Study of the Influence of Doping on the Structural, Optical and Electrical Properties of zinc oxide thin Films Produced by by Spray Pyrolysis for Solar Cell Applications

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ABSTRACT

In the present study, the effect of Al doping with 0.5 % Al (AZO-0.50), 1 % Al (AZO-1.00), and 1.5 % Al (AZO-1.50) have been successfully synthesized by Spray Pyrolysis method. The structural, optical and electrical properties of the obtained films was studied. The obtained films are characterized by different techniques such as X-ray diffraction (XRD), UV-visible and electrical Hall Effect measurements. The X-ray diffraction confirmed that the Al doping did not change the ZnO Hexagonal Wurtzite structure. Spectroscopic measurements in the UV-VIS-IR wavelength range were found to give good average transmittance values of about 73%, with a high transmittance of 75% with 0.5% Al doping. The optical gap value increases in the range of 3.23 to 3.26 eV with increasing aluminium content. The electrical analysis shows that the conductivity improved with doping compared to the pure ZnO film.

I. Introduction

In recent years, zinc oxide (ZnO) has been of increasing interest in many research works because of its many potential applications [1]. It has a relatively large exciton binding energy (60 meV) at room temperature [2], zinc oxide (ZnO) is a n-type compound semiconductor with a direct wide band gap [3, 4], zinc oxide represents an important basic material due to its low cost as well as its electrical, optical and luminescent properties [5]. Overall, ZnO is of importance for fundamental research, and relevant for various fields of industrial and high technological applications such as gas sensors [6], optoelectronic [7], solar cell [8]. ZnO thin films have been prepared using various methods such as pulsed laser deposition [6], thermal evaporation [9], sputtering [10], sol gel [11] and spray pyrolysis [12]. In this work, the effect of aluminum (Al) doping on the structural, optical and electrical properties of ZnO thin films produced by the spray pyrolysis technique was studied.

II. Experimental details

The thin films of Al-doped ZnO are deposited on the glass substrates at 350±10 °C. Before the deposition, the substrates of dimensions 75 × 25 mm^2 were cleaned with acetone and double-distilled water. The sputtered solutions were obtained by dissolving zinc nitrate (Zn (NO3)2,6H2O), aluminum nitrate (Al (NO3)3,9H_2O), in

double distilled water at a concentration of 1.00 M, Different syntheses are performed with different concentrations of aluminum (x= 0.5, 1 and 1.5%). Furthermore, all the thin ZnO films obtained were manufactured under the same conditions summarized in Table 1.

Table 1: Conditions for depositing thin films of ZnO doped Al.

Precursor of solutions	zinc nitrate:($Zn(NO_3)2,6H_2O$) aluminum nitrate: ($Al(NO_3)_3$, $9H_2O$)
Composition of the spray solutions	ZnO : 100% Zn ,$(NO_3)_2$ ZnO doped 0.50% Al : 99.5% Zn ,$(NO_3)_2$ + 0.5% Al $(NO_3)_3$ ZnO doped 1.00% Al : 99.0% Zn ,$(NO_3)_2$ + 1.0% Al $(NO_3)_3$ ZnO doped 1.50% Al : 98.5% Zn ,$(NO_3)_2$ + 1.5% Al $(NO_3)_3$
Name	Pure (un-doped) ZnO ZnO doped 0.50% Al : AZO-0.5 ZnO doped 1.00% Al : AZO-1.0 ZnO doped 1.50% Al : AZO-1.5
Substrate	glass
Temperature	325±10 °C
Distance	substrate-heating plate: 30 cm
Air flow rate	2 ml /min
Flow rate	6.104 Pa
Volume	75 ml

The structural characterization was performed at room temperature using a Bruker X-ray diffractometer model D2 Phaser with CuKα radiation (λ =1.5406 Å). The optical transmittances have been recorded between 200 and 2500 nm wavelength using a JASCO 570 type UV–vis-NIR double-beam spectrophotometer. The electrical parameters were measured by using the ECOPIA HMS-5000 Hall Effect measurement system at room temperature.

II.1 Results and Discussion

II.1.1 *Structural properties and morphology*

Figure.1. Summarized X-ray diffraction (XRD) spectra of un-doped and Al-doped ZnO thin films with different concentrations, the presence of several peaks indicating the polycrystalline structure of the obtained films. All the peaks observed in these spectra correspond to the wurtzite structure of ZnO according to the comparison with JCPDS map No. 36-1451 [13]. The results revealed the existence of the preferred orientation (002) with the c-axis perpendicular to the substrate surface. Such a preferred basal orientation is generally observed in aluminum-doped ZnO films [14-15]. No peaks corresponding to other phases such as aluminum, aluminum oxide or other tin compounds were detected in these XRD spectra; this shows the good incorporation of Al atoms in the ZnO matrix and therefore the success of the doping.

The grain sizes, lattice constants, strains and dislocation density have been evaluated according to Fig. 3. For the estimation of crystallite size the Sherrer formula is used [16]:

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

Where k = 0.9, λ = 1.5406 Å is the x-ray wavelength, β is the full width at half maximum (FWHM) of the XRD peak, and θ is Bragg's diffraction angle.

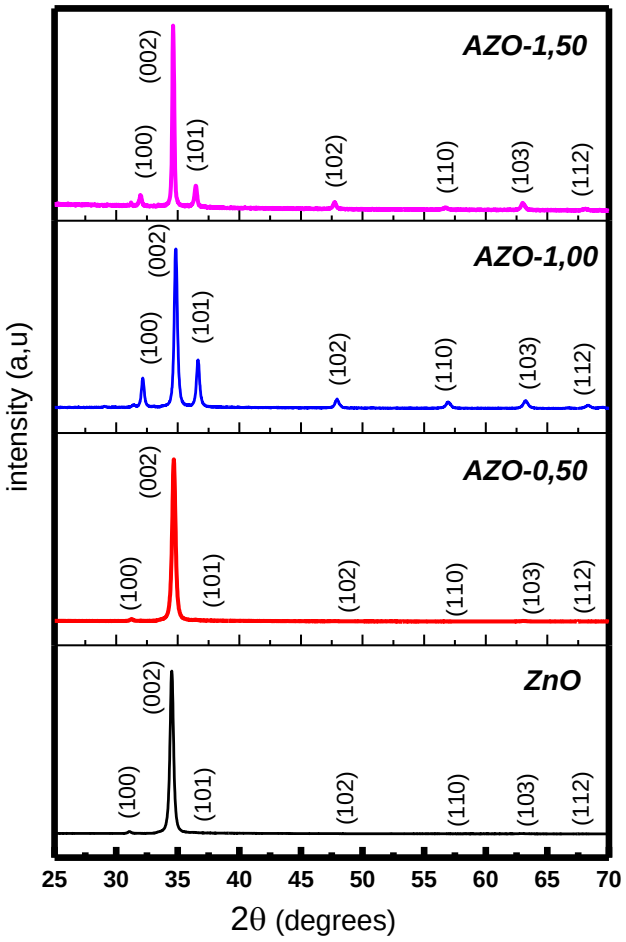

Figure 1. XRD of thin layers of ZnO and AZO different concentrations of aluminum.

Table 2: Structural parameters of ZnO and Al-doped ZnO thin films with different concentrations.

Samples	$2\theta^0$ (002)		FWHM $.10^{-3}$ (Degree)	Crystal size (nm)	a (Å)	c (Å)	(ε) deformation (10^{-4})	(δ) dislocation density (10^{-4} Line/nm^2)
JCPDS card N ° 36-1451	34.422		-	-	3.24	5.20	-	-
ZnO	34.521		5.093	28.508	3.241	5.192	12.157	12.300
AZO-0.50	34.537		5.388	27.021	3.240	5.188	12.824	13.898
AZO-1.00	34.574		5.460	26.595	3.239	5.184	13.033	14.138
AZO-1.50	34.599		5.411	26.094	3.238	5.182	13.283	14.986

The lattice parameters of the films are determined by the following relation [17]:

$$\frac{1}{d^2_{hkl}} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\left(\frac{l^2}{c^2}\right) \quad (1)$$

The micro-strain (ε) has been estimated using the following formula [18]:

$$\varepsilon = \frac{\beta cos\theta}{4} \quad (2)$$

The dislocation density of the films has been estimated using the following formula [19]:

$$\delta = \frac{1}{D^2} \quad (3)$$

All the structural parameters, i.e. full width at half maximum (FWHM), crystallite sizes, lattice constants (a and c), strains and dislocation density are summarized in Tab. 2.

From (Tab.2), the degradation of the grain size was attributed to the incorporation of aluminum in the ZnO site. This degradation has already been observed by several authors [20,21] which implied a decrease of the lattice parameters and consequently a compressive stress, the authors explained this behavior by the ionic size effects of the dopants occurring in the substitution sites since the ionic radius of Al^{3+} (0.54 Å) is smaller than Zn^{2+} (0.74 Å) [22].

II.1.2 *Optical properties*

The transmittance spectra for ZnO, AZO-0.5, AZO-1.00 and AZO-1.5 were measured in the wavelength range 200-2500 nm (Fig.2). As shown, the optical transmission spectra of zinc oxide films prepared on a glass substrate at a substrate temperature of 350 ^{0}C for different aluminum doping concentrations. All films are highly transparent in the visible range (400-750 nm) of the optical spectrum, with average values up to 75%. It should be noted here that the resulting films will give a satisfactory optical window in the visible range for optical applications [23].
All the spectra show the presence of very weak interference fringes, due to reflections at the surface of the layer, at the layer/substrate interface as well as to light scattering which is favoured by the small grain sizes, also observed the absence of interference fringes in the transmission spectra is due to the roughness of the surface of our films caused by the spray pyrolysis technique [24]. This may be due to very small droplets resulting from this technique that vaporise above the glass substrates and condense into clusters [25].

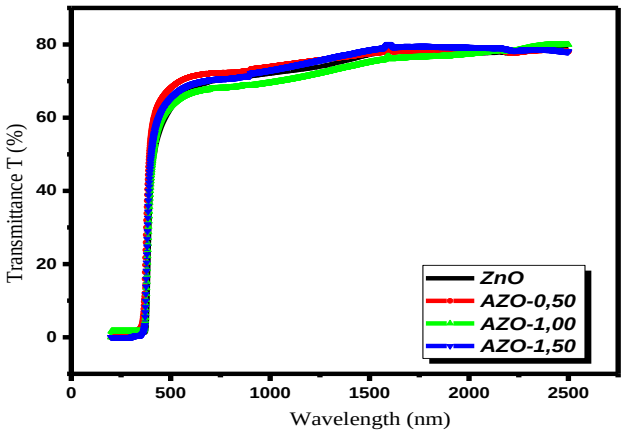

Figure 2. Transmittance spectra of the obtained films.

The band gap of thin ZnO films is an important parameter for estimating the limit of their absorption band, From the transmittance spectra we calculated the optical gap ,the optical band gap was determined using the following formula [26-27]:

$$(ahv)^n = A(hv - Eg) \quad (5)$$

Where is the absorption coefficient, hv the photon energy, A, a relation constant and Eg the optical band gap.
We have usually taken n = 0.5 for indirect band gap semiconductors and n = 2 for direct band gap semiconductors, as ZnO is considered as a direct semiconductor. The intersection of the extrapolation of the linear region of $(\alpha h\upsilon)^2$ on the energy axis, which makes it possible to determine the optical gap (Fig.3). According to (figure.3), we observe a shift of the gap energy towards the large band gap energies after the increase of the aluminum concentration from 3.23 eV to 3.26 eV. This shift towards the large values is in agreement with the literature [25] and could be explained by the increase in carrier concentration [28].

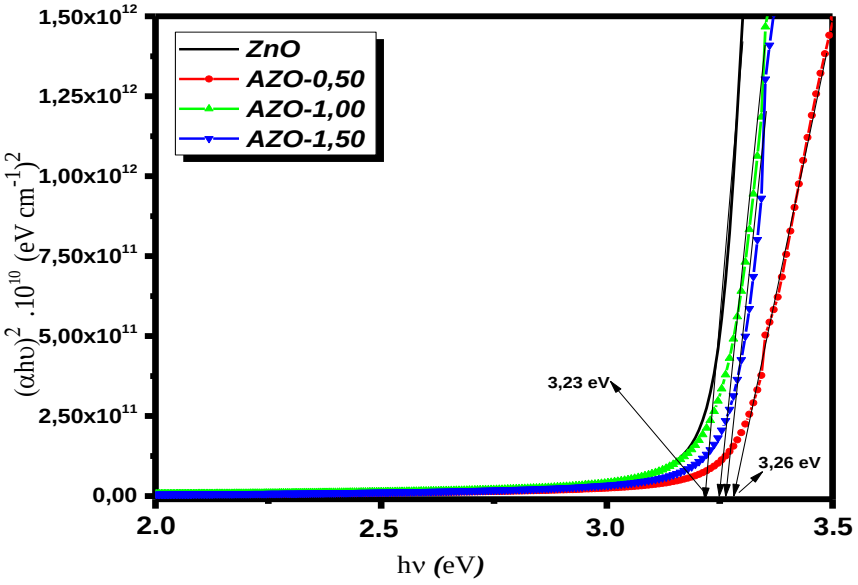

Figure 3. Variation of $(\alpha h\nu)^2$ versus energy of the obtained films.

The disorder is characterized by the Urbach energy measurement. The value of this energy (Eu) has been calculated with using equation (29).

$$\alpha = \alpha_0 \exp(\frac{h\nu}{E_U}) \quad (6)$$

Where E_U is the Urbach energy, α is the absorption coefficient and α_0 is a constant.
The increase of the Urbach energy with the increase of the aluminum concentration in ZnO can be attributed to the degradation of the structural quality of the doped layers, in agreement with the XRD data previously. Comparing our results with those of the literature [30], the reported Eu variation range (0.92-1.44 meV) correlated with those of the optical band gap, confirms the slight loss of crystallinity. The values of the band gap (Eg) and Urbach energy (Eu) for ZnO and AZO at different aluminum concentrations are summarized in Table 3.

Table 3: Urbach energy of ZnO and Al-doped ZnO thin films with different concentrations.

Samples	Urbach energy (Eu) (eV)
ZnO	0.092
AZO-0.50	0.108
AZO-1.00	0.120
AZO-1.50	0.131

II.1.3 *Electrical properties*

The electrical properties of ZnO and AZO thin films with different aluminum concentrations are measured at room temperature using the Hall Effect measurement.

The values of electrical conductivity (σ), carrier concentration (n) and Hall mobility (μ) are summarised in (Table.4). The negative values of the carrier concentrations show that the deposited films are of type (n). The un-doped ZnO sample has a low conductivity which is $4.06.10^{-03}$ $(\Omega\ .cm)^{-1}$, in agreement with the literature [31]. From (Table.4) it can be seen that the electrical conductivity increases rapidly with (Al) doping and takes a maximum value of $1.27.10^{-01}$ (Ω.cm-1) for the AZO-1.00 sample (Fig.4).This electrical enhancement is due to the increase of the carrier concentration which is about $2.54.10^{+18}$ cm^{-3}. While the mobility remained about the same, this improvement in the conductivity of aluminum-doped (ZnO) is noted in the work of A. Crossay et all [34].

Table 4: Electrical parameters of ZnO and Al-doped ZnO thin films with different concentrations.

Samples	Mobility (cm^2/V_S)	Carrier concentrations (cm^{-3})	Conductivity $(\Omega\ .cm)^{-1}$
ZnO	$4.30.10^{-01}$	$-5.91.10^{+16}$	$4.06.10^{-03}$
AZO-0.50	$4.04.10^{-01}$	$-2.14.10^{+18}$	$1.01.10^{-01}$
AZO-1.00	$3.14.10^{-01}$	$-2.54.10^{+18}$	$1.27.10^{-01}$
AZO-1.50	$4.78.10^{-01}$	$-1.39.10^{+18}$	$3.98.10^{-02}$

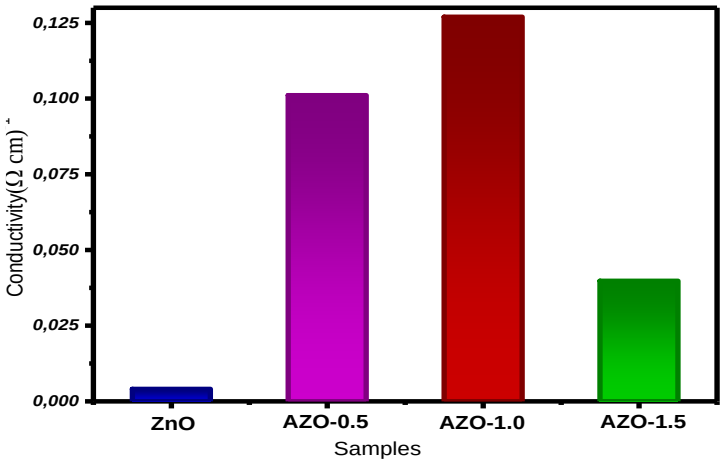

Figure 4. Evolution of the electrical conductivity of ZnO and Al-doped ZnO thin films with different concentrations.

III. Conclusion

Thin films of pure and Al doped ZnO have been successfully prepared with the spay pyrolysis. The structural, optical and electrical properties of un-doped and Al- doped ZnO thin films with different concentrations were investigated out. The aim of this contribution is to see the effect of aluminum incorporation in the ZnO lattice as transparent conducting oxides in photovoltaic cells. The XRD analysis confirmed that the deposited films have a hexagonal wurtzite structure with a preferred orientation of (002) no peaks corresponding to other phases was observed. The crystallite sizes are calculated using the scherrer's formula, which shows that the doped ZnO layers have the smallest crystallite size. UV-visible analysis showed that all layers have high transparency with an average transmission value of about 75% after doping; the highest band gap value 3.26 eV was obtained for the doped film (AZO-0.50). Electrical measurements were also carried out giving a maximum electrical conductivity of the order of $1.27.10^{-01}$ $(\Omega.cm)^{-1}$ for the thin film (AZO-1.00). This suggests that the deposited Al doped ZnO thin films are a good candidate for optoelectronic applications such as photovoltaic applications.

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