

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

3.1 Introduction

It has been seen in the Chapter two that the zinc oxide (ZnO), a non-toxic and inexpensive semiconductor material, can be successfully deposited onto glass at relatively lower substrate temperature (473K) using novel advanced spray pyrolysis technique. The various preparative parameters such as, core temperature substrate temperature etc. of the advanced spray pyrolysis system used, are optimized in order to realize optimum properties of ZnO thin films. These undoped ZnO films have shown great potentials for hazardous hydrogen sulphide gas sensing. However, ZnO-based gas sensors have shown some limitations, such as low sensitivity, high working temperature and restricted detection of low concentration gas.

Over the years, substantial efforts have been devoted to make ZnO films selective, bring down its operating temperature and decrease the response time. For this, two approaches, either decreasing the material size into nanoscale or introducing proper dopants, have been demonstrated to be effective. One of the effective ways of improving the gas sensing properties of ZnO sensor is the addition of certain impurities/dopants. Transition metal elements have been successfully employed as dopants in ZnO. In particular, the group IB transition element copper (Cu) with similar ionic radius to that of Zn^{2+} ion (0.074nm) and electronic shell structure, has many physical and chemical properties similar to those of Zn [1]. Cu has observed to cause significant effects on the electrical, chemical, and optical properties of ZnO [2]. The Cu-doped ZnO (ZnO: Cu) is one of the most promising electrical conductivity-controlled metal oxide due to its variable electrical resistance properties [3] and it has been demonstrated that ZnO films doped with Cu have higher electrical resistance [4]. Such high resistivity effect has been revealed to increase the sensitivity of the metal oxide gas sensors [5]. Earlier ZnO: Cu films have been shown to sense carbon monoxide [6, 7], ethanol [8] at high working temperatures. Therefore, doping

ZnO with Cu might be a promising selection to improve the gas sensors sensitivity.

In the present investigation, an effort has been made to synthesize ZnO: Cu thin films at low substrate temperature by simple and inexpensive advanced spray pyrolysis technique. The structural, morphological, and optical properties of ZnO: Cu thin films are studied as a function of copper doping concentration.

3.2. Experimental Details

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

3.2.1. Substrate Cleaning

The glass microslides substrates were cleaned by the procedure explained in Section 2.2.1 of Chapter two.

3.2.2. Deposition of Copper Doped Zinc Oxide Thin Films

The schematic experimental set up of advanced spray pyrolysis system for ZnO: Cu 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: Cu 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 [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] (Thomas Baker) and cupric chloride [$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$] (s.d Fine-Chem) in methanol. The total solution of 150 ml is sprayed. In order to dope Cu in ZnO thin films, four different concentrations (1, 2, 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, 2, 3, and 4 at % Cu doped ZnO thin films were denoted as 1CZO, 2CZO, 3CZO and 4CZO respectively.

3.2.3. Characterization Techniques

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

3.3 Results and Discussion

3.3.1 X-ray Diffraction studies

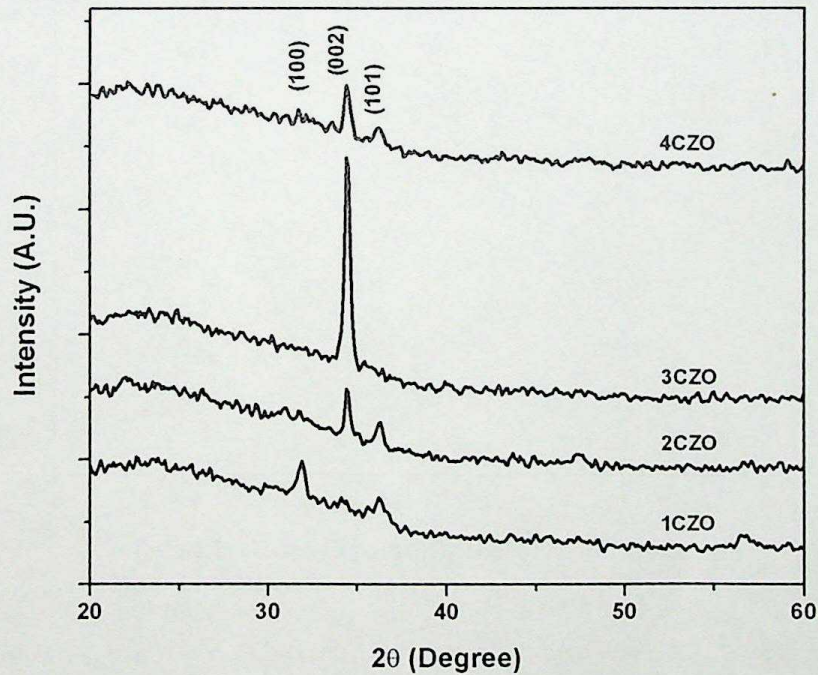


Figure 3.1: XRD patterns of the advanced sprayed ZnO: Cu thin films deposited at 473K with different Cu doping concentrations.

Figure 3.1 shows the XRD patterns of ZnO: Cu films fabricated at different Cu doping concentrations. In Figure , the peaks at 31.9° , 34.4° and 36.3° are identified as (100), (002) and (101), reflections of wurtzite structure of ZnO, confirming that all the polycrystalline films retain the similar ZnO structure and are randomly oriented at low Cu concentrations. At 1 at%, the (002) peak is very pathetic as compared to the (100) and (101) peaks. However, with increase in Cu

doping concentrations intensity peak corresponding to (002) is improved and the 3 at% film exhibits the most intense single peak corresponding to (0 0 2) plane. Further at 4 at%, the (002) peak intensity observed to decrease. Earlier, an improvement in the c-orientation of ZnO films as an effect of Cu doping has been reported by others [9, 10]. According to Lee et al. the increase in the extent of c-orientation may be due to the fact that a moderate quantity of Cu atoms exist as interstitials sharing the oxygen with Zn atoms and hence improve the (002) orientation [10].

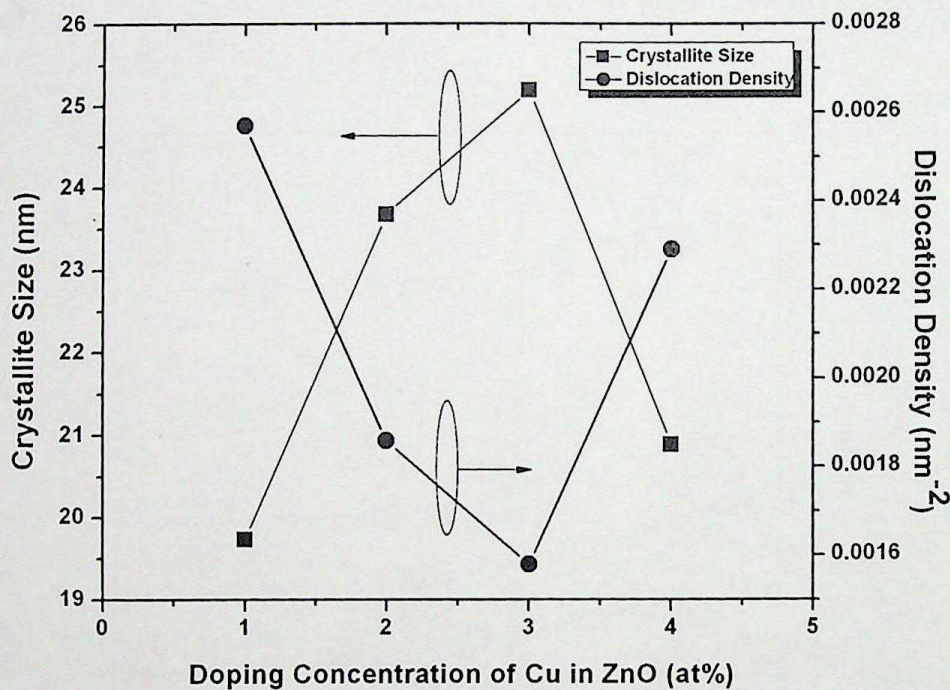


Figure 3.2: Crystallite size and dislocation density in ZnO: Cu thin films as a function of Cu doping concentration.

The microstructural parameters such as crystallite size (D) and dislocation density (d) for ZnO: Cu films were estimated using the relevant formulae [11, 12] and represented in Figure 3.2. Figure shows the variation of average crystallite size and corresponding dislocation density as a function of Cu doping concentration. From Figure, it can be seen that the crystallite size increases from ~20 to ~25 nm, when the Cu doping concentrations increases from 1 to 3 at%. However, for further increase in Cu concentrations i. e. at 4 at% the crystallite size shows a decreasing trend. The results imply that the

crystallinity and degree of orientation of the ZnO: Cu films were closely associated to the Cu doping concentration. Moreover, the structural parameters like dislocation density (d) show a decreasing trend with the Cu doping concentration up to 3 at%, which leads to the reduction in the concentration of lattice imperfections.

3.3.2. Surface Morphology

3.3.2.1 Field Emission Scanning Electron Micrograph (FESEM) Study

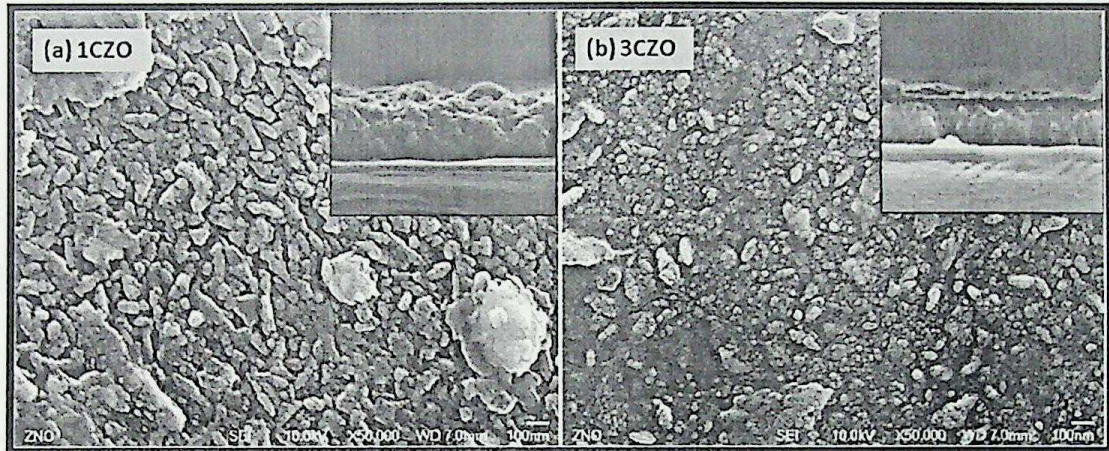


Figure 3.3: Plain view FESEM micrographs for ZnO: Cu films prepared at different Cu concentrations: (a) 1 at %, and (b) 3 at%.

The FESEM in-plane and cross-sectional images of the 1 and 3 at% Cu doped ZnO thin films shown in Figure 3.3 are utilized to support the observations from the XRD characterization and directly characterize the growth mode of the ZnO: Cu films. From the plain view images it is seen that the 1 at% Cu doped ZnO sample surface consists of irregular sized structures and it is not dense too. However, the 3 at% sample exhibits comparatively compact surface well covered with the granular structures. Further, the cross-sectional FESEM images of the 1 and 3 at% Cu doped ZnO thin films are shown in their respective insets. From the images, it is noted that Cu doping has a profound influence on the cross-sectional structure and growth mode of the ZnO: Cu films. As can be seen from insets, 3 at% Cu doped ZnO film exhibits better columnar growth perpendicular to the surface than the 1 at% Cu doped ZnO film. It is well-known that columnar growth has improved crystalline structure and thus morphology observations clear the crystalline behavior understood from the XRD patterns.

The film thicknesses measured by profilometer do not show much variation and found to vary in the range 140 to 180nm.

3.3.2.2 Atomic Force Micrograph (AFM) Study

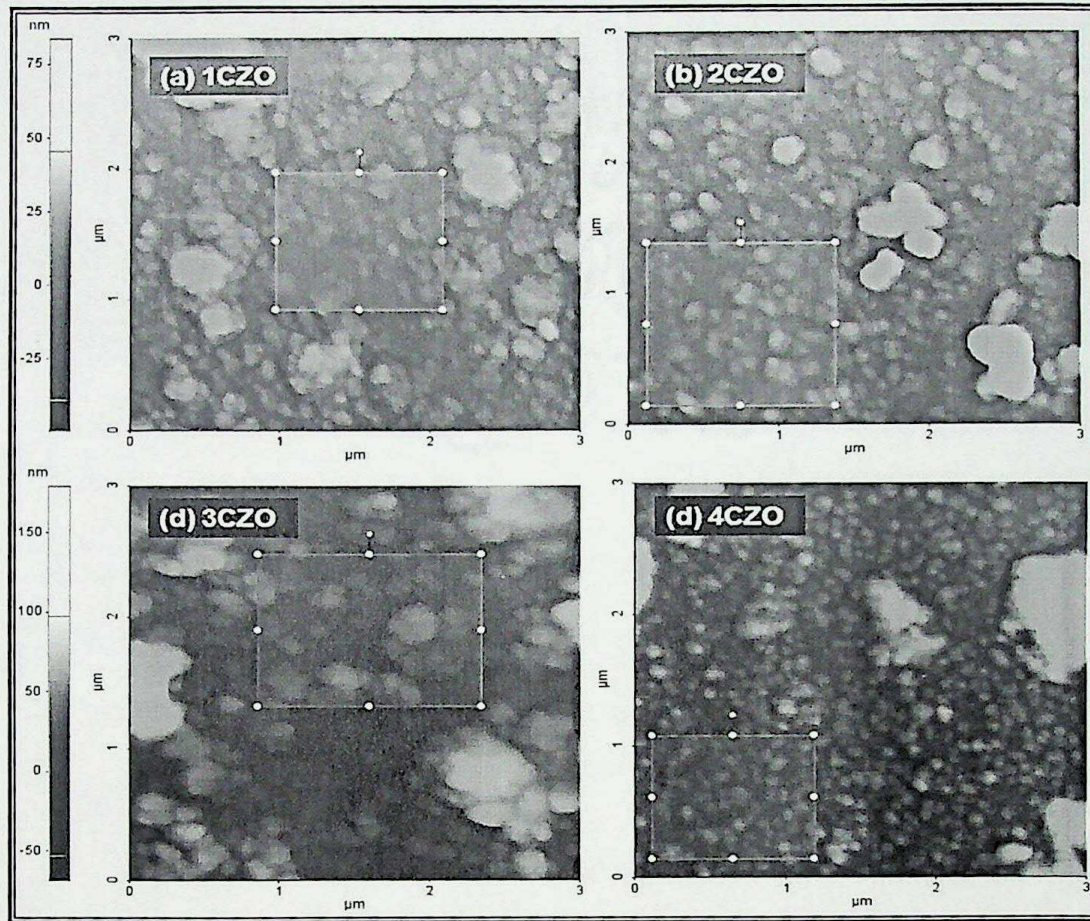


Figure 3.4: AFM images for ZnO films prepared at various Cu doping concentrations: (a) 1 at%, (b) 2 at%, (c) 3 at% and (d) 4 at%.

Figure 3.4 shows the two-dimensional atomic force microscopy (AFM) images of zinc oxide thin films deposited for different preheating temperatures. The images are recorded on $3 \times 3 \mu\text{m}^2$ planar in contact mode at the scan rate of 10.17 Hz. From the images it is seen that all the film surfaces are well covered with the uniformly distributed spherical grains of varying sizes. It is evidently seen that grain size increased with incorporation of copper up to 3 at% doping concentration; however grain size decreased for 4 at% Cu doped ZnO sample. Thus, the 3 at% Cu doped ZnO films exhibits highly dense morphology with the highest grain sizes correlated with the FESEM and XRD observations. Further, some overgrown agglomerates are also seen in all AFM images. The evaluated

RMS surface roughness is 4.89, 3.74, 6.32 and 4.97 nm for 1, 2, 3 and 4 at% Cu doped ZnO samples, respectively.

3.3.3 Optical Absorption Studies

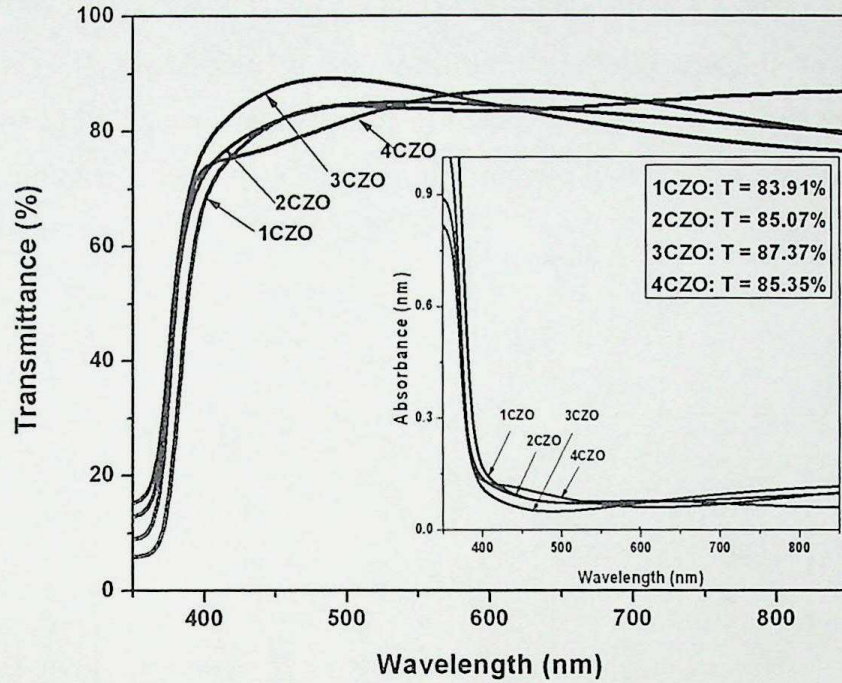


Figure 3.5: Optical transmission spectra of ZnO: Cu samples at different Cu doping concentrations.

Figure 3.5 shows the optical transmittance spectra of ZnO: Cu thin films with different Cu doping concentrations in the wavelength range of 350 to 850 nm. The inset of the Figure shows the corresponding optical absorption of ZnO: Cu films. The transmittance of all copper doped ZnO films stays over 80% at 550nm. The optical transmittance is observed to increase with Cu doping concentration up to 3 at%; however it again decreases slightly for 4 at% sample. The observed change in transmittance may be the effect of change in film thickness and consequent surface scattering of incident photons with variation in Cu doping concentration in ZnO.

The variations of the absorption coefficient of ZnO: Cu films with respect to the incoming photon energies are given in Figure 3.6. It is seen that the dependence of the $(\alpha h\nu)^2$ on $(h\nu)$ is linear about the fundamental absorption region which can be taken as an indication of the direct transition. The

absorption coefficient being about 10^6 cm^{-1} , which is deduced from the absorption spectra, is also a suggestion of the direct transition. The optical band gap values are determined from these plots by means of the extrapolation of the linear portion of $(\alpha h\nu)^2$ vs. $(h\nu)$ curves. As can be seen in the plot, the optical band gap of 1, 2, 3 and 4 at% Cu doped ZnO films are $\sim 3.27 \text{ eV}$, $\sim 3.26 \text{ eV}$, $\sim 3.25 \text{ eV}$ and $\sim 3.26 \text{ eV}$, respectively. Similar effect of Cu incorporation in ZnO on band gap was demonstrated by K.-S. Ahn et al [13]. The observed behavior of band gap variation with the Cu doping concentration is likely to be attributed to a variation of crystallite size and a modification of the grain boundary configuration during growth.

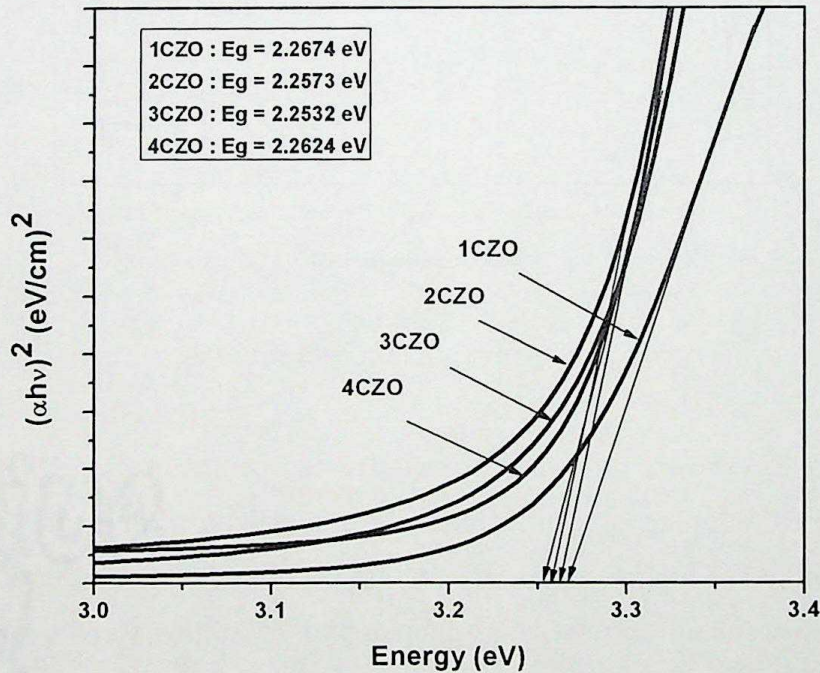


Figure 3.6: Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for ZnO: Cu samples with different Cu doping concentrations.

References

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