

Growth of $Zn_{1-x}Cd_xO$ nanocrystalline thin films by sol-gel method and their characterization for optoelectronic applications

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This paper describes the growth of Cd doped ZnO thin films on a glass substrate via sol-gel spin coating technique. The effect of Cd doping on ZnO thin films was investigated using X-ray diffraction (XRD), UV-Vis spectroscopy, photoluminescence spectroscopy, I-V characteristics and field emission scanning electron microscopy (FESEM). X-ray diffraction patterns showed that the films have preferred orientation along (002) plane with hexagonal wurtzite structure. The average crystallite sizes decreased from 24 nm to 9 nm, upon increasing of Cd doping. The films transmittance was found to be very high (92 to 95 %) in the visible region of solar spectrum. The optical band gap of ZnO and Cd doped ZnO thin films was calculated using the transmittance spectra and was found to be in the range of 3.30 to 2.77 eV. On increasing Cd concentration in ZnO binary system, the absorption edge of the films showed the red shifting. Photoluminescence spectra of the films showed the characteristic band edge emission centred over 377 to 448 nm. Electrical characterization revealed that the films had semiconducting and light sensitive behaviour.

Keywords: X-ray diffraction; optical material; semiconductor; chemical synthesis; sol-gel

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1. Introduction

Wide band gap transparent semiconducting oxide materials have recently attracted much attention due to their excellent structural, optical and electrical properties. Nowadays, thin films of transparent conducting oxide (e.g. n-type, such as ZnO, NiO, CdO, InO, ITO, SnO₂, and p-type: CuAlO₂, SrCu₂O₂, tin-gallium oxide) are used in a variety of potential applications. Among them, ZnO based thin films are one of the promising candidates due to their brilliant physical, optical and electrical properties, which are very useful in transparent electronics, thin films photovoltaics, window layers, heat reflectors, photo detectors and many other opto-electronic devices [1–5]. ZnO has a direct wide band gap (~3.30 eV) and high excitonic binding energy (60 meV) at room temperature. As the threshold voltage of ZnO is low, it could be used

as a light-emitting diode (LED), diode laser and radiation resistance. ZnO has unique and diverse properties comparable to other wide band gap semiconducting materials, such as piezoelectricity, chemical stability, biocompatibility, optical transparency exceeding 90 % in the visible region of solar spectrum and high voltage-current nonlinearity. Therefore, the main aim of this work is to tailor optical and electrical properties of ZnO thin films for optoelectronic applications, by doping transition metal elements. On incorporation of Cd into ZnO binary system, Cd⁺² ions can uniformly substitute Zn⁺² or interstitial sites inside ZnO lattice [6]. The radii of zinc and cadmium ions are 0.074 nm and 0.097 nm, respectively. Cd ion has larger radius than that of zinc ion hence, lattice distortion may occur in ZnO lattice system. This may lead to the narrowing of electronic structure of ZnO binary system and, as a result, to some decrease in the band gap of ZnO thin film. Hence, the optical properties of ZnO on Cd doping make it more attractive for optoelectronic devices [7, 8].

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ZnO thin films have been deposited by various methods, such as thermal evaporation, MOCVD, CVD, spray pyrolysis [9–11], pulse laser deposition [12], r. f. sputtering [13], sol-gel [14, 15] etc. Among these methods, the sol-gel spin coating technique is highly attractive for the fabrication of metal oxide semiconducting material thin films due to its simplicity and convenience in handling. In the present work, ZnO and Cd doped ZnO thin films with different concentrations of Cd were deposited on glass substrates by sol-gel spin coating method. The influence of Cd doping on structural, optical and electrical properties of ZnO thin films was investigated in details.

2. Experimental

All the reagents used for the deposition of thin films were of analytical grade and purchased from Merck. The glass substrates used for the deposition of the thin films were cleaned ultrasonically with a soap solution and rinsed with distilled water and then with acetone. Thin films of Zn_{1-x}Cd_xO ($0 \leq x \leq 0.25$) were deposited on glass substrates by sol-gel spin coating method. In the preparation of sol-gel, we used zinc acetate dehydrate and cadmium acetate dehydrate as starting materials. Initially, 0.75 M of zinc acetate dehydrate and cadmium acetate dehydrate were dissolved in 2-methoxyethanol and monoethanolamine (MEA) as a solvent and a stabilizing material, respectively. The molar ratio of MEA to zinc acetate dehydrate and cadmium acetate dehydrate was maintained to be unity and the doping was done according to the atomic weight percentage. Homogeneous and transparent solution was obtained after constant magnetic stirring for 90 minutes at 65 °C. A freshly prepared solution was used for thin films deposition at 4000 rpm for 30 s. After each deposition the film was preheated at 265 °C. This process was repeated for ten times. Finally, the films were post annealed at 400 °C for 2 h. The optical properties of Zn_{1-x}Cd_xO thin films were investigated by UV-Vis-NIR spectroscopy (double beam JASCO V570 spectrophotometer). The photoluminescence of thin films with different Cd concentrations was measured by He–Cd laser, operating at 325 nm

with an output power of 50 mW and the structural properties were investigated by X-ray diffraction (model: Philips analytical diffractometer PW3710 with Cu K α radiation, $\lambda = 0.15405$ nm) in the 2θ range of 10° to 70°. Surface morphology of thin films was recorded by FESEM model Quanta. The temperature dependent electrical resistivity of thin films was measured in a temperature range of 300 to 500 K. The area of thin films was 0.5 cm². The dark and illuminated I-V measurements were made using a dc Keithley 487 multimeter. Tungsten halogen lamp, emitting white light, was used for illumination at 200 W. To avoid any heating effects in the samples, the lamp was placed at a height of 35 cm.

3. Results and discussion

3.1. X-ray diffraction analysis

X-ray diffraction (XRD) spectra of thin films with different Cd concentrations (Zn_{1-x}Cd_xO, $x = 0 \%$, 10% , 20% , 25%) are shown in Fig. 1. The growth of thin films was found to be along (002) diffraction plane. The characteristic ZnO peak, observed at an angle of $2\theta \sim 34.57^\circ$ shows a good agreement with the internationally reported data in JCPDS6-314 for ZnO wurtzite structure. The intensity of the (002) peak decreases, while the FWHM of (002) peak increases as the Cd concentration is increased in the ZnO binary system. This confirms that the crystalline nature of the thin films gradually degrades on increasing Cd concentration in ZnO. The crystallites size (D) and lattice parameters of thin films were calculated using the following formulae:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where k is a constant, λ is the wavelength of X-ray used and β is the full width at half maximum of (002) peak;

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

It is observed from the calculated lattice parameters that the value of 'c' increases linearly from 5.208 Å

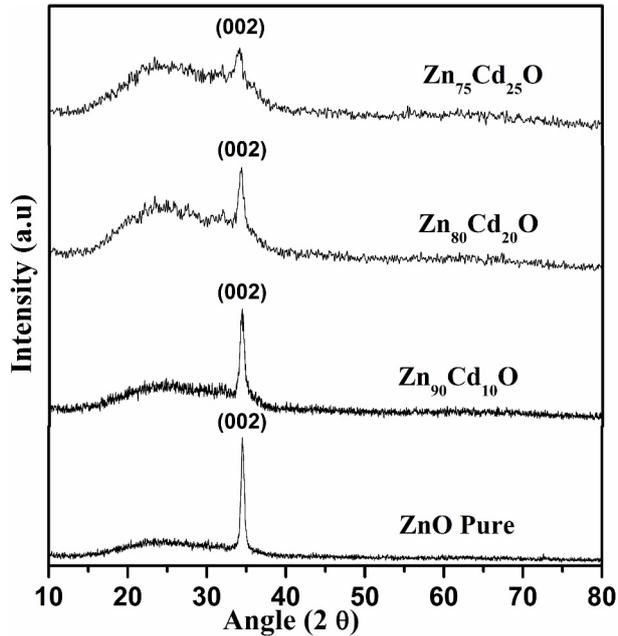


Fig. 1. XRD patterns of ZnO and $Zn_{1-x}Cd_xO$ thin films.

(pure ZnO) to 5.265 Å (25 % Cd). The increasing values of ‘c’ lattice parameter confirm the substitution of Cd ions with Zn ions in the hexagonal wurtzite ZnO structure. The calculated structural parameters of ZnO and Cd doped ZnO thin films are shown in Table 1 and Table 2.

3.2. Optical properties

The transmission spectra of ZnO and Cd doped ZnO thin films deposited on glass substrate in the range of 300 to 1100 nm are shown in Fig. 2. High transmittance of 92 to 95 % in the visible region of solar spectrum is observed in the figure. The significant red shift can be observed in the band edge with the increase in Cd concentration. The Urbach relation near the fundamental absorption edge is given as follows [16]:

$$\alpha hv = A(hv - E_g)^m \quad (3)$$

where m is a constant determining the nature of interband transitions, which may be allowed or forbidden transition between the top of the valence band to the bottom of the conduction band; the values of m : 2, 0.5, 3, 1.5 correspond to allowed direct transitions, allowed indirect transition, forbidden direct transition and

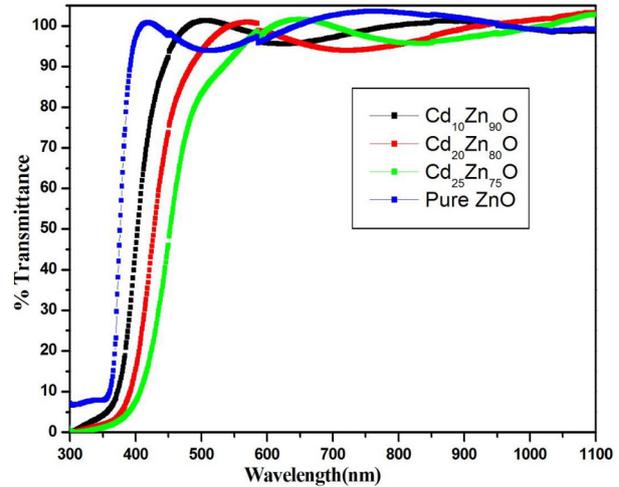


Fig. 2. Transmission spectra of ZnO and $Zn_{1-x}Cd_xO$ thin films.

forbidden indirect transition, respectively [17], A is the energy independent constant, E_g is the optical band gap and α is the absorption coefficient. The plots of $(\alpha hv)^2$ vs. hv are shown in Fig. 3. The energy band gap in case of a film, is determined by extrapolation of the linear portion of the plot $(\alpha hv)^2$ vs. hv on the energy axis to zero absorption coefficient. The calculated optical band gaps of thin films showed shift from 3.30 eV to 2.77 eV. Similar result on Cd doped ZnO thin films was also reported by A. Singh *et al.* [18]. When Cd content increases in a ZnO binary system, a contraction of the band gap of the thin film is observed. It may be due to the Zn ions replacement with the Cd ions in the ZnO lattice site. Both the ions have the same outer electronic structure but the core structure of these ions are entirely different and this difference may give rise to an electron trap level (exciton levels), close to the conduction band. ZnO acts as an isoelectronic centre, which is neutral. An injected electron is first trapped at this centre. Then, this negative center captures the hole from the valence band to form a bound exciton. The subsequent annihilation of this electron-hole pair yields a photon with energy equal to the band gap. The first order derivatives of transmission spectra with respect to wavelength of ZnO and Cd doped ZnO thin films are shown in Fig. 4. From the plots of $dT/d\lambda$ vs. wavelength in Fig. 4 we have concluded two

Table 1. Structural parameters of ZnO and Zn_{1-x}Cd_xO thin films.

Thin film samples	Interplanar spacing (Å)	FWHM (β) (002)	Crystallite size D(nm)
ZnO	2.60486	6.01	24
Cd ₁₀ Zn ₉₀ O	2.61508	10.52	12
Cd ₂₀ Zn ₈₀ O	2.63105	8.63	17
Cd ₂₅ Zn ₇₅ O	2.63259	15.03	09

Table 2. Lattice parameter 'c' of ZnO and Zn_{1-x}Cd_xO thin films.

Thin film samples	Lattice parameters c (Å) calculated	Lattice parameter c (Å) of ZnO standard
ZnO	5.208	
Cd ₁₀ Zn ₉₀ O	5.230	5.190
Cd ₂₀ Zn ₈₀ O	5.261	
Cd ₂₅ Zn ₇₅ O	5.265	

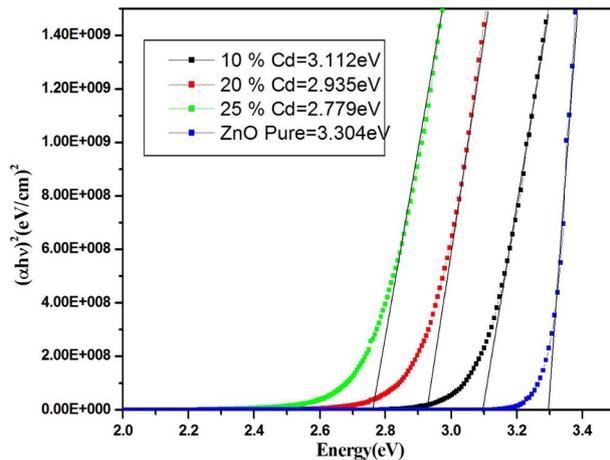
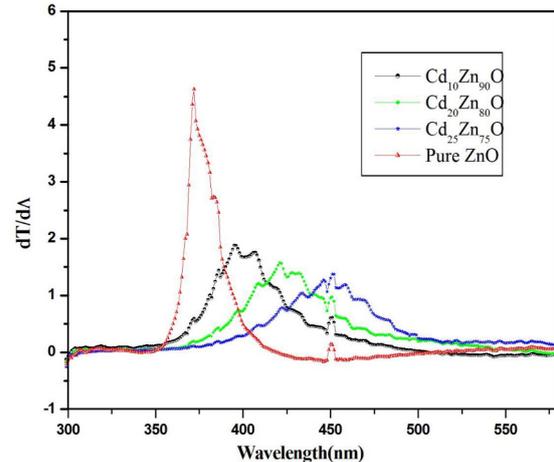
Fig. 3. Plots of $(\alpha h\nu)^2$ vs. photon energy of ZnO and Zn_{1-x}Cd_xO thin films.

Fig. 4. First derivative plots of transmittance of thin films as a function of Cd concentration.

interesting things. Firstly, the pure ZnO fundamental absorption peak is observed at 372 nm i.e in UV region and as the doping concentration increases the peak is shifted towards higher wavelengths that is into a visible region, as reported by Y. Caglar et al. [19]. Secondly, the band gap decreases on increasing the Cd concentrations. This may be due to creation of trap levels below the conduction band, which results in narrowing the band gap.

3.3. Photoluminescence

The room temperature PL spectra of ZnO and Cd doped ZnO thin films are shown in Fig. 5. In

the PL spectrum of ZnO thin film we observe a high intense peak centred at 380 nm, which corresponds to band to band transition. Broad low intense shoulder is observed at 650 nm. This hump of low intensity may be due to oxygen vacancy created during the growth of the samples [20]. From Fig. 5 we can see that due to the doping of Cd into ZnO binary system, the characteristic peaks near the band edge shifted towards the red wavelength region. This confirms the narrowing in band gap due to the Cd incorporation [21]. Similar results were obtained from UV-Vis spectroscopy. The bandgaps of ZnO and Cd doped ZnO thin films,

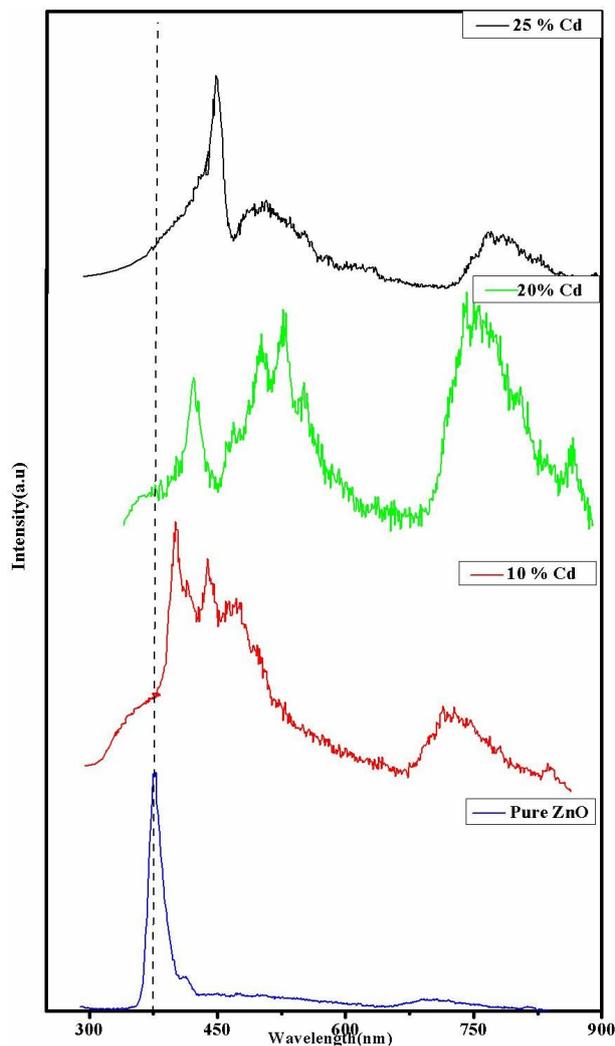


Fig. 5. Photoluminescence spectra of ZnO and $Zn_{1-x}Cd_xO$ thin films.

estimated from PL and UV-Vis spectra, are presented in Table 3. The intensity of near band edge (NBE) peak decreases with the increase in Cd concentration in the ZnO binary system. Cd doped ZnO thin films showed a few more emission peaks centred over the wavelengths ~ 500 nm, 650 nm and 700 nm [22]. These peaks might originate from the defects and impurities arising due to the Cd dopant incorporation. This emission, also explained by the first principle study of native point defects in ZnO, may be due to oxygen anti-site defects [23]. Recently, S. Vijayalakhmi et al. [20] reported that the near band edge emission peak vanished at 25 % Cd doping, but in the present study

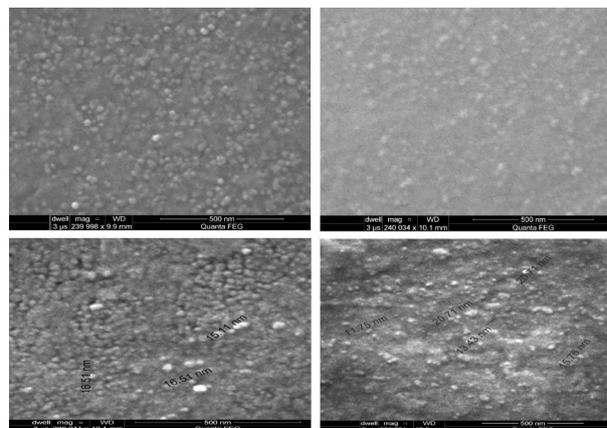


Fig. 6. SEM micrographs of thin films: (a) ZnO, (b) 10 % Cd doped, (c) 20 % Cd doped, (d) 25 % Cd doped.

NBE peaks with low intensity have been clearly observed.

3.4. Surface morphology analysis

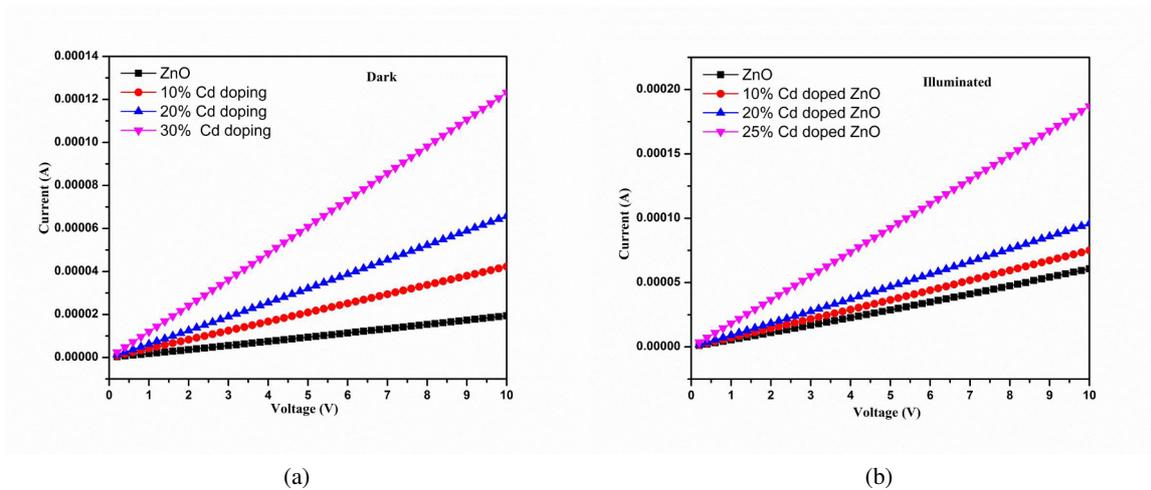
The surface morphologies of ZnO and Cd doped ZnO thin films are illustrated in Fig. 6. The SEM pictures suggest that the growth of the films consisting of spherical particles was uniform. The films are free from voids and cracks. No significant influence of Cd doping is observed. The average particle size of ZnO and Cd doped thin films was estimated in the range of few nanometers. It is consistent with the XRD results.

3.5. Electrical conductivity

I-V characteristics of ZnO and Cd doped ZnO thin films under illumination and in dark are shown in Fig. 7. In both conditions the thin films show the ohmic behaviour. The current measurements under the illuminated condition show an enhancement in conductivity of the thin films. The conductivity of the thin films increases with an increase of Cd content in ZnO lattice. This confirms that the Cd doped ZnO thin films have significant light sensitive properties. Similar properties were reported by the Y. Caglar et al. [19]. The electrical resistivity (ρ) of ZnO and Cd doped ZnO thin films have been measured in the temperature range of 300 to 500 K. The plots $\ln \rho$ versus $1/T$ of ZnO and Cd doped ZnO

Table 3. Optical parameters of ZnO and $Zn_{1-x}Cd_xO$ thin films.

Thin film samples	Energy band gap (eV) from UV-Vis	Energy band gap (eV) from photoluminescence	Stoke shift (meV) $ \Delta E = E_{Abs} - E_{PL}$
ZnO	3.304	3.281	23
Cd ₁₀ Zn ₉₀ O	3.112	3.093	19
Cd ₂₀ Zn ₈₀ O	2.935	2.932	3
Cd ₂₅ Zn ₇₅ O	2.779	2.767	12

Fig. 7. I-V characteristics of ZnO and $Zn_{1-x}Cd_xO$ thin films: (a) dark, (b) illuminated: 200 Watt light source.

thin films are shown in Fig. 8. The electrical resistivity of the films has been estimated by the well known exponential relation. The activation energy of the films has been calculated using the graphs presented in Fig. 8. The shifting in Fermi level indicates that the semiconductors are intrinsic in behaviour at high temperature. However, at low temperature they behave like pseudo-intrinsic, with an energy gap equal to the gap between the impurity level and the band edge. It is observed that the resistivity of the films decreases with an increase in temperature. This confirms the typical semiconducting behaviour of the films. The electrical resistivity of the films shows the non linear behaviour. This non-linear behaviour may be due to the defects.

4. Conclusions

The structural, optical and electrical properties of ZnO and Cd doped ZnO thin films grown by sol-gel spin coating method on glass substrates

have been investigated in the present work. XRD patterns showed the growth of thin films along the (002) plane with hexagonal wurtzite structure. The average crystallite sizes of the films were found to be in the range of 24 to 9 nm. The transmittance of the films was found to be very high, ranging from 92 to 95 % in the visible region of solar spectrum. The band gap of the films decreased with increasing Cd content in ZnO lattice. PL spectrum of ZnO thin films revealed a strong characteristic peak near band edge emission, centred over the 380 nm wavelength. On Cd doping in ZnO thin films, the characteristic emission peaks shifted towards the red wavelength. The surface morphologies of the films showed nano spherical shaped particles, uniformly distributed over the surface. The I-V measurements under dark and illumination conditions showed photosensitive behaviour of thin films. The resistivity of thin films decreased with the increase in the thin film temperature, which confirmed the semiconducting behaviour of the films.

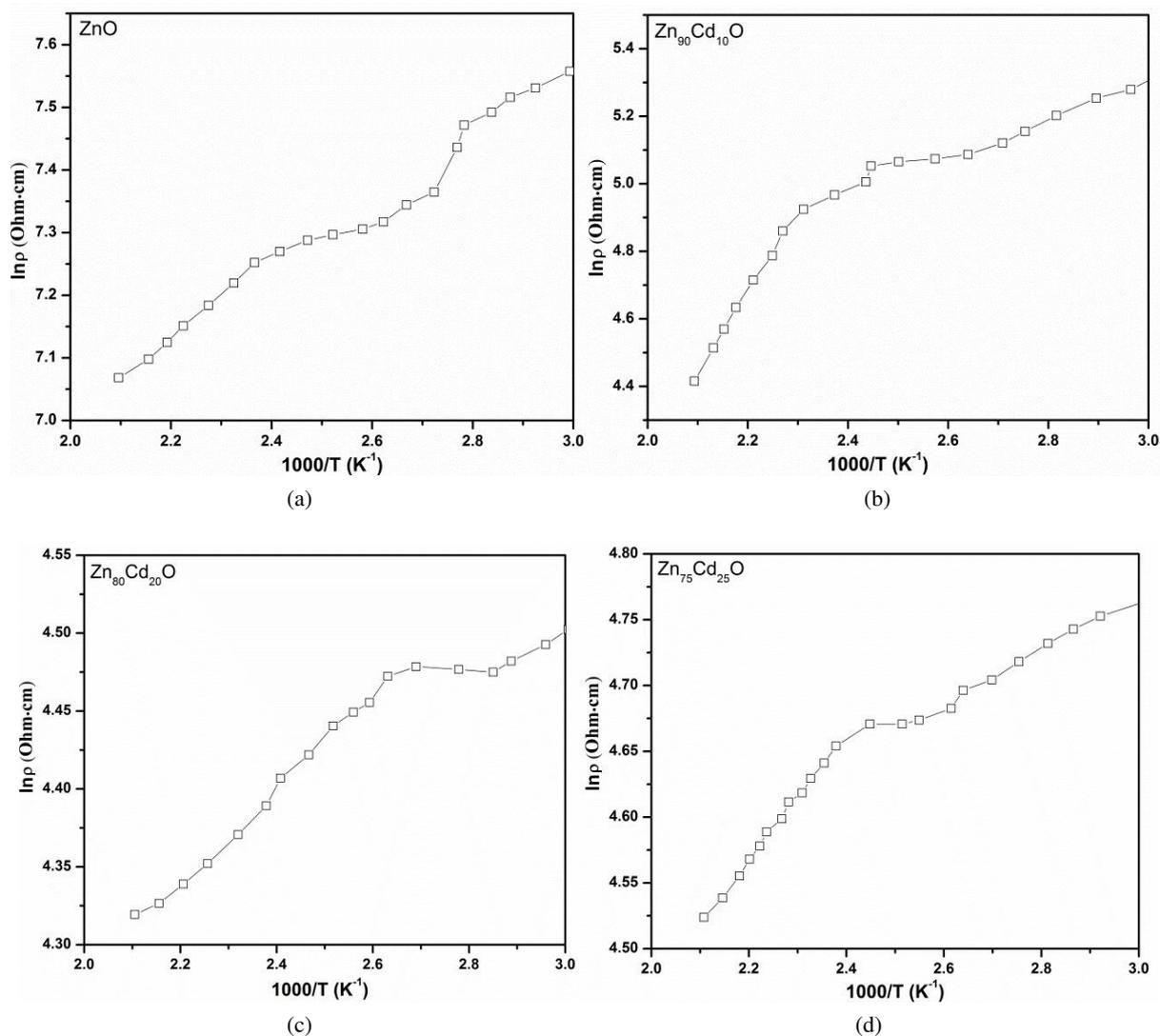


Fig. 8. Plots $\ln \rho$ vs. $1/T$ of ZnO and Zn_{1-x}Cd_xO thin films: (a) ZnO, (b) 10 % Cd doped, (c) 20 % Cd doped, (d) 25 % Cd doped.

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