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STRUCTURAL AND OPTICAL CHARACTERIZATION OF ZnO FILMS DOPED WITH Ni

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ABSTRACT. Zinc oxide (ZnO), and Ni-doped ZnO (NZO) thin films were deposited on glass substrates by radio frequency (RF) magnetron sputtering for three different distances between substrate-target. The influence of the distance between substrate-target upon structure of the thin films was analyzed by X-ray diffraction (XRD) and the grain size was determined by theoretical calculations. Optical transmission measurements show the influence of doping and distance between substrate-target on the optical band gap.

Keywords: *XRD, transmittance, Ni-ZnO thin films, RF magnetron sputtering*

INTRODUCTION

It is not a novelty that zinc oxide is used to generate energy, however, its field of application has never ceased to expand by doping with various impurities to improve its optical and electrical qualities. Because

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ZnO is cheaper, non-toxic and more abundant in nature it has more advantages compared to ITO films (indium tin oxide). Also, being chemically stable to hydrogen plasma processes, doped-ZnO thin films are used to produce solar cells [1], gas sensors [2-4], diodes [5], display devices [6], spintronics [7], air filters [8] etc. These impurities work as a donor for the metallic ZnO when it replaces an occupied Zn^{2+} state or a state in between the zinc oxide composition structures, the donor offering the optical transparency.

The Ni-doped ZnO (NZO) can be analyzed in many forms such as powders, nanostructures, nanoparticles and thin layers. Some recent articles regarding Ni-doped ZnO thin films, it was found that a lower Ni concentration (3% -5%) possesses better crystallinity and a higher magnetic moment [9]. Furthermore, a concentration of 12% Ni show that with the introduction of Ni, the refractive index (ne) decreases as a result of doping. This decrease can be explained by the annihilation of oxygen vacancies, but the same method shows that the prepared samples also showed ferromagnetic properties [10]. Thus, NZO study still leaves room for progress. Although Ms has values smaller than those of ZnO: Co, Ni remains one of the most promising and most used dopants in the transitional metals group.

For fabricating metal oxide thin films and related materials, radio-frequency magnetron sputtering technique is considered one of the best deposition methods, as it allows growth of uniform thin films at low temperature with high reproducibility and with strong adhesion to substrates over large area surfaces [11].

In the present study, we present the structural and optical characterization of NZO thin films obtained by FR magnetron sputtering. This technique is often used to deposit thin films because of its efficiency, low cost and good reproducibility [12]. Thus, taking into account the decrease of the distance between the target substrate and the residual compressive stress at the film-substrate interface arising during the film growth, significant changes in the structural and optical properties have occurred.

EXPERIMENTAL DETAILS

We prepared two ceramic targets, one undoped using just ZnO of 99.99% purity, that acts as a reference for the next one that was doped with NiO (3% w.p.) obtained by solid state reaction method, using mechanically mixed powders of ZnO (99.99% purity), NiO (99.99%). They were mechanical processed at a pressure of 490 MPa and annealed at a temperature of 930 °C for 60 minutes. The deposition was performed on soda-lime glass substrates heated at a constant temperature of 150 ^{o}C and a controlled atmosphere of O_2 and Ar, having the mass flows d_{Ar} and d_{O2}. The RF-power density was 19.72 W/cm^2 and the deposition pressure was maintained at 6×10^{-2} mbar and the deposition time was maintained constant at **a value of 90 minutes**.

The films thicknesses, t, measured with a quartz monitor were around t=105 nm for d=4 cm, t=45 nm for d=6 cm and t=15 nm for d=8 cm, respectively. This result show that the growth rate (*R*) decreases as the substrate to target distance increases.

The crystal phases were identified by comparing the 2θ values and intensities of reflections on X-ray diffractograms with JCP data base using the Diffraction AT-Brucker program. Optical transmission measurements were done with a Carry 500 Spectrometer (300 nm – 1000 nm range). From the transmission spectra, the optical constants were calculated using the program PARAV-V2.0 [13].

RESULTS AND DISCUSSIONS

A. Structural measurements

For the preparation of films, we started by synthesizing two ceramic targets, the zinc oxide first, and the second was prepared by adding nickel oxide to the ZnO composition with 3% NiO (99.99% purity) and 97% percent ZnO mass (purity 99.9%). The percent fraction calculated from the diffractogram respects the percentages in the recipe used by 97% ZnO and 3% NiO, respectively. However, the fact that the calculated percentage of the diffractogram is 2.2% (*table 1*) shows that in the solid phase reaction method NiO did not react completely, as emphasized in the experimentally obtained diffractogram (see *figure 1*).

Table 1. Calculated phase percentage

Name	Formula	Matched phase	Quantity (%)
Zinc oxide	O Zn	Zincite	97.8
Nikel oxide	Ni O		2.2

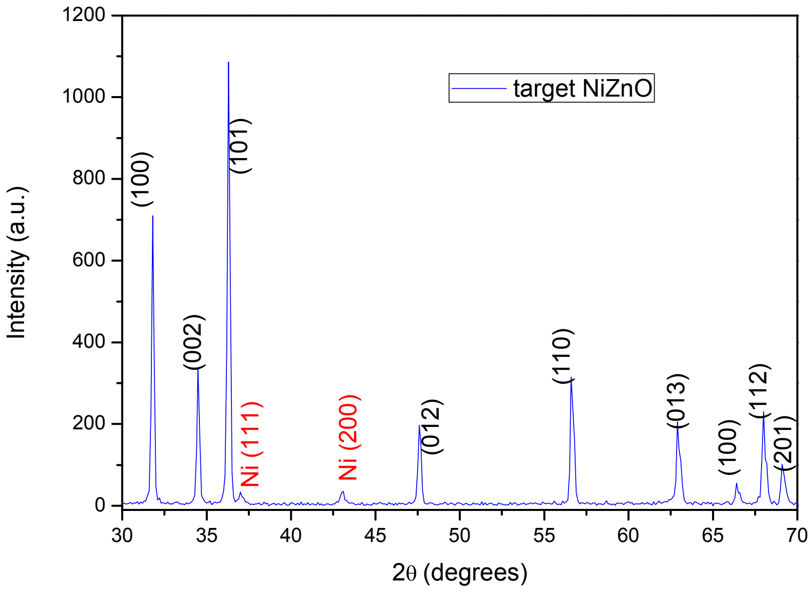

Figure 1. XRD pattern of NZO target

Targets were analyzed by X-ray diffraction, and the diffraction peaks obtained for an angle scan of 2Θ, in the range of 30° and 70°, with the Miller indeces (100), (002), (101), (012), (110), (013), (112) and (201) are assigned to the crystalline planes of ZnO. NiO, (111) and (200) diffraction peaks are also observed, which means that the parameters of the solid phase reaction method used for target synthesis were not optimal.

Films were deposited at three different distances between target-substrate, namely 4 cm, 6 cm and 8 cm respectively, aiming to optimize the manufacturing parameters as well as improving their structural and optical properties.

The crystallite size was calculated with Scherrer's equation: $D = \dfrac{0.9\lambda}{B\cos\theta}$

where λ, ϑ, and B are: the X-ray wavelength $\lambda_{CuK\alpha1}$, diffraction angle and FWHM (full width at half maximum) of the (002) diffraction peak, respectively [14].

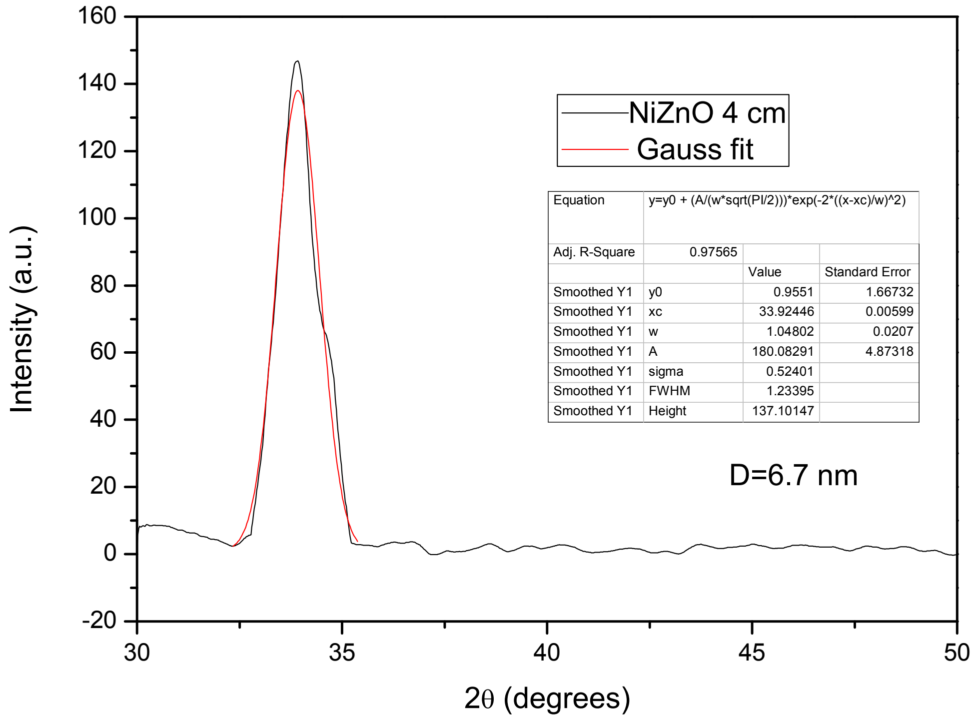

Figure 2. Diffractogram pattern of NZO film deposited at a distance of 4 cm

The films deposited at d = 4 cm (figure2) and d = 6 cm (figure3) have a preferential orientation along the c axis, perpendicular to the surface of the substrate, and the diffraction peaks correspond to 33.9 ° and the wound structure, according to the study of the literature [15]. The crystallite size is influenced by the distance between substrate-target, *d,* for NZO doped films (see *Table 2*).

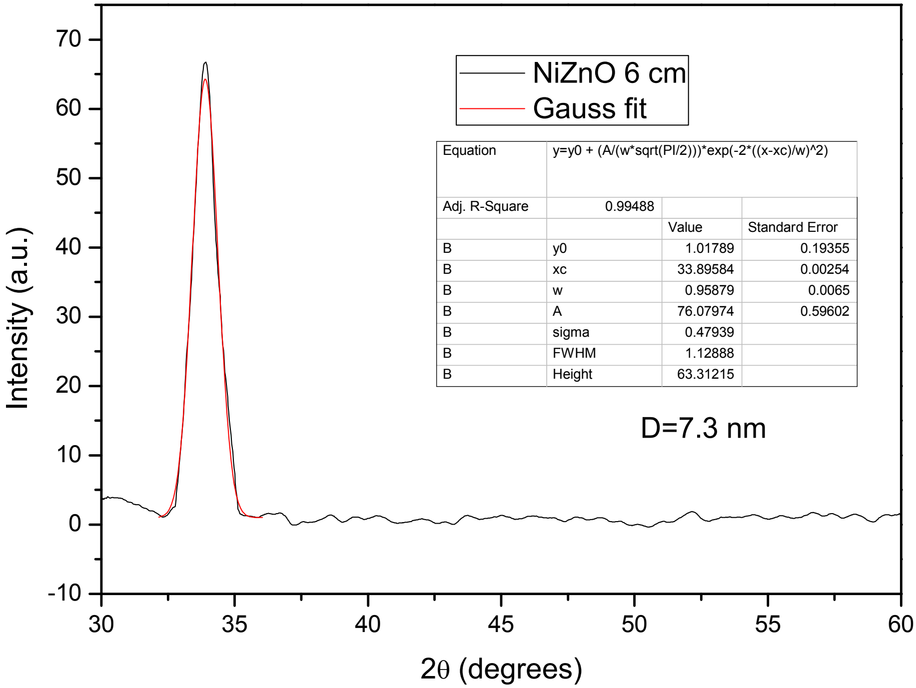

Figure 3. Diffractogram pattern of NZO film deposited at a distance of 6 cm

Table 2. Structural and optical characteristics of NZO thin films

Sample name	d (cm)	D (nm)	t (nm)	E_g (eV)	n (nm)
NZO	4	6.7	105	3.23	1.92
NZO	6	7.3	45	3.26	
NZO	8	-	15	3.28	

Diffractograms belonging to the above-mentioned films are made up of a single maximum of diffraction, which corresponds to the crystalline planes with Miller indices (002). In the case of the film deposited at d = 8 cm, the X-ray diffraction was inconclusive because it is the thinnest, respectively 15 nm.

The values of the thin film parameters shown in *Table 2*, with respect to the size of the crystals obtained using the Scherrer equation. These values increase with the increase of the distance between target-substrate, the ***optimum distance with the best crystallinity being 6 cm*** in agreement with the result of the correlation coefficient illustrated in *Figure 3.*

B. Transmittance measurements

Optical transmittance measured as function of wavelength (in the region 375-1000 nm) for NZO films using an ellipsometer J.A. Wollam, the results are illustrated in *Figure 4* and *Figure 5.* By ellipsometry measurements we determined the optical band gap and the thickness of NZO thin films. Optical constants were determined from reflection, and then the thickness of each film was calculated*. Using the Complete EASE program, a fitting process was made between the measurements and the model, thus determining the thickness of the films.* The data shows that the films are transparent in the visible region. The effect of distance between target- substrate on the optical transmittance, thickness of the films, t, and the band gap (E_g) values of the films have been studied by using the program PARAV [13].

The optical band gap is given by the energy difference between Fermi pulse states in the band and the valence band.

The linearity of the plot of (▯h▯)^2 versus 'h▯' indicates a direct transition [16]. By increasing d from 4 cm to 8 cm, the optical band gap E_g value were the same for all samples, which is in accordance with other literature results (*see table 2*).

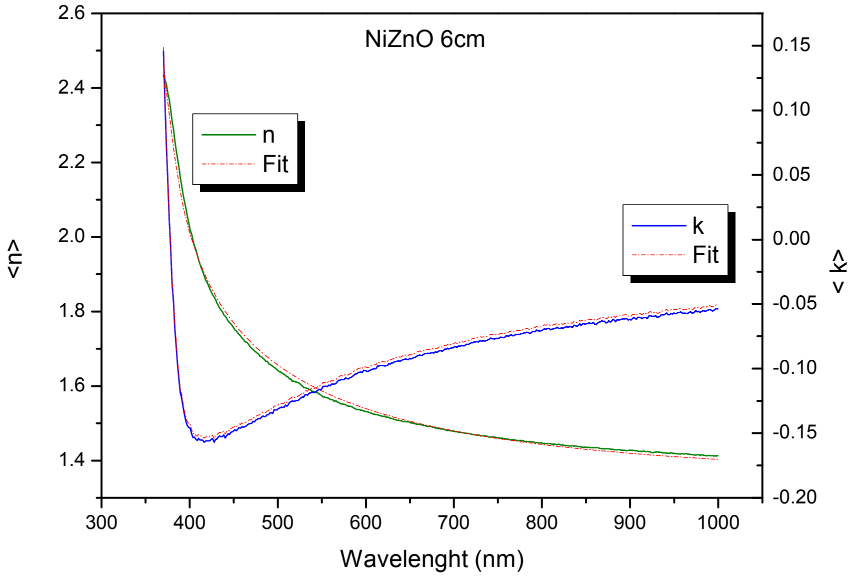

Figure 4. Ellipsometric measurements and fitting pattern for NZO film deposited at d = 6 cm

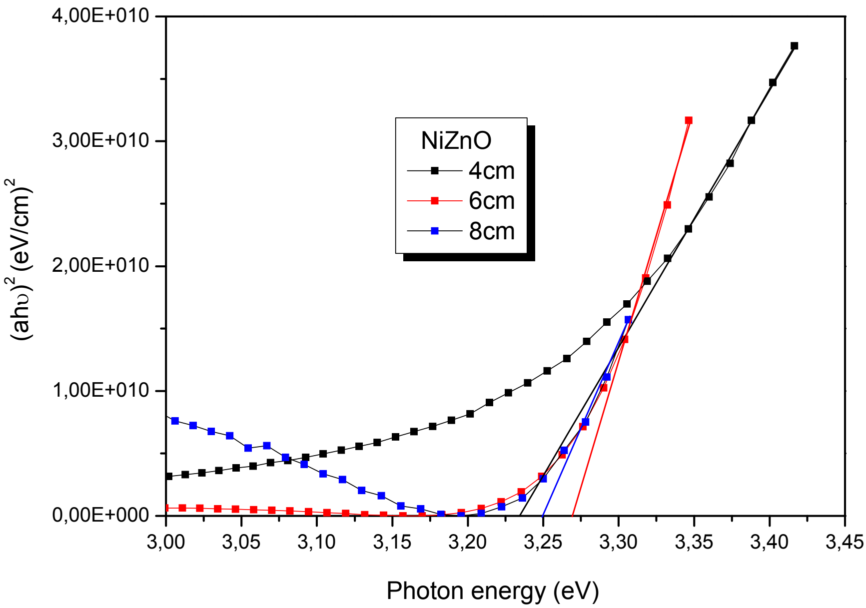

Figure 5. Tauc plotting of NZO thin films obtained for three distances

The band gap, E_g, was determined according to the Tauc relation:

$$(\alpha h\nu)^2 = A^2(h\nu - E_g),$$

where A is a constant that depends on the electron-hole mobility, h is Planck's constant. The optical absorption coefficient is defined as $\alpha = \frac{1}{t}\ln\frac{(1-R)^2}{T}$, where t is the thickness of the thin films [17].

To entail, the optical band gap and the absorption limit of the nanostructured materials is shifted due to the quantum effects because of the dimensions (the electronic properties differ with particle size reductions) [18].

For the film deposited at 4 cm, the value of E_g is 3.23eV and with the increase of the target-substrate distance, the E_g value increases as shown in *table 2.*

CONCLUSIONS

Ni doped ZnO thin films were deposited on glass substrates by RF magnetron sputtering method. The effect of Ni doping on the optical and structural properties of ZnO films was analyzed.

From the XRD measurements it was found that the values for the grain size was between 6.7 nm and 7.3 nm depending on the target-substrate distances used. The diffraction pattern of to the films deposited at d = 4 cm and d = 6 cm show a single peak, corresponding to the crystalline planes with Miller indices (002). Furthermore, the films deposited at d = 4 cm and d = 6 cm have a preferential orientation along the c axis, perpendicular to the surface of the substrate, and the diffraction peaks correspond to 33.9 ° of the wurtzite structure.

The maximum value of E_g was obtained for the film deposited at a distance of 6 cm, this being 3.26 eV. The refractive index, n, calculated at the specific wavelength of 632.8 nm, has the same value for all three films obtained.

Thus, these results emphasize that the optimum distance between target-substrate was 6 cm, where the crystallinity as well as optical properties show good results.

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