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Influence of Cu Doping on Physical Properties of Nanocrystalline Spray Deposited Zinc Oxide Thin Films

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ABSTRACT

Nanotechnology is critical in today's world of technology and research. Structures are becoming more miniature in every field, which reduces circuit size and cost while also increasing working efficiencies. In the present research work, the influence of Cu doping on physical properties of nanocrystalline spray deposited zinc oxide thin films were studied. The structural and morphological investigations revealed that, the films are nanocrystalline in nature with pure hexagonal lattice and mixed cubic lattices and exhibits direct band gap of the order of 3.32 eV which decreases to 2.52 eV with increase in doping concentration. The electrical resistivity of the pristine films was found to be $3.81\times10^{-1}\Omega cm$ which decrease to $4.80\times10^{-2}\Omega cm$ with higher Cu doping. The thermo-emf measurement confirms that both undoped and doped thin films own n-type conductivity.

Keywords: Thin films, Nanostructures, Structural properties, Optical properties, Electrical properties.

I. INTRODUCTION

In the field of spintronics wide band gap semiconductor materials play a vital role. These materials may be utilized in manufacturing and development of devices such as sensors [1], biosensors [2], supercapacitors [3], photodiodes [4] and different types of solar cells [5-9] etc., One of such wide band gap semiconductor material is zinc oxide (Eg=3.31eV) which belongs to II–VI group. Several researches have already deposited zinc oxide films by using numerous techniques which includes chemical vapor deposition [10], molecular beam epitaxy [11], reactive magnetron sputtering [12], sol–gel [13], pulsed laser deposition [14] and spray pyrolysis [15]. Influence of transition metals can play a significant part in exceptional tuning the physical properties of metal oxide thin films. In the present research work, the influence of Cu doping on physical properties of nanocrystalline zinc oxide thin films were studied by using a simple and economic spray pyrolysis deposition technique.

II. Experimental Details

The development of simple and cost-effective thin film deposition technologies has always piqued the interest of researchers. Spray pyrolysis is one of the most cost-effective and simple ways for depositing thin films of oxides, selenides, and other materials [16]. In 1982, Bates et al. [17] used the aforementioned process to deposit $CuInSe_2$ films with a thickness of around 1 μm. Using a 0.05M solution of $ZnCl_2$ produced in methanol and doubly distilled water, pristine and Cu doped zinc oxide thin films were formed on ultrasonically cleaned glass substrates, and copper doping was achieved by adding a sufficient amount (1 at. %) of $CuCl_2$ to the starting solution. A total of 15 mL of solution was sprayed at a steady flow rate of 5 mL/min throughout the deposition procedure. When deposited above the stated spray rate, the films are uneven and show cracks, whereas when deposited at a lower spray rate than the optimal value, the films are irregular. The optimal temperature for deposition was found to be 573 K, with a distance of 30 cm between the nozzle and the glass substrate. The average thickness of the film was calculated using the gravimetric weight difference technique. The structural properties of CuKα radiations of wavelength 1.5404 were studied using a PAN analytical X'Pert Pro MPD diffractometer. The optical characterization was done with a Perkin Elmer lambda 25 spectrophotometer, and the surface morphology of the deposited film was studied with a JEOL-6380A scanning electron microscope.

III. RESULTS AND DISCUSSION

Structural Analysis

Fig. 1 shows the XRD patterns of the undoped and Cu doped zinc oxide thin films deposited at 573K. The intense diffraction peaks of the ZnO deposition appear at 31.890°, 34.230°, 36.236°, 47.708°, 56.712°, 62.630° and 69.182°, which correspond to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (2 0 1) peaks with hexagonal lattice and having preferred orientation along (1 0 1) plane while the diffraction peaks of the copper oxide also appears at 29.451°, 36.521°, 42.182°, 52.620° and 61.830° which correspond to the (1 1 0), (1 1 1), (2 0 0), (2 1 1) and (2 2 0) corresponding to cubic phase with no preferred orientation observed after matching with JCPDS data file: 05-0667. It was also observed that there is shifting of peaks with Cu doping. The (002), (102), (110) and (201) peak positions 2θ of the doped sample were shifted to a lower value after doping which may be due to the extrinsic doping in pure zinc oxide films.

Table 1: Comparison of observed and standard XRD data of Pure zinc oxide thin films (JCPDS card 36-1451) and Cu doped Zinc oxide thin films (JCPDS card 05-0667)

Film	Observed data		Standard data		h k l	phase
	2θ (deg.)	d (Å)	2θ (deg.)	d (Å)		
Pure ZnO Films	31.890 34.230 36.236 47.708 56.712 62.630 69.182	2.760 2.701 2.496 1.826 1.590 1.513 1.329	31.770 34.422 36.253 47.539 56.603 62.864 69.100	2.814 2.603 2.475 1.911 1.624 1.477 1.358	1 0 0 0 0 2 1 0 1 1 0 2 1 1 0 1 0 3 2 0 1	Hexagonal Hexagonal Hexagonal Hexagonal Hexagonal Hexagonal Hexagonal
Cu Doped ZnO Films	29.451 33.998 36.236	3.121 2.718 2.496 2.414 2.249 1.813	29.555 34.422 36.253	3.020 2.603 2.475	1 1 0 0 0 2 1 0 1	Cubic Hexagonal Hexagonal Cubic

	36.521	1.681	36.419	2.465	111	Cubic
	42.182	1.641	42.298	2.196	200	Hexagonal
	47.490	1.401	47.539	1.911	102	Cubic
	52.620	1.411	52.455	1.743	211	Hexagonal
	56.590		56.603	1.624	110	Cubic
	61.830		61.345	1.510	220	Hexagonal
	69.108		69.100	1.358	201	

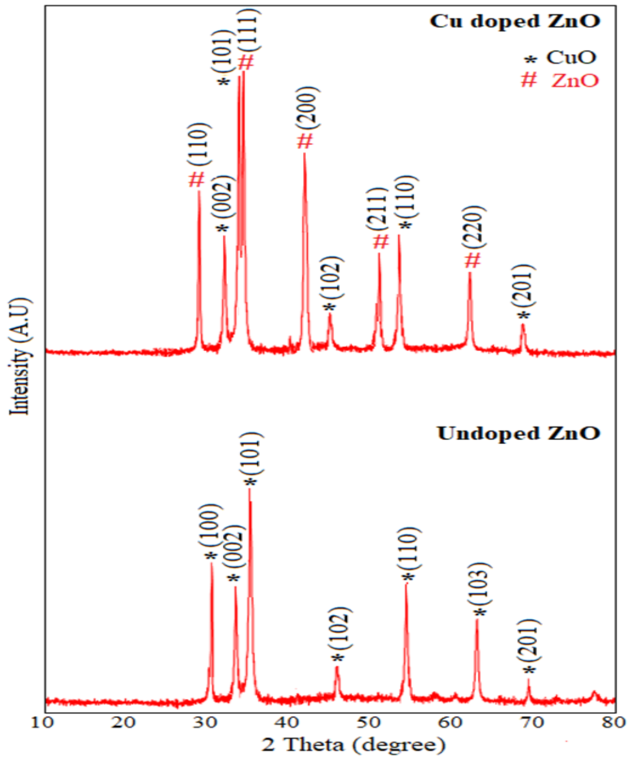

Figure 1: XRD pattern of pure and Cu doped ZnO thin films

The crystallite size was calculated by using FWHM data and Debye Scherrer's formula [18]. For the undoped ZnO film it was found to be 43.35nm whereas this value reduces to 36.12nm for Cu doped zinc oxide films.

$$d = \frac{K\lambda}{\beta \cos\theta} \quad \text{------- (1)}$$

where d, λ, β and θ are the grain size, X-ray wavelength (0.154 nm), the full width-at-half-maximum and Bragg's angle, respectively. The comparison of the observed and standard XRD data for selected peaks at different angle (2θ) was given in the Table 1.

Surface morphology

Scanning electron microscopy (SEM) is an appropriate approach for studying the microstructure of deposited thin films. SEM micrographs of undoped and Cu doped ZnO thin films are shown in Figure 2. The SEM pictures of the as-pure zinc oxide films reveal a well-covered, regular, dense, and continuous cauliflower-like surface structure with very small grains, which could be owing to rapid crystallization between the precursors during the drying process. While doping causes a change in overall structure, resulting in a compact mesh type with small voids.

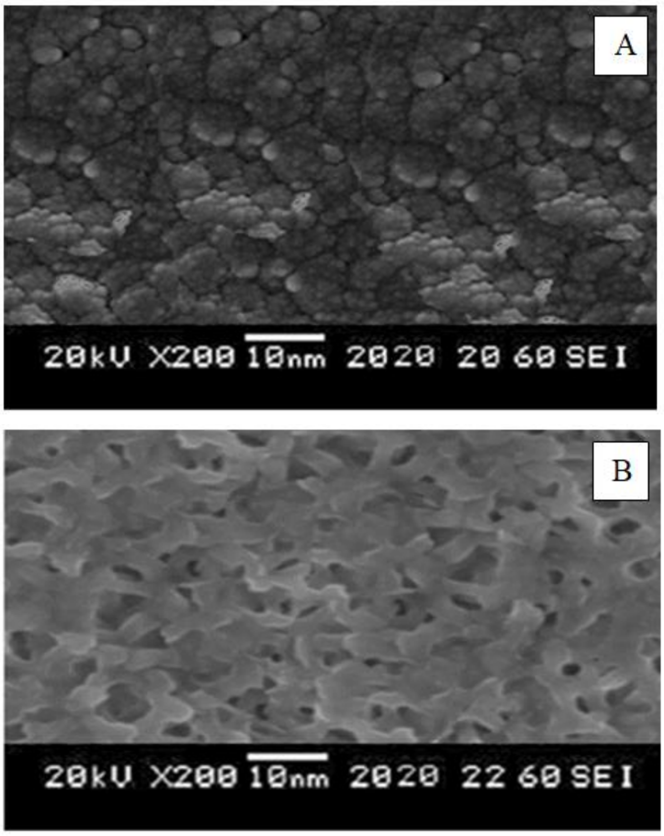

Figure 2: SEM micrographs of (A) undoped and (B) Cu doped ZnO thin films

Optical properties

The optical characteristics of pure and Cu doped ZnO thin films were studied using a Lambda 25 UV-VIS spectrophotometer. In order to determine the optical band gap, optical absorption spectra in the wavelength range 300nm-1100nm are acquired. The plot of variation of optical absorbance vs. wavelength for deposited undoped and Cu doped ZnO thin films is shown in Figure 3. Figure 4 shows the plots of $(\alpha h\upsilon)^2$ vs photon energy (hυ) for direct transition.

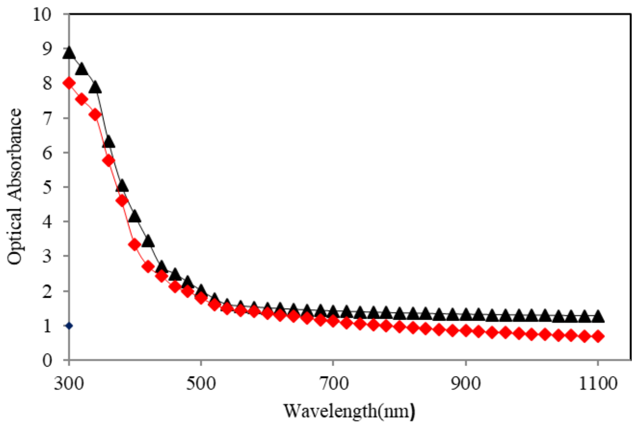

Figure 3: Variation of optical absorption vs. wavelength for spray deposited undoped and Cu doped ZnO thin films

The nature of the transition is determined by using the formula,

$$\alpha = \frac{A(h\upsilon - Eg)^n}{h\upsilon} \qquad \text{------- (2)}$$

where hυ is the photon energy, Eg is the band gap energy, A and n are constants. For allowed direct transitions n =1/2 for allowed indirect transitions n =2. The nature of plots indicates the existence of direct transition.

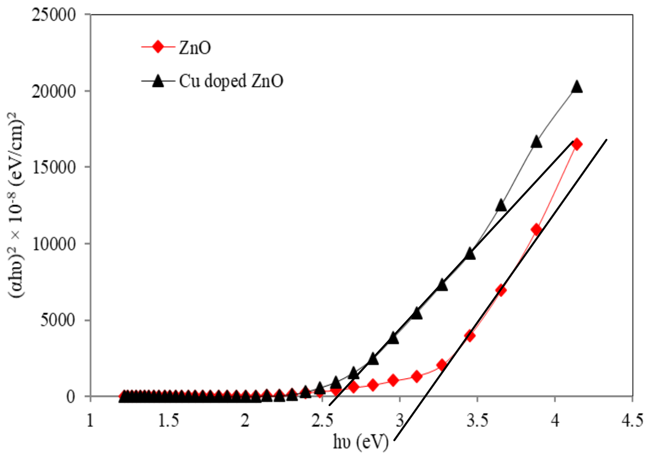

Figure 4: Plot of $(\alpha h\upsilon)^2$ versus hυ for spray deposited undoped and Cu doped ZnO thin films

The predicted band gap for pure zinc oxide film was found to be in the range of 3.32eV, decreasing to 2.52eV. This decrease in the band gap could be attributed to the inclusion of a dopant, which can be amplified to improve conductivity without affecting other zinc oxide properties.

Electrical properties

We used two probe techniques to analyse the electrical characteristics of pure and doped zinc oxide thin films in this investigation. The ohmic contact between silver and ZnO is confirmed by the linear form of I–V characteristics (Figure 5), showing that the work function of metal Ag is higher than that of semiconductor ZnO thin film.

The variation of dc-electrical resistivity with temperature was studied for both doped and undoped ZnO thin films in the temperature range 303 to 483 K. The room temperature electrical resistivity for pristine films was found to be $3.81\times10^{-1}\Omega$cm and it decrease to $4.80\times10^{-2}\Omega$cm with Cu doping. The deposited thin films are semiconducting in nature is well understand by the fact that the resistivity of the film decreases as the film temperature increases.

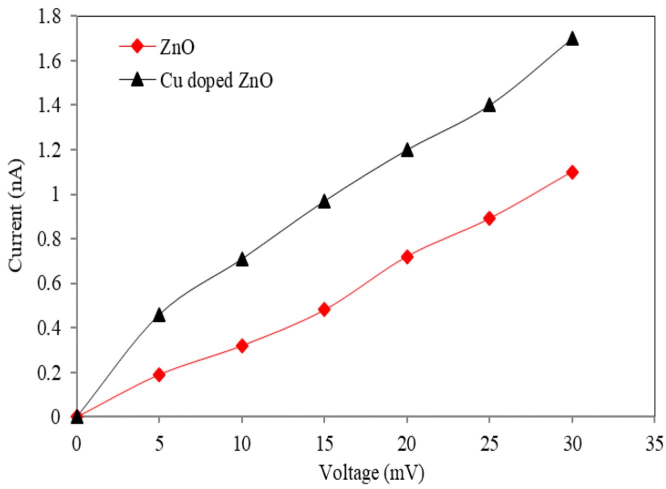

Figure 5: I-V characteristics for spray deposited undoped and Cu doped ZnO thin films

Figure 6 shows the variation of log (ρ) with reciprocal of temperature (1/T) for spray deposited undoped and Cu doped ZnO thin films. The dependence of resistivity on temperature is almost linear indicating the presence of only one type of conduction mechanism in the film. The thermal activation energy was calculated using the relation,

$$\rho=\rho_o \exp(Ea/KT) \text{ --------- } (3)$$

where ρ is resistivity at temperature T, ρ_o is a constant, K is Boltzmann constant.

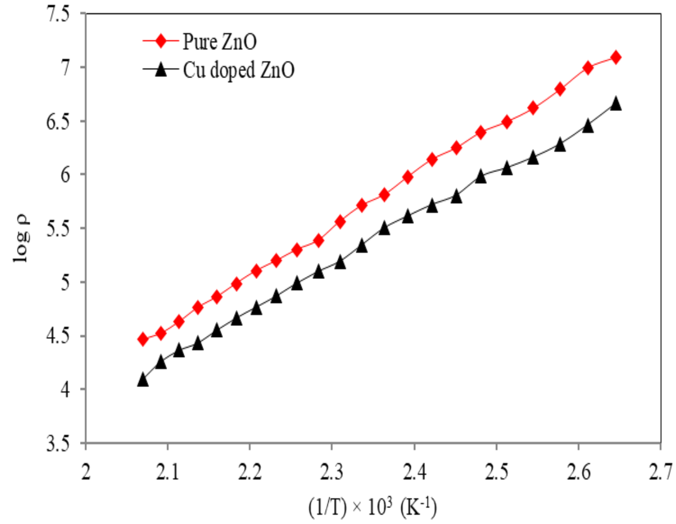

Figure 6: Variation of Log of resistivity with 1/T for spray deposited undoped and Cu doped ZnO thin films

The activation energy (Ea) was calculated from the resistivity plot which shows that the value of activation energy decreases from 0.081eV to 0.0472eV with the addition of dopant.

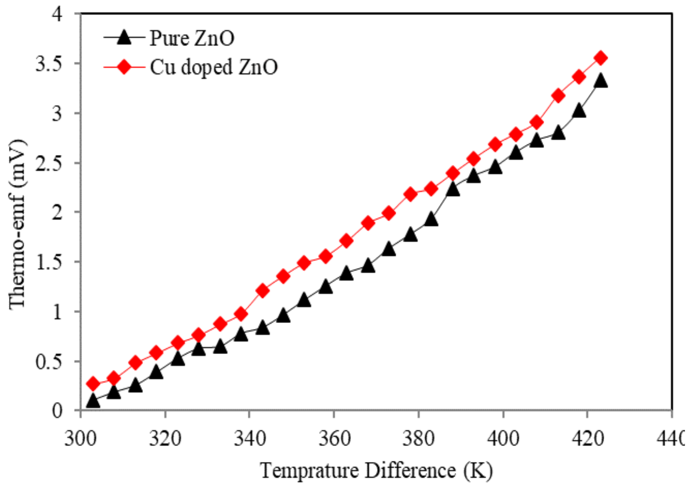

Figure 7: Variation of thermo emf (mV) with temperature difference for spray deposited undoped and Cu doped ZnO thin films

The TEP of the deposited thin films was measured as a function of temperature in dark in the temperature range of 304-423K (Figure 7). The thermo-emf measurement confirms that both undoped and doped thin films own n-type conductivity.

IV. CONCLUSION

Nanostructured pristine and Cu doped zinc oxide thin films were successfully deposited by spray pyrolysis technique and the influence of Cu doping on physical properties of nanocrystalline spray deposited zinc oxide thin films were studied. The structural and morphological investigations revealed that, the films are nanocrystalline in nature with hexagonal lattice and exhibits direct band gap of the order of 3.32 eV which decreases to 2.52 eV with increase in doping concentration. The electrical resistivity of the pristine films was found to be $3.81\times10^{-1}\Omega$cm which decrease to $4.80\times10^{-2}\Omega$cm with higher Cu doping. The thermo-emf measurement confirms that both undoped and doped thin films own n-type conductivity.

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