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Effect of the precursor solution on the structural morphological and optical properties of ZnO thin films deposited by Spray Pyrolysis technique for solar cell application

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***Abstract*—The objective of this research is to study the structural, morphology and optical properties of zinc oxide thin films deposited by spray pyrolysis technique. The ZnO thin films were prepared and grown on glass substrate at 400°c, using two different precursor solutions namely zinc acetate, and zinc chloride with a molarity of 0.2M/L. Our interest is on the investigation of the precursor solution on structural; morphological and optical properties of ZnO thin films. The X-ray diffraction patterns indicated that the thin films were almost pure and are relatively uniform the preferential orientation of ZnO growth was (002). The nanostructure images obtained by scanning electron microscopy show the whole samples have a homogenous distribution of ZnO product on the substrates.**
The spectrophotometer UV-Visible confirms that it is possible to get good transparent ZnO films with a transmission of 80 to 95% in the visible. The values of optical gaps Eg deduced from the spectra of UV-Visible transmissions vary between 3.209 and 3.288 eV.

***Keywords*—ZnO; Spray Pyrolysis, Thin film, XRD, OTC**

I. INTRODUCTION

Transparent conducting oxide (TCO) thin films have been very important concerning the design of devices with immediate applications in sensors, photovoltaics, catalysis, micro- and opto-electronics, among others [1], [2].

ZnO thin films is one of the most studied TCO materials, since it exhibits distinct advantages like abundance in nature, non-toxicity, high optical transmittance in the visible region and high chemical and thermal stability, among others [3].

Zinc oxide (ZnO) is a binary, n type- semiconductor material with a large direct gap varying between 3.20 and 3.35 eV [1] and large exciton binding energy (60 meV) [4].

Its properties make it an important base material for the synthesis of many technological devices such as: solar cells, gas sensors, piezoelectric sensors, guides of waves, etc. [5] and transparent layers in photovoltaic solar cells due to the high transmittance in the visible region and its low electrical resistivity Also, a ZnO layer may work as an antireflection coating as it absorbs the UV radiation such that lower energy photons are able to reach the absorber layer [6].

ZnO thin films can be produced by several techniques, including: electrodeposition [7], spray, thermal evaporation, reactive spraying, sol gel [8] and laser ablation etc. [9].

The technique of spray pyrolysis is a simple, less expensive and allows the production of highly pure and ultrafine nanoparticles with a high degree of transparency [10], [11]-[12].

Different morphologies can be produced including nanorods [13], [14], nanowires [15], [16], nanotubes [17] and nanostructured thin films [18].

Accordingly, the preparation of ZnO films by spray an aqueous solution has been seen to attract increasing interest over the last few years.

Most research is based on the study of the influence of different precursor solution on physical and chemical properties of ZnO thin films [19], [20].

II. EXPERIMENTAL

ZnO thin films were grown on glass substrates by the spray pyrolysis technique. Two different precursor solutions were used. In the precursor solution 1, the zinc acetate ($Zn(CH_3COO)_2.2H_2O$) dehydrate was dissolved in ethanol and the solution was magnetically stirred at 60°c temperature for 20min. The resulting solution was highly transparent and stable. For the precursor solution 2, zinc chloride ($ZnCl_2$) was dissolved in distilled water and the solution was stirred with a magnetic stirrer at 60 °C for 20min.

Glass slides (2.2 * 2*0.08) cm were used as substrates, Prior to the deposition of the films, the glass substrates were cleaned rinsing them in acetone, and then in ethanol.

The precursor's solutions are ejected onto glass substrates positioned onto a substrate holder. The deposition temperature (Ts) (temperature at the substrate surface) was maintained at 400 °C with an accuracy of ±5°C. The latter is measured using a Chrome–Nickel thermocouple.

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Two series of thin films were grown on glass substrates, one series for each solution.

During the pyrolytic process, the following possible reactions take place.

$$ZnCl_2 + H_2O \rightarrow ZnO + 2HCl \quad (1)$$

$$(Zn(CH_3COO)_2.2H_2O) + 2(C_2H_5OH) \rightarrow ZnO + 2(CH_3COC_2H_5) + 3H_2 + \frac{5}{2}O_2 \uparrow \quad (2)$$

The crystal structure of the ZnO thin film was determined by X-ray diffraction (XRD) using (Siemens D-5000) diffractometer with CuKα X-ray source with Cu anode (wavelength λ=1.54056 Å).

The morphology and composition of the sprayed films were analyzed by scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) using a JEOL JSM-6400 model operating at 7 kV.

The optical transmission spectra are used to study the optical properties of deposit thin films and have been analyzed using UV–Visible spectrophotometer with double beam ‘‘UV–visible SHIMADZU’’ in a wavelength range of 300–1100 nm at room temperature.

III. RESULTS AND DISCUSSION

A. *Structural characterization*

The XRD patterns of the samples grown by the spray technique on glass substrates using different precursor solutions are presented in Fig. 1. It can be seen that the films are polycrystalline with a hexagonal wurtzite structure.

The samples grown using precursor solution 1 present four peaks at: 31.83°, 34.33°, 56.55° and 56.65° that correspond to the diffraction planes of hexagonal ZnO (1 0 0), (0 0 2), (1 0 1) and (1 1 0) respectively. In the patterns of the samples 2, three peaks can be clearly seen at 34.84°, 36.78° and 47.87° this peaks correspond to the (002), (101) and (102) diffraction planes of ZnO wurtzite structure.

The films were in good agreement with those reported in JCPDS data cards [36–1451].

Fig. 1(a) shows that the (100) direction is the preferential growing orientation for the ZnO film. However, one can see in Fig. 1.b for ZnO films that the preferential orientation is (002). Sagar et al. [21], [22] reported preferentially oriented films in the (0 0 2) direction obtained from Zinc Acetate precursor.

Thus Zinc Acetate promotes the growth of crystals in the (0 0 2) direction.

The mean crystallite size of the sample is estimated by using the Scherrer formula (3)[23]:

$$D = \frac{k\lambda}{\beta cos\theta} \quad (3)$$

Where:

D: Crystallite size (nm).

K: Crystallite shape factor a good approximation is 0.9.

λ :Wavelength (1.5406 Å, 0.15406nm).

ß: Full width at half maximum (FWHM) of the peak (in radian).

θ: Bragg angle (in radian).

The lattice constants can be calculated using the formula (4) [9].

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

Where;

d: Plane spacing, obtained by the Bragg law (5)

$$\lambda = 2dsin\theta \quad (5)$$

h k l: Miller indices.

a and c: Lattice parameters(nm).

The calculation results for the crystallite sizes (D) and the values of lattice parameters (a and c), are presented in Table 1.

The lattice parameters give a = 0.3243nm, and c = 0.5209 nm for all the samples. These values are in good agreement with the reported values in the literature [24].Similar results were also obtained by [25], [26].

The texture coefficient (TC) was calculated using Eq. (6).

$$T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{\frac{1}{n}\sum_n I(hkl)/I_0(hkl)} \quad (6)$$

Where:

I_0: Represents the standard intensity.

I: The observed intensity of (hkl) plane.

n: The reflection number

The value of TC calculated for the diffraction peaks of ZnO, are shown in Table 1. It was observed that the (002) peak has the highest TC value for the sample 2

The volume of the ZnO hexagonal cell was calculated using the formula [3], [27] (7).

$$V = 0.866a^2c \quad (7)$$

Where:

a and c: Lattice parameters (nm).

All the calculated parameters are summarized in Table 1.

Table 1 Different parameters obtained from XRD (Bragg’s angle (2θ), lattice parameters (a and c), crystallite size (D), the texture coefficient (TC) and the volume (V).

	Zinc Chloride	Zinc Acetate
2θ(°)	34.84 36.78 47.87	31.83 34.33 36.55 56.65
hkl	(002) (101) (102)	(100) (002) (101) (110)
a(nm)	0.3250	0.3245
c(nm)	0.5206	0.5190
c/a	1.60	1.59
D(nm)	33.11	15.28
TC	2.738	1.266
$V(nm)^3$ $V(Å)^3$	0.0476 47.6	0.0473 47.3

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The ratio of lattice constants c/a was found to be around 1.60 for all layers. This is in good accord with values of the bulk wurtzite ZnO. Similar results were also obtained by [28]

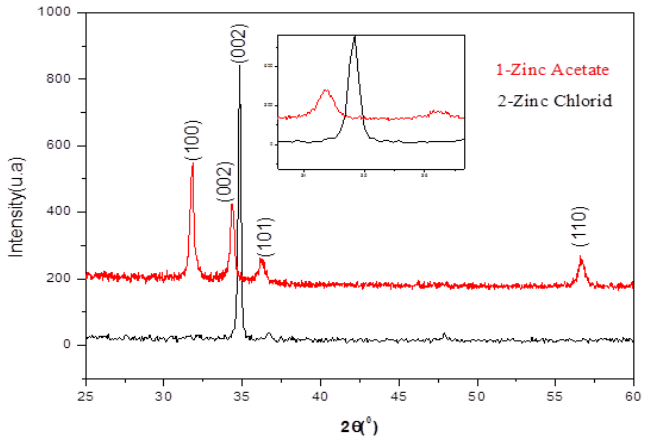

Fig.1 X-ray diffractograms of ZnO thin films using different precursor solutions (1) Zinc Acetate, (2) Zinc Chloride with M=0.2M/L and Ts=400°C

B. Optical characterization

Fig.2 shows the transmittance spectra of the samples. As it can be seen the films with the highest transmission are the samples grown using precursor solution 1 with a value of about 96%. These results are consistent with the observed in the precursor solutions. An absorption edge is observed between 300 and 400 nm, this edge could be related to the band gap value of the ZnO films. The glass substrate was measured in order to determine the absorption edge of glass, this was found to be near 300 nm, and thus the observed edge in the films at 300 nm corresponds to the absorption of the glass substrate used in the experiments.

The relationship between the absorption coefficient (α) and photon energy (hυ) for direct transition [29], [30] is:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (8)$$

Where:

A: Constant

Eg: The band gap value (eV).

Eg can be determined by extrapolating the straight line portion at a = 0 as indicated in Fig.3.

The band gap (Eg) of the samples was calculated from the absorption spectra also known as optical density of the films Fig.3. An extrapolation of the linear part of the curves intercepting the hν axis gives the band gap value [32], [32].

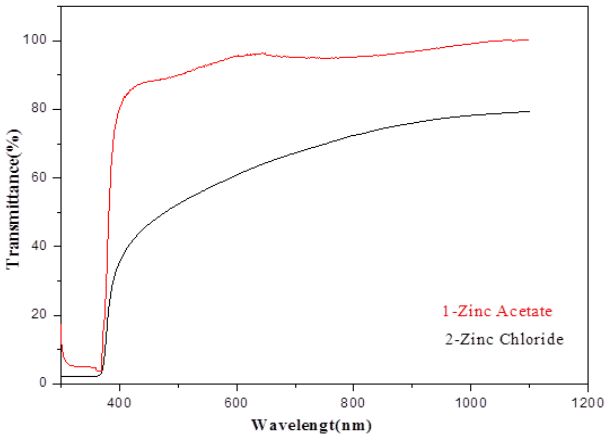

Fig.2 Optical transmittance spectra for ZnO thin films using different precursor solutions (1) Zinc acetate, (2) Zinc Chloride with M=0.2M/L and Ts=400°C

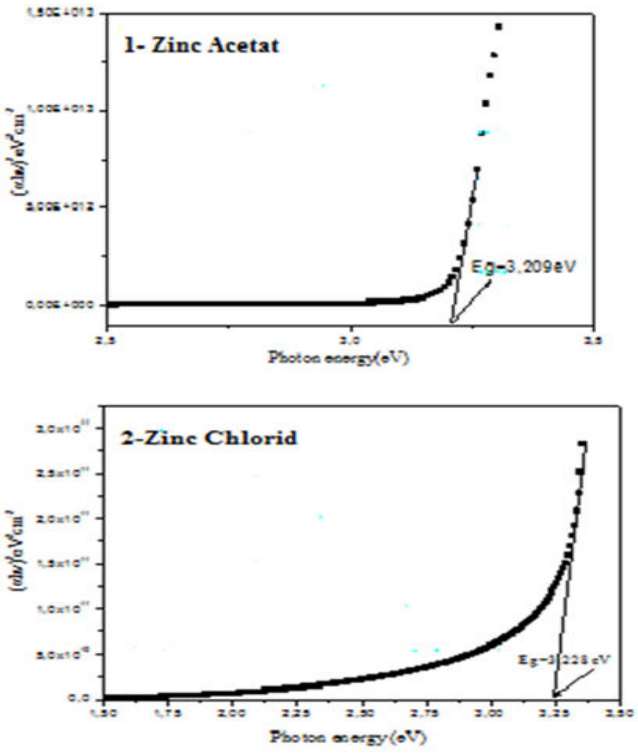

Fig.3 The plots of $(\alpha h\upsilon)^2$ vs. photon energy for ZnO thin films using different precursor solutions (1)Zinc acetate, (2) Zinc Chloride with M=0.2M/L and Ts=400°C .

The refractive index (n) of a semiconductor decreases with increasing band gap energy Eg.

The refractive index (n) is calculated using the model of M. Berruet and M. Va´zquez using Eq. (9)[33] and it is found to vary from 2.29 to 2.42, which is within the values reported in the literature [33].

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$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_g}{20}} \qquad (9)$$

We summarize the average values of the transmission (T%) the band-gap energies (Eg) and the refractive index in Table 2.

Table2 Different parameters obtained from transmittance spectra transmission (T%), band gap (Eg) and refractive index (n)

	T(%)	Eg(eV)	n
Zinc Chloride	64	3.228	2.33
Zinc Acetate	96	3.209	2.34

C. Morphology

Fig. 3 displays a typical SEM micrographs series of the surface morphologies of the ZnO thin films deposited by spray pyrolysis. The zinc oxide film surface is rough and is composed of fine particles. Furthermore, the surface morphologies of the ZnO films are intimately correlated to precursor solution. All images show homogeneous and dense surfaces. All the films deposited in the optimized conditions exhibit a good adherence [31].

The results show that the different solvents used in the preparation of ZnO solution strongly affect the properties of the ZnO thin film surface. The same results were remarked in the literature [34].

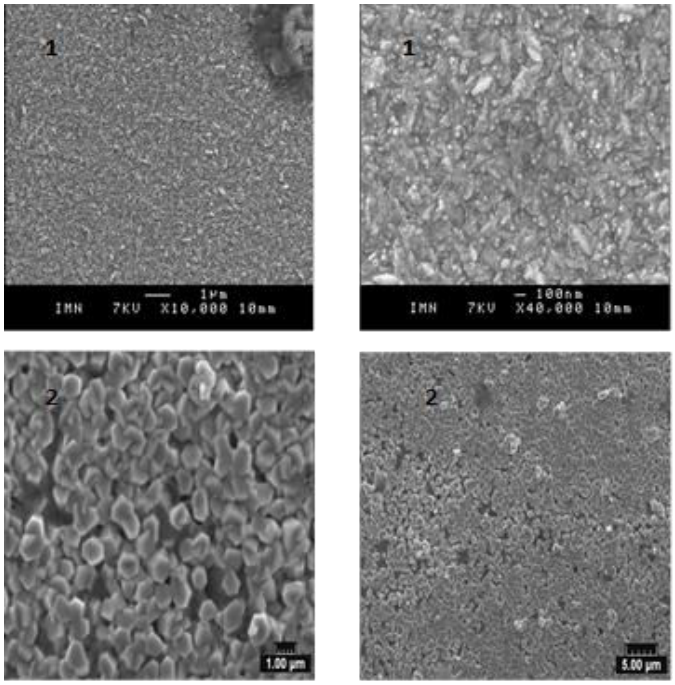

Fig.4. SEM micrographs visualization of ZnO thin films using different precursor solutions (1)Zinc acetate, (2) Zinc Chloride.

The chemical composition of the elements of two ZnO samples is presented in Table 3

It is observed that for the solution of zinc chloride the chemical reactions are not complete hence the presence of Cl, but for the solution (zinc acetate) the composition is almost stoichiometric. The presence of Si is due to the glass substrate

Table 3 Atomic and weight percentage of the chemical composition for ZnO thin films

Precursor solution	Zinc chlorure		Zinc Acetat	
	Wt%	At%	Wt%	At%
Zn	82.23	55.77	81.38	51.86
O	13.57	37.61	18.32	47.72
Cl	2.22	4.10	-	-
Si	1.98	2.52	0.30	0.54
O/Zn	0.67		0.92	

IV. CONCLUSION

Two different precursor solutions were used to obtain ZnO thin films. The influence of the precursor solution on the physical properties of the thin films was studied. Transparent polycrystalline thin films were obtained.

the structural properties such as crystallite size, grain size and surface morphology depend on both the precursor solution, thus the choice of the proper solution depends on the application wanted for the films.

The calculated band gap of the films is in agreement with the expected value for ZnO thin films. It was shown that the band gap can be modified when using different solutions, this is important because the use of ZnO thin films for solar cell applications requires the control of the band gap.

Both precursor solutions give good quality ZnO thin films. Thus two simple and effective ways to produce ZnO thin films were developed. Based on the results from XRD the thin films grown using Zinc Acetate based solution have better crystallinity than the ones grown with the Zinc Acetate based solution.

UV–Vis transmittance spectra results show that the films obtained from the Zinc Acetate solution are more transparent than the films obtained from Zinc Chloride solution.

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