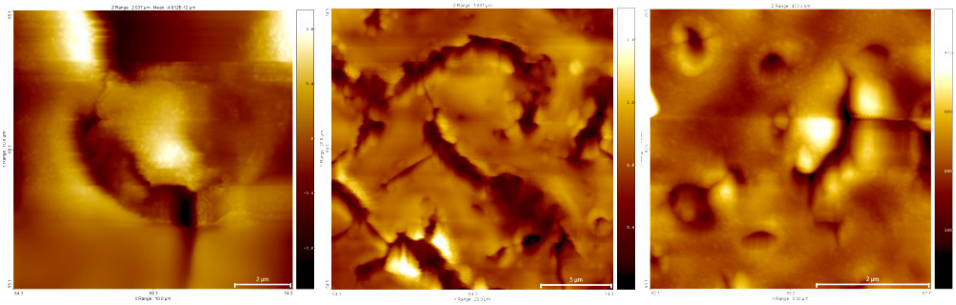

Fig. 7. AZO-Gd spray coated on Si(100) and annealed at temperatures: 600ºC, 800ºC, 1000ºC (left to right).

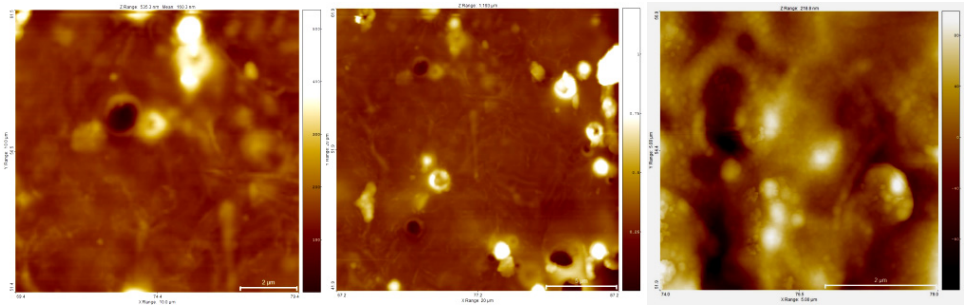

Fig. 8. AZO-Nd spray coated on Si(100) and annealed at temperatures: 600ºC, 800ºC, 1000ºC (left to right).

Furthermore, by using different RE dopants we could observe a slight effect in how compact the surface was formed, revealing better quality for the samples doped with Nd ions, that could be related to the fact that Nd has a smaller ionic radius compared to the other RE used, making it more likely to incorporate into the ZnO lattice.

CONCLUSIONS

ZnO thin films co-doped with Al and RE ions were grown using spray coating technique and deposited on quartz glass and Si(100) single crystal. The films were annealed at three different temperatures (600ºC, 800ºC, 1000ºC), and characterized by XRD, SEM and AFM.

The type of RE-ions, substrate and annealing temperatures, induce changes in the structure and especially in the morphology of thin films.
The growth of film and crystallographic plane orientation is differently influenced by Si(100) substrate and quartz glass substrate respectively.

All films deposited on quartz glass are polycrystalline with random orientation. For films deposited on Si(100) substrate, anisotropic growth with a preferred c-axis orientation was emphasized. The degree of c-axis epitaxy and the stress along this direction is influenced by the type of RE ion and annealing temperature. Along the c-axis, for Er and Gd dopants the tension stress decreases with increasing annealing temperature, while for Nd dopant the change from tension stress to compressive stress was evidenced.

AFM and SEM revealed that the sprayed samples forms cracks on the surface and the number of crystallites increases with increasing the annealing temperature. Also, the type dopant used had a slight effect in how compact the surface was formed after the annealing process, revealing better quality for the samples doped with Nd ions.

EXPERIMENTAL SECTION

Spray coated technique and two different types of substrates were used to obtain ZnO co-doped with Al and RE ions using a constant concentration of 0.15 M. Solid nitrides were measured after the specific concentration (c=0.15 M) and quantities were calculated, then mixed with equal quantities of ethanol and distilled water using the ultrasonic bath for 5 minutes for better homogeneity. Two types of substrates were used, quartz glass and Si(100) kept at a temperature of 210°C and a pressure of 2 bars, for 10 minutes time of deposition. After the spraying process, the samples were annealed at three different temperatures (600°C, 800°C, 1000°C) for 5 minutes each to eliminate any impurities and mechanical stress in the films. The structure of films was determined by XRD analysis, using a Brucker D8 X-ray diffractometer with a CuK_{α} radiation. The 2θ range was recorded at the rate of 0.02º and 2θ / 0.5 s. The crystal phases were identified by comparing the 2θ values and

intensities of reflections on X-ray diffractograms with JCP data base using Diffraction AT-Brucker program. Scanning electron microscopy technique was used to illustrate the morphology of film surface. SEM images were recorded using FEI Quanta 3D FEG 200/600 microscope.

The sample topography was analyzed by atomic force microscopy (AFM) in order to analyze the structure of the surface. AFM images were taken with a Ntegra Spectra commercial microscope (NT-MDT, Russia) at room temperature in semicontact mode with anticorrosive rectangular monocrystalline silicon Sb doped cantilever for static charge dissipation, electrical resistivity 0.01-0.025 Ω×cm, resonant frequency in the range 240-440 kHz (typically 320 kHz), a constant force of 22-100 N/m (typical 40 N/m), peak radius <10 nm (typical 6 nm). After acquisition, image processing was performed using the Nova v1.1.0.1837 (NT-MDT) program.

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