Effect of Concentration of Precursor on Intrinsic ZnO Thin Films by Spray Pyrolysis

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Abstract: In this work, we have prepared chemically sprayed zinc oxide thin films (ZnO) on microscopic glass substrates. The films were deposited from a starting solution containing zinc acetate dehydrate. The influence of concentration of starting solution on the structural, morphological, optical and electrical properties of the ZnO thin films was studied. The structure of all the ZnO thin films was polycrystalline, and a variation in the intensity of preferential growth with the concentration of the solution was observed. The crystallite size was found to increase with precursor concentration and ranges from 56 to 95nm. The optimal deposition conditions leading to conductive and transparent ZnO thin films were also found. In this way a resistivity of 1.88×10^{-2} Ω-cm with a (0 02) preferential growth, were obtained in optimized ZnO thin films. Due to their excellent optical and electrical properties, ZnO films are promising contender for their potential use as transparent window layer and electrodes in solar cells

Keywords: *Spray pyrolysis, Structural, morphological, optical properties, wurtzite, ZnO;*

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1. Introduction:

Spray deposition is well established and widely used technique for thin film processing. It is a chemical deposition that has been successfully used for the deposition of various oxides based materials [1,2]. Two major interests in this method are the operating at atmospheric pressure and the deposition on a large surface.

The spray deposition is based on the mechanical transformation of the solution to a droplets stream by using compressed gas or ultrasonic waves. The droplets are then sprayed onto a heated surface where they react to form a solid film. Thereafter, the properties of the used solution and the thermodynamics at the interface droplet/substrate are key parameters controlling the spray deposition processes and the deposited films properties [3].

A large number of thin films materials have been deposited by spray pyrolysis namely SnO_2, ITO, ZnO ZnS, $CuInSe_2$, CdTe, CdS onto varied of nature of substrate. Investigations of deposition parameters influence on ZnO thin films properties have been intensively carried. Parameters such as: substrate temperature [4-6], solution molarity [7,8], substrate nature [9], flow rate [10], annealing [11] and doping [12,13] were studied in the literature. In the present paper we address a comprehensive study of the influence of the solution concentration on the characteristics of ZnO thin films deposited by spray pyrolysis technique.

2. Experimental details

Spray pyrolysis is an effective method for the deposition of thin films of metallic oxides, as is the case with the ZnO material. In this deposition technique, a starting solution, containing Zn precursors (Zinc acetate dehydrate), was sprayed by means of a spray nozzle, assisted by a carrier gas, over a hot substrate. When the fine droplets arrived at the substrate, the solid compounds reacted to become a new chemical compound. ZnO thin films were deposited on to ultrasonically cleaned glass substrates using the spray pyrolysis method with various molar variation of precursor.

A solution (each molar) of $Zn(CH_3COO)_2:2H_2O$ was used as a precursor, prepared by dissolving in mixture of deionized water and methanol. In this mixture, methanol concentration was 25ml in 100 ml solution. The nozzle was at a distance of 30cm from the substrate during deposition. The solution flow rate was held constant at 12ml/min. Compressed air was used as the carrier gas, at the pressure of 2mbar. When aerosol droplets were close to the substrates, a pyrolytic process occurs and highly adherent ZnO films were produced. The ZnO thin films were deposited at constant 450°C substrate temperature with variation in solution molarity from 0.2M to 0.6M at the equal steps of 0.1M.

These deposited ZnO thin films were characterized for structural elucidation using X-ray diffraction pattern. The X-ray diffraction spectra were recorded with Rigaku (Japan) X-ray

diffractometer equipped with monochromatized Cu-Kα radiation (λ=0.154 nm) at the scanning rate of 0.03^0 S^{-1} ranging from 20^0 to 80^0 (2θ) operated at 40kV, 100mA . The surface morphology using scanning electron microscopy (FESEM, JEOL 6700F or Sirion 200) and optical properties of the films were estimated by using the instrument JASCO UV- VIS-NIR spectrophotometer. The thickness of films were measured using simple gravimetric weight difference method which is further used for electrical resistivity measurement using Four probe setup Model DFP-02.

3.   Results and discussion

The ZnO thin films formed using variation in concentration of precursor by which metal to oxide ratio in ZnO is varied and which is responsible for formation of nucleation and growth of precursor using spray pyrolysis. With the initial constant airflow rate 10 lpm, 50 ml quantity of solution and substrate temperature 450°C. We have varied concentration of precursor from 0.2M to 0.6M and the structural, morphological, optical and electrical properties of film were studied [14].

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3.1 X-ray diffraction

The X-ray diffraction analysis of undoped ZnO films deposited at different molar concentrations of zinc acetate solution (0.2 M to 0.6 M) of which 0.2M, 0.45M and 0.6M films were analyzed and shown in Figure 1. Polycrystalline structure due to intense diffraction peaks was evidenced from the XRD spectra. Films were hexagonal wurtzite structure type over the whole range of molar concentrations with peak orientation along (100), (002), (101), (113), (200), (110) and (112) plane. The ZnO films fabricated at molar concentrations 0.2 M were bear a less intense preferred orientation along (002) plane. However, with increase in molar concentration from 0.2M to 0.45M peak orientation along (002) plane enhanced.

This showed the formation of highly crystalline films with increase in concentration. But further increase in concentration decreases the crystal orientation along (002) plane due to lattice saturation effect.
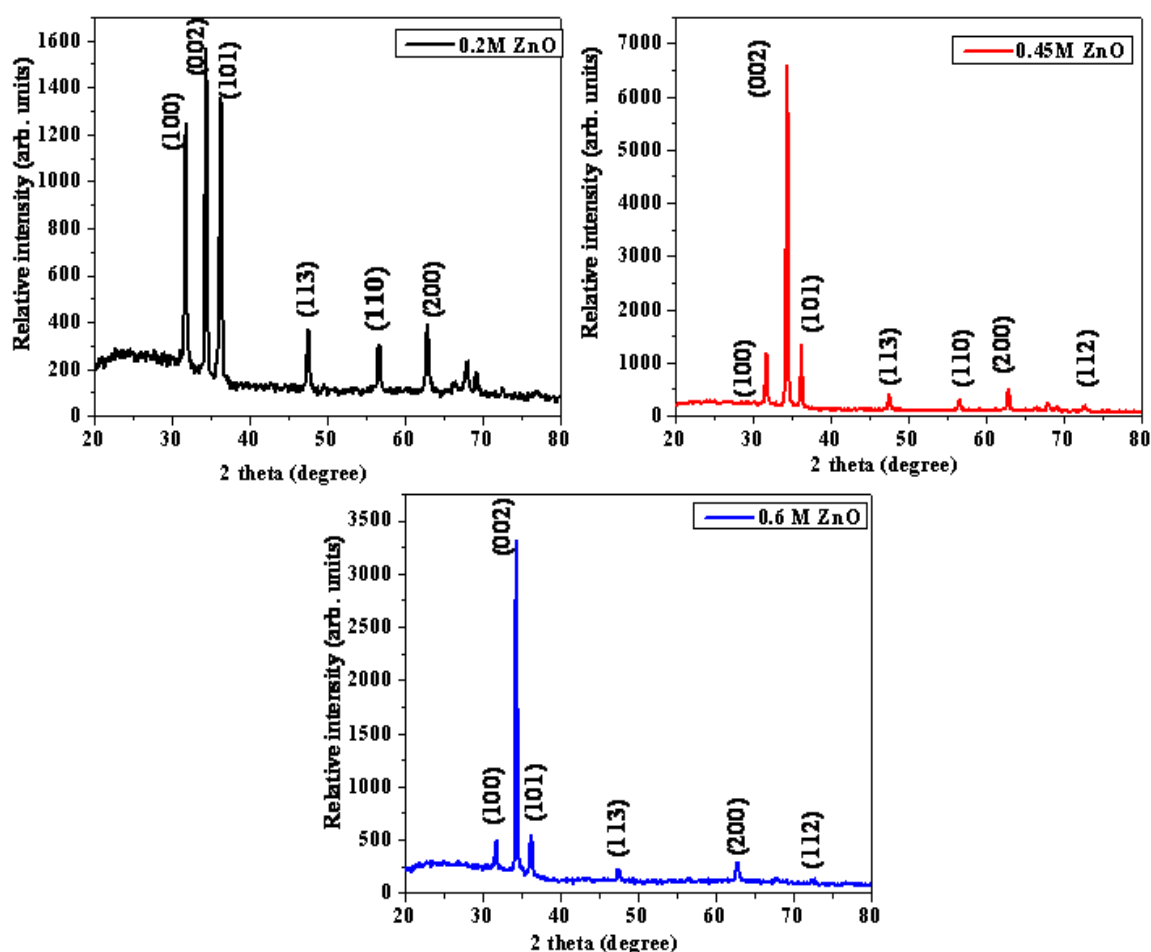

Figure 1: X-ray diffraction pattern of concentration dependent ZnO thin films

The crystallite size of the deposits is estimated from the full width at half maximum (FWHM) of the most intense diffraction line by Scherrer's formula as follows [15];

$$d = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$
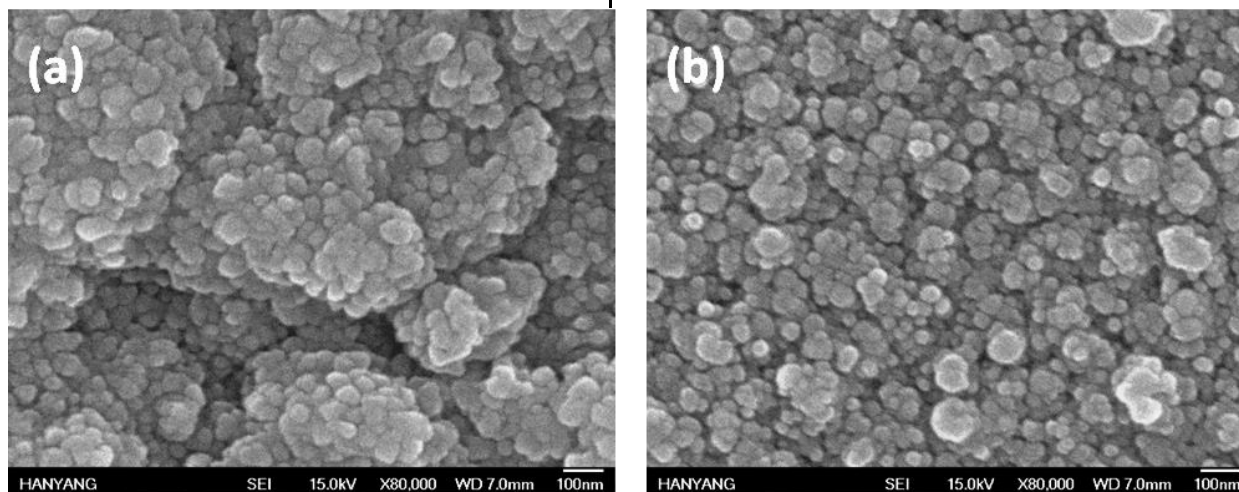
where,

'd' = crystallite size,

λ = wavelength of X-ray used,

β = full width at half maxima of the peak (FWHM) in radians,

θ = Bragg's angle.

The crystallite size increases with increase in molarity of ZnO thin films from 56nm to 95nm due to enhancement in crystallinity of the films.

3.2 Scanning electron microscopy

The surface morphology analysis using SEM for concentration variation of ZnO thin films were shown in figure 2. The variations of concentration of precursor have influence on the morphology of deposited ZnO thin films. Initially at 0.2M concentration of precursor figure 2 (a) well covered substrate surface revealing agglomeration of grains over the film substrate occurs with average grain size of 80nm. With increase in concentration of precursor to 0.45M figure 2 (b) formation of spherical, uniform grain growth having grain size of order of 30nm-40nm in size. At lower concentration agglomeration of grains with voids over the film surface decreased and well coverage of grains over film substrate occurs as concentration of precursor increases.

Figure2: SEM images of ZnO thin films deposited by spray pyrolysis with precursor concentration a) 0.2 M, b) 0.45 M.

3.3 Uv-Vis analysis

The concentration effect on the transparency and homogeneity of the prepared samples was evaluated and depicted in figure 3. Regardless of the concentration, all films are highly transparent in the VIS (400–800nm) region with a total transmittance over 70%. The optical transparency is slightly reduced at higher concentration owing to the segregated OH_2 phase, agglomeration of grains and porous structures formed in the ZnO films whose grain size are varied for all doping concentration as revealed by SEM photographs in figure 3. In addition, the threshold of optical absorption for ZnO thin films shifts to shorter wavelength in comparison to intrinsic band gap of ZnO (3.3eV). The observation might be ascribed to the Burstein–Moss effect for heavily doped zinc oxide films. Here the electrons require an additional energy to be excited from

conduction band to higher energy states in the conduction band where the bottom of the conduction band has already been occupied by photoelectrons. That is, the Fermi level was lifted in to the conduction band of the ZnO thin film, which leads to the band gap broadening effect. The optical absorption coefficient (α), is defined as[16]:

$$\alpha = \frac{1}{d} \ln\left(\frac{I_O}{T}\right) \qquad (4)$$

Where d is the film thickness and I_0 and I are the intensities of the initial and transmitted beams, respectively.
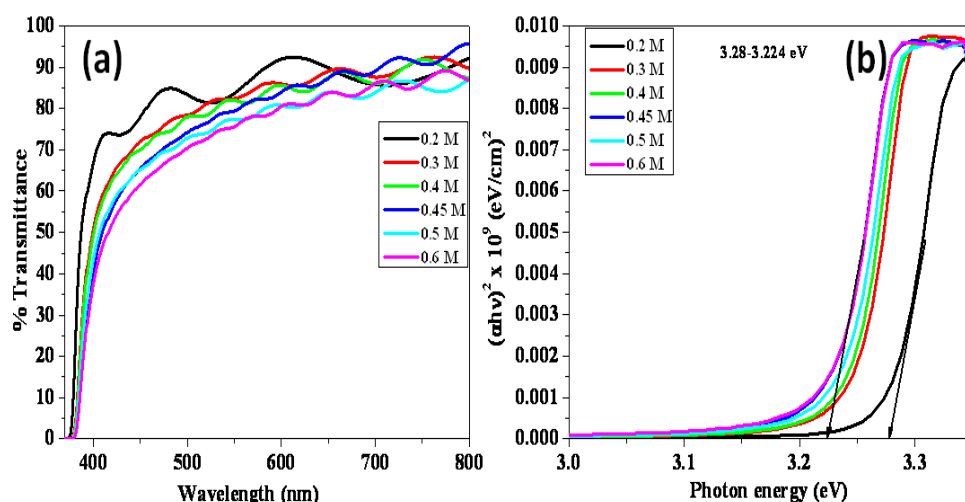
Figure 3: Concentration dependent a) Optical transmittance spectra and b) plot of $(\alpha h\nu)^2$ against photon energy variation of ZnO thin films

Being a direct gap semiconductor, the optical band gap (Eg) of the films can be described by the Tauc relationship: An extra polation of the linear plot of $(\alpha h\nu)^2$ on the y-axis versus photon energy (hν) on the x-axis gives the value of band gap Eg at $(\alpha h\nu)^2 = 0$ as depicted in figure 3(b). The Eg obtained using the variation showed values between 3.28eV and 3.224eV. In our study, the concentration has little impact on the red-shifted Eg [17]. It is noteworthy that the decrease in Eg as the Zn exceeds suggests that excess atoms do not contribute for conduction band filling due to the Zinc oxides segregation at the grain boundaries.

3.4 Thickness measurement

The thickness of deposited ZnO thin films with variation in concentration of precursor measured using weight difference method before and after deposition of precursor over the substrate films.

The well cleaned microscopic glass substrate initially weighed using microbalance and the weight of slides before deposition was noted. Then these samples were used to deposit ZnO thin films. After deposition of precursor substrates were cooled and finally weighed giving weight after deposition. Using gravimetric method the weight difference, area of deposition and density of material is used to calculate the thickness. The measured thickness of samples is presented in table 1

Table 1: Thickness measurement form weight difference of deposited ZnO thin films with variation in concentration of precursor.

Sr. No.	Molarity in M	Weight difference (gm)	Thickness T=$\frac{M}{2A\rho}$ (cm)
1	0.2	0.007	0.2336 x10⁻⁴
2	0.3	0.010	0.3667 x10⁻⁴
3	0.4	0.025	0.8679x10⁻⁴
4	0.45	0.028	0.9680x10⁻⁴
5	0.5	0.019	0.6676 x10⁻⁴
6	0.6	0.018	0.6342 x10⁻⁴

Form table 1 it is observed that the thickness of deposited ZnO thin films increases with increase in concentration of precursor concentration. The maximum thickness of film measured for film deposited with 0.45M concentration of order of 968nm. With further increase in concentrations of ZnO thin film thickness of film decreases due to saturation of grains over the film substrate and less adhesive film formation.

3.5 Electrical measurements

The ZnO in thin film form possess semiconducting material property having various applications in opto-electrical devices. The electrical resistivity of ZnO thin films deposited at various precursor concentrations were measured using four-probe resistivity apparatus. The enhanced conducting ZnO thin films can be used for electrical device applications [18].

Table 2 : Resistivity and resistance measurement of ZnO thin films using four-probe method

Sr. No.	Molarity in M	Voltage V (mV)	Current I (mA)	$R = \dfrac{V}{I}$ (Ω)	Resistivity R =Rs*thickness (Ω-cm)
1	0.2	152	0.11	1381.8	0.1462
2	0.3	630	0.11	5727.27	0.9526
3	0.4	105	1.16	90.52	0.0273
4	0.45	110	4.06	27.093	0.0188
5	0.5	101	0.16	631.25	0.1813
6	0.6	108	0.11	981.81	0.3860

The measured current across the point probe for applied potential were measured forming resistance used to calculate resistivity of the deposited ZnO thin film. The measured resistivity of ZnO thin films indicated in table 2:

Form table 2 it is observed that sheet resistance decreases with increase in concentration of precursor from 0.2M to 0.45M forming resistivity change from 14.62×10^{-2} to 1.88×10^{-2} Ω-cm. But with further increase in concentration of precursor to 0.6M resistivity increase to 38.6×10^{-2} Ω-cm. Resistivity of ZnO thin film deposited at 0.45M precursor concentration showed formation of good conducting film formation.

4. Conclusions

Transparent conductive ZnO thin films were successfully prepared by the spray pyrolysis technique using an aqueous solution of zinc acetate [Zn $(CH_3COO)_2$, $2H_2O$] on microscopic glass substrate. The prepared films are reproducible, adherent to the substrate, pinhole free and uniform. The X-ray diffraction analysis showed that films are polycrystalline in nature. It is also found that with increasing molarity of precursor solution the preferred orientation along [002] in ZnO films enhanced for 0.45M and further reduced with increase in concentration. All the films are optically active having higher optical transmittance and revealing decrease in band gap with concentration. Electrical characterization of these films was measured with sheet resistance and electrical resistivity. The molarity of 0.45 M appears to be an optimum molarity of precursor solution for the growth of highly transparent (~ 82 %) and low resistivity (~1.88×10^{-2} Ω-cm) ZnO films. These films can be used as a conductive electrode as well as a transparent window filter in amorphous silicon based solar cells.

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