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STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF RE-DOPED AZO THIN FILMS (RE=Nd, Gd, Er) GROWN BY RF MAGNETRON SPUTTERING

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ABSTRACT. In this paper we describe the influence of substrate-target distance of AlZnO films doped with rare earth (RE= Nd, Gd, Er) ions, on structural, morphological and optical properties. The transparent conductive RE doped AZO thin films were fabricated by radio frequency (RF) magnetron sputtering using a power of 100 W and the deposition pressure of 2.1 × 10^{-2} mbar. The deposition was performed on glass substrates heated at 150^0C and with a time deposition of 90 minutes. Therefore, we obtained AZO thin films doped with RE ions. The influence of substrate-target distance for each rare earth ions on the structure of thin films was analyzed by X-ray diffraction (XRD). Scanning electron microscopy (SEM) shows the uniformity of the surface which consists of well-defined spherical crystallites. The decreasing of target-substrate distance leads to an increase in grain size. However, there is a slight change in the size and topography of films by doping with different 4f elements. The energy dispersive X-ray spectroscopic analysis (EDX) results show presence of an oxygen deficiency (oxygen stoichiometry lower than 50 wt.%). The optical transmittance through the films was measured in the wavelength range 375–1000 nm. The refractive index, transparency and thickness of obtained films were determined.

***Keywords**: RE doped AZO thin films, XRD, SEM, EDX, optical transmission.*

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INTRODUCTION

As an II-VI semiconductor material, zinc oxide (ZnO) with band gap energy (3.37 eV at room temperature), similar to TiO_2, has attracted considerable attention due to its unique properties, such as high electron mobility and conductivity, high transmittance in visible and IR region of the spectrum. Therefore, transparent conductive oxide (TCO) thin films are considered promising materials for light emitting materials [1, 2], transistors [3], gas sensors [4], magnetic semiconductors [5, 6] and photocatalyts [7]. Also, ZnO doped with aluminium, (AZO), have some new domains of application, in the electromagnetic spectrum as terahertz spectroscopy and imaging are becoming potential tools for characterizing various materials including semiconductor, high-temperature, superconductor and biomaterial specimens [8-11], nanowires [12, 13] and coatings for energy-efficient windows or organic solar cells [14, 15].

In this work, we prepared AZO thin films doped with rare earth (RE=Nd, Gd, Er) ions, due to its wide applications such as solar cells [15, 16], flexible organic light-emitting diodes [17-19], spintronic devices [20] data storage, radiation detection and even biomedical applications [21, 22]. These thin films were synthesized in RF magnetron sputtering, at different distances between substrate and target and they were analysed using XRD measurements for structural properties, SEM and EDX for surface and stoichiometry properties. Optical measurements were studied using PARAV program for calculating the transmittance spectra and refractive index [23]. The results shows that the thickness of thin films depends on the distance between the target-substrate and also, the nature of the dopant components (Nd, Gd, Er), according with other studies [24].

RESULTS AND DISCUSSION

Structural properties

Figure 1 shows the diffraction patterns of the obtained films. As seen in these figures, all the films are polycrystalline with hexagonal wurtzite type structure.

According to the literature [25, 26], it was observed that the location of 4f elements atoms in analyzed thin films was not possible due to the large difference between the atomic radii of the elements (Zn, Al, Er, Gd, Nd), resulting in distortion and displacement of the peaks in the X-ray diffractogram. Also with increasing target-substrate distance a (100) preferential orientation in was observed for Gd and Nd dopants. However, doping affects the growth of crystallites, damaging the structure, which for AZO films is more evident than in the case of doping with Er.

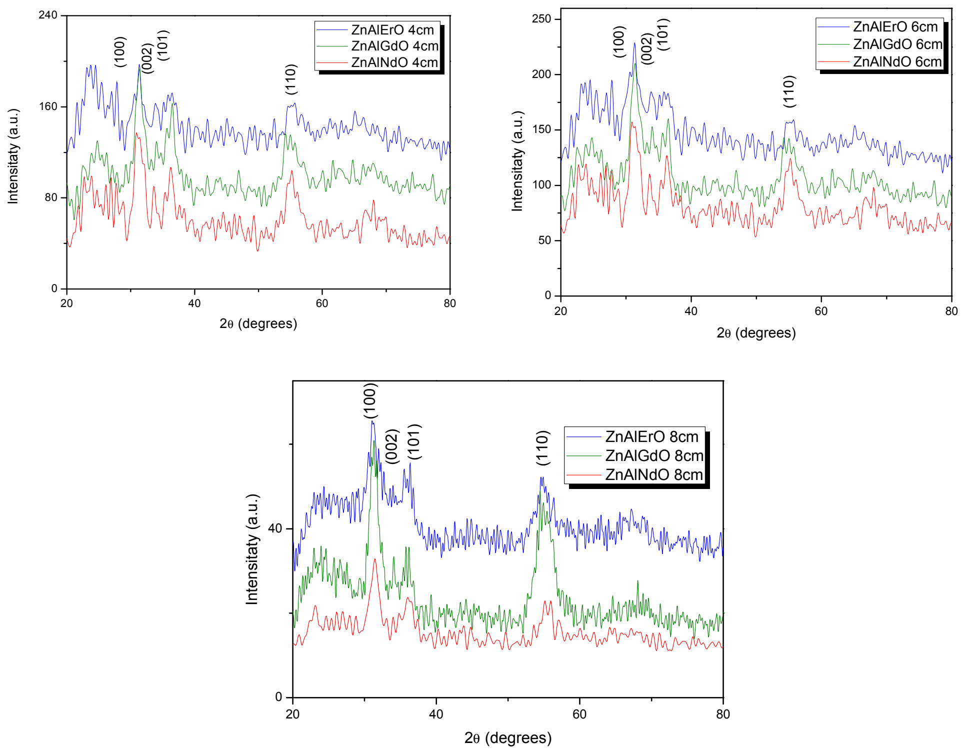
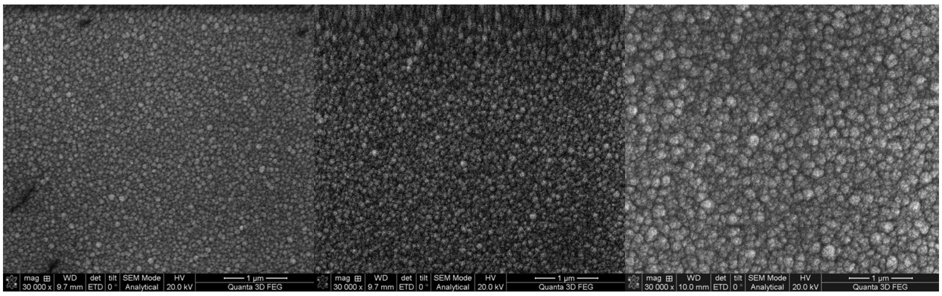


Figure 1. X-ray diffraction spectra of AZO-Er, AZO-Gd and AZO-Nd with three different target-substrate distances.

All diffraction peaks are consistent with previously reported data for ZnO, suggesting that most of the rare earth ions might have been incorporated in the Zn^{2+} sites of the ZnO lattice. This can be understood considering the larger ionic radii of Er^{3+} (0.89 Å), Gd^{3+} (0.938) and Nd^{3+} (0.983) in comparison to that of Zn^{2+} (0.74 Å), which makes the replacement more and more difficult, thus distorting the ZnO lattice. [27, 28].

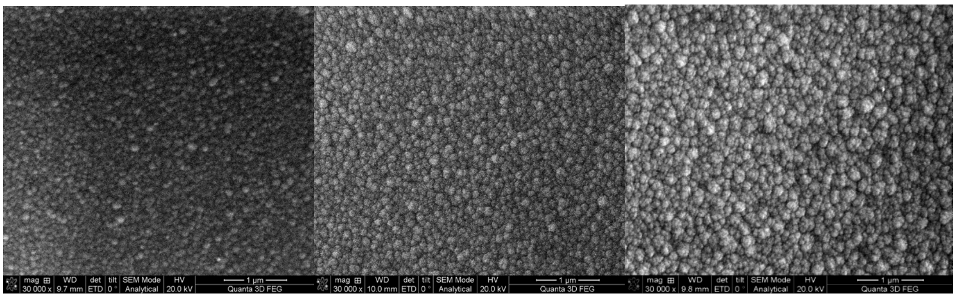
Morphological properties

SEM images show that the surface of all thin films is smooth, uniform and consists of spherical grains. With the decrease of the distance between target-substrate, we observed an increase in grain size that is well emphasized for the thin films doped with Gd (Figure 3) and Nd (Figure 4). However, addition of rare earth ions varies the structure in general and a kind of disorder is noticed in the images in accordance with the literature [29]. Also, the images of AZO thin films doped with Er (Figure 2) point out a more homogeneous distribution of the grains in size, keeping the same deposition conditions [30].



8 cm **6 cm** **4 cm**

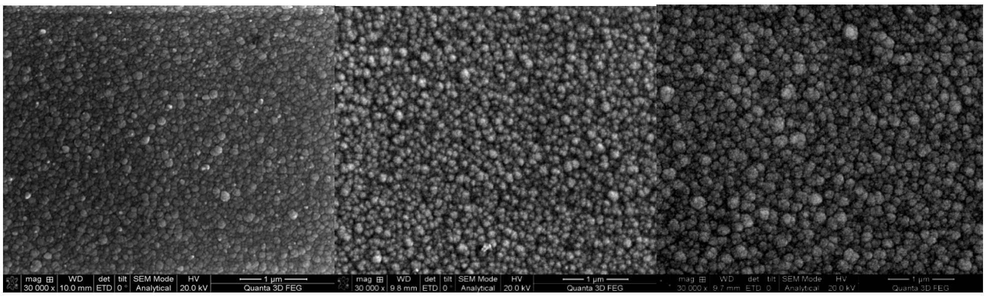
Figure 2. SEM image of AZO-Er thin films



8 cm **6 cm** **4 cm**

Figure 3. SEM image of AZO-Gd thin films

In Figure 5 we present the EDX spectra for Er, Gd, Nd doped AZO thin films. Therefore, with the increase of distance between target-substrate (small thickness of the films), we received signals for the components of the glass substrate.



8 cm **6 cm** **4 cm**

Figure 4. SEM image of AZO-Nd thin films

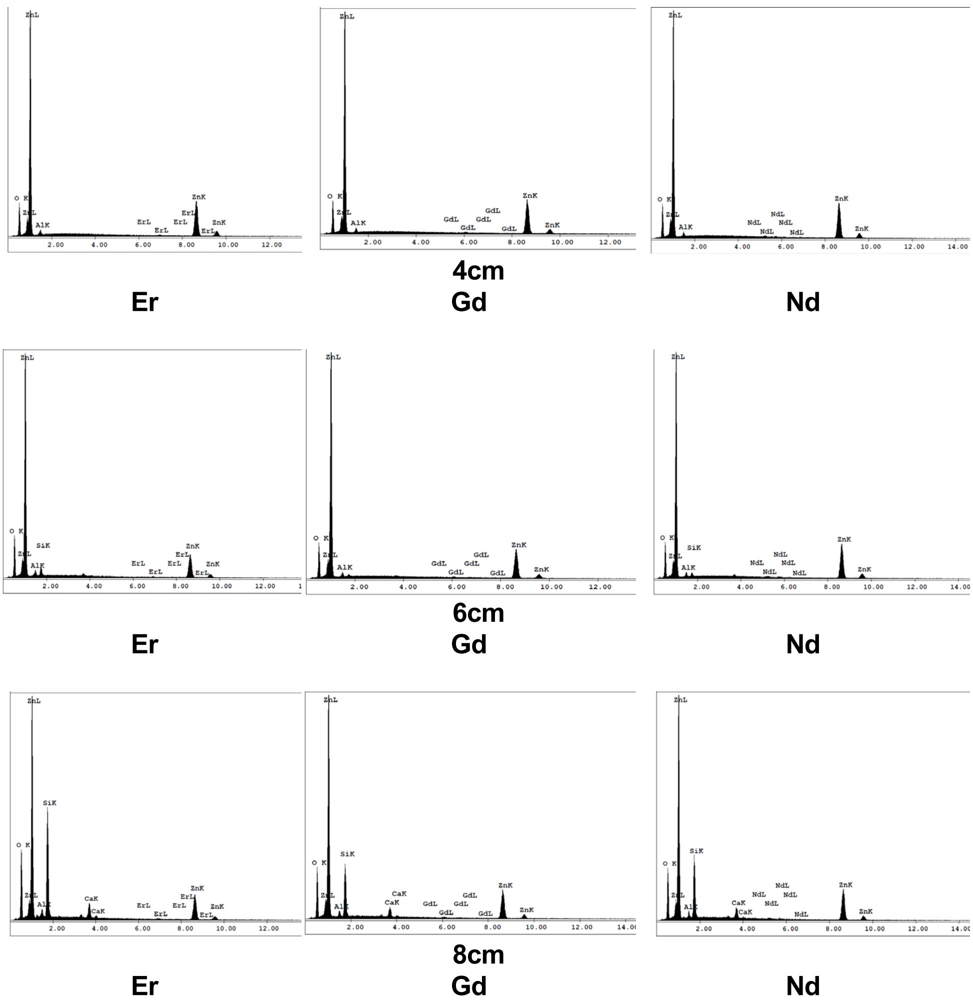


Figure 5. EDX spectra of the studied films

Energy dispersive X-ray (EDX) analysis and elemental mapping images displayed the existence of rare earth ions in the structure of AZO thin films. The percentage of rare earth ions is better observed for thicker films that were obtained for the smallest distance between target-substrate (4 cm) is presented in Table 1. EDX measurements highlight a lack of oxygen, 50% lower than that for Zn, for a constant gas flow in the chamber [25].

Table 1. Elemental weights (wt.%) of Zn, O and dopant elements in the thin films.

Sample	Distance (cm)	Dopant wt.%	Oxygen wt.%	Zinc wt%
AZO-Er	**4**	1.63	13.32	82.37
	6	2.80	20.79	68.19
	8	2.31	24.43	42.72
AZO-Gd	**4**	2.32	14.28	80.74
	6	2.03	16.39	78.82
	8	1.85	20.06	56.72
AZO-Nd	**4**	1.45	14.08	81.95
	6	1.63	14.74	79.37
	8	1.46	19.04	57.11

Optical properties

In Figures 6, Figure 7 and Figure 8 are presented the transmittance spectra and the refractive index of AZO-RE doped thin films. It is shown that the transmittance spectra decreases with the increase of the distance between target-substrate highlighting that the transmittance is influenced of the film thickness and also, the nature of the doping component, in accordance with the literature [31-33]. Furthermore, the refractive index shows a decrease with the increase of wavelength spectra.

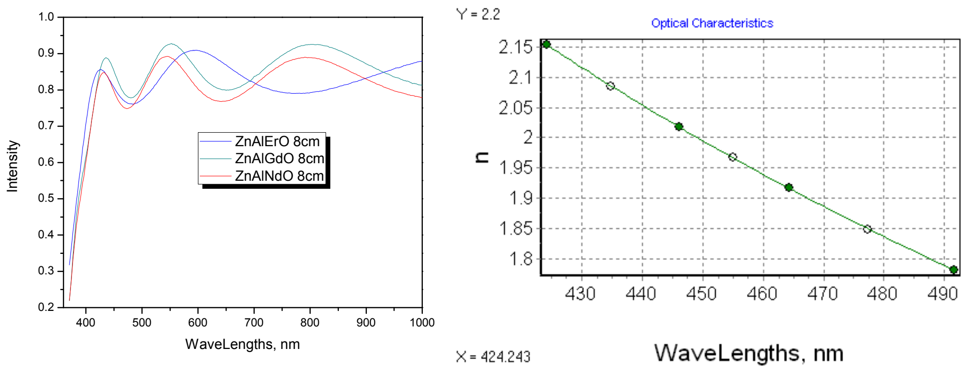


Figure 6. Spectroscopic measurements of the AZO-RE thin films deposited at a distance of 8 cm and refractive index chart

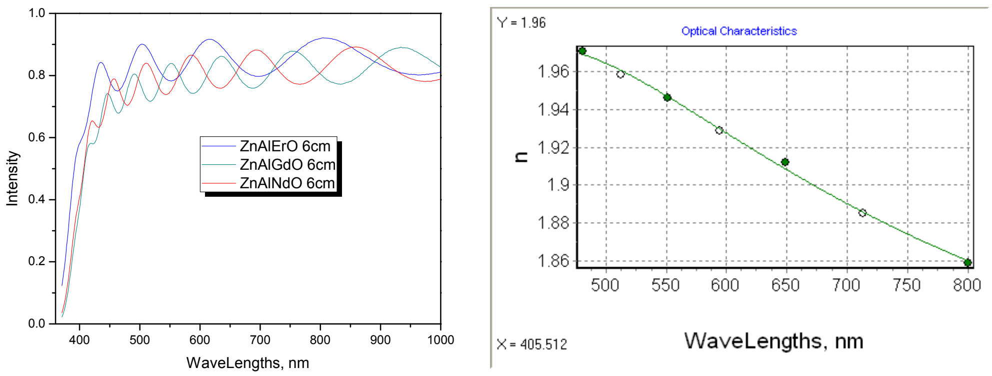


Figure 7. Spectroscopic measurements of the AZO-RE thin films deposited at a distance of 6 cm and refractive index chart

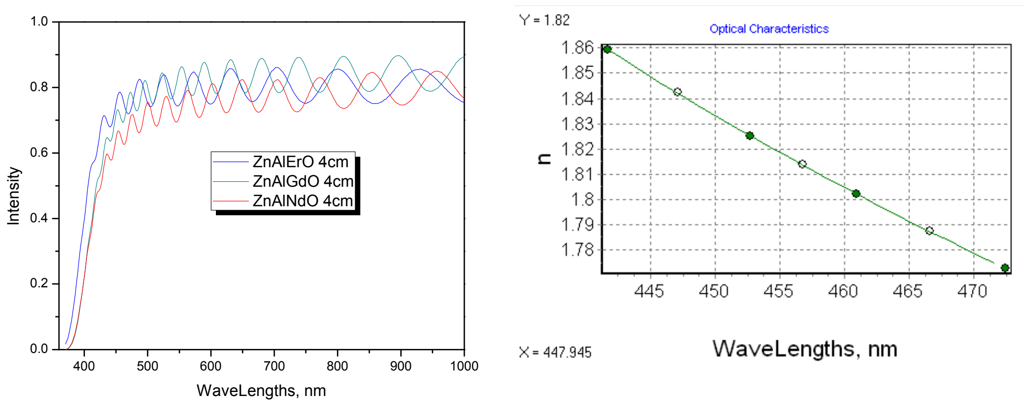


Figure 8. Spectroscopic measurements of the AZO-RE thin films deposited at a distance of 4 cm and refractive index chart

Table 2 shows the thickness dependence of AZO-RE films deposited at different distances.

Table 2. The thickness of the AZO films doped with Er, Gd, Nd deposited at different distances

d (cm)	h (nm) Er	h (nm) Gd	h (nm) Nd
8	346	485	496
6	668	833	811
4	1600	2286	2529

It is found that the film thickness for the same target-substrate distance is influenced by the nature of the dopant (the highest values are obtained for Nd and lowest for Er). The film thickness increases dramatically with decreasing of the target-substrate distance. By decreasing the distance from 8 cm to 4 cm, the film thickness increases approximately 4.6 times in case of the films with Er and Gd and 5.1 times for Nd doped films.

CONCLUSIONS

High quality transparent Er, Gd and Nd doped AlZnO thin films were grown using the RF sputtering technique on glass substrate starting from polycrystalline targets and characterized by XRD, SEM and EDX techniques. The effect of 4f elements and target-substrate distance on structural and morphological properties was studied.

XRD measurements show that all the deposited films are polycrystalline in nature. The increase of target-substrate distance has a (100) preferential orientation, observed for Gd and Nd doped AlZnO thin films. The 4f doping affects the growth of crystallites, damaging the structure, which for AlZnO films is more evident than for Er doping.

The SEM images of the thin films showed the uniformity of the surface which consists of well-defined spherical grains. With decreasing of target-substrate distance the grain size increases.

The EDX analysis results show that the oxygen stoichiometry is lower than 50 wt.% and the stoichiometry of the amount of Zn is more than 50 wt.%. These results highlight the presence of an oxygen deficiency.

Optical measurements highlight a slight decrease of the transmittance spectra (about: 83%) with the decrease of the target-substrate distance, because the increase of film thickness. Also, the refractive index decreases with the increase of wavelength from 400 nm to 1000 nm.

EXPERIMENTAL SECTION

Ceramic preparation

We prepared three ceramic targets obtained by solid state reaction method, using mechanically mixed powders of 97 wt. % of ZnO (99.99% purity), 2 wt. % of Al_2O_3 (99.97%), 1 wt.% of Gd_2O_3 (99.9%), Er_2O_3 (99.9%), Nd_2O_3 (99.9%). They were mechanical processed, pressed at a pressure of 490 MPa and annealed at a temperature of 930 °C for 90 minutes.

Deposition process

The RE-doped AZO thin films were fabricated by RF magnetron sputtering using a power of 100 W. The deposition was performed on glass substrates heated at a constant temperature of 150 ^{0}C, the deposition pressure was maintained at 2.1 × 10^{-2} mbar. The films were deposited in an oxygen–argon atmosphere with the ratio $Ar:O_2$=10:6 sccm. By modifying the distance between target and substrate for 4 cm, 6 cm and 8 cm and the type of dopant (Nd, Gd, Er), we obtained nine different thin films. The films' thickness was measured with a piezoelectric sensor.

Measurements

To emphasize structural properties we analyzed the surface of the thin films using Bruker Advance D8 XRD diffractometer in Bragg-Bretano (ϴ - 2ϴ) configuration with an CuK_{α} anode ($\lambda_{CuK\alpha}$ = 0.154 nm). XRD patterns were obtained with a step size of 0.1 and an integration time of 5 s/step.

The microstructure and stoichiometry of the thin films deposited under different distances between substrate and target were evaluated using SEM and EDX. For this type of measurements we used a FEI Quanta 3D FEG 200/600 with double electron beam in vacuum module with EDT (Everhart Thornley Detector) from ICEI Cluj Napoca.

Optical measurements of the AZO-doped thin films were performed using a J.A. Woollam M2000V ellypsometer in transmission mode in the range of wavelengths between 375-1000 nm from INCDTIM Cluj Napoca. To highlight the optical properties of the thin films we used the PARAV program.

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