Contribution to the study of ZnO films properties prepared by spray pyrolysis

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Transparent conducting oxides (TCOs) are widely used as electrodes in optoelectronic devices due to their optical transparency in the visible range and to their electrical conductivity. They can be found in various applications such as photovoltaic solar cells, liquid crystal displays, sensors and organic light emitting devices. Indium tin oxide (ITO) and zinc oxide (ZnO) are the two major TCO materials to be used. In our case, we have deposited Zinc oxide onto pyrex substrates by Spray Pyrolysis technique at temperatures ranging from 350 to 450°C by step of 25°C. The structural properties of the films were studied by X-Ray diffraction (XRD) and confirmed by selected area electron diffraction (SAED) mode. Surface morphology of ZnO thin films was analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The films appear to be composed of ZnO nanoparticles (ZnO NPs), whom size increases with temperature. The results showed the presence of the wurtzite phase of ZnO with an orientation along the c-axis of the crystallites. Morphology images of the films obtained by Scanning electron microscopy revealed that pure ZnO film grew as quasi-aligned hexagonal shaped microrods with diameters varying between 100 and 400 nm. UV- visible spectroscopy measurements were also performed to determine the optical band gap.

1. Introduction

Transparent conductive oxide (TCO) thin films have received more attention from many researchers and scholars because of its industrial optoelectronic applications. Tin-doped indium (ITO) was the most commonly used TCO material because of its excellent optical and electrical properties. But today, it has application problems related to its high cost, toxicity and low stability [1]. Zinc oxide (ZnO) has therefore attracted considerable attention on account of its good electrical and optical properties in combination with its abundance in nature and its non toxicity and can also be taken as promising alternative candidate to ITO [2].

ZnO is an II-VI group semiconductor material with a hexagonal wurtzite crystal structure. It has broader direct band gap energy at 3.37 eV and a higher excitation binding energy at about 60 meV under room temperature. With these notable physical characteristics and low cost, it has broader applications such as in gas sensors, surface acoustic wave components and short-wavelength light-emitting materials [2].

Various deposition techniques have been widely used to produce ZnO thin films. However, seeking the most reliable and economic deposition technique is the main goal. The most studied techniques include thermal evaporation [3, 4], sputtering [5, 6], chemical vapor deposition [7, 8], sol–gel [9, 10], pulsed laser deposition [11,12]. Electrochemical deposition [13,14] and Spray Pyrolysis [15,16]. Among these techniques, spray pyrolysis is one of the most widely used methods because of its many advantages such as simplicity, low cost, high purity, excellent control of chemical uniformity and stoichiometry in multi-component system. It can be performed at atmospheric pressure and does not require any vacuum set up. Very common compounds can be used as starting material, such as zinc nitrate [17], zinc acetate [17, 18], or zinc chloride [19].

Another major advantage of spray pyrolysis is that it can achieve excellent thickness uniformity of the films, and also can be easily adapted for production on large-area substrates.

In this study, ZnO thin films were deposited by spray pyrolysis on Pyrex substrates starting with an aqueous solution containing zinc chloride. The influence of substrate temperature on the structural, morphological and optical properties of ZnO thin films was investigated without any post annealing.

2. Experimental details

2.1 Deposition conditions

The depositions were performed onto Pyrex substrates, which were previously ultrasonically cleaned and kept at temperatures from 350 °C to 450 °C by step of 25°C during the deposition. The starting solution is

obtained by adding zinc chloride in deionised water and stirred at 60°C during 30 min before its introduction in the spraying apparatus. The nozzle was located at 30 Cm above the substrates and the solution flow rate was held constant at 1 mL/min, thanks to compressed air flow maintained at the pressure of 2.4×10^5 Pa.

2.2 Characterization technique

The structural properties were studied by X-Ray diffraction measurements using Panalytical X'celerator diffractometer with Cuk$_\alpha$ radiation (λ = 1.5418Å). The Crystallite orientation was confirmed by transmission electron microscope (Tecnai12 from FEI Company at 120 KV) and the average crystal size was determined from the peaks on the diffraction spectra using the Scherrer's method [20].

Thickness and surface morphology was investigated using Scanning electron microscope (SEM) Quanta 200 from FEI Company. All measurements were carried out on films with thickness in the range 166-380 nm. The optical measurements of the ZnO thin films were carried out at room temperature using (spectro PerkinElmer Lambda 900 UV/Vis/Nir wavelength range 200nm-2500nm) spectrometer in the wavelength range 300 to 1000nm.

3. Results

3.1 Structural properties

Fig.1 shows the XRD patterns obtained for undoped ZnO thin films prepared by spraying the precursor solution on Pyrex substrates at temperatures ranging of 350°C to 450°C by step of 25°C.

For All the as-deposited films, we can see some peaks corresponding to (002), (101), and (110) plans representing a hexagonal structure of ZnO powder (zincite phase of the JCPDS file n° 36-14519). All ZnO thin films showed a polycrystalline wurtzite structure with a preferential orientation along the [002] direction (c-axis).

Fig.1. XRD patterns of ZnO thin films with different substrate temperatures.

The study of XRD measurements reveals that the films deposited at the temperature 425°C exhibit the good

crystallinity with a sharp peak located at 34.42°. These results were confirmed by TEM images (Fig.2) and a diffraction simulation (Fig. 3). The SAED pattern projected to the [010] axis confirms the presence of the zincite phase and shows that the crystallites are oriented along the c-axis.

Fig.2. TEM diffraction image showing a family orientation in accordance with (00-2), (00-1), (001), (002) plans.

Fig.3.Simulation of electron diffraction by selecting the zone axis [010] which is perpendicular to the [002] axis in concordance with real TEM image.

The Crystallites size of these samples was estimated using the following Scherrer's formula applied to the (002) peak [20]:

$$d = \frac{0.9\lambda}{\Delta(2\theta)\cos\theta} \qquad (1)$$

Where d is the crystallite size, λ is the X-Ray wavelength, θ the Bragg's diffraction angle and Δ (2θ) the full width at half maximum of the peak corresponding to the θ value. These values are listed in Table 1. The crystallites size increases from 33.44nm of the film grown at 350°C up to 45.05nm of the film deposited at 425°C indicating that the substrate temperature of 425°C is the best deposition condition confirmed by the XRD results (Fig.1). One can observe from the table that the thickness of films decreases

when the substrate temperature increases. This may be due to the more evaporation of the solvent on the substrate at high temperatures giving place to very thin films.

Table1. Variation of film thickness, crystallite size strain, stress and lattice parameters with substrate temperatures

Temperature	cristallite size (nm)	thickness (nm)	c(Å)	a(Å)	epsilon z	sigma (Gpa)
T350°C	33,44	380,00	5,21	3,26	0,10	2074,26
T375°C	37,24	315,00	5,22	3,26	0,16	3506,48
T400°C	44,42	250,00	5,22	3,25	0,18	3843,96
T425°C	45,05	189,00	5,21	3,25	0,08	1670,93
T450°C	42,31	166,00	5,20	3,25	-0,04	-831,35

The lattice constants c and a of the ZnO films are in agreement with standard value from JCPDS-ASTM No .01-1136 c_0= 5.21Å and a_0= 3.242 Å. They are calculated using the following equation: [21].

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

(2)

The average uniform strain (epsilon z) in the lattice along the c-axis has been estimated using the following expression:

$$\varepsilon_z = \frac{c - c_0}{c_0} x100\%$$

(3)

The stress (σ) in the plane of the film can be calculated using the biaxial strain model: [22]

$$\sigma_{film} = \frac{2C_{13}^2 - C_{33}(C_{11} + C_{12})}{2C_{13}} \varepsilon_Z$$

(4)

Where C_{11}=209.7GPa, C_{12}=121.1GPa, C_{13}=105.1GPa, and C_{33}= 210.9 GPa are the elastic stiffness constants of bulk ZnO. Minimum stress was observed at Temperature 425°C, due to higher orientation of crystallites along the c-axis, The negative values of strain for the films indicate that the lattice constant c is compressed, as compared to the unstressed powder sample.

3.2 Morphological characterization

Fig.4 shows the SEM images of samples elaborated at 350°C, 375°C, 400°C, 425°C and 450°C. For all the deposited films, one can see nanocrystals with densely packed grains distributed evenly throughout the entire surface of the film. The grain size increases with increasing the substrate temperature as shown in table 1. These images show clearly a compact and homogenous surface for films deposited at all temperatures. The films are very uniform, with a dense surface without visible holes or faulty zones.

The EDAX analysis showed that all the layers are stoichiometric (50% of Zn and 50% of O) (Fig. 4).
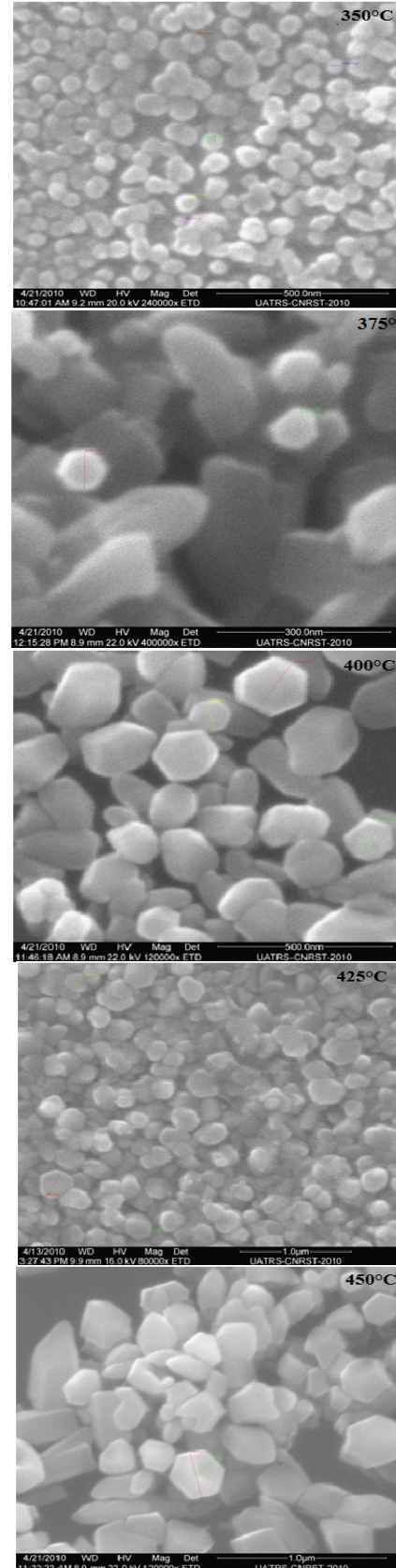

Fig.4. SEM images of ZnO thin films synthesized at different substrate temperatures
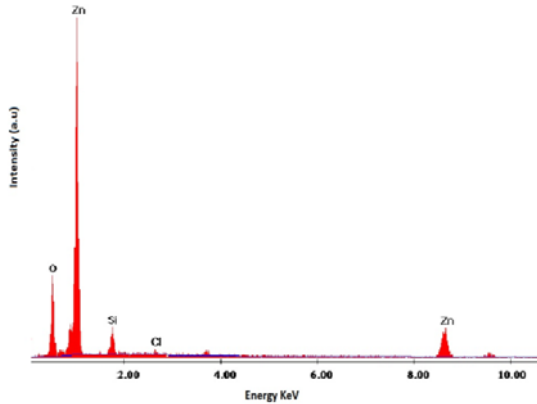
Fig.5. EDAX analysis spectrum of the ZnO thin film.

Fig.7. Variation of $(\alpha.h.\nu)^2$ as a function of h.υ of ZnO thin film elaborated at 425°C

3.3 Optical properties

Fig.6 displays the transmittance spectra of ZnO thin films deposited onto Pyrex substrates by Spray pyrolysis at different substrate temperatures. The transmissions in the visible range (400nm-800nm) reach values of the order of 90%. In a general way, an increase in substrate temperature improved the transmission as can be observed on the deposits performed at temperature 350ºC, 375°C and 450°C in comparison to those prepared at 400°C and 425   °C.
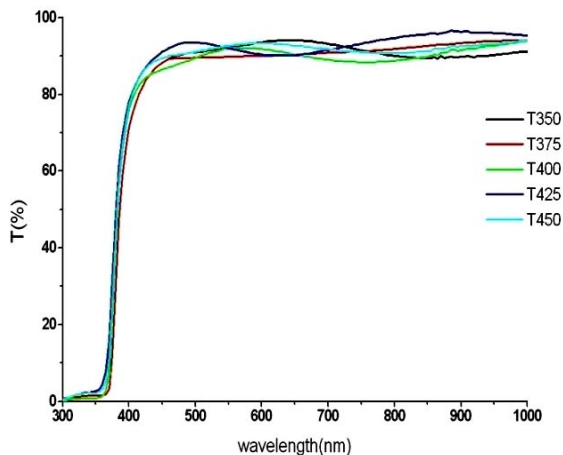
Fig.6. Transmission spectra of ZnO thin films.

A sharp absorption edge can be observed at about 375 nm, which corresponds to an energy gap of 3.305 eV, as determined for the film deposited at 425°C presented in Fig.7. And it can be observed that this improvement can be attributed to either the decrease in thickness or the improvement in structural homogeneity and crystalline quality.
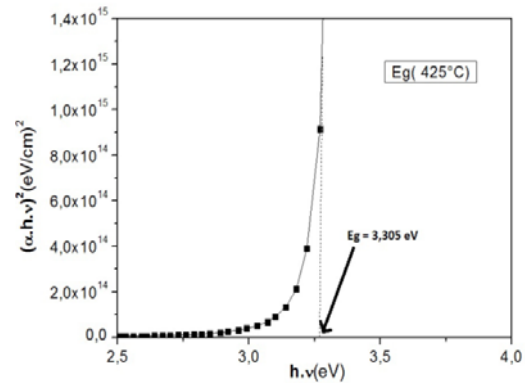
In Fig. 7, one can see the variation of $(\alpha.h.\nu)^2$ as a function of h.υ of ZnO thin film elaborated at 425°C since it is the best elaboration temperature. The absorption coefficient α is calculated from the relation [23].

$$T = (1 - R)\,e^{-\alpha t}. \tag{5}$$

Where T is the transmittance, R is the reflectance and t is the film thickness. The optical band gap of film is determined by applying the Tauc model in the high absorption region.

$$\alpha h\nu = A\sqrt{h\nu - E_g}. \tag{6}$$

Where $h\nu$ is the photon energy, E_g the optical band gap, and A is a constant. The band gap of the film has been calculated using Tauc's plot of $(\alpha.h.\nu)^2$ versus h.υ as shown in **Fig.7** and by extrapolating the linear part of the absorption edge to find the intercept with energy axis. A band gap of 3.305 eV has been obtained for the film deposited at 425°C.

4. Conclusion

In this study, we have deposited ZnO thin films by spray pyrolysis technique on a Pyrex substrate at different temperatures using Zinc chloride dissolved in deionised water. The results showed that the deposited ZnO thin films are uniform. The structural analysis of X-rays diffraction and TEM analysis showed that the films deposited are of wurtzite structure (phase zincite, JCPDS 01-1336) with a preferential orientation along the [002] direction. The study of the microscopic structure at different temperatures revealed a homogeneous and uniform grain structure. In the other case Particle size increases with increasing substrate temperature from 350 °C to 450 °C. The transmittance spectra show that the films prepared at 400°C and 425°C exhibit a transmission higher than 90% in the visible region with a sharp

fundamental absorption edge at about 375 nm, corresponding to gap energy of 3.305 eV. The films prepared at temperature 350ºC, 375°C and 450°C have a low transmission, and those prepared at 400°C 425 ºC have a higher one. It can be observed that, in general, an increase in substrate temperature improved the transmission. This improvement can be attributed to either the decrease in thickness or the improvement in structural homogeneity and crystalline quality.

Acknowledgments

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