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Synthesis and Characterization of Co doped ZnO Nanocrystalline Thin films

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ABSTRACT

ZnO and Co doped ZnO nanocrystalline thin films have been prepared by sol-gel dip coating method. X-ray diffraction analysis reveals that the ZnO and Co doped ZnO nanocrystalline thin films exhibit hexagonal structure. The lattice constants of Co doped ZnO was observed to decrease slightly with incorporation of Co. The surface morphology of the ZnO and Co doped ZnO films suggests that the films are homogeneous and are made of uniform deposit free of cracks and pores. The composition analysis results show that Zn, Co and O are present in the samples. Photoluminescence properties of undoped ZnO and Co doped ZnO nanocrystalline thin films have been studied.

Keywords: Co doped ZnO nanocrystalline thin films, Sol-gel, X-ray diffraction,

I. INTRODUCTION

ZnO has a variety of applications in optoelectronics, laser diodes, surface acoustic wave guides (SAW), solar cells, and gas sensors because of its wide band gap (3.37 eV) and a large exciton binding energy of 60 meV at room temperature. For room temperature ferromagnetism, the transition metal (TM) doped ZnO is a most promising candidate in accordance with theoretical predictions. Nowadays, Co doped ZnO nanomaterial's [1-3] are widely used for studying Dilute Magnetic Semiconductors (DMS). A variety of techniques have been used so far for fabricating ZnO films such as thermal deposition [4], Sputtering [5], metal organic chemical vapour deposition (MOCVD) [6], Spray pyrolysis [7], Sol-Gel technique [8-9]. From these methods, the sol- gel method is more popular because of its cheapness, reliability, repeatability, and simplicity. In this paper, we report about the preparation and characterization of nanocrystalline $Zn_{1-x}Co_xO$ thin films prepared by sol – gel method.

II. EXPERIMENTAL

In the present study, ZnO and Co doped ZnO nanocrystalline thin films have been prepared by sol-gel dip coating method. The precursors were used Zinc acetate dihydrate, cobalt chloride hexahydrate, Isopropyl alcohol, and diethanolamine. A sol was prepared by mixing thoroughly the calculated amount of the Zinc

acetate dihydrate in Isopropyl alcohol on a magnetic stirrer at room temperature. The cobalt chloride hexahydrate was used as a dopent at concentrations (Co=0.01M). Total concentration of the metal ions was maintained as 0.1M.The solutions were stirred about 30 min, an equimolar quantity of diethanolamine was added as a sol stabilizer until it becomes transparent [10 – 13]. This sol was used to coat on Si (100) substrates by dip –coating process. Totally 10 dipping (1 min) were carried out. After each dipping, the film has been dried at 110ºC in hot oven for 15 minutes. This process of coating and subsequent heat treatment has been repeated for 10 times to give the film thickness of 125nm. Finally, as deposited films were annealed at 550ºC for 1 hour.

III. RESULTS AND DISCUSSION

The X-ray diffraction patterns of ZnO and Co doped ZnO thin films are shown in figure 1. From the figure 1 the pure ZnO films exhibits poor crystallanity for 2θ values from 30º to 40º. But for Co doped ZnO thin film (figure 1b) have been shown that the existance of low intensity peaks for 2θ values from 30º to 40º, which corresponds to the ZnO wuritze structure [12]. In $Zn_{1-x}Co_xO$ thin film at low concentration of Co, secondary phases namely CoO and Co_3O_4 are also found out along with poor crystalline phases of ZnO. A secondary phase dominants at 2θ= 67.7º represents CoO with (220) planar orientation. The average grain size of the samples has been determined using full width at half-maximum (FWHM) of the diffraction peaks using Scherrer's equation. Grain size of ZnO and Co doped ZnO have been found to be lie in the range of 25- 35 nm.

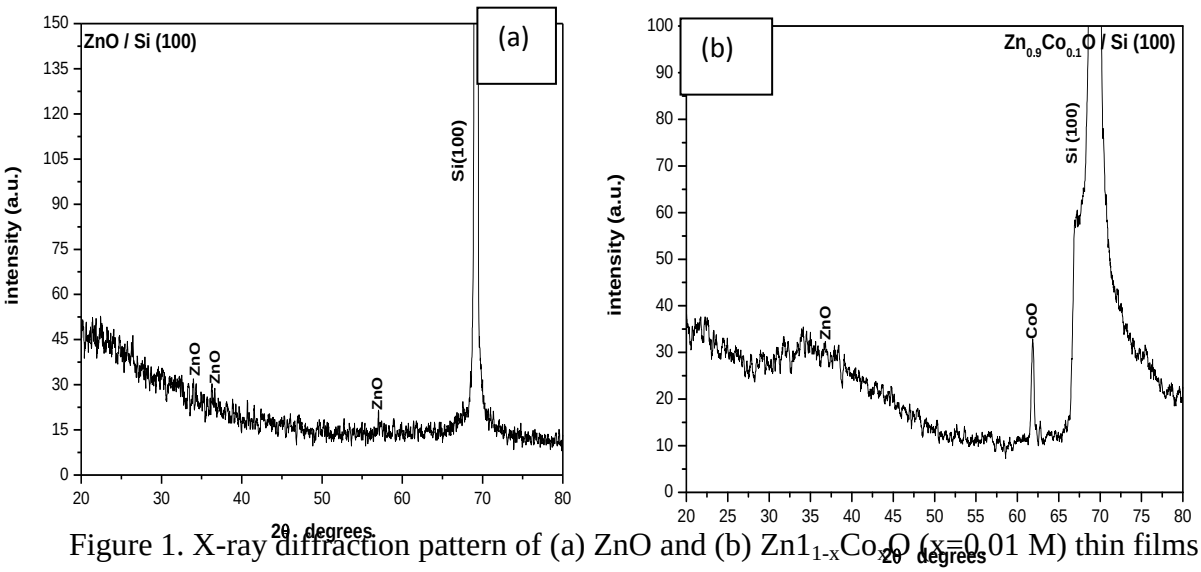

Figure 1. X-ray diffraction pattern of (a) ZnO and (b) $Zn1_{1-x}Co_xO$ (x=0.01 M) thin films

Scanning electron microscope (SEM) was used to investigate surface morphology of the ZnO and Co doped ZnO thin films prepared by sol-gel dip coating method The surface morphology of undoped and Co doped ZnO thin films are shown in figure 2. The surface morphology of the ZnO and Co doped ZnO films suggests that the films are homogeneous and are made of uniform deposit free of cracks and pores. Figures 3 shows the energy

dispersive x-ray analysis (EDAX) of undoped ZnO and Co doped ZnO. EDAX analysis reveals that Zn, O and Co is present in the sample.

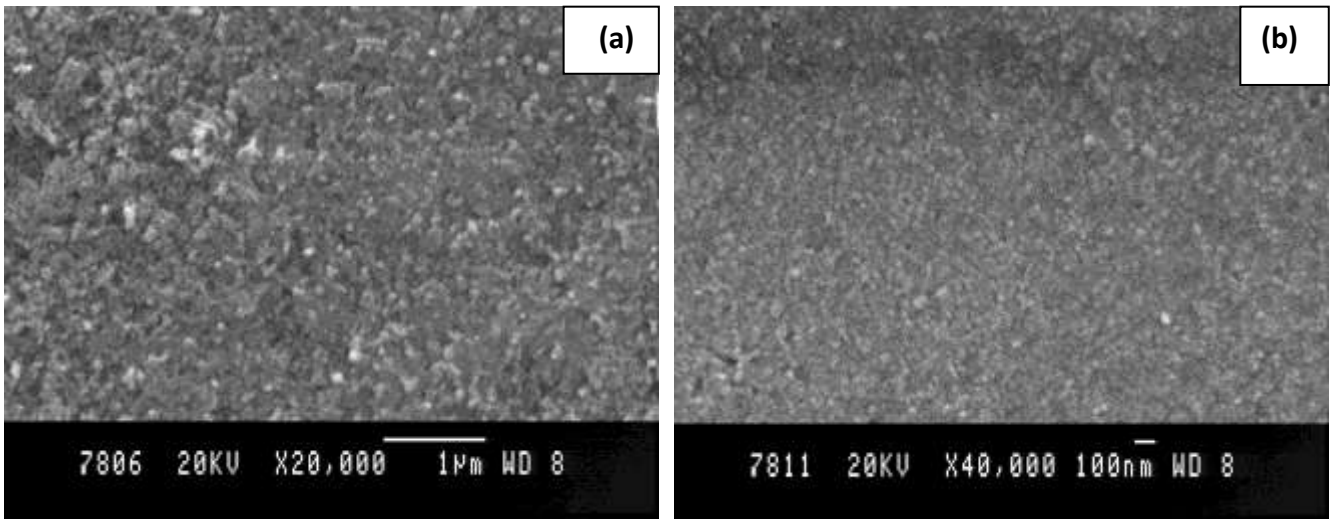

Figure 2. SEM images of (a) ZnO and(b) $Zn1_{1-x}Co_xO$ (x=0.01 M) thin films

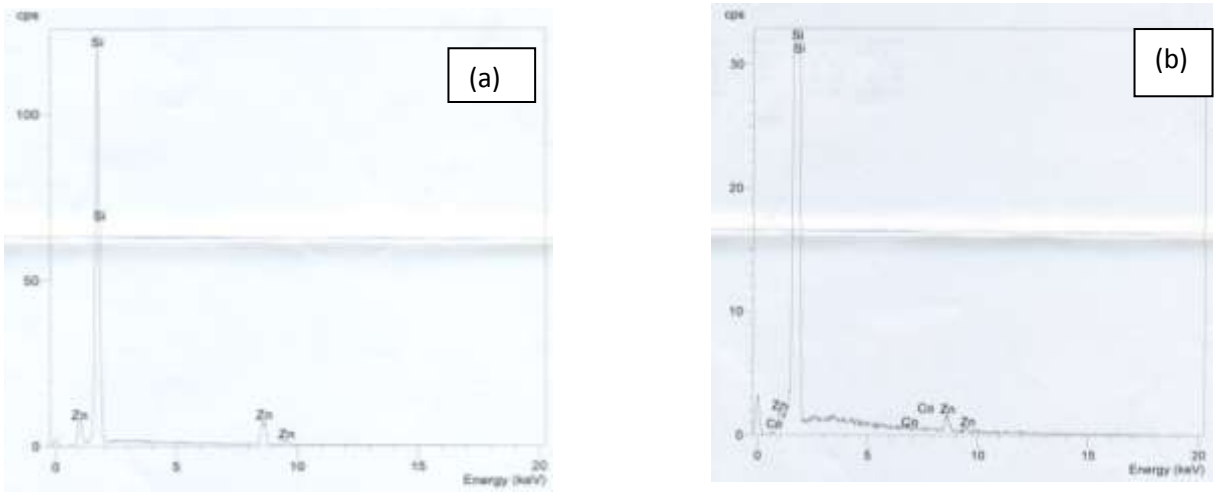

Figure 3.EDAX pattern of (a) ZnO and (b) $Zn1_{1-x}Co_xO$ (x=0.01 M) thin film

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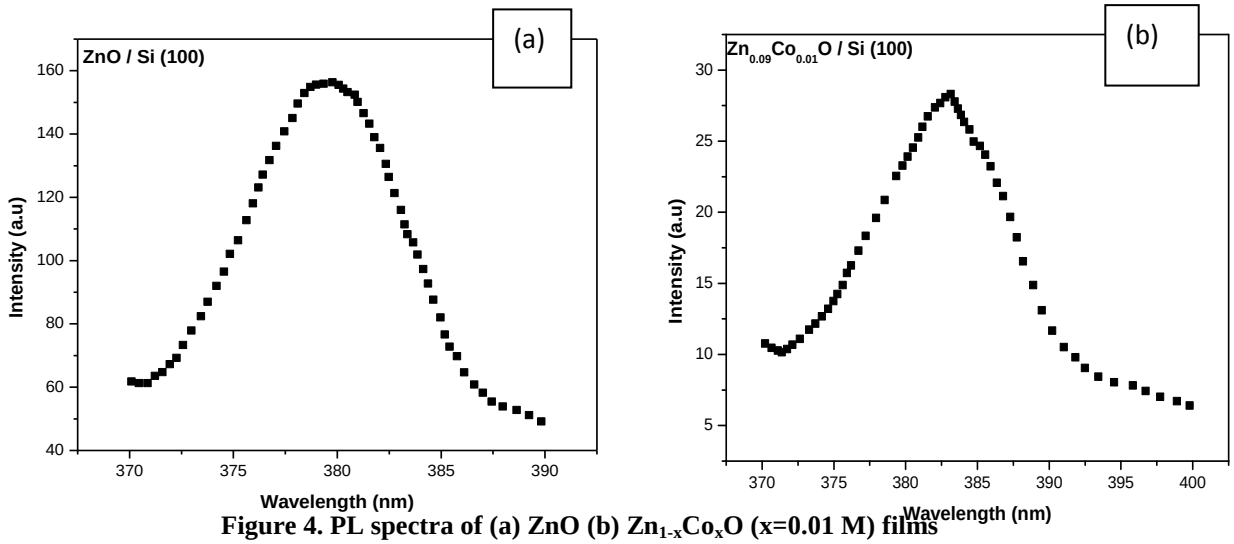

Figure 4. PL spectra of (a) ZnO (b) $Zn_{1-x}Co_xO$ (x=0.01 M) films

Figure 4 shows room temperature photoluminescence (PL) spectra for ZnO and Co doped ZnO/Si at concentration (0.01M) has been carried out. The intensity (a.u) Vs Wavelength (nm) plot for pure ZnO (figure 4a) shows emission peak at λ=380nm (E_g =3.267eV). This strong emission peak corresponds to near edge emission of ZnO material. Encouraged by the recent demonstration of ultrasensitive and highly sensitive gas sensors, its sensing capability may yield positive results [14]. In sol-gel process, since the decomposition was done in air at 550^{o}C, ZnO surface strongly adsorbs oxygen. Adsorbed oxygen at the grain boundaries of the polycrystalline ZnO/Si film was known to give rise to surface acceptor states which are the trap states. Annealing in air increases the density of the trap states in the interface, which indirectly support the violet emission in ZnO is linked to recombination between trapped electrons at the grain boundary related interface traps and holes in the valence band.

The intensity (a.u) Vs Wavelength (nm) gives the emission spectra (figure 4b) of ZnCoO/Si films [15-16]. PL spectra of Co doped ZnO peak shifts towards higher wavelength side.

IV. CONCLUSION

ZnO and Co doped ZnO nanocrystalline thin films have been prepared by sol-gel dip coating method. X-ray diffraction analysis reveals that the ZnO and Co doped ZnO thin films exhibit hexagonal structure. The surface morphology of the ZnO and Co doped ZnO films suggests that the films are homogeneous and are made of uniform deposit free of cracks and pores. The composition analysis results show that Zn, Co and O are present in the samples.

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