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Structural, morphological and electrical properties of spray deposited $CdIn_2Se_4$ thin films

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ABSTRACT

Semiconducting n-$CdIn_2Se_4$ thin films have been deposited on to the amorphous and fluorine doped tin oxide (FTO) coated glass substrates using spray pyrolysis technique. The influence of solution concentration on to the photoelectrochemical, structural, morphological, compositional, thermal and electrical properties has been investigated. The PEC characterization shows that the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) are at their optimum values (I_{sc} = 1.04 mA and V_{oc} = 409 mV) at the optimized precursor concentration (12.5 mM). The structural analysis shows the films are polycrystalline in nature having cubic crystal structure. The average crystallite size determined was in the range of 50–66 nm. Surface morphology and film composition have been analyzed using scanning electron microscopy and energy dispersive analysis by X-rays, respectively. The addition of solution concentration induces a decrease in the electrical resistivity of $CdIn_2Se_4$ films up to 12.5 mM solution concentration. The type of semiconductor was examined from thermoelectric power measurement.

1. Introduction

Recently, ternary compounds of II–III–VI group attract many researchers due to their applications in optoelectronic devices and solar cells [1–3]. Among II–III–VI group ternary compounds, Cadmium indium selenide ($CdIn_2Se_4$) is one of the interesting semiconductors due to its optical absorption property with a narrow band gap and a low electrical resistance [4,5]. Because of its narrow band gap, $CdIn_2Se_4$ compound is also widely used in optoelectronic devices [2], non-linear optics [6], semiconducting devices, radiation detectors, laser materials, thermoelectric devices, solar energy converters etc. [7,8]. $CdIn_2Se_4$ is a direct band gap semiconductor with an energy gap of 1.73 eV which make them interesting for solar cells through photoelectrochemical route [2,9]. The basic requirements of good thin film photoelectrode for photoelectrochemical cells are low resistivity and large grain size. Large grain size leads to reduction of grain boundary area of thin films with important consequences for efficient energy conversion. The low resistivity of photoelectrode is required to minimize the series resistance of PEC cell. Due to its wide applications, this compound is always prepared as thin film via many methods such as electro-deposition [10], slurry pasting technique [11], vacuum evaporation [3] and spray pyrolysis [12,13]. The deposition of $CdIn_2Se_4$ thin films have been carried out using relatively inexpensive, simple and convenient for large area deposition, spray pyrolysis technique. Furthermore, synthesis of $CdIn_2Se_4$ thin film by spray pyrolysis technique obtained a good photovoltaic activity. An obtained thin film has high crystallinity with low electrical resistivity, which leads to high thermoelectric power [14]. Tenne et al. have prepared $CdIn_2Se_4$ single crystals and studied their properties using optical and photoelectrochemical techniques, respectively [2]. An analysis of published data signifies that large amount of literature is available concerning the preparation and properties of bulk $CdIn_2Se_4$ [2,10] single crystals, but very few are available regarding thin films. Number of methods such as vacuum evaporation [15], slurry pasting technique [11] have been attempted to prepare $CdIn_2Se_4$ thin films and studied their properties. Mahalingam et al. [3] reported electro synthesis of $CdIn_2Se_4$ films on ITO substrates. The dependency of microstructural parameters such as crystallite size, strain and dislocation density with deposition potential has been studied. Adpakpang et al. [4] studied synthesis and characterization of $CdIn_2Se_4$ by aqueous chemical reduction at low temperature. El-Nahass have prepared $CdIn_2Se_4$ thin films by vacuum evaporation method and studied their properties [15]. The preparation of $CdIn_2Se_4$ thin films by slurry pasting technique and their properties have been investigated by Tenne et al. [11]. Thin and continuous $CdIn_2Se_4$ films with desired electrical and optical properties are required for photoelectrochemical solar cells. It is difficult to obtain thin and continuous single phase $CdIn_2Se_4$ films by above mentioned techniques. $CdIn_2Se_4$ thin films obtained using electrodeposition method and their structural, morphological, compositional properties have been investigated earlier [16,17]. In the above mentioned works, the structural parameters such as crystallite size, texture coefficient, strain, thermal and electrical parameters have not been discussed.

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The purpose of this work is to synthesize stoichiometric n-$CdIn_2Se_4$ films using a simple and low cost spray pyrolysis technique on to the amorphous and fluorine doped tin oxide coated conducting glass substrates. Influence of solution concentration on to the photoelectrochemical, structural, compositional, microstructural and electrical properties has been investigated by PEC, X-ray diffraction, Scanning electron microscopy, Energy dispersive analysis by X-rays and two probe resistivity techniques, respectively. Variation of dislocation density, strain and texture coefficient w.r.t. concentration has been investigated. The importance of $CdIn_2Se_4$ material is to deposit the good quality photoanode (working electrode) for photoelectrochemical solar cells.

2. Experimental

The cadmium indium selenide ($CdIn_2Se_4$) thin films were deposited on to the ultrasonically cleaned glass and fluorine doped tin oxide (FTO) coated glass substrates using simple and inexpensive chemical spray pyrolysis technique. The deposition method involved the decomposition of aqueous solution of A.R. grade cadmium chloride ($CdCl_2$) supplied by S. D. Fine Chem., Ltd, Mumbai, indium trichloride ($InCl_3$) and selenourea [$(NH_2)_2CSe$] (99.99%, A.R. grade, Aldrich) in appropriate volumes in order to obtain Cd:In:Se ratio as 1:2:4, respectively. Only double distilled and deionized water was used for solution preparation. $CdIn_2Se_4$ thin films were deposited at various solution concentrations 5–20 mM by keeping constant optimized substrate temperature of 553 K. Compressed air was used as a carrier gas. Other preparative parameters viz. spray rate: 2 cm^3 min^{-1}, nozzle to substrate distance: 33 cm, nozzle diameter: 0.05 cm was kept constant for all experiments.

The prepared films were characterized for optimization by using photoelectrochemical, structural, morphological, compositional, thermal and electrical characterization etc. The PEC cell was fabricated by using $CdIn_2Se_4$ thin film as active photoelectrode, polysulphide (1 M NaOH–1 M Na_2S–1 M S) solution as an electrolyte and graphite as a counter electrode. By using this arrangement V_{oc} and I_{sc} were measured for the $CdIn_2Se_4$ thin films deposited at different solution concentrations. The structural characterization of deposited thin films was carried out, by analyzing the X-ray diffraction patterns obtained under Cu-Kα (λ = 1.5406 Å) radiation from a Philips X-ray diffractometer model PW-1710 and surface morphology was studied using JEOL JSM-6360 scanning electron microscope (SEM), Japan attached with an energy dispersive analysis by X-ray (EDX) analyzer to measure quantitatively the sample composition. The resistivity of the film was measured using two-probe method in the temperature range 300–500 K. The TEP measurement was carried out in the temperature range 300–500 K.

3. Results and discussion

In the spray pyrolysis technique, the clear precursor solution was sprayed onto the preheated hot glass substrates and pyrolytic decomposition of solution occurs, thereby resulting well adherent dark brown $CdIn_2Se_4$ thin films. Every sprayed droplet reaching the surface of the hot substrate undergoes pyrolytic decomposition and split up into its constituent components. The other volatile components get evaporated in the form of vapour and the only desired compound containing the Cd, In and Se chemical species deposit on the surface of substrate in the film. The depositions of $CdIn_2Se_4$ thin films were carried out at various solution concentrations 5, 10, 12.5, 15, 17.5 and 20 mM at the optimized substrate temperature of 553 K. The film formation does not observe below the 5 mM solution concentration. This may be due to extra low concentration of the precursor solution. At high concentration the complete thermal decomposition of the solution does not take place. However, the $CdIn_2Se_4$ thin films deposited at intermediate solution concentration (5–20 mM) are uniform and adherent to the glass substrates with dark brown in colour. The mechanism of formation of $CdIn_2Se_4$ is described by the following equation [18].

$$Cd^{2+} + 2In^{3+} + 4Se^{4+} + 9e^- \rightarrow CdIn_2Se_4 \quad (1)$$

Optimization of preparative parameters for the deposition of good-quality and stoichiometric $CdIn_2Se_4$ thin films is most essential. Optimization of preparative parameters is carried out by noting the maximum values of I_{sc} and V_{oc} of the PEC cell. Fig. 1 shows the variation I_{sc} and V_{oc} with solution concentration; from the graph, it

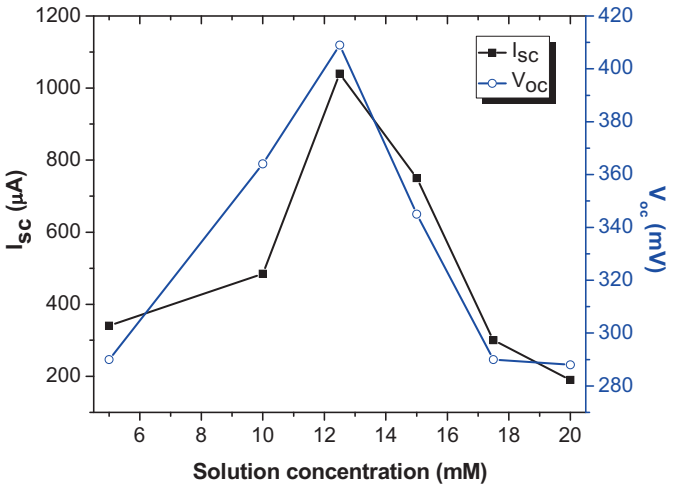

Fig. 1. Variation of I_{sc} and V_{oc} with precursor solution concentration for the $CdIn_2Se_4$ thin films.

is observed that I_{sc} and V_{oc} increases with increase in solution concentration, attains maximum values for film deposited at 12.5 mM solution concentration indicating probably a better formation of stoichiometric semiconducting compound. On further increasing solution concentration, both I_{sc} and V_{oc} decrease, this indicates the formation of a poor quality films. The lower values of I_{sc} and V_{oc} may be originated due to increase in resistivity and non-stoichiometric growth of $CdIn_2Se_4$ thin films due to insufficient thermal energy provided during the deposition [19]. The PEC cell with configuration $CdIn_2Se_4$/0.1 M polysulfide/graphite is used to check the type of conductivity exhibited by $CdIn_2Se_4$ thin films. The polarity of dark voltage is negative toward $CdIn_2Se_4$ photoelectrode and positive toward the graphite electrode for all samples showing n-type semiconducting behavior.

A detailed kinetics study was carried out by changing the solution concentration. Fig. 2 shows the growth kinetics of $CdIn_2Se_4$ thin film deposited for various solution concentrations from 5 to 20 mM. The film thickness was slowly built up at the initial stages linearly and finally gets to a maximum of about 1.24 μm at 12.5 mM concentration and then decreases for higher concentrations. The film deposited at 12.5 mM was found to be uniform, thick and well adherent to the substrate.

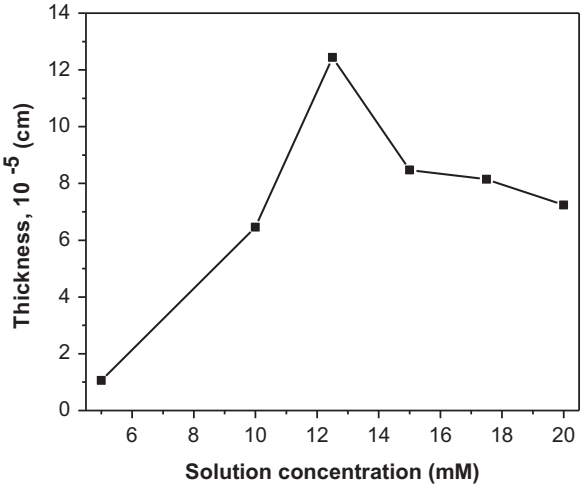

Fig. 2. Variation of thickness with precursor solution concentration for the $CdIn_2Se_4$ thin films.

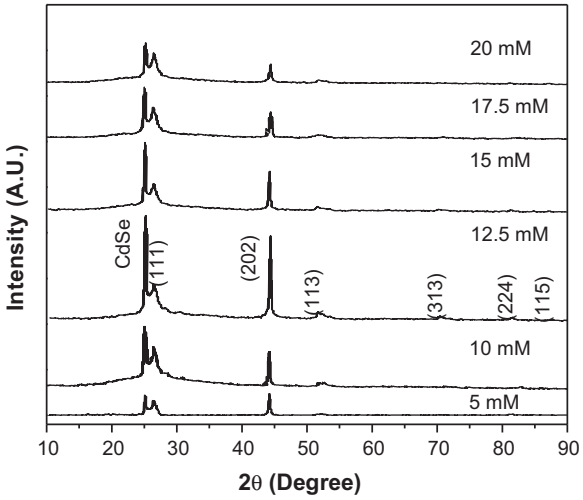

Fig. 3. X-ray diffraction patterns of the $CdIn_2Se_4$ thin films at various solution concentrations.

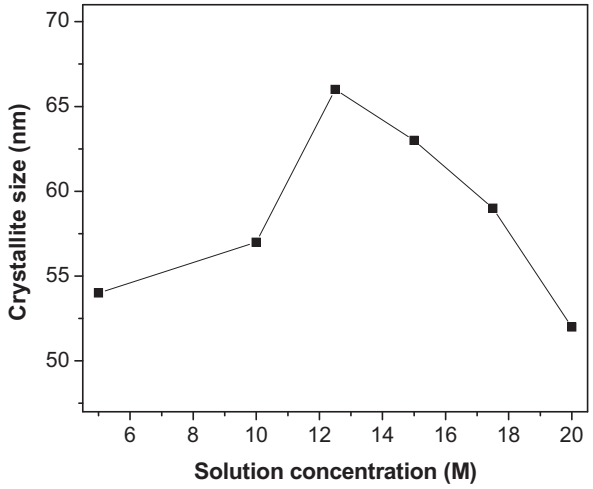

Fig. 4. Variation of crystallite size with respect to solution concentration of $CdIn_2Se_4$ thin films.

3.1. X-ray diffraction studies

Fig. 3 shows the X-ray diffraction patterns of deposited films at different precursor solution concentrations. The films are polycrystalline and fit well with the cubic crystal structure with preferred orientation along (2 0 2) plane (JCPDS card No. 8-267 and 8-459). The reason for relatively lower peak intensities is the lower film thickness and formation of amorphous plus nanocrystalline phase in thin films. Some weak reflections such as (1 1 1), (1 1 3), (3 1 3), (2 2 4) and (1 1 5) have also been observed but with small intensities. However (1 1 1) orientation of CdSe phase has been also observed. When the solution concentration increases, the intensity of the (2 0 2) peak increases up to 12.5 mM concentration and then decreases for higher concentrations. Comparison of standard [20,21] and calculated d values of the $CdIn_2Se_4$ thin films is shown in Table 1. As the solution concentration increases, crystallinity of the films increases may be due to the sufficient increase in growth of the grains. Further increase in solution concentration peak intensity decreases is attributed to the non-uniform and porous nature of the films. Observed full width at half maximum (FWHM) is corrected using the single crystal Si peak broadening. The crystallite size 'D' is calculated using Scherrer's formula [22,23]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{2}$$

where D is the crystallite size, β is the broadening of the diffraction line measured at half of its maximum intensity (rad) FWHM and λ is the X-ray wavelength (1.5405 Å). From Fig. 4, it is seen that as solution concentration increases the average crystallite size increases up to 12.5 mM concentration and tends to decrease afterwards. The tendency of a decrease in crystallite size with increase in concentration after 12.5 mM may be due to super-saturation of atoms.

The strain generated in deposited films are calculated by using formula [25]

$$\beta = \left[\frac{\lambda}{D\cos\theta}\right] - \left[\varepsilon \tan\theta\right] \tag{3}$$

where D is the crystallite size, β is the broadening of the diffraction line measured at half of its maximum intensity (rad) FWHM, λ is the X-ray wavelength, θ is Bragg's diffraction angle and ε is the strain. Dislocation density is defined as the length of dislocation lines per unit volume of the crystal [26]. The dislocation density is calculated using the formula given below [27]

$$\delta = \frac{1}{D^2} \tag{4}$$

where δ is the dislocation density. Fig. 5 shows the variation of dislocation density and strain generated in films with solution concentration. It is seen that, as solution concentration increases the dislocation density and strain generated in the films decreases with solution concentration and films prepared at a 12.5 mM is found to have minimum value of dislocation density and strain, thereafter the dislocation density and strain increases. Due to the fewer defects in the lattice, the strain in the films gets released and minimum value of strain is obtained for films prepared at a 12.5 mM. $CdIn_2Se_4$ thin films with lower strain and dislocation density improve the stoichiometry of the films which in turn causes volumetric expansion of films. The variation of crystallite size, strain and dislocation density with respect to solution concentration represents that the strain and dislocation density decreases whereas the crystallite size increases.

The texture coefficient (TC), represents the texture of a particular plane, whose deviation from unity implies the preferred growth. Quantitative information concerning the preferential crystallite orientation is obtained from different TCs ($h\,k\,l$) defined by

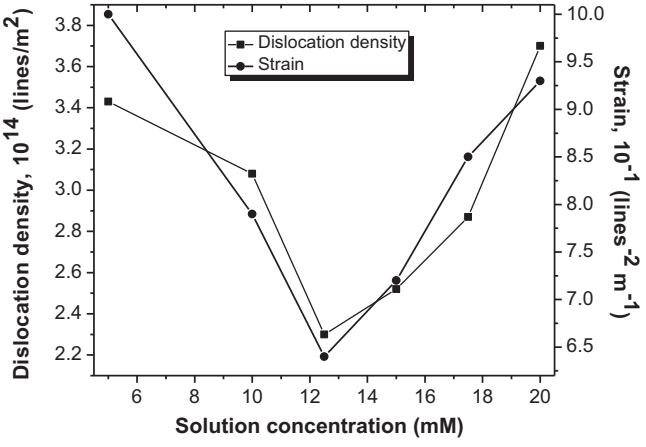

Fig. 5. Variation of dislocation density and strain with respect to solution concentration of $CdIn_2Se_4$ thin films.

Table 1
Comparison of observed and standard '*d*' values for the $CdIn_2Se_4$ thin films deposited at various solution concentrations.

Sr. no.	Standard '*d*' values (Å)	Observed '*d*' values (Å)					(*h k l*) planes
		0.005 M	0.01 M	0.0125 M	0.0150 M	0.0175 M	
1	3.3640	3.3502	–	3.3607	3.3576	3.3751	(1 1 1)
2	2.0600	2.0474	2.0485	2.0492	2.0487	2.0485	(2 0 2)
3	1.7510	1.7549	1.7498	1.7741	1.7724	1.7716	(1 1 3)
4	1.3340	1.3350	1.3312	1.3400	1.3361	1.3411	(3 1 3)
5	1.1839	1.1815	1.1831	1.1824	1.1837	1.1839	(2 2 4)
6	1.1200	1.1155	1.1185	1.1189	1.1191	1.1192	(1 1 5)

well-known relation [23,24]

$$TC(h\,k\,l) = \frac{I(h\,k\,l)/I_0(h\,k\,l)}{(1/N)\sum_N (I(h\,k\,l)/I_0(h\,k\,l))} \quad (5)$$

where $I(h\,k\,l)$ is measured intensity, $I_0(h\,k\,l)$ the JCPDS [20] intensity and N is the reflection number. Fig. 6 depicts the variation of the texture coefficient with solution concentration for the (2 0 2) plane. It is seen that, TCs of the (2 0 2) plane for the films deposited initially increases up to 12.5 mM solution concentration and decrease later. The observed TC along (2 0 2) plane is about 1.95 at optimized solution concentration due to formation of crystalline and stoichiometric films.

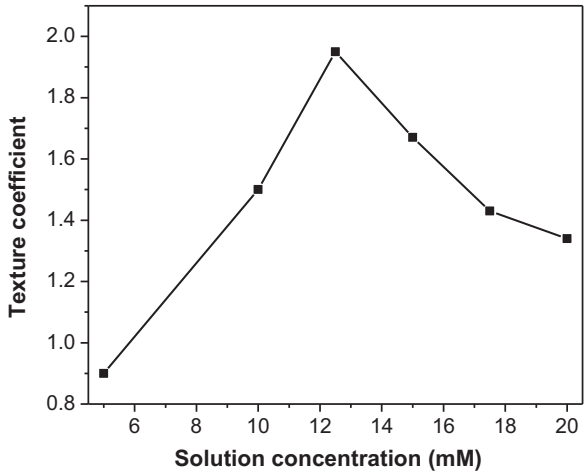

Fig. 6. Variation of texture coefficient along (2 0 2) plane with respect to solution concentration of $CdIn_2Se_4$ thin films.

3.2. Surface morphology

The surface morphology of $CdIn_2Se_4$ thin films has been analyzed using scanning electron microscope. Fig. 7(a–d) shows the morphology of the films deposited 5, 10, 12.5 and 15 mM solution concentrations. The micrograph shows polycrystalline nature of the film, with surface covered by non-uniformly distributed grains of varying sizes. At low solution concentration, film shows very thin and smooth growth surface. As we increase the solution concentration film thickness increases having non-uniformly distributed grains of varying sizes at optimized concentration, well covered smooth, uniform and pinhole free granular and rounded densely packed grains on the surface are observed. For higher concentrations the rough and randomly scattered with various sized grains are seen with some overgrown of particles. Moreover the growth

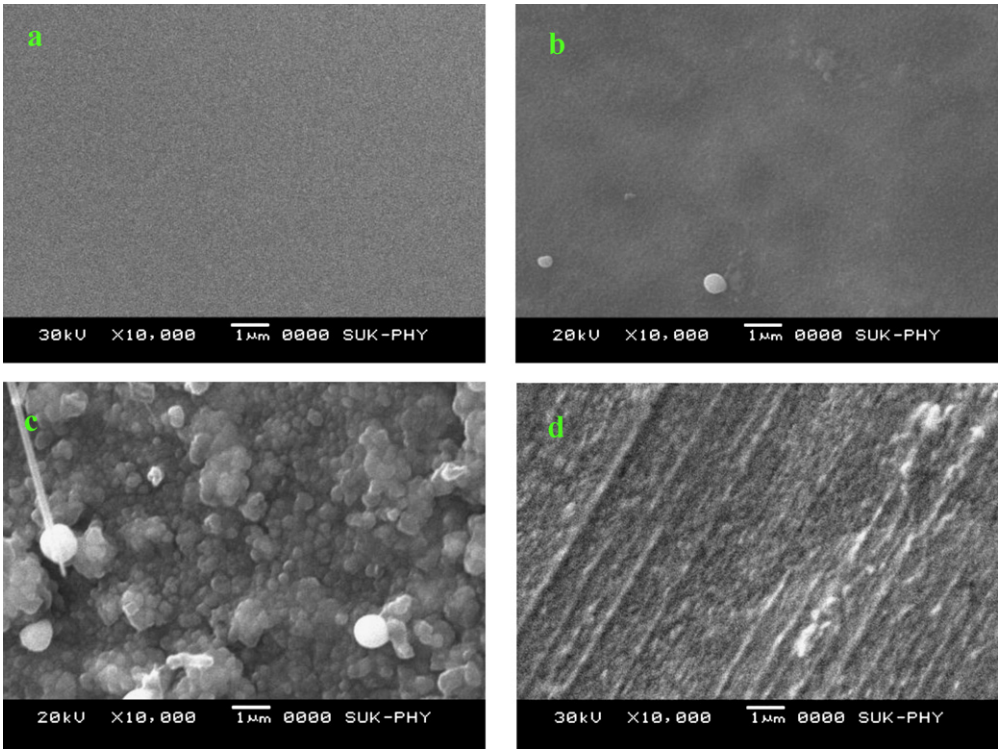

Fig. 7. Surface morphology of deposited $CdIn_2Se_4$ films at (a) 5 mM, (b) 10 mM (c) 12.5 mM and (d) 20 mM.

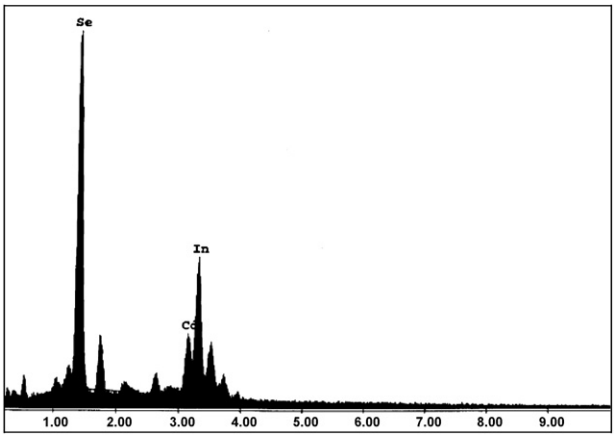

Fig. 8. EDX spectrum of $CdIn_2Se_4$ thin films deposited at optimized 12.5 mM solution concentration.

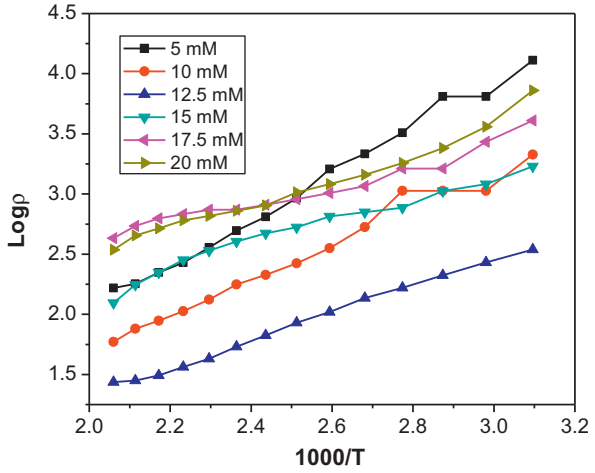

Fig. 9. Plot of log ρ vs. 1000/T for $CdIn_2Se_4$ thin films deposited at various solution concentrations.

rate of the films increases with the solution concentration. Hence, at high concentration, there is small probability of rearrangement of the arriving material and the inhomogeneity increases with solution concentration. The grains are dull grey in appearance with low specular reflectivity. The average size of the grains is found to be 70–150 nm. The film composition has been analyzed using an energy dispersive analysis by X-rays set up attached with scanning electron microscope. The EDX analysis has been taken out in order to determine elemental analysis of deposited film. The variation of Cd, In and Se content at 12.5 mM solution concentration for $CdIn_2Se_4$ thin films is shown in Fig. 8. The atomic molar ratio (Cd:In:Se) for $CdIn_2Se_4$ thin films prepared at a 12.5 mM is found to be 1.0:1.984:4.26 indicates the stoichiometric formation of $CdIn_2Se_4$ thin films. The elemental analysis of $CdIn_2Se_4$ thin film is tabulated in Table 2.

3.3. Electrical resistivity

The variation of log ρ vs. (1000/T) for the films deposited at various solution concentrations is shown in Fig. 9. The dc electrical resistivity decreases with increasing temperature confirms the semiconducting behavior of deposited $CdIn_2Se_4$ thin films. It shows that, as the solution concentration increases, the resistivity of the films decreases up to 12.5 mM and then increases for higher solution concentrations, because of the carrier concentration is a rapidly increasing with solution concentration. After 12.5 mM solution concentration the substrate temperature 553 K is insufficient to complete decomposition of the sprayed droplets of the solution results into non-uniform and porous films. The dc resistivity increases with increasing temperature because of the addition of thermal energy, electron could be set free from O^{2-} ions. The lowest resistivity achieved for films deposited at 12.5 mM concentration is about $3.9 \times 10^1\ \Omega$ cm. The randomly oriented grains possess higher trap density, leading to increase in resistivity for higher concentrations [28]. As the crystallinity increases, grain size increases thereby minimizing the grain boundary scattering losses and defects in the films. So the number of electron trap states reduces and hence the carrier concentration increases [22]. For the films deposited at relatively low solution concentrations (<12.5 mM) due to lower grain size of $CdIn_2Se_4$ particles, scattering at the grain boundaries result into higher resistivity of the films. As thickness increases grain boundary effect decreases leading to large mean free path, which in turn decreases, the scattering and thus the resistivity. The mean free path decreases up to 12.5 mM and then increases with solution concentrations might be due to the increase in the conductivity and carrier concentration of the films. The values of mean free path are 0.86, 0.071, 0.59, 0.68, 0.89 nm for solution concentration 5, 10, 12.5, 15, 17.5 mM, respectively.

For analysis of defect levels generated in the samples, the activation energy is calculated by using the relation [29]

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{kT}\right) \quad (6)$$

where ΔE is the activation energy, ρ is the resistivity at room temperature, k is the Boltzmann constant and ρ_0 is temperature independent constant. Fig. 10 shows the variation of activation energy with respect to solution concentrations. As the solution concentration increases up to 12.5 mM the activation energy decreases showing lowest value 0.00668 eV and then again increases for higher concentrations. It is interesting to notice that the activation energy increases due to grain relaxation with porosity. As the fraction of isolated grains increases, series resistance due to pore surface trapped in the grains, start to dominate grain or bulk relaxation, resulting into the increase in activation energy. The shallow

Table 2
Compositional analysis of $CdIn_2Se_4$ thin films deposited at 12.5 mM solution concentration.

Elements/solution concentration	Se (at%)	Cd (at%)	In (at%)
0.0125 M	58.84	13.79	27.37

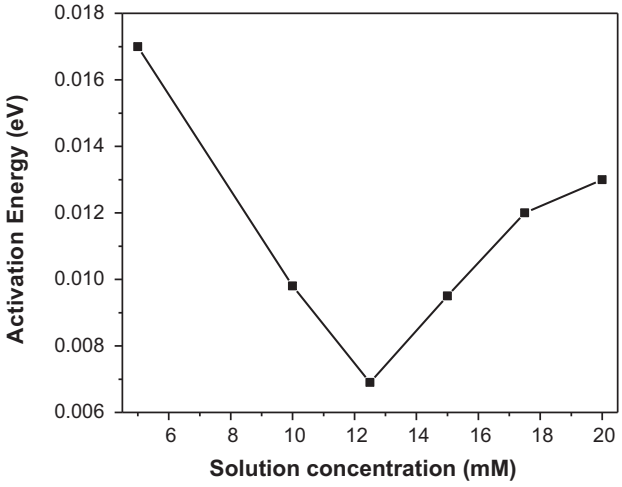

Fig. 10. Variation of activation energy w.r.t. solution concentrations of $CdIn_2Se_4$ thin films.

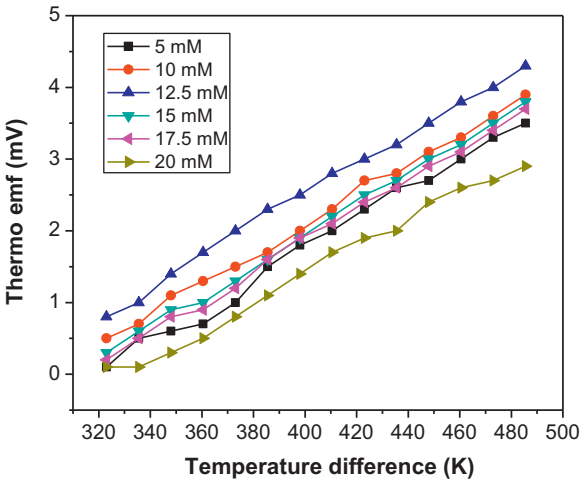

Fig. 11. Variation of thermo emf with temperature difference for spray deposited $CdIn_2Se_4$ thin films deposited at various solution concentrations (viz. 5–20 mM).

defects levels slightly disperse toward the Fermi level due to significant achievement of stoichiometry.

3.4. Thermoelectric power measurement

The type of conductivity exhibited by the spray deposited $CdIn_2Se_4$ thin films is determined from thermoelectric power measurement. The polarity of thermally generated voltage at the hot end is positive indicating that the films are of n-type. Fig. 11 shows the variation of thermo emf with respect to temperature difference for the films deposited at various solution concentrations. It is seen that, the thermo emf increases with solution concentration up to 12.5 mM concentration and then decreases for higher concentrations varies linearly with difference in temperature. Relatively higher thermo-emf is observed for the film prepared at 12.5 mM solution concentration may be due to higher crystallinity and well stoichiomtery of the film. Seebeck coefficient depends upon the location of Fermi energy in the material and the type of scattering mechanism. It increases as the Fermi energy moves further into the energy gap from the bottom edge of conduction band.

4. Conclusions

We have successfully deposited well adherent and stoichiometric thin films of the semiconducting n-$CdIn_2Se_4$ using a simple and inexpensive spray pyrolysis technique. The films of n-$CdIn_2Se_4$ are good photoactive and photoactivity is better for the film deposited at optimized solution concentration. X-ray diffraction patterns shows the films are polycrystalline in nature with cubic crystal structure. The crystallinity and texture coefficient increases up to optimized solution concentration and then decreases later and vice versa for dislocation density and strain. Micrographs shows the film surface is well covered by non-uniformly distributed grains with varying sizes. The stoichiometry of deposited films is confirmed by using EDX analysis. The lowest resistivity and activation energy achieved for films deposited at 12.5 mM concentration is about $3.9 \times 10^1\ \Omega$ cm and 0.0068 eV, respectively. The deposited thin films of $CdIn_2Se_4$ are of n-type confirmed with the help of TEP measurements.

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