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Structural Properties of ZnO Thin Films Prepared by Spray Pyrolysis Method

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Abstract *- Zinc Oxide (ZnO) thin films were prepared on corning (7059) glass substrates by Spray Pyrolysis technique. The deposition was carried out at room temperature after which the samples were annealed in Nitrogen atmosphere at temperatures of 300°C and 400°C. The structural properties of ZnO thin films were studied by X-ray diffraction (XRD). The XRD analysis of the films showed that thin films are characterised by the appearance of (002) and (101) diffraction peaks. The intensity of the peaks was observed to increase with annealing temperature. The values of the lattice constants,* ***a*** *and* ***c*** *agree strongly with International centre for diffraction data (ICDD). Furthermore, the structural parameters such as micro-strain, dislocation density, full width at half maximum (FWHM) and grain size were found to be dependent on annealing temperature. Therefore the annealing effects on the structural properties of ZnO thin film will be useful for the formation of ZnO-based hetero-structure for application in fabrication of optoelectronic and other photovoltaic devices.*

Key words: ZnO, Spray Pyrolysis, Annealing, Lattice Parameters, Substrate Temperature

1.0 INTRODUCTION

ZnO is an important wide band-gap optoelectronic material because it has high chemical and thermal stability at room temperature (27°C) and a large exciton binding energy of 60 meV. These characteristics made ZnO thin film a good candidate for ultraviolet emission applications (Mandalapu et al., 2008; Zhu et al., 2009). ZnO thin films usually show high transmittance in the visible range and possess excellent n-type conductivity when doped with Al, Ga and In, thus they can be used as transparent electrodes (Oh et al., 2006) and window layers of solar cells (Hagiwara et al., 2001). ZnO-based homostructure and heterostructure are attractively increasing attention because of their promising optoelectronics applications, and it is important work for the realization of ZnO optoelectric devices that to investigate the properties of ZnO films deposited various semiconductor substrates. ZnO has good lattice matching with the indium Phosphide (InP) crystal substrates, which has high solar conversion efficiency and high radiation resistance.

Many growth methods such as, thermal oxidation (Rakhesh et al., 2009), Spin coating (Godbole et al., 2011), vacuum evaporation (Eya et al., 2006), electron beam evaporation (Rusu et al., 2011), sputtering (Janotti and Vande, 2008; Suchea et al., 2009), have been used in the preparation of ZnO thin films. The physical deposition routes have the advantages of producing high-quality materials, but also the disadvantage of the need for high temperature. Spray pyrolysis technology is a convenient chemical deposition method for the deposition of semiconductor thin films and has the several advantages in comparison with other deposition techniques such as low cost of the source materials, producing high- quality films using comparatively simple deposition equipment, moderate substrate temperatures, deposition scaled for large area and uniform deposition with very thin layers with specific composition, morphology, good adhesion between the deposited film and controlling the shape and sizes. The morphology of the material depends on the thermal treatment. Usually, as-deposited films require a thermal treatment to improve stability and reduce the possible undesirable influence of the substrate. It has been reported previously that high-purity crystalline ZnO thin films can be fabricated by spray pyrolysis. The key success of spray pyrolysis is using a single-solid organic zinc fountain as a precursor with the physical and chemical properties required depositing a pure film at the substrate. Thermal annealing is a widely used method to improve crystal quality and to study structural defects in materials. During an annealing process, dislocations and other structural defects will move in the material and adsorption/decomposition will occur on the surface, thus the structure and the stoichiometric ratio of the material will change. Such phenomena can have major effects on semiconductor device properties, light emitting devices being particularly affected. In this paper, the preliminary results on the growth of ZnO thin films on glass substrates using hydrated zinc acetate [Zn $(CH_3COO)_2 . 4H_2O$] as precursor in ethanol with tri-ethylene glycol (TEG) is reported. The aim of the present study is to investigate the general features of the annealing effect of the prepared ZnO thin films.

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2.0 MATERIALS AND METHOD

Graded chemicals (Aldrich) were used for the deposition of ZnO thin films, soda lime glass was used as substrate, and film thickness was measured using Profilometer (**STYLUS TAYLOR HOBSON MODEL**). Zinc oxide thin films were prepared on soda lime glass substrates using **KM 150** spray pyrolysis deposition machine. Before deposition the substrates, the beakers and measuring cylinders were washed first with detergent and rinsed with distilled water, then washed with acetic acid and finally rinsed with ethanol, dried and rubbed gently with cotton. A 1.10g of Zinc Acetate was dissolved in 15ml of H_2O. 50ml of Acetone, 30ml of Ethanol and few drop of Acetic Acid precisely 5ml were poured in the same beaker containing the Zinc Acetate making a total volume of 100ml. 1ml of the mixture was placed in a syringe which is attached to the spray chamber. Before deposition the substrate temperature was fixed at 300^{o}C. The nozzle to substrate distance was set at 11.0cm. The precursor solution was then sprayed on substrate and zinc oxide thin films were deposited on the substrate at a flow rate of 0.8ml/min. After deposition, samples were removed from the spray Chamber. One sample was kept as deposited and two samples were subjected to a thermal annealing by inserting them into a horizontal Carbolite oven one after the other at temperatures 300℃ and 400℃ respectively under nitrogen atmosphere for one hour at the ramp rate of 6℃/sec. The samples were allowed to cool at room temperature. The structural characterization was then studied by X-ray diffraction XRD using **PANALYTICA XPERT PRO** Diffractometer with Cu-Kα radiation (λ = 1.54056Å) for the 2θ ranging from (20^0 – 100^0). The average crystallite sizes of the films deposited at various thicknesses have been estimated using the following Scherer's formula (Moreh et al., 2013).

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

Where K is the shape factor of a value having 0.94, (λ=1.5406 Å) is the wavelength of X-ray, β is full width at half maxima (FWHM) of (002) peak of XRD pattern in radians and θ is the Bragg's diffraction angle. The dislocation density (δ), defined as the length of dislocation lines per unit volume, are estimated using equation (2) (Momoh et al., 2015);

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

Where D is the crystallite size.

Micro-Strain (ε) of the thin films is estimated using equation (3) (Momoh, et al., 2015)

$$\varepsilon = \frac{\beta\cos\theta}{4} \qquad (3)$$

Where θ, and β are the Bragg diffraction angle and full width at half maximum of (002) diffraction peak, respectively.

Using XRD data, the lattice parameters (**a** and **c**) are calculated from equation (4) (Ibrahim et al., 2013)

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

3.0 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction Analysis

Figures 1, 2 and 3 depicts XRD patterns for un-annealed ZnO thin films and ZnO thin films annealed at 300°C and 400°C respectively under nitrogen atmosphere. It can be seen that under all conditions ZnO thin films are characterised by the appearance of (002) and (101) diffraction peaks. Comparing the XRD pattern with International Centre for Diffraction Data (ICCD) a typical hexagonal Wurtzite structure of thin films has been inferred. This suggests that all the deposited ZnO thin films were found to be ZnO thin film structure and are preferentially oriented along the c-axis perpendicular to the substrate surface.

For as deposited films as illustrated in figure 1, the intensity of peaks is low. When the films are annealed at 300°C as shown in figure 2, the intensity of each peak is observed to increase. It should be noted that in addition to 002 and 101 diffraction peaks there exist a peak identified to be 100 which might be due to an unknown phases. As the annealing temperature is increased to 400°C as illustrated in figure 3, the sharpest and strongest 002 and 101 peaks were observed and the 100 peak disappear. The disappearance of 100 at 400°C may be due disappearance of Phases/impurities at an elevated annealing temperature. The strong preferential growth observed along (002) plane is a clear indication that the films are oriented along c-axis. Similar observation was reported by other researchers such as Ibrahim et al., 2013 who investigated the effect of annealing temperature on the structural and optical properties of Nano-crystalline ZnO thin films prepared by Sol-gel method.

The XRD results which showed the appearance of sharp 002 and 101 peaks belonging to standard ZnO, when compared with XRD pattern with only 002 peak reported by Pay-yu et al., (2013), Hassan and Hashim (2013) and Sameem (2015), who studied the effect of annealing temperature on the properties of Nano-crystalline ZnO thin films prepared by Chemical bath deposition, Oxidation and Successive ionic layer adsorption and reaction (SILAR) methods respectively, attest the advantage of spray pyrolysis over other methods in producing quality films.

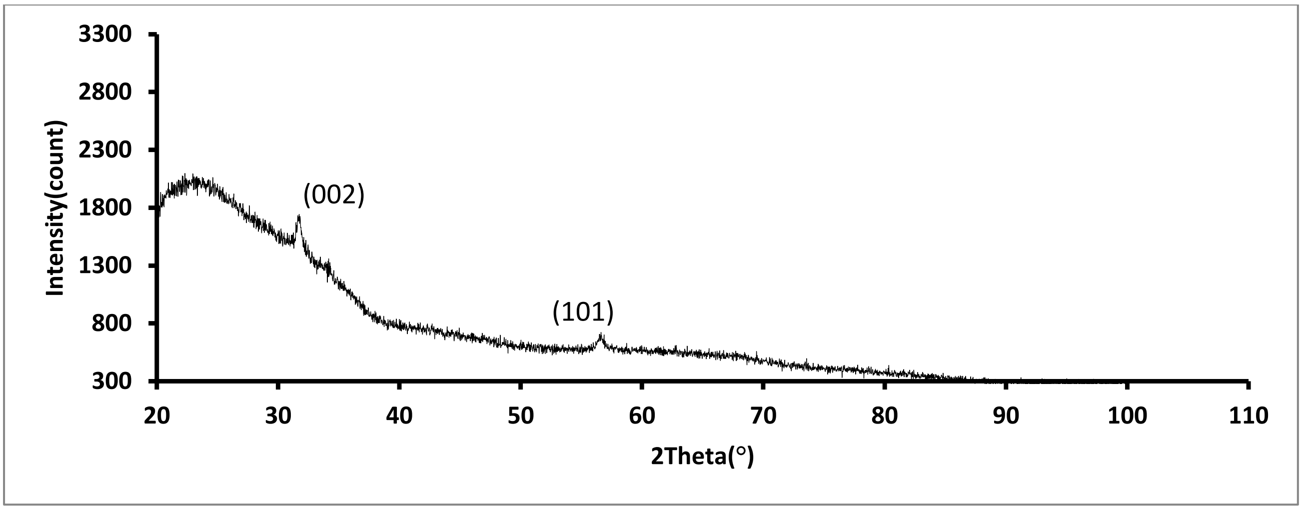

Figure 1: XRD patterns for as deposited ZnO thin films

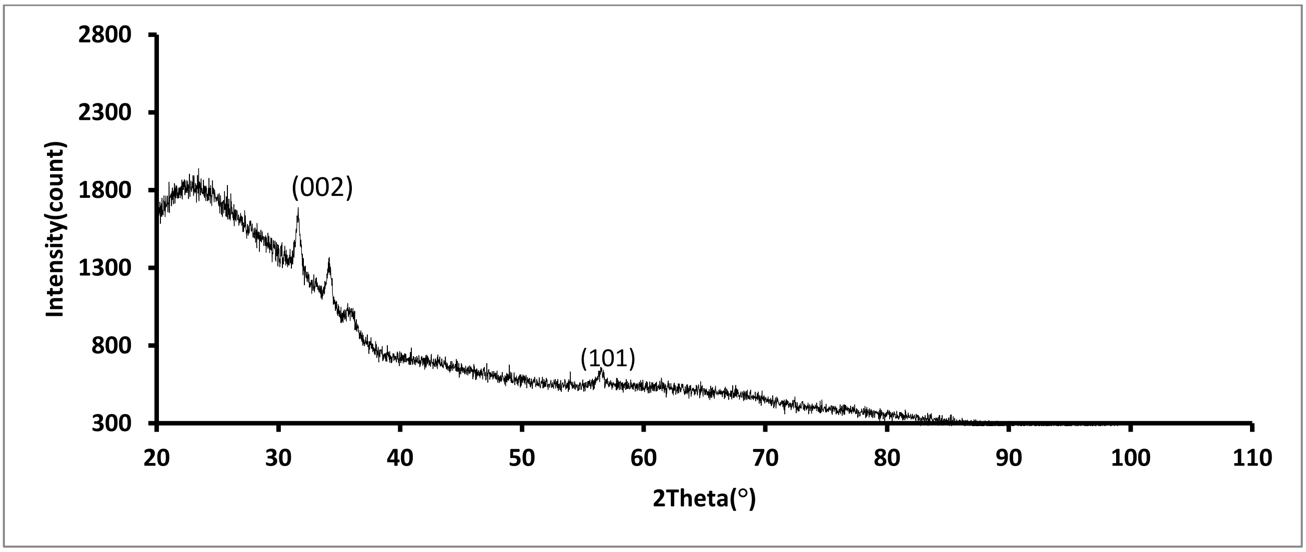

Figure 2: XRD patterns for ZnO thin films annealed at 300°C under N_2 atmosphere

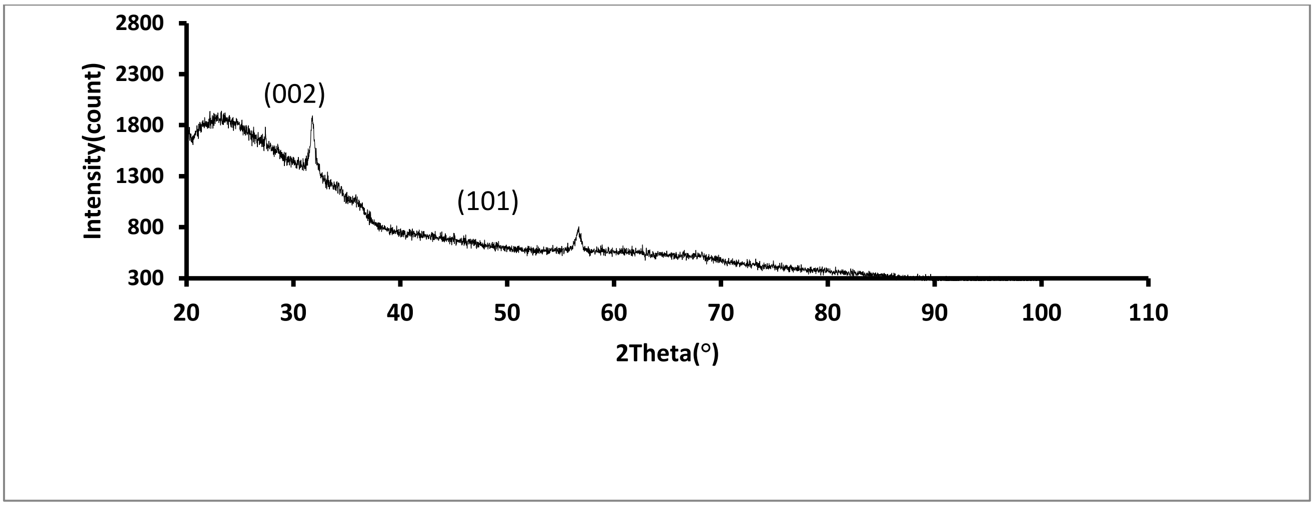

Figure 3: XRD patterns for ZnO thin films annealed at 400°C under N_2 atmosphere

3.2 Grain size (D)

The average crystallite sizes were calculated to be 0.4873nm, 0.6953nm and 0.6959nm for the as-deposited, films annealed at 300°C and films annealed at 400°C respectively. This shows that crystallite size increase with annealing. Increase in crystallite size implies increase in crystallinity. According to Pawan et al., 2010, the increase in particle size could be due to the merging of the smaller particles into larger ones and is as a result of potential energy difference between small and large particles.

3.3 Dislocation density (δ)

The values of δ for as deposited, annealed at 300°C and annealed at 400°C ZnO thin films as presented in table 1.0 are 42.1 $\times10^{17}$lines/m^2, 20.7$\times10^{17}$lines/m^2 and 20.6$\times10^{17}$lines/m^2 respectively. This shows that dislocation density decreases with annealing, which implies that annealing reduces imperfection/defects. This is because annealing lead to reduction in the interplanar spacing and thus minimizes the stacking fault (irregularity in the planar stacking sequence of atoms) in the films. Similar observation was reported by Moreh et al., (2013), but for $CuAlS_2$ thin films.

3.4 Micro-strain (ε)

From table 1.0 it can be seen that for as deposited the ε is 7.1$\times10^{-2}$, for films annealed at 300°C ε is 4.9$\times10^{-2}$ and for films annealed at 400°C ε is 4.98$\times10^{-2}$. Like δ, ε is observed to decrease with increase in annealing temperature. Thus, indicating an improved crystallinity. Similar behaviour was observed by Ibrahim et al., 2013. This is attributed to decrease in disorder and defect density in the structure as annealing temperature increases, which give rise to increase in crystallinity.

3.5 Lattice constants (a and c)

The values for lattice constants **a** and **c** are presented in table 1.0. The lattice parameter '**a**' for as deposited, annealed at 300°C and annealed at 400°C thin films are 3.2547A^0, 3.2576A^0 and 3.2660A^0 respectively. Similarly, the values of the lattice parameter **'c'** for as deposited, annealed at 300°C and annealed at 400°C thin films are 5.637A^0, 5.642A^0 and 5.657A^0 respectively. These values are in fair agreement with the lattice constants of ZnO powder sample of ASTM card: a= 3.2648A^0 and C = 5.2194A^0.

Table1: Structural parameters of ZnO thin films

Sample	Grain size D (nm)	Micro strain ε $X10^{-3}$	Dislocation density(δ) $x10^{17}$lines/m^2	FWHM β (0 0 2) (degrees)	2theta(°)	Lattice parameter (Å) a	c
ZnO as deposited	0.4873	71.1	42.1	0.3346	31.7467	3.254	5.637
ZnO annealed under N2 at 300°c	0.6959	49.8	20.6	0.2342	31.7173	3.257	5.642
ZnO annealed under N2 at 400°c	0.6953	49.9	20.7	0.2342	31.6335	3.266	5.657

Full width at half maximum (β)

From table 1.0 it is observed that FWHM (β) for the three samples are 0.3346, 0.2342 and 0.2342 respectively. This means that β decreases with increase in annealing temperature. Decrease in β is a good manifestation of improved crystallinity, implying that as annealing temperature increase, thin films becomes more crystalline. This is attributed to the relaxation of the misfit strain, as the film annealing temperature increases, the misfit strain decreases resulting in better crystallinity (Myoung et al., 2002).

4.0 CONCLUSION

The study of structural characterization of ZnO thin films grown by Spray pyrolysis technique was successfully carried out by x-ray diffraction. XRD characterizations reveal that annealing temperature has a great influence on the structure of films.It was discovered that the crystallinity of the grown films increase with increasing annealing temperature. Similarly, lattice parameters were found to depend largely on annealing temperature: the grain size D of the thin film increases with increasing film thickness, while micro strain, dislocation density, and FWHM were found to decrease appreciably with increasing annealing temperature. This work promises a potential application of spray pyrolysis deposited ZnO thin films for the Photovoltaic and Optoelectronics devices fabrication.

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