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Effect of Cd Doping on the Structural, Optical and Electrical Properties of ZnO Thin Films Deposited by Spray Pyrolysis Technique

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Abstract: *Thin films of cadmium doped zinc oxide (Cd : ZnO) with different cadmium concentrations have been prepared by spray pyrolysis method on glass substrates at 400 °C using zinc acetate and cadmium chloride as precursors for Zn and Cd ions, respectively. The deposition parameters have been optimized to obtain smooth and good quality films. Structural, optical and electrical properties of these films have been studied for photovoltaic applications. Effect of Cd doping concentration on various properties was studied. Visible spectroscopy. X-ray diffraction analysis shows that the films werehexagonal wurtzite structure with the preferential orientation of (100) plane. Optical absorption measurements werecarried out in the visible region (380 – 800 nm) and opticalenergy band gap values were obtained 3.18 to 3.12. Electrical properties of the films have been studied within the temperature range 305 K to 465 K. The resistivity decreases with increase of the temperature and it varies with the doping concentrations.*

Keywords: *ZnO,Cd concentration, Spray pyrolysis, Thin films.*

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I. Introduction

There are many transparent oxide materials studied for solar cell and other applications among these ZnO is one of the most promising Transparent conducting oxide (TCO) currently available in electronic and optoelectronic application such as transparent electrodes, solar cell, liquid crystal displays, gas sensors etc. has high transparency in the visible region of the electromagnetic spectrum to oxygen vacancies. Zinc oxide is an inexpensive n-type semiconductor of the II–VI semiconductor group having direct band gap of 3.37 eV at room temperature. Various techniques have been used for depositing ZnO thin films, are available in literature such as sol – gel method[1-3], pulse laser deposition (PLD)[4-5], chemical bath deposition,sputtering[6], spray pyrolysis[7] etc.

Impurity doping is necessary for the successful manipulation of the physical and electrical properties of ZnO doped with Cd[8]. This work aims to study the effects of doping concentration and annealing on the structural, morphological, and optical properties of Cd-doped ZnO thin films.

II. Experimental Process

For the deposition of undoped and Cd doped ZnO thin films, 0.1 M zinc acetate dehydrate ($(CH_3.COO)_2.Zn.2H_2O$) was used as a source of zinc and cadmium chloride ($CdCl_{2.}2H_2O$) was used as a source of Cd. Zinc acetate dehydrate and Cadmium Chloride were dissolved in distilled water in order to prepare the spray solution. The 0.1 M solutions of zinc acetate and cadmium chloride was used to obtained proper doping concentration. The zinc concentration in spray solution was kept constant and the Cd doping amount was varied from 0% to 2%. All prepared solutions were maintained under continuous magnetic stirring at room temperature for 1 h. Prior to all films deposition, glass substrates were washed with a liquid detergent, rinsed with distilled water and dried with hot air.

The distance between the tip of the nozzle and surface of the substrate was kept 20 cm. The deposition temperature was kept constant at 400ºC for the deposition of all films. The temperature was measured by using thermocouple fixed to the hot plate.

The crystalline quality and crystal orientation of the ZnO thin films were investigated by XRD (Bruker D2) with CuK_α radiation having the wavelength of 0.1542 nm and in the range of 2θ=20 to 70° with step value 0.02° . The experimental peak positions were compared with the standard JCPDS files card no. 2100100.

The Optical properties were measured using UV–vis spectrophotometer in the wavelength range 380-800 nm. Electrical measurements were performed by increasing the temperature slowly in the van der Pauw configuration and Hall measurement system.

III. Results And Discussion

3.1 Structural properties

The structural properties of pure and Cd:ZnO films for different concentration of cadmium were studied by XRD and are shown in**Fig 1.**The preferential orientation of all the films has been found to be along (100) plane. Other peaks were obtained along (002), (101), (102), (110), (103) and (112) respectively. The analysis revealed that all the films are of crystalline in nature having a hexagonal wurtzite type crystal structure according to the JCPDS files.

The moderate order of intensity indicates the good crystallinity of the samples. Comparing the intensities and full width at half maximum (FWHM) of (100) peak for undoped and doped samples, it is found that the intensity of three major peaks for 2 % Cd doped sample is much higher than others which indicates the best crystalline quality of 2% Cd doped sample.

It is also observed from XRD pattern the peak intensity of (101) is higher compared to other peaks except for 1% Cd doped samples. There is a small competition of intensities of (100) and (101) for 1% Cd doped sample which indicates that the crystal structure habit is mainly along (100) direction. A small deviation from (100) for 1% Cd doped samples may be due to the variation of temperature during growth rather than doping concentration.

The crystalline size of the films was calculated by using Debye Scherer formula

$$\zeta = \frac{0.94\lambda}{\beta \cos\theta}$$

where: ζ is the crystallite diameter,
λ is the wavelength,
θ is the Bragg's angle,
β is the full-width at half-maximum (FWHM) of the peak.

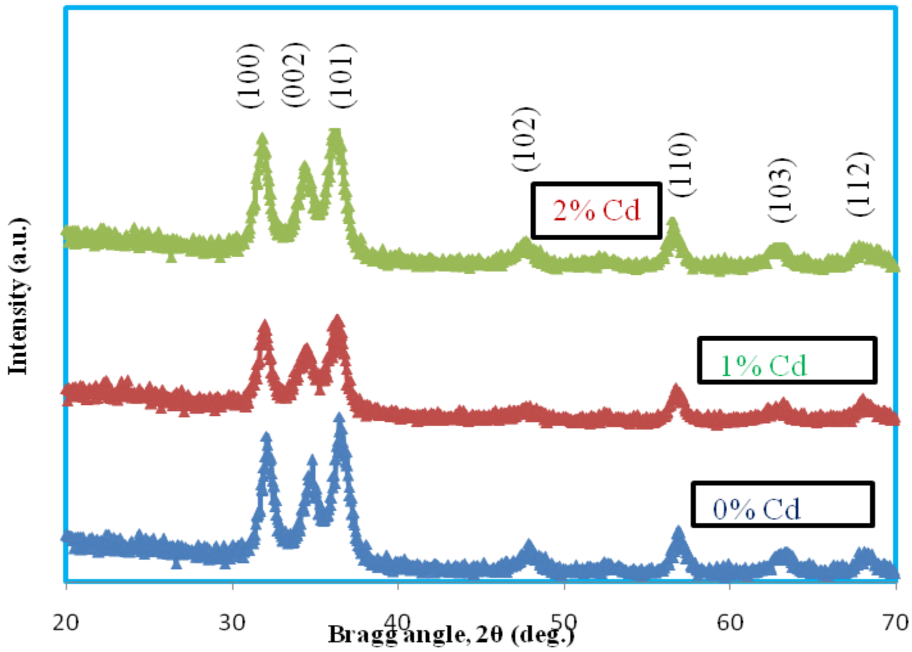

Fig. 1: X-ray diffraction pattern for undoped and Cd:ZnO thin films.

3.2.Optical Properties

The optical transmission and reflection spectra versus wavelength curves of ZnO thin film with different doping concentration of Cd deposited onto glass substrate at 400^0C at air ambient were taken in the wavelength range 380-800 nm using UV-visible spectrometer.

The transmittance spectra shows that the transmittance are low at lower (visible) wavelength region and it increases moderately at the absorption edge region and become almost constant at higher wavelength region. From the **Fig 2.**it is also seen that the transmittance of ZnO thin films decreases with the increase of Cd doping concentration. This result may be caused by the scattering of photon by the crystal defects created by doping[10]. It is found that the absorbance of the film decrease sharply in the lower wavelength region (visible) and then decrease slowly for a wide range of wavelength. It is also seen from the **Fig 3.** that the absorbance increases with the increase of Cd doping concentration.

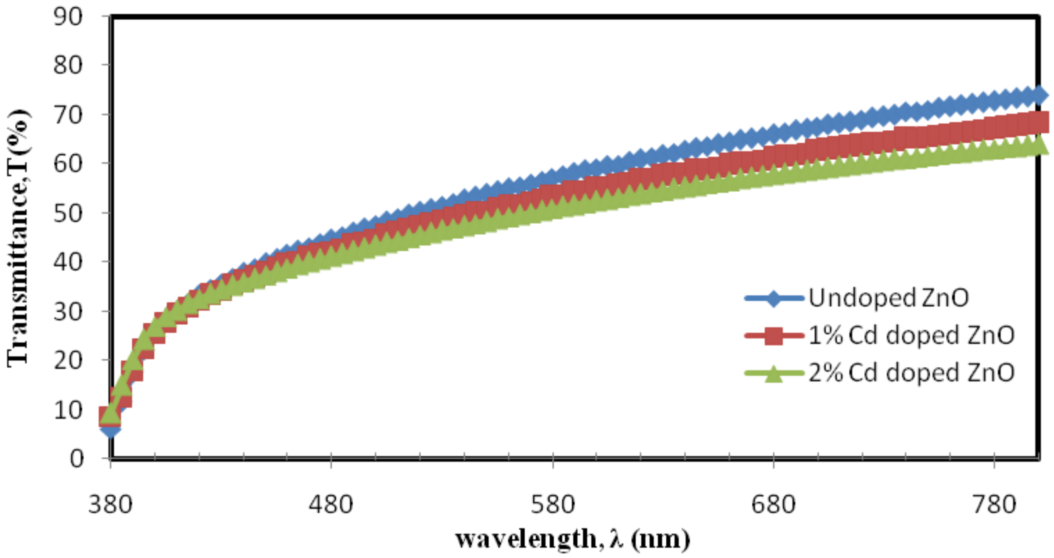

Fig. 2: Variation of optical transmittance with wavelength for undoped and Cd:ZnO thin films.

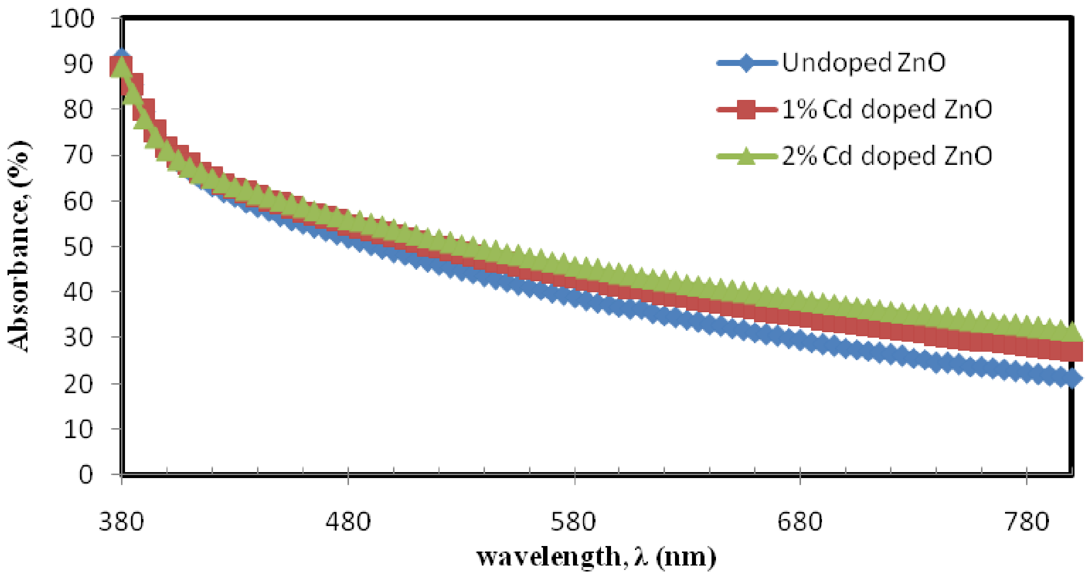

Fig. 3: Variation of optical absorbance with wavelength for undoped and Cd:ZnO thin films.

The optical band gap energy of the films has been obtained from the intercept on the energy axis after extrapolation of the straight line section from the energy curve. The optical band gap energy of this film has been calculated using the Tauc's relationship [11-12] .

$$(\alpha h v) = A(hv - E_g)^m$$

where, α *is* the absorption co-efficient, A is a constant, hv is the photon energy, E_g is the optical band gap of the semiconductor and m is the index related to the density of states for the energy band.

From the table 1it is clear that the band gap energy for direct transition decreases with the increase of Cd doping concentration, but 2 % doesn't maintain the sequence because some other factors may be influenced here. The observed optical band gap depending on the doping concentration varies from 3.12-3.18 eV.

Table no 1: Values of direct band gap energy for undoped and Cd:ZnO thin films.

Cd concentration in ZnO (mol%)	Direct band gap, E_g (eV)
0	3.18
1	3.12
2	3.16

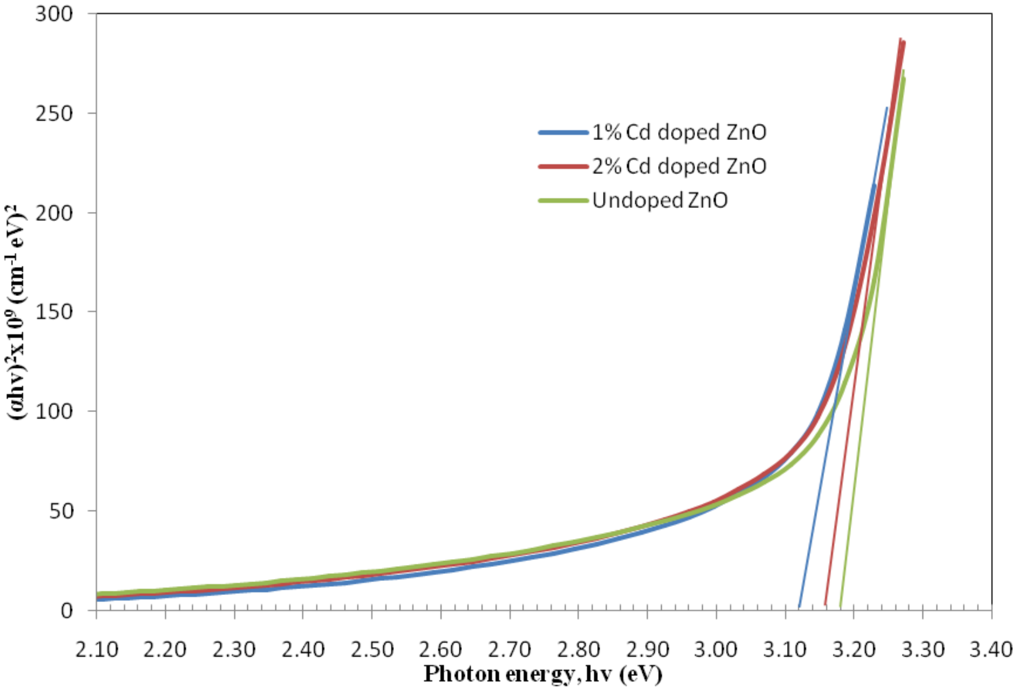

Fig. 4: Variation of $(\alpha h\nu)^2$ with photon energy for undoped and Cd:ZnO thin films.

3.3 Electrical Properties

The resistivity of undoped and Cd:ZnO thin films were measured by Van der Pauw method [13]and data were taken by increasing the temperature slowly. Before measurement, samples were annealed at 400°C for two hour and then cool down slowly to room temperature so that constituent atoms sits their lattice site properly and to remove any structural disorder may present during growth process.

Fig 5.represents the variation of resistivity with temperature for undoped and Cd:ZnO thin films. It is observed that the resistivity decreases with the increase of temperature that confirms the semiconducting nature of the samples. It is also seen that the resistivity of the samples decreases with increasing the doping concentration of Cd. The room temperature (RT) resistivity of all the films is found to be in the order of $\mathbf{10^{-2}}\Omega$-cm. The decrease of resistivity of undoped and Cd:ZnO thin films with increasing temperature may be due to increase of transition of donor electrons to conduction band. The decrease of resistivity with increase of Cd concentration may be due to increase of donor electron by substitution of Cd at 0 lattice site forming solid solution.

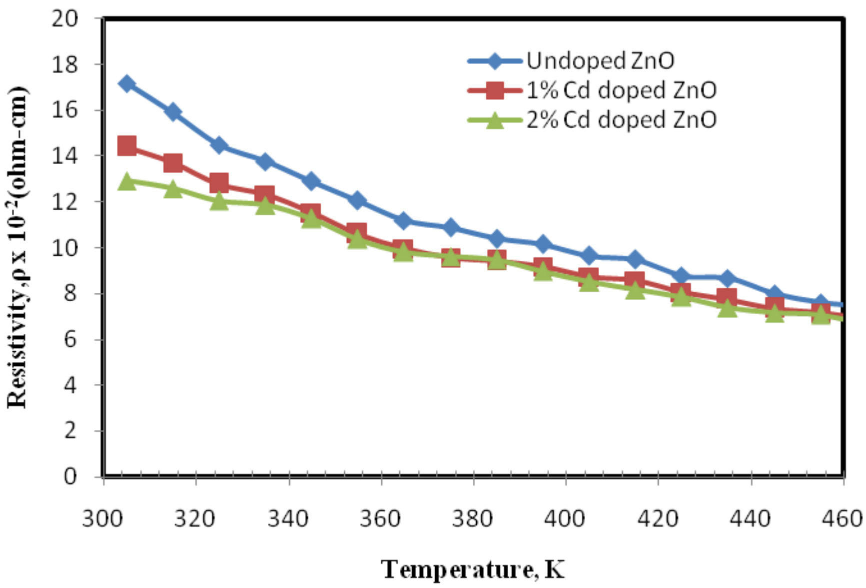

Fig 5: Variation of resistivity with temperature for undoped and Cd:ZnO thin films.

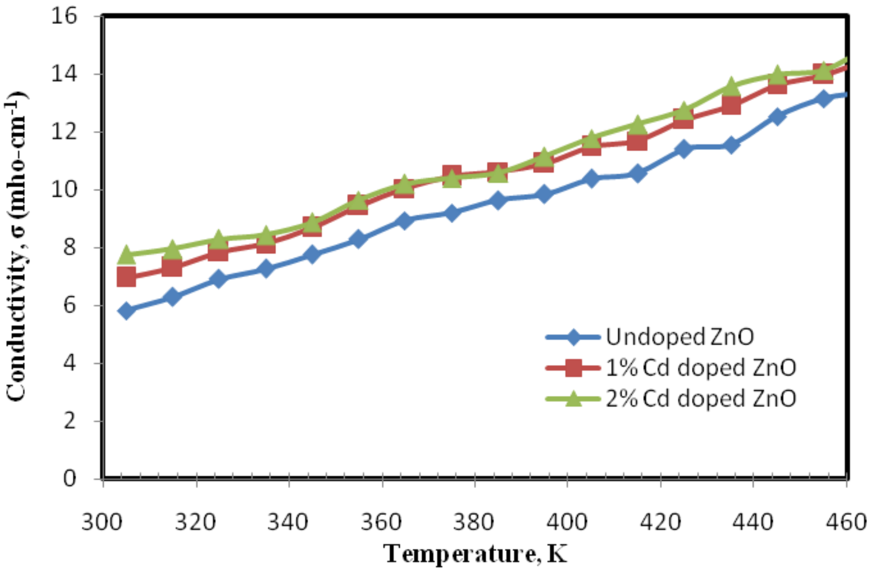

Fig 6: Variation of conductivity with temperature for undoped and Cd:ZnO thin films

The conductivity (σ) of all the pyrolized samples has been calculated from resistivity data. The plot of conductivity as a function of temperature for undoped and Cd:ZnO thin films is shown in **Fig 6**. From this figure it is clear that the conductivity is inversely related to the resistivity (according to the equation σ=1/R). The conductivity was found to be increased continuously with the increase of temperature and with increase of Cd concentration as well.

The activation energy ΔE can be calculated using the relation,

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{2k_B T}\right)$$

Where, ΔE is the activation energy, $\sigma_0$is a constant and $\sigma$is the electrical conductivity, K_B is the Boltzmann constant and T is the absolute temperature.

In the lower temperature region, as the temperature is increased, the electrons are excited thermally from donor levels to conduction band. Thus more charge carriers overcome the activation energy barrier causing the electrical conduction.

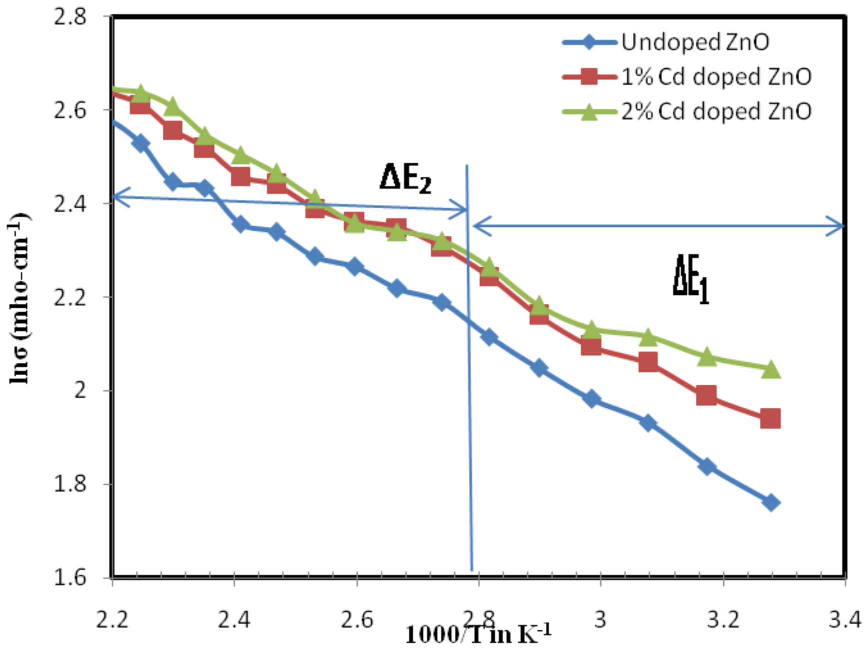

Fig 7: Variation of lnσ with 1000/T for undoped and Cd:ZnO thin films.

In the higher temperature region, the trapped charge carriers induce the electrical conduction at the grain boundaries with donor electron. Thus with the increase of temperature, the conduction mechanism changes from only thermally activated charge carriers to the grain boundary trapped charge conduction mechanism.

Table 2: Activation energy of undoped and Cd:ZnO thin films.

Cd concentration in ZnO (mol%)	Activation energy, ΔE (ev)	
	ΔE_1 (303-358)K	**ΔE_2** (358-453)K
0	0.0242	0.0321
1	0.0208	0.0280
2	0.0153	0.0277

Hall voltage measurements were done for undoped and Cd: ZnO thin films using Van der Pauw's method in ambient air temperature and in a constant field of 9.185kG. The different Hall parameters such as Hall constant (R_H), carrier concentrations (N), resistivity (ρ), conductivity (σ), and Hall mobility (μ_H) haves been calculated and tabulated in **Table 3**for all the samples. The positive values of Hall constant corresponds to p-type carrier and the negative values correspond to the n-type carrier. The type of carriers has also been determined and it is found that it is n-type carrier according to the sign of the Hall constant. The carrier concentrations of undoped and Cd:ZnO thin films are found in the order of 10^{19} cm^{-3}.

Table 3: Resistivity, Conductivity, Hall constant, Carrier concentration and Hall mobility.

Cd concentration in ZnO (mol%)	Resistivity, at (RT) $\rho x10^{-2}$ (ohm-cm)	Conductiviy, σ $(ohm\text{-}cm)^{-1}$	Hall constant, R_H $(cm^3/coul)$	Carrier concentration,$Nx10^{19}$ (cm^{-3})	Hall mobility,μ_H (cm^2/Vs)
0	17.18	5.82	-0.375	1.6666667	2.18
1	14.39	6.95	-0.237	2.637130802	1.65
2	12.91	7.75	-0.155	4.032258065	1.20

From the table it is clear that the carrier concentrations increase with the increase of Cd doping concentrations. It is also seen that Hall mobility decreases with the increase of Cd doping concentration. The observed carrier concentrations and Hall mobility are comparable with that of reported14for Cd:ZnO thin films prepared by chemical spray pyrolysis technique. The reported carrier concentration and hall mobility are about 6.12×1020and 13.8 cm2/Vs respectively.

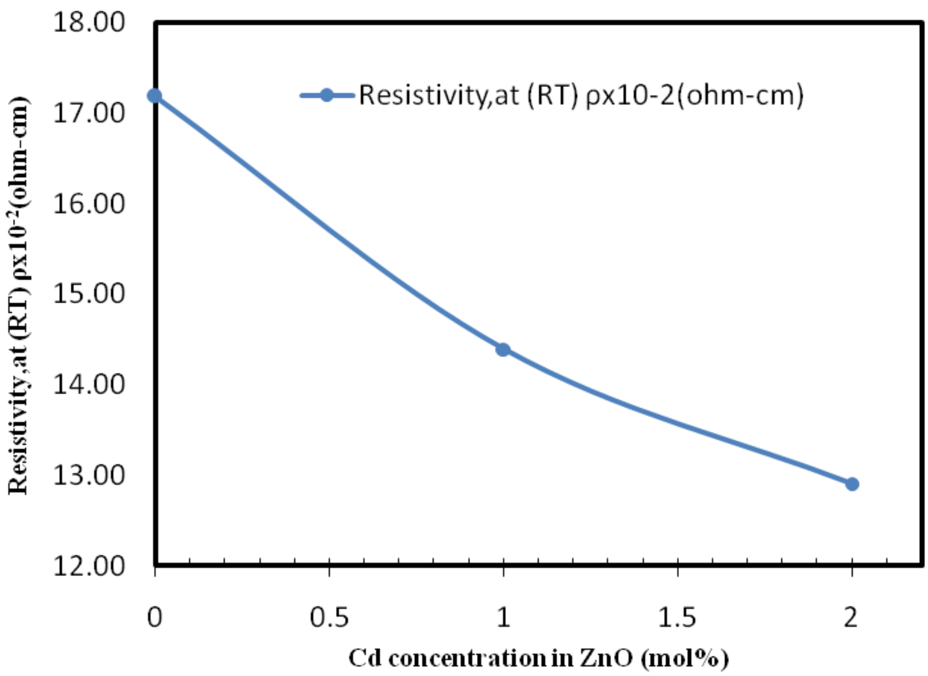

Fig 8: Variation of Resistivity with Cd concentration in ZnO films.

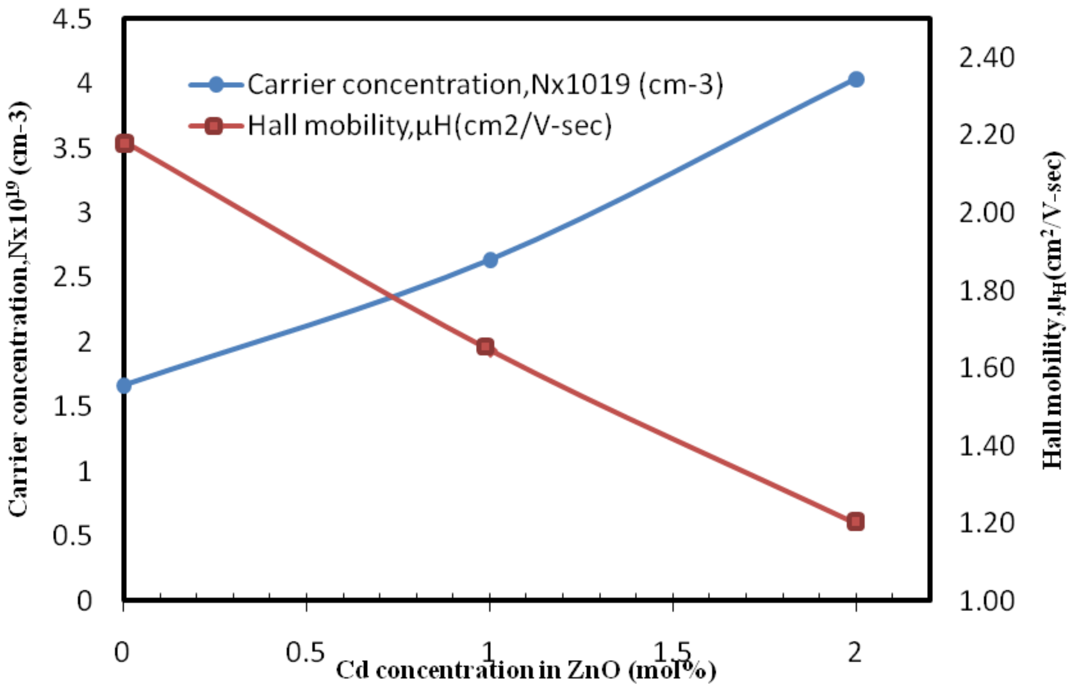

Fig 9: Variation ofCarrier concentration, and Hall mobilitywith Cd concentration in ZnO films.

IV. Conclusion

In the work, transparent conducting ZnO thin films doped with Cd have been successfully fabricated on ordinary glass substrate using lowcost spray pyrolysis technique at substrate temperature 400 ^{0}C. The prepared thin films were examined by various techniques in terms of their structural, optical, electrical properties. The XRD result confirms the formation of ZnO with a hexagonal wurtzite crystal structure. The UV-Vis study confirms the undoped and Cd:ZnO films are direct band gap semiconductor. The optical band gap energy 3.18 eV is obtained for undoped ZnO sample. The Van der Pauw electrical measurements confirms Cd doped ZnO thin films are semiconducting in nature and resistivity as low as $12.91 \times 10^{-2}\,\Omega - \text{cm}$. Hall measurement reveals undoped and Cd:ZnO films are n-type semiconductor.

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