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Influence of indium doping on the properties of spray deposited $CdS_{0.2}Se_{0.8}$ thin films

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ABSTRACT

Polycrystalline indium doped $CdS_{0.2}Se_{0.8}$ thin films with varying concentrations of indium have been prepared by spray pyrolysis at 300 °C. The as deposited films have been characterized by XRD, AFM, EDAX, optical and electrical resistivity measurement techniques. The XRD patterns show that the films are polycrystalline with hexagonal crystal structure irrespective of indium doping concentration. AFM studies reveal that the RMS surface roughness of film decreases from 34.68 to 17.76 with increase in indium doping concentration up to 0.15 mol% in $CdS_{0.2}Se_{0.8}$ thin films and further it increases for higher indium doping concentrations. Traces of indium in $CdS_{0.2}Se_{0.8}$ thin films have been observed from EDAX studies. The optical band gap energy of $CdS_{0.2}Se_{0.8}$ thin film is found to decrease from 1.91 eV to 1.67 eV with indium doping up to 0.15 mol% and increase after 0.15 mol%. The electrical resistivity measurement shows that the films are semiconducting with minimum resistivity of $3.71 \times 10^4\ \Omega$ cm observed at 0.15 mol% indium doping. Thermoelectric power measurements show that films exhibit n-type conductivity.

1. Introduction

In recent years, the growth of II–VI based ternary and quaternary compound semiconductors has attracted considerable attention because of their novel physical properties and many applications in optoelectronic devices [1], photoelectrochemical solar cells [2], photovoltaics [3], visible light emitting diodes and lasers [4]. In particular, considerable attention has been devoted to the possibility of tailoring the optical and electrical properties of these materials. This purpose has been mainly achieved by means of two different processes: (i) fabrication of ternary and quaternary alloys, whose band gap can be modulated by controlling the relative concentrations of two elements forming the alloy (for example, CdS_xSe_{1-x}, ZnS_xSe_{1-x}, $Cd_xZn_{1-x}Se$, etc.) [5]. and (ii) doping with different dopant density, which causes the broadening of intra-gap impurity bands and the formation of band tails and band gap renormalization [6].

CdS and CdSe are two very important wide band gap semiconductors, because of their wide applications in optoelectronics, such as non-linear optics, visible-light emitting diodes and lasers [7,8]. Previously, we have successfully grown CdS_xSe_{1-x} ($0.0 \le x \le 1.0$) ternary alloy thin films by means of chemical spray pyrolysis technique, which has become a widespread deposition method for its advantages as the simplicity, low cost and possibility of grow highly oriented stoichiometric thin films with good optical properties [9]. Although a considerable improvement in the photoelectrochemical cell performance has been noted at $x = 0.8$ [2], the observed conversion efficiency is much smaller as compared to the existing literature values. The lower conversion efficiency has been attributed partly to the higher resistivity of the photoelectrode material that could be effectively reduced by a suitable donor impurity concentration. The resistivity of polycrystalline material mainly depends upon the grain boundary or surface scattering mechanisms [10]. The photoelectrodes based on CdSe have been observed to show electrochemical corrosion [6]. In order to get low resistance contact, it is essential to obtain CdSSe thin films which are doped with a suitable donor impurity concentration. Recently, much attention has been given to tailor the optical and electrical properties of these materials by using suitable dopants such as Fe, In and Sb [6,5,11,12]. The process of doping with different dopants causes the broadening of intra gap impurity bands and the formation of band tails and band gap renormalization [11]. Pawar et al. have prepared Fe doped CdSe (CdSe:Fe) thin films from non-aqueous electrolytic bath using electrodeposition technique and reported its structural, optical and photoelectrochemical properties [6]. Masumdar et al. have reported the growth mechanism, crystallographic, microscopic observations, optical and electrical properties of Sb doped CdSe thin films prepared using solution growth process [12]. Indium, an III group element, has shown pronounced effects in a number of host lattices [11].

The ternary II–VI thin films can be prepared by variety of techniques such as electrodeposition [3], chemical bath deposition [13–16], evaporation [17–20], solvothermal route [21], sputtering [22] and chemical spray pyrolysis [23,24]. Among these various

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deposition techniques available for preparation of thin films, the spray pyrolysis, which has the advantages of low cost, easy-to-use, safe and can be implemented in a standard laboratory, has been known to be suitable for many scientific studies and technological applications. This method is based on the preparation of solutions of some salt of the material whose films are to be prepared.

The aim of present study is to deposit indium doped $CdS_{0.2}Se_{0.8}$ thin films using chemical spray pyrolysis technique. The effect of indium doping on the structural, morphological, optical and electrical transport properties of spray deposited $CdS_{0.2}Se_{0.8}$ thin films have been studied and results obtained are discussed.

2. Experimental details

The spray pyrolysis method is basically a chemical deposition technique in which fine droplets of the desired material are sprayed onto preheated substrates. Continuous films are formed on the hot substrate by thermal decomposition of the material droplets. The chemical reactants are selected in such a way that the products other than the desired compound will volatile at the temperature of deposition. The indium doped $CdS_{0.2}Se_{0.8}$ thin films with varying concentration of indium were deposited onto the amorphous glass substrates by using well known chemical spray pyrolysis method at optimized substrate temperature of 300 °C [9]. The 0.025 M aqueous solutions of cadmium chloride hydrate ($CdCl_2{\cdot}H_2O$), thiourea (H_2NCSNH_2) and selenourea ($H_2NCSeNH_2$) along with various concentrations of $InCl_3$ were used as starting materials. Glass microslides of the size 7.5 cm × 2.5 cm were used as substrates. Prior to deposition these substrates were washed with water, then boiled in concentrated (2 M) chromic acid and kept in double distilled water for 48 h. Finally the substrates were ultrasonically cleaned for 10 min. The substrate temperature was controlled by an iron–constantan thermocouple. The spray rate employed was 3 ml/min and kept constant throughout the experiment. Air was used as carrier gas. After deposition, the films were allowed to cool at room temperature. The adhesion of the films onto the substrate was quite good.

The structural characterization of the films was carried out by analyzing the X-ray diffraction (XRD) patterns obtained using Philips PW-3710 X-ray diffractometer with Cu-K_α radiation, within the 2θ range of angles between 20° and 60°. Atomic force microscopy (AFM) was carried out in air at ambient condition (300K) using Nanoscope III from Veeco. The compositional analysis of the spray deposited indium doped $CdS_{0.2}Se_{0.8}$ thin films on glass substrate was carried out using JOEL–JSM 5600. A UV–Vis spectrophotometer (SHIMADZU UV-1700) was used to record the optical absorption spectra of the samples in the wavelength range 350–950 nm. Electrical resistivity and thermo electric power measurements were done using D.C. two point probe method. Silver paste was employed to films to ensure good ohmic contacts.

3. Results and discussion

3.1. Structural studies

The as deposited indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium were characterized by X-ray diffraction with Cu-K_α radiation (1.5406 Å). The range of 2θ angle was from 20° to 60°. Fig. 1 shows X-ray diffractogram of indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium. The diffractograms show that as-deposited films are polycrystalline in nature and the crystallinity increased with indium doping concentration up to 0.15 mol% and then decreased for higher doping concentrations. A comparison of observed and standard d values for $(h\,k\,l)$ planes ensures that indium doped $CdS_{0.2}Se_{0.8}$ thin films show hexagonal crystal structure [25,26]. For pure $CdS_{0.2}Se_{0.8}$ the preferential orientation was along (1 0 0), (0 0 2), (1 0 1), (1 1 0), (2 0 0) and (1 1 2) as matched with standard JCPDS data cards [25,26]. In case of indium doped $CdS_{0.2}Se_{0.8}$ thin films all peaks occur at the same positions with modifications in the intensity and peak width. As there is no appreciable change in the peak positions of $CdS_{0.2}Se_{0.8}$ thin films with indium doping; it is concluded that indium acts as dopant in the host lattice. After refinement the cell constants were calculated to be $a = b = 4.2343$ Å and $c = 6.8865$ Å.

The effect of indium doping concentration on the orientation of polycrystalline $CdS_{0.2}Se_{0.8}$ thin films was investigated by evaluating the texture coefficient ($T_c(h\,k\,l)$) of the $(h\,k\,l)$ plane using Eq. (1).

$$T_c(h\,k\,l) = \frac{I(h\,k\,l)/I_0(h\,k\,l)}{(1/N)\left(\sum_N I(h\,k\,l)/I_0(h\,k\,l)\right)} \quad (1)$$

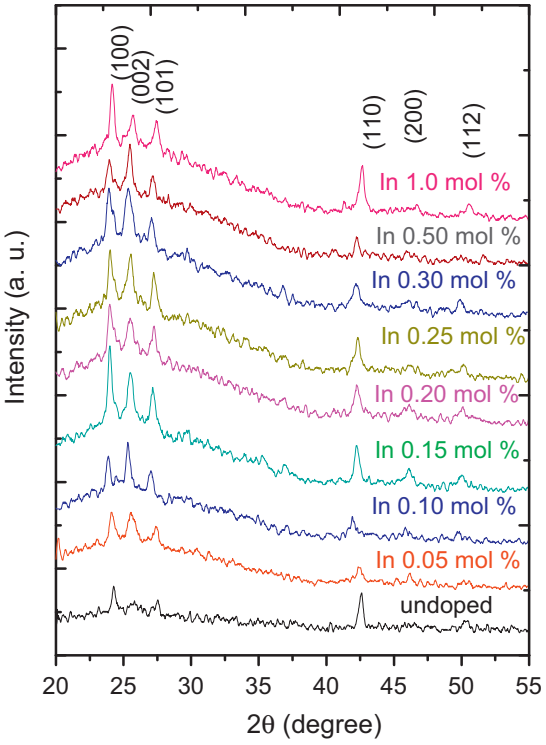

Fig. 1. X-ray diffraction patterns of spray deposited indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium.

where $T_c(h\,k\,l)$ is the texture coefficient of the $(h\,k\,l)$ plane, I is the measured intensity and I_0 is the JCPDS standard intensity, N is the number of diffraction peaks. From Eq. (1), it is seen that the value of texture coefficient approaches unity for a randomly distributed powder sample, while $T_c(h\,k\,l)$ is greater than unity when the $(h\,k\,l)$ plane is preferentially oriented. Fig. 2 shows the variation of texture coefficient for (1 0 0) plane with respect to indium doping concentration in $CdS_{0.2}Se_{0.8}$ thin films. From Fig. 2, it is clear that the lower value of texture coefficient represents that the films have poor crystallinity and the crystallinity may be improved by increasing indium doping concentration from 0.05 to 0.15 mol%. Further increase in indium concentration above 0.15 mol%; the value of texture coefficient slightly decreases as shown in Fig. 2. Hence, indium doped $CdS_{0.2}Se_{0.8}$ thin films obtained at 0.15 mol%

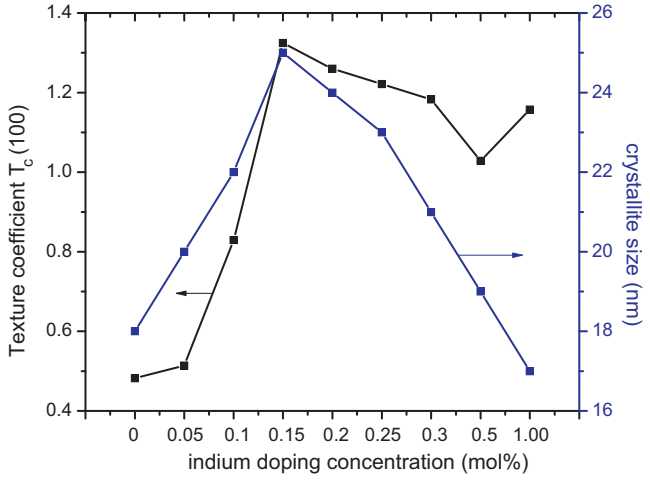

Fig. 2. Variation of texture coefficient along the (1 0 0) plane and crystalline size for In:$CdS_{0.2}Se_{0.8}$ thin films prepared at various indium doping concentrations.

concentration have better crystallinity as well as better adherence to the substrates.

Crystallite size was estimated by using Debye–Scherrer's formula given by [27],

$$D = \frac{k\lambda}{\beta \cdot \cos\theta} \quad (2)$$

where k varies from 0.89 to 1.39. But in most of the cases it is closer to 1. Hence for grain size calculation it is taken to be one, λ is wavelength of X-ray, β is the full width at half of the peak maximum in radians and θ is Bragg's angle. The crystallite size was estimated for the standard (1 0 0) reflection. The crystallite size in the present work is found to increase up to 25 nm for 0.15 mol% indium doping concentration in $CdS_{0.2}Se_{0.8}$ thin films and it is decreased for further increase in indium doping concentration. The variation of crystallite size with indium doping concentration is shown in Fig. 2.

3.2. Surface morphology and compositional analysis studies

The surface morphology was studied by atomic force microscopy; root mean square (RMS) roughness of the films was extracted from AFM data. The AFM micrographs obtained for

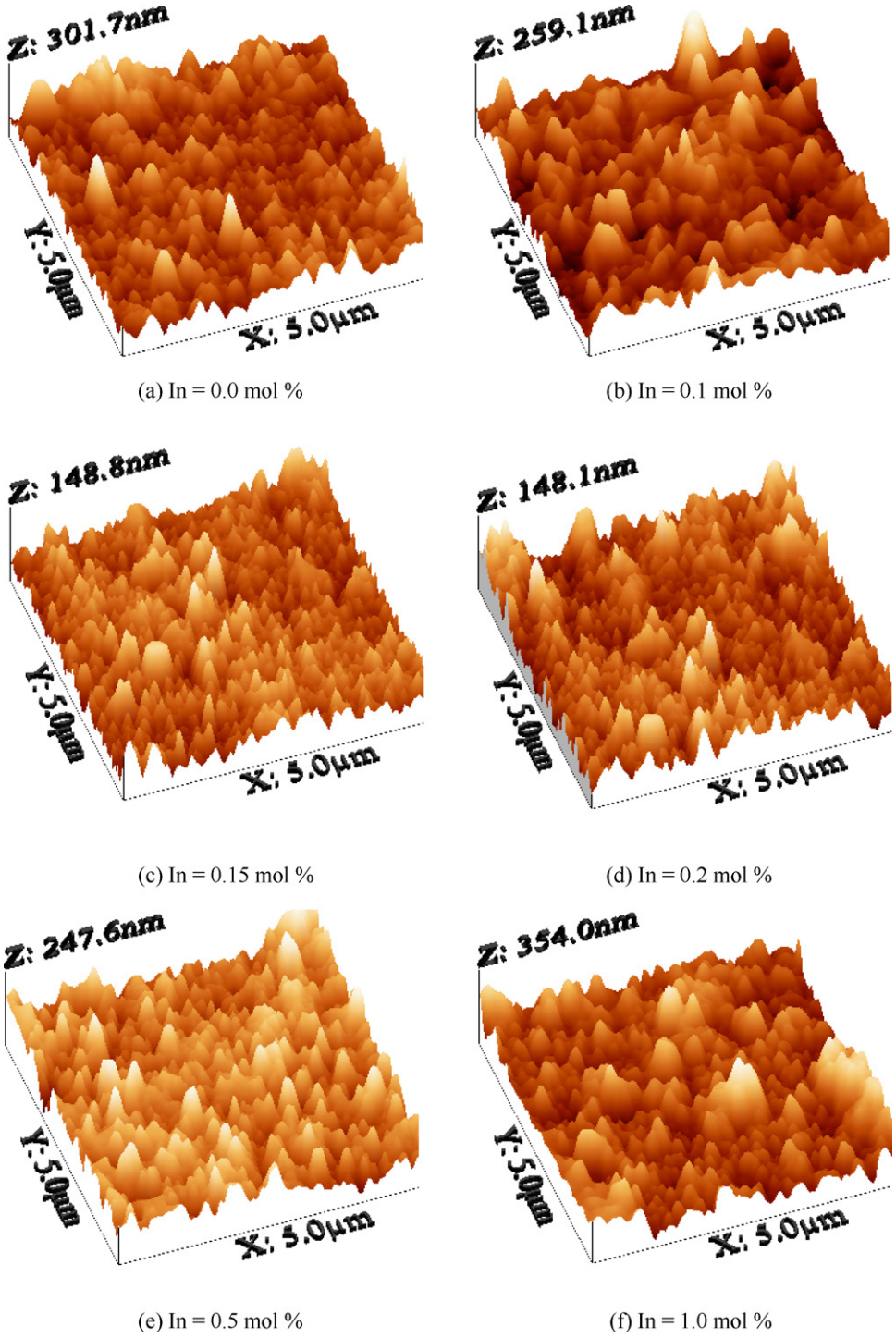

Fig. 3. Atomic force micrographs of spray deposited indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium.

Table 1
Optical and electrical parameters of spray deposited indium doped $CdS_{0.2}Se_{0.8}$ thin films.

Doping concentration mol%	RMS surface roughness	E_g (eV)	Activation energy		Electrical resistivity	
			LT (eV)	HT (eV)	300 K ($\times 10^5$ Ω cm)	500 K ($\times 10^2$ Ω cm)
0.00	34.68	1.91	0.214	0.323	1.62	2.17
0.05	33.26	1.80	0.292	0.322	1.39	1.85
0.10	32.52	1.71	0.240	0.317	0.74	1.07
0.15	17.76	1.67	0.216	0.308	0.37	0.59
0.20	19.20	1.74	0.222	0.310	0.47	0.63
0.25	23.18	1.77	0.226	0.313	0.55	0.74
0.3	29.68	1.79	0.236	0.314	0.63	0.89
0.5	34.02	1.87	0.266	0.315	1.00	1.11
1.0	48.19	1.91	0.267	0.319	1.05	1.21

indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium are shown in Fig. 3. The values of RMS surface roughness for various compositions are given in Table 1. The RMS roughness of 34.56 nm obtained for undoped $CdS_{0.2}Se_{0.8}$ thin film has been reduced drastically to a minimum of 17.76 nm with 0.15 mol% indium doping in $CdS_{0.2}Se_{0.8}$ films. This clearly indicates that the surface of undoped $CdS_{0.2}Se_{0.8}$ thin films is rougher than that of doped film. It is perceptible from the figure that the surface of film has been improved with indium doping in $CdS_{0.2}Se_{0.8}$ thin film. The RMS surface roughness is found to increase with further increase in indium doping in $CdS_{0.2}Se_{0.8}$ thin films above 0.15 mol%. Detailed analysis shows that the RMS roughness is dependent on doping concentration of indium.

The quantitative analysis of the undoped and 0.15 mol% indium doped $CdS_{0.2}Se_{0.8}$ thin films were carried out by using EDAX technique, to study the stoichiometry of the films. The details of relative analysis are given in Table 2. From EDAX study, it is concluded that the indium is incorporated in $CdS_{0.2}Se_{0.8}$ thin film.

3.3. Optical absorption studies

The optical absorption spectrum of the indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium on glass substrate was studied in wavelength range 350–950 nm. The absorption coefficient, band gap and nature of the transition involved (direct or indirect) during the absorption process were determined by studying the dependence of the absorption coefficient α, on photon energy $h\upsilon$ as [28]

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad (3)$$

where A is the constant, E_g is the band gap energy, $h\upsilon$ is the photon energy, $n = 1/2$ or 2 for direct or indirect transition. The value of absorption coefficient is found to be of the order of 10^4 cm^{-1} for indium doped $CdS_{0.2}Se_{0.8}$ thin films. The optical data was further analyzed to determine the nature of transition that takes place in indium doped $CdS_{0.2}Se_{0.8}$ thin films. The plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium are shown in Fig. 4. The straight line nature of the graphs supports the direct band gap nature of the semiconductor. The straight-line portion was extrapolated to the energy axis at $\alpha = 0$, to obtain the band gap energy. It is observed that for undoped $CdS_{0.2}Se_{0.8}$ thin film, the band gap energy is found to be 1.91 eV and it is decreased up to 1.67 eV with increase in indium doping concentration up to 0.15 mol%, which further increases to 1.91 eV for further increase in indium doping concentration up to 1.0 mol% in $CdS_{0.2}Se_{0.8}$ films. The decrease in band gap may be attributed to the improved grain structure of the film due to segregation of the impurity atoms along the grain boundaries [11,12], whereas the increase in band gap at higher indium doping concentrations can be attributed to the increased amount of disorder caused by addition impurity atoms in host lattice [11]. The values of band gap energy (E_g) for various indium doped $CdS_{0.2}Se_{0.8}$ thin films are given in Table 1.

Table 2
Atomic percentage composition of undoped and 0.15 mol% indium doped $CdS_{0.2}Se_{0.8}$ thin films from EDAX analysis.

Element	Atomic percentage in film	
	Undoped $CdS_{0.2}Se_{0.8}$	(0.15 mol%) In:$CdS_{0.2}Se_{0.8}$
Cd	49.47	50.23
Se	40.75	39.06
S	09.78	09.32
In	–	01.39

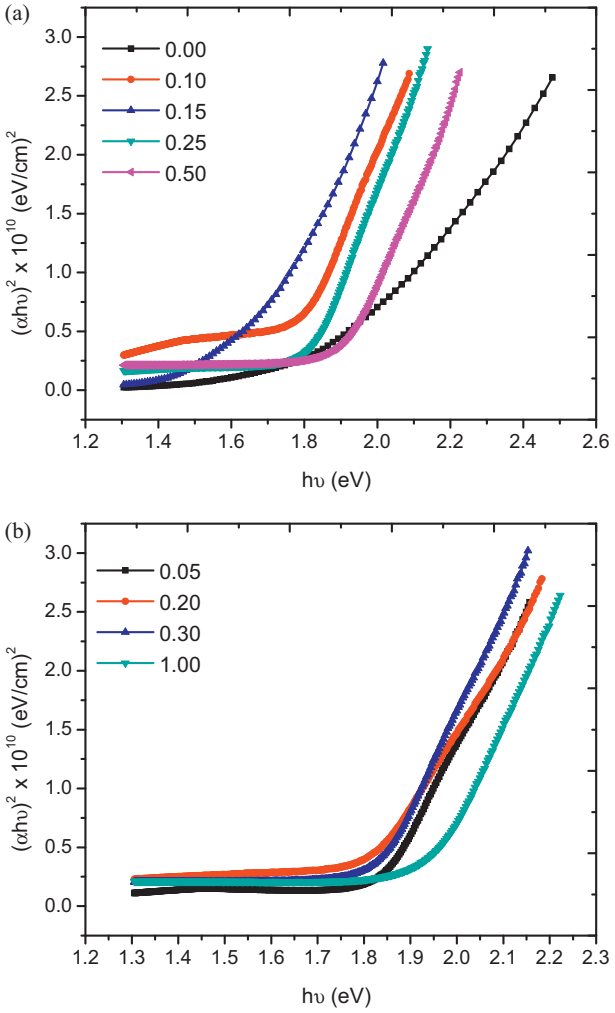

Fig. 4. Variation of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for spray deposited indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium.

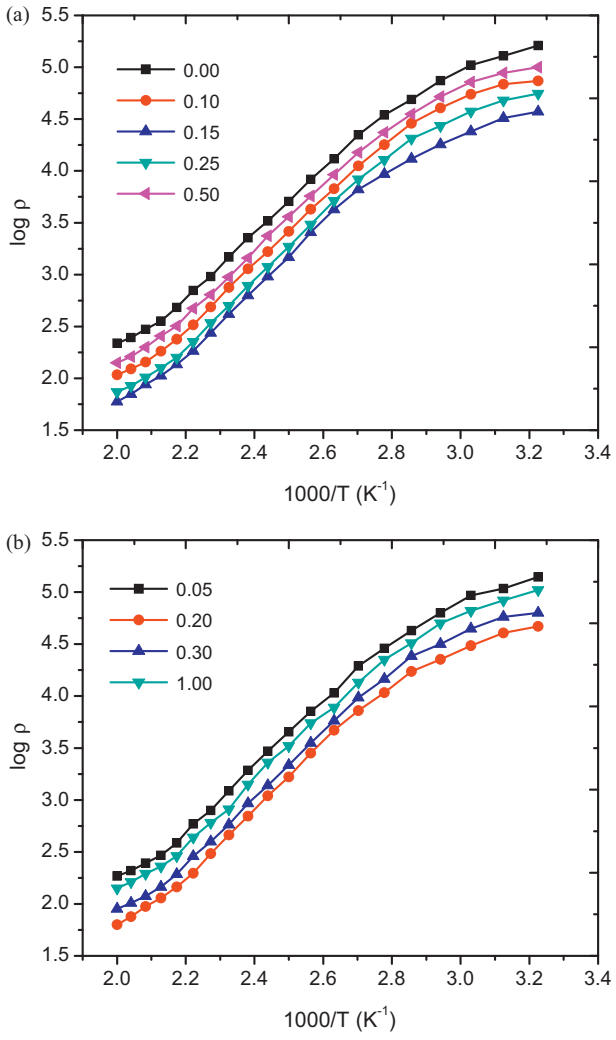

Fig. 5. Plots of log ρ versus 1000/T for spray deposited indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium.

3.4. Electrical transport studies

The measurements on electrical resistivity of the indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium were carried out in the temperature range 300–500 K on rectangular-shaped samples with typical size of 100 mm^2, using a standard DC two point probe method under dark. The variations of log ρ versus inverse of absolute temperature (1000/T) for indium doped $CdS_{0.2}Se_{0.8}$ thin films are shown in Fig. 5. It is found that this resistivity variation obeys the relation,

$$\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right) \quad (4)$$

where E_a is the activation energy and k is the Boltzmann constant. It is well known that the resistivity of a semiconducting material strongly depends on the temperature, carrier concentration and mobility. In a semiconductor, carrier concentration is a rapidly increasing function of temperature. This increase is due to thermal excitation of electrons, either from imperfections or across the band gap. It is clear from Fig. 5, that the resistivity decreases as the temperature increases, showing semiconducting behaviour of the indium doped $CdS_{0.2}Se_{0.8}$ thin films [29]. Also from Fig. 5 the variation indicated two distinct temperature zones with two different characteristic regions. The first region from room temperature up to 370 K is identified with low temperature and extends upwards as far as the impurity exhaustion temperatures. This region is identified with the extrinsic conductivity of semiconductor due to the ionization of impurity atoms. The second region from 370 up to 500 K is identified with the transition to intrinsic conduction in semiconductor. Within this region, the density of carriers is equal to that of intrinsic carriers. The values of activation energy E_a are found to be in the range between 0.214 and 0.292 eV in the low temperature region and 0.308–0.323 eV in the high temperature region. The values of the activation energy for indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium are given in Table 1 indicates that the prepared samples are semiconductors.

The values of dark electrical resistivity for various indium doped $CdS_{0.2}Se_{0.8}$ thin films at 300 and 500 K are given in Table 1. It is seen that the room temperature resistivity 1.62×10^5 Ω cm of pure $CdS_{0.2}Se_{0.8}$ thin film decreases with increase in indium doping concentration from 0.0 to 0.15 mol% to 3.71×10^4 Ω cm and then again increases for higher doping concentrations to 1.05×10^5 Ω cm for 1.0 mol%. Similar results have been reported earlier for doped and mixed thin films [30,31]. The decrease in resistivity with increase in indium doping concentration up to 0.15 mol% can be explained as follows: Incorporation of indium in the host structure ($CdS_{0.2}Se_{0.8}$) has two possibilities; (1) substitution of divalent cadmium by a trivalent indium and (2) possibility of formation of Cd-vacancies. Since Cd^{2+} and In^{3+} are deposited simultaneously, there is less chance for forming the Cd-vacancies [30]. Thus substitution of divalent cadmium by a trivalent indium is more predominant which

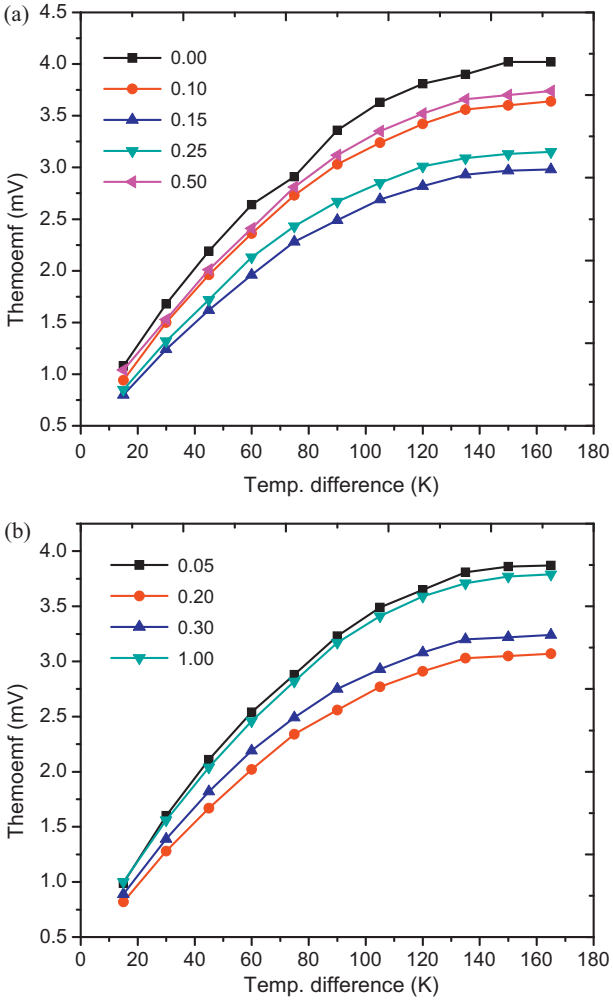

Fig. 6. Plots of thermo-emf versus temperature difference for spray deposited indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium.

makes the indium atom act as a donor [31]. This causes electrical resistivity to decrease up to 0.15 mol% indium doping concentration in $CdS_{0.2}Se_{0.8}$ thin films. At higher indium doping concentration (i.e. >0.15 mol%), the $CdS_{0.2}Se_{0.8}$ films may become greatly disordered and substitute indium does not now contribute as donor and results in increase in film resistivity.

3.5. Thermoelectric power measurement studies

The thermoelectric power (TEP) is defined as the ratio of thermally generated voltage to the temperature difference across a piece of semiconductor. The type of conductivity exhibited by the spray deposited indium doped $CdS_{0.2}Se_{0.8}$ thin films with various concentrations of indium are determined from TEP measurement. The polarity of thermally generated voltage at the hot end is positive indicating that the films are of n-type. Fig. 6 shows the variation of thermo-emf with temperature difference for the films deposited with various concentrations of indium in $CdS_{0.2}Se_{0.8}$ thin films.

4. Conclusions

Thin films indium doped $CdS_{0.2}Se_{0.8}$ with various concentrations of indium can be deposited by simple and inexpensive spray pyrolysis technique. XRD patterns reveals that the deposited films exhibit hexagonal crystal structure with preferential orientation along (1 0 0) plane irrespective of indium doping concentration. The microstructural parameters such as texture coefficient and crystallite size are calculated using XRD data and their dependency with indium doping concentration is investigated. From AFM studies it is observed that the surface of film has been improved with indium doping in $CdS_{0.2}Se_{0.8}$ thin films. EDAX studies confirmed that $CdS_{0.2}Se_{0.8}$ thin films can be doped with indium. Optical properties of the deposited films indicate that decrease in the value of band gap energy with indium doping in $CdS_{0.2}Se_{0.8}$ thin film initially and increase afterwards for more than 0.15 mol% indium doping. The indium doping in $CdS_{0.2}Se_{0.8}$ thin film results in considerable decrease in the film resistivity up to 0.15 mol%.

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