

Synthesis of Tin Doped Nanocrystalline ZnO Thin Films and its Influence on Physical Properties

4.1 Introduction

As it has been reported in the opening two chapters, several semiconducting oxides are employed as gas sensors by utilizing the changes of the electrical conductivity of these materials upon exposing to target gases. Especially, the oxides of some metals, such as zinc (Zn) and tin (Sn), have been exploited as active materials in chemiresistor sensors due to their unique electrical properties and process flexibility, which are normally operated at high temperature ($>373\text{K}$). Among these, ZnO is one of the earliest discovered and the most widely applied gas sensing material. However, ZnO-based gas sensors have shown some limitations, for example, low sensitivity, high working temperature and limited response towards low gas concentrations. The gas sensing properties of zinc oxides, which are difficult to elucidate, depend naturally on their catalytic or surface chemical properties, in addition to their physical or morphological properties. Because of the surface reaction, this type of gas sensor shows a lack of selectivity resulting in an indefinite gas detection mechanism and several reducing gases can be sensed at once. Moreover, the majority reactions involved in the gas detection depends on the reaction between the adsorbed oxygen and the test gas, and thus usually resulting in quite high working temperature [1]. Therefore, incorporation of particular dopants/impurities was reported to make it selective, bring down its operating temperature and decrease the response time [2].

Recently, the synergistic effects of dopants, for example, Al [3], Ga [4], In [5], Sn [6], and Sb [7] on the undoped nanocrystalline ZnO were reported to enhance the sensing performances. Among these dopants, tin (Sn) with ionic radius of $0.69\text{\AA}$ comparable to zinc ($0.74\text{\AA}$) seems to be appropriate substitutional impurity in the ZnO wurtzite structure to modify its electrical properties [8, 9]. Thereby, it is anticipated that a significant resistance change can be obtained in doped ZnO rather than in undoped ZnO, which results in a higher sensor response. Recently, Sn doped ZnO film has been successfully used for gas sensor applications. Shishiyanu et al. [10] reported conductometric gas sensors based on Sn doped ZnO film as sensitive

layer which are of great interest for NO₂ detection. Paraguay and Yoshida [11] prepared ZnO by spray pyrolytic process and the effect of doping by various metals on the sensing behavior to ethanol vapor was studied. It showed that doping ZnO by tin (Sn) improved the sensing properties of the prepared sensor.

In this chapter, the effects of Sn doping on the physical properties of advanced sprayed ZnO films are studied from the morphology, crystal structure, optical properties point of view.

4.2. Experimental Details

Deposition of ZnO: Sn films by advanced spray pyrolysis method include the substrate cleaning, solution preparation and deposition etc. The earlier optimized preparative parameters were applied in order to get nanocrystalline and feasible ZnO: Sn films for gas sensor application. The ZnO: Sn films were characterized using various techniques in order to get information on their structural, surface morphological, electrical and optical properties.

4.2.1. Substrate Cleaning

The details of the cleaning procedure of glass microslides substrates were given in Section 2.2.1 of Chapter two.

4.2.2. Deposition of Tin Doped Zinc Oxide Thin Films

The schematic experimental set up of advanced spray pyrolysis system for ZnO: Sn thin film deposition is shown in Figure 1.2. It consists of mainly a reaction chamber, a substrate heater, temperature controllers and nozzle assembly. For synthesis of ZnO: Sn thin films, initially, the spraying solution was prepared by mixing appropriate volumes of equimolar (0.1M) non-aqueous solution made by dissolving high purity zinc acetate [Zn (CH₃COO)₂·2H₂O] (Thomas Baker) and stannic chloride [SnCl₄·5H₂O] (Loba Chemie) in methanol. The total solution of 150 ml is sprayed. In order to dope Sn in ZnO thin films, three different concentrations (1, 3, and 4 at% measured as atomic weight percentage) were selected. At the time of deposition, the other previously optimized deposition parameters such as core temperature (598K) spray rate (6ml min⁻¹), nozzle to substrate distance (37 cm) and carrier gas pressure (10 LPM) were kept constant. The resulting solution (150 ml) was sprayed at an optimized substrate temperature of 473 K. Throughout the experimentation, the

both the substrate and core temperature were controlled using electronic temperature controllers. Hazardous gases evolved during the thermal decomposition were expelled out.

For simplicity, 1, 3, and 4 at % Sn doped ZnO thin films were denoted as 1SZO, 3SZO and 4SZO respectively.

4.2.3. Characterization Techniques

The spray deposited ZnO: Sn films were characterized for structural, surface morphological, electrical and optical properties by the techniques explained in Section 2.2.4 of chapter two.

4.3 Results and Discussion

4.3.1 X-ray Diffraction (XRD) studies

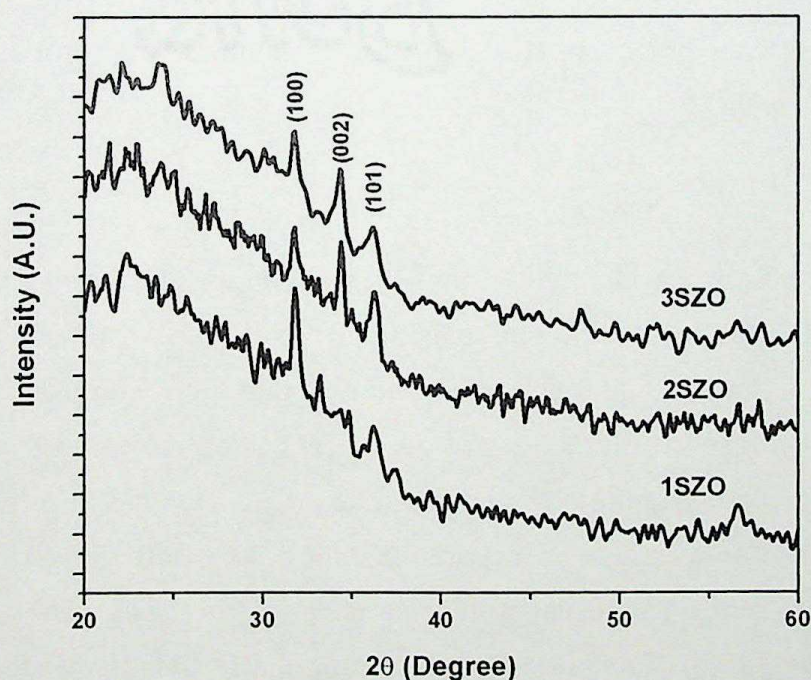


Figure 4.1: XRD patterns of the advanced sprayed ZnO: Sn thin films deposited at 473K with different Sn doping concentrations.

The effect of tin concentration on the crystallographic properties of Sn-doped ZnO thin films is studied using X-ray diffractometry. Figure 4.1 shows the XRD patterns of the ZnO: Sn films doped with 1, 3 and 4 at% tin doping concentrations. The 2θ values were varied from 20 to 60° . The peaks with the

Miller indices (100), (002) and (101) belong to the ZnO [12]. With these peaks, the XRD pattern of the films shows hexagonal wurtzite structure with a polycrystalline nature. No other peaks corresponding to tin oxide or tin are observed. As it is seen from patterns, the 1 at% Sn doped ZnO film is oriented along (101) plane; however for further increase in Sn doping, say 3 and 4 at%, the films possess dominant orientation along (002) plane. No change in position of (100) and (101) peaks (observed at 31.8 and 34.2° Bragg angles respectively) was observed due to variation in Sn doping concentration. However, the (002) peak slightly shifts to lower angle by ~1° with increase of Sn doping concentration. This suggests the lattice distortion incorporated in the film with Sn doping. Meanwhile, throughout such reorientation effect with the increase of Sn concentration intensities of dominant diffraction peaks declined and the crystallinity is observed to be affected to some extent.

The average crystallite size (D) of these samples was calculated using Scherrer's formula [13]:

$$D = \frac{0.9\lambda}{\beta \cos \theta_B} \text{-----} (4.1)$$

where λ is the X-ray wavelength of 1.54 Å, θ_B is the Bragg diffraction angle and β is the FWHM (full width at half maximum) of θ_B . The estimated average crystallite sizes of 1, 2 and 3 at% Sn-doped ZnO thin films were ~21.60, 21.30 and 19.06 nm, respectively. When the Sn concentration increased from 1 to 4 at%, the average crystallite size decreased about ~2.54 nm. Thus, from these calculations it is clear that incorporation of Sn into ZnO films caused the crystallinity to somewhat degenerate. The discrepancy in the ion radius between (0.074 nm) and Sn⁴⁺ (0.069 nm) might have caused a small lattice distortion and hence for that reason reduced the XRD Bragg peak intensity with the crystallite size [14]. In literature, similar results were reported [9, 14, 15].

Additionally to know more about the amount of defects in the films, the simple approach of Williamson and Smallman [16] was used and the dislocation density was evaluated by following relation,

$$\delta = \frac{1}{D^2} \text{-----} (4.2)$$

The δ values along with the crystallite size (D) values are also shown in Figure 4.2. The better crystallization of the films indicated by larger D and δ values. As can be seen in figure, the decreasing crystallite size and increasing dislocation density confirms the degradation of the crystallinity with the increase of Sn doping concentration in ZnO.

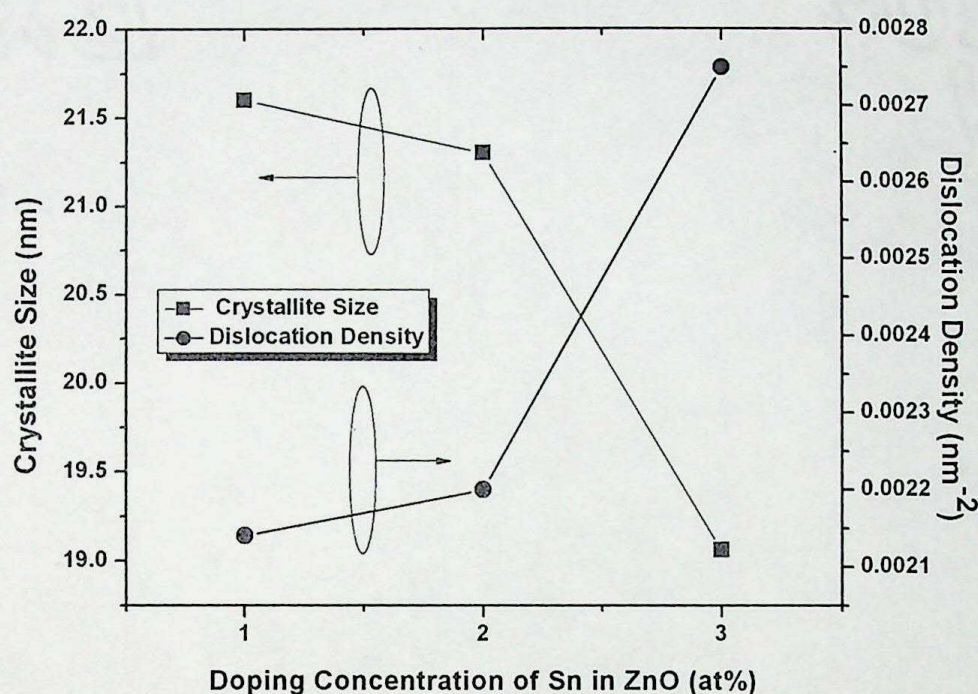


Figure 4.2: Crystallite size and dislocation density in ZnO: Sn thin films as a function of Sn doping concentration.

4.3.2. Surface Morphology

The influence of the Sn doping level in ZnO films on their surface morphologies was investigated using the field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM).

4.3.2.1 Field Emission Scanning Electron Micrograph (FESEM) Study

Figure 4.3 displays the representative in-plane FESEM images of the ZnO: Sn thin films at 1, 3 and 4 at% Sn doping concentrations. The images were performed at 50, 000 $\times$ magnifications. All the film surfaces are free from cracks, highly dense and homogeneous. As seen in these micrographs, the surface morphology of the ZnO: Sn films observed to exhibit some modification with Sn doping concentration increase. For the 4 at% Sn doped ZnO sample, the grains

are seen to agglomerate to form uniformly distributed clusters. The average particle size on the surface of ZnO: Sn decreased slightly with increase in Sn doping level. This is in a good agreement with X-ray diffraction results. This could play an important role in the surface reactions resulting in an increase in the sensitivity of the films.

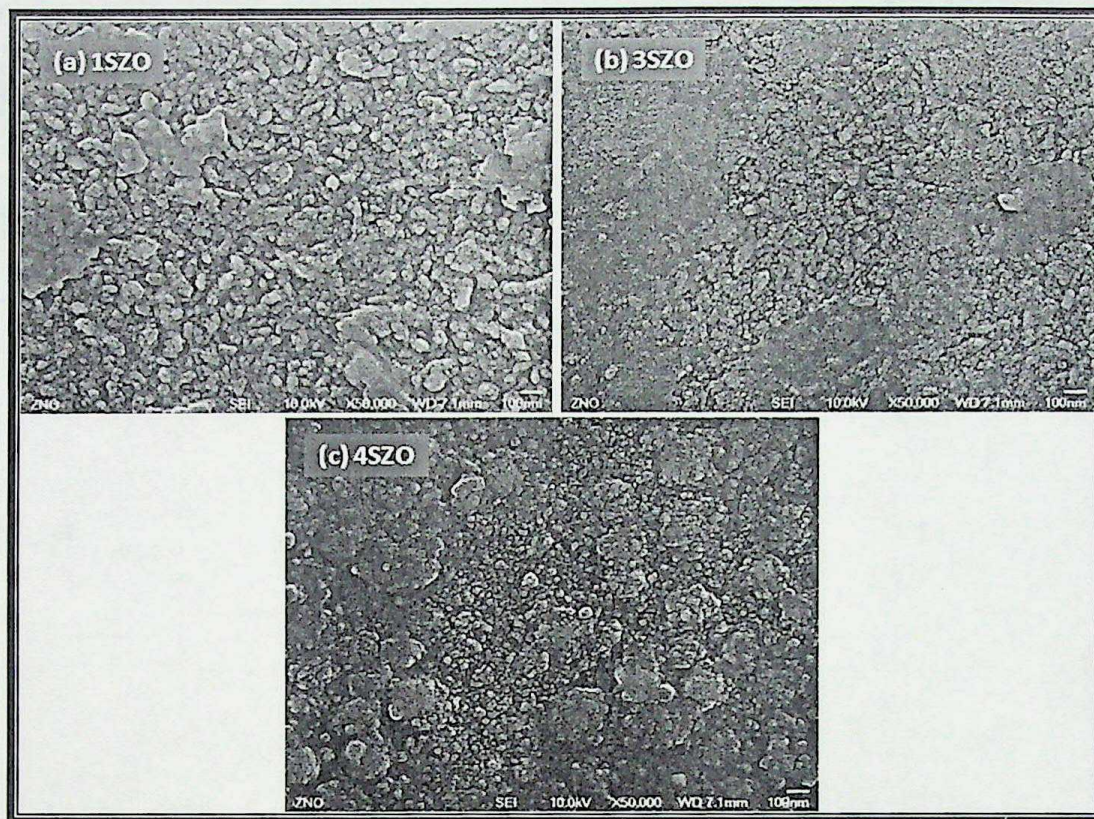


Figure 4.3: Plain view FESEM micrographs for ZnO: Sn films prepared at different Sn doping concentrations: (a) 1 at %, (b) 3 at %, and (c) 4 at%.

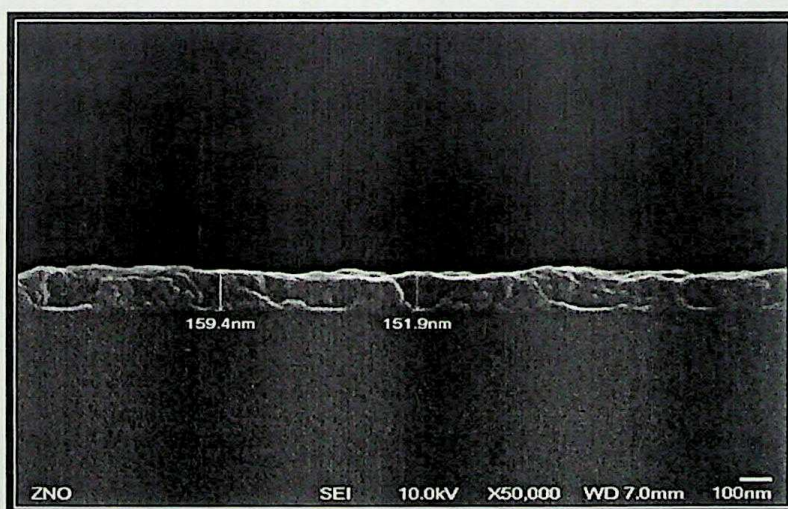


Figure 4.4: Typical cross-sectional view FESEM image of 4 at% Sn doped ZnO film.

The film thickness of the ZnO: A Sn film was measured by taking the cross-sectional view FESEM images. Figure 4.4 shows a typical cross-sectional view FESEM micrograph of ZnO: Sn film at 4 at% Sn doping. From the image it is seen that the film adheres well to the glass substrate. The measured average film thickness of the film is $\sim 156\text{nm}$. The film thickness of the other film viz. 1 at% and 3 at% Sn doped films are $\sim 204\text{nm}$ and 163nm respectively.

4.3.2.2 Atomic Force Micrograph (AFM) Study

To support the observations from the FESEM images of the samples, the atomic force microscopy images were obtained. Figure 4.5 shows two-dimensional AFM images of ZnO: Sn films at different Sn doping concentrations. Depending on the increasing Sn concentration, the surface morphologies of the films were seen to be deteriorated. This result supports the XRD and FESEM observations.

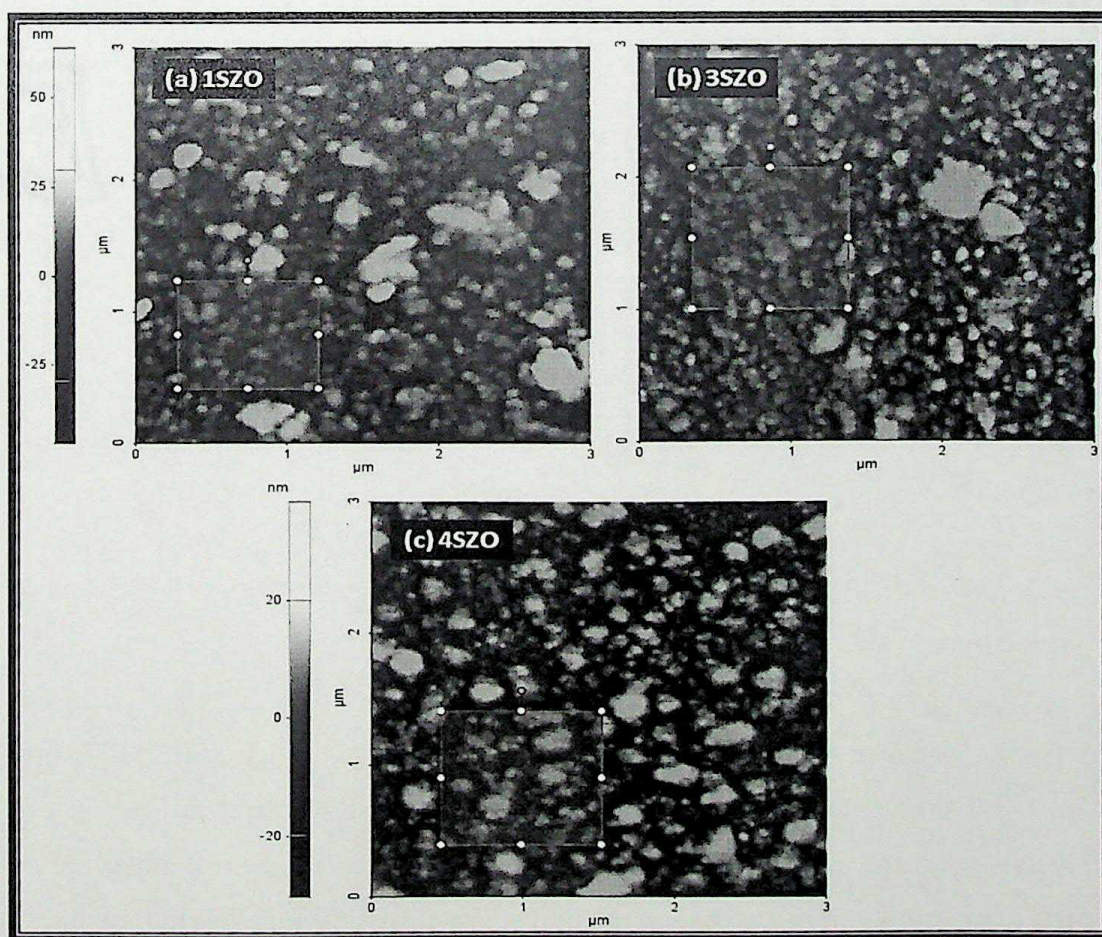


Figure 4.5: AFM images for ZnO: Sn films prepared at various Sn doping concentrations: (a) 1 at%, (b) 3 at%, and (c) 4 at%.

Moreover, Root mean square roughness of the ZnO: Sn film extracted from the AFM. It is apparent that the reduction of average crystallite/particle size in the ZnO films after Sn substitution results into the decrease in surface roughness. A noteworthy improvement of surface RMS roughness with Sn doping can be seen. The root-mean square (RMS) roughness decreased with Sn concentrations. The ZnO: Sn films at 1, 3 and 4 at% Sn doping level exhibit 5.171, 2.271 and 0.897 nm surface RMS roughness.

4.3.3 Optical Absorption Studies

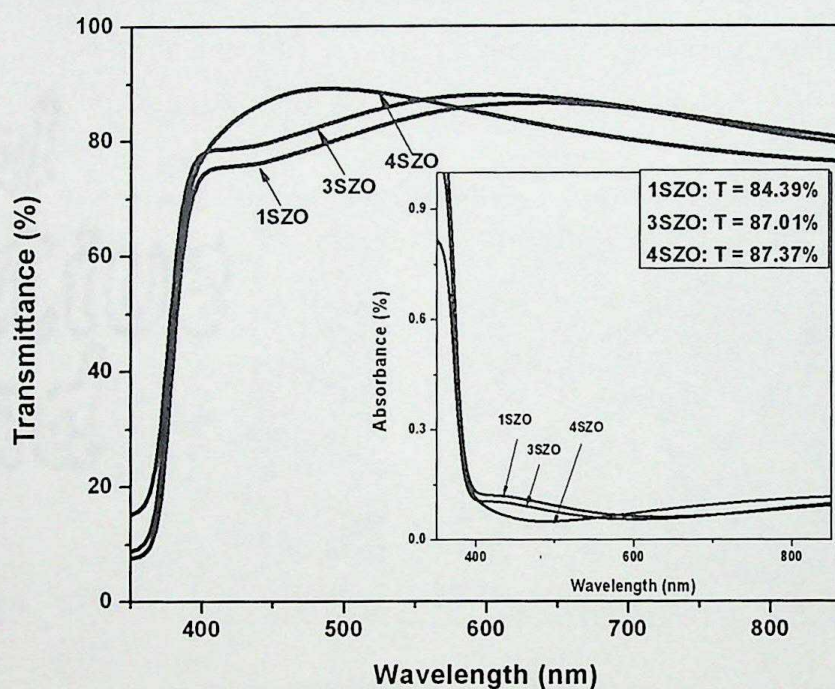


Figure 4.6: Optical transmission spectra of ZnO: Sn films at different Sn doping concentrations.

The optical properties of ZnO: Sn films were studied by measuring the optical absorbance spectra of samples in the wavelength range 350 to 850 nm. Figure 4.6 shows the optical transmittance spectra of ZnO: Sn thin films in the wavelength range of 350 to 850 nm. The corresponding optical absorbance spectra are shown in the inset of the Figure. The transmittance of Sn doped ZnO films stay over 84% at 550nm. The optical transmittance is observed to increase from ~84% to ~87% as the Sn concentration increases from 1 to 4 at%. This increase in transmittance may be attributed to the decrease in film thickness and

RMS roughness with increase in Sn doping level. With a relatively smother surface, the 4 at% Sn doped sample exhibit highest transmittance and thus demonstrates minimum scattering loss of incident beam light. Further investigation of the Figure indicates that there is a slight shift in the optical band gap along with the increase in the transparency of the samples, which is appropriate with the concentration of Sn doping.

The optical band gap E_g of the films can be determined from the theoretical relation between E_g and the absorption coefficient (α)

$$\alpha = A(h\nu - E_g)^{1/2} \text{-----} (4.3)$$

where, A is a constant, h is Planck's constant and ν is the frequency of the radiation [17]. The values of the direct optical band gap E_g values of the films were obtained from the intercept of $(\alpha h\nu)^2$ versus $h\nu$ curves plotted in Figure 4.7. The determined optical band gaps are increased from ~3.28 to 3.29 eV as the Sn doping concentration increases from 1 at% to 4 at%. The increase in band gap is attributed deterioration of crystallinity [18]. The trends of energy gap are similar to those reported in the literature [9].

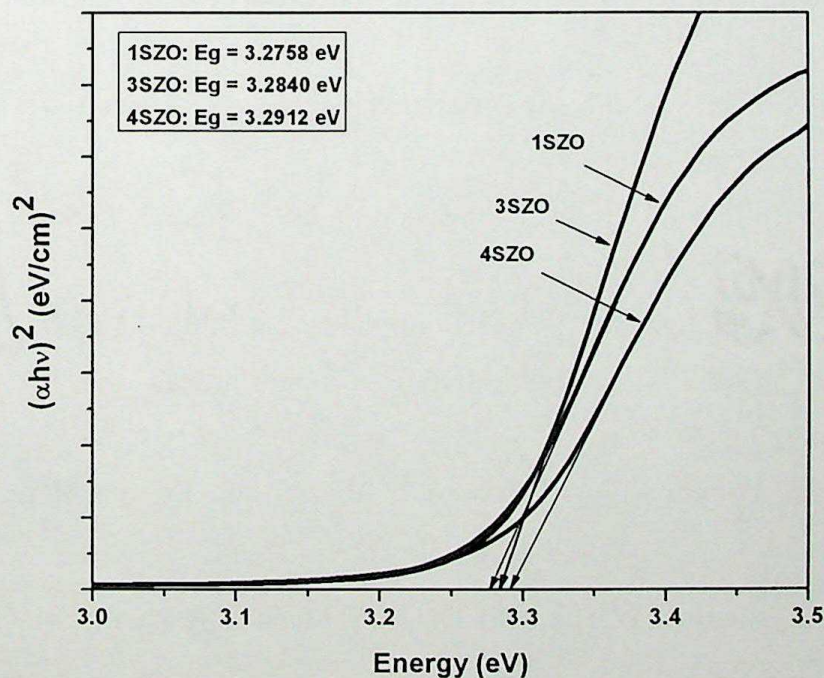


Figure 4.7: Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for ZnO: Sn films at different Sn doping concentrations.

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