



Electrosynthesis and studies on Cadmium-Indium-Selenide thin films

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ABSTRACT

Thin films of Cadmium Indium Selenide (CdIn_2Se_4) have been deposited on indium doped tin oxide coated conducting glass (ITO) substrates using potentiostatic cathodic electrodeposition technique. Cyclic voltammetry has been carried out in order to fix the deposition potential in the range between -1500 and $+600$ mV versus SCE. X-ray diffraction pattern shows that the deposited films exhibit tetragonal structure with most prominent reflection along (200) plane. The dependency of microstructural parameters such as crystallite size, strain and dislocation density with deposition potential has been studied. Surface morphology and film composition have been analyzed using scanning electron microscopy and energy dispersive analysis by X-rays, respectively. EDX analysis reveals that films with well defined stoichiometry has been obtained at a deposition potential -950 mV versus SCE. The optical band gap, refractive index and extinction coefficient are evaluated from optical absorption measurements. The experimental observations are discussed in detail.

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1. Introduction

Recently, ternary compounds of II-III-VI group attracts 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) has found applications in optoelectronics and solar cells due to its higher value of absorption coefficient. 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 [2–4]. Thin films of CdIn_2Se_4 are usually crystallized in tetragonal structure (JCPDS-ICDD, 08-0267) with lattice constants ($a = 5.820$ Å; $c = 5.8125$ Å). Tenne et al have prepared CdIn_2Se_4 single crystals and studied their properties using optical and photoelectrochemical techniques, respectively [2]. The preparation of CdIn_2Se_4 single crystals using Bridgmann method and their optical properties have been analyzed by Choe et al [3]. An analysis of published data signify that huge amount

of literature is available concerning the preparation and properties of bulk CdIn_2Se_4 [2–4] single crystals, but very few are available regarding thin films. Number of methods such as vacuum evaporation [6], slurry pasting technique [5] have been attempted to prepare CdIn_2Se_4 thin films and studied their properties. El-Nahass have prepared CdIn_2Se_4 thin films by vacuum evaporation method and studied their properties [6]. The preparation of CdIn_2Se_4 thin films by slurry pasting technique and their properties have been investigated by Tenne et al [5]. 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 the above mentioned techniques. CdIn_2Se_4 thin films obtained using electrodeposition method and their structural, morphological, compositional properties have been investigated earlier [7,8]. In the above mentioned works, the structural parameters such as crystallite size, strain, dislocation density and optical parameters such as refractive index and extinction coefficient have not been discussed. Electrodeposition is one of the suitable methods to prepare thin and continuous semiconductor films. Electrodeposition provides many advantages over vacuum and other process such as low temperature growth, control of film thickness and morphology, potentially low capital cost, etc., One obvious requirement is that the substrate must be conductive. This is not a problem for thin film

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solar cells, since they are deposited on a conducting substrate [9–11].

In the present work, thin films of CdIn_2Se_4 have been deposited on indium doped tin oxide coated conducting glass substrates at various deposition potentials using potentiostatic cathodic electrodeposition technique. The deposited films are subjected to X-ray diffraction, Scanning electron microscopy, Energy dispersive analysis by X-rays and Optical absorption techniques for their structural, morphological, compositional and optical properties. The effect of deposition potential on the above properties of the films are studied and the results are discussed.

2. Experimental Details

The chemicals used in the present work were of Analar grade reagents. Thin films of CdIn_2Se_4 were electrodeposited on indium doped tin oxide coated conducting glass substrates from an aqueous solution mixture containing 0.025 M CdSO_4 , 0.05 M $\text{In}_2(\text{SO}_4)_3$ and 0.005 M SeO_2 using potentiostatic electrodeposition technique. All the depositions were carried out using a PAR scanning potentiostat/galvanostat unit (Model 362, EG & G, Princeton Applied Research, USA) employing three electrode configuration with indium doped tin oxide coated conducting glass substrate as cathode, graphite plate as anode and saturated calomel electrode (SCE) as reference electrode, respectively. The electrolytic processes were monitored using cyclic voltammetry and governed potentiostatically. In cyclic voltammetric studies indium doped tin oxide coated glass substrate was used as cathode with constant potential plating. The depositions were carried out at various deposition potentials in the range between -750 and -1050 mV versus SCE. The bath temperature and solution pH were fixed as 70°C and 3.0 ± 0.1 , respectively.

Thickness of the deposited films was measured using stylus profilometer (Mitutoyo SJ 301). An X-ray diffractometer with $\text{CuK}\alpha$ radiation with wavelength ($\lambda = 1.540 \text{ \AA}$) was used to analyze the crystalline nature and phases of the deposited films. The surface morphology and film composition were analyzed using an energy dispersive analysis by X-rays set up attached with scanning electron microscope (JEOL JSM 840). Optical absorption measurements of the deposited films was recorded using an UV-Vis-NIR spectrophotometer (HR-2000, M/S Ocean Optics).

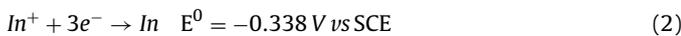
3. Results and Discussion

3.1. Electrochemistry of CdIn_2Se_4 thin films

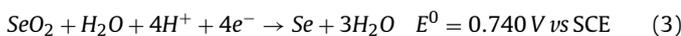
The electrodeposition of CdIn_2Se_4 thin films is carried out potentiostatically from an aqueous acidic bath containing CdSO_4 , $\text{In}_2(\text{SO}_4)_3$ and SeO_2 . The electrochemical reactions involving the codeposition of Cd, In and Se are described as follows [12]



$$E_{\text{Cd}} = E_{\text{Cd}}^0 + \left[\frac{RT}{2F} \right] \ln \left[\frac{a_{\text{Cd}^{2+}}}{a_{\text{Cd}}} \right]$$



$$E_{\text{In}} = E_{\text{In}}^0 + \left[\frac{RT}{3F} \right] \ln \left[\frac{a_{\text{In}^{3+}}}{a_{\text{In}}} \right]$$



$$E_{\text{Se}} = E_{\text{Se}}^0 + \left[\frac{RT}{4F} \right] \ln \left[\frac{a_{\text{SeO}_2}}{a_{\text{Se}}} \right] + \left[\frac{RT}{4F} \right] \ln (a_{\text{H}^+})^4$$

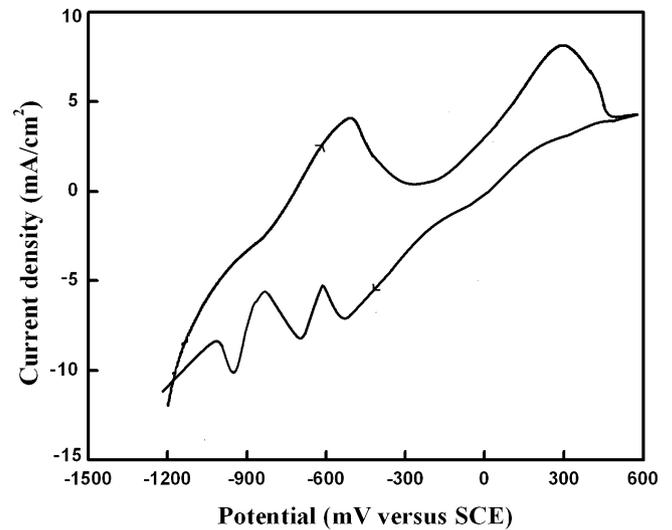
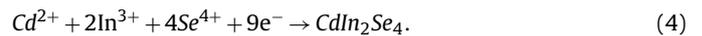


Fig. 1. Cyclic voltammogram of ITO glass electrode in an aqueous solution mixture containing 0.025 M CdSO_4 , 0.05 M $\text{In}_2(\text{SO}_4)_3$ and 0.005 M SeO_2 .

where E_{Cd}^0 , E_{In}^0 , E_{Se}^0 are the standard reduction potential of Cd, In and Se respectively with respect to SCE and $a_{\text{Cd}^{2+}}$, $a_{\text{In}^{3+}}$ are the activities of Cd and In ions present in the electrolyte. a_{Cd} , a_{In} are the activities of respective atoms present in the deposited films. The deposition of Cd and In occurs at potentials more positive than their standard reduction potentials by gaining free energy in the compound formation. It has been reported that under potential deposition of less noble constituent here (In) of a compound (CdIn_2Se_4) is brought about by the gain of free energy by its formation. Hence, in order to obtain co-deposition of CdIn_2Se_4 , we have used a higher concentration of less noble constituent (here In) and lower concentration of noble metal (here Cd) and too lower concentration of more noble constituent (here Se) in order to bring the electrode potentials of three deposits closer. The mechanism of formation of CdIn_2Se_4 is described by the following equation [12].



Cyclic voltammetric studies has been carried out in a standard three compartment cell comprising of indium doped tin oxide coated conducting glass substrate as cathode, graphite plate as anode and saturated calomel electrode as reference electrode, respectively. The scan rate employed is 20 mV/sec. The voltammetric curves are scanned in the potential range from -1500 to $+600$ mV versus SCE. A typical cyclic voltammogram recorded for ITO glass electrode in an aqueous solution mixture containing 0.025 M CdSO_4 , 0.05 M $\text{In}_2(\text{SO}_4)_3$ and 0.005 M SeO_2 is shown in Fig. 1. It is observed from Fig. 1 that the voltammetric curve shows the reduction of all three precursors. A reduction peak I observed at -520 mV versus SCE may be responsible for the reduction of H_2SeO_3 to Se according to Eq. (3). The reduction peak II observed at -710 mV versus SCE may be due to the reduction of cadmium ion according to the Eq. (1). Reduction peak III observed at -950 mV versus SCE displays strong (cathodic) photoeffect. This may be ascribed to the formation of CdIn_2Se_4 system according to the following Eq. (4). On further decreasing the deposition potential, an oxidation peak observed at -520 mV versus SCE which may be due to the stripping off of the metallic indium layer. The reoxidation of In produced during the forward scan would be impossible when covered completely by CdIn_2Se_4 which is only stripped off at more positive potentials such as 300 mV versus SCE. On more positive potential an anodic photoeffect is observed, whereas at more negative potential cathodic photoeffect is observed. The photo effects observed in the above process produces an intrinsic semi-

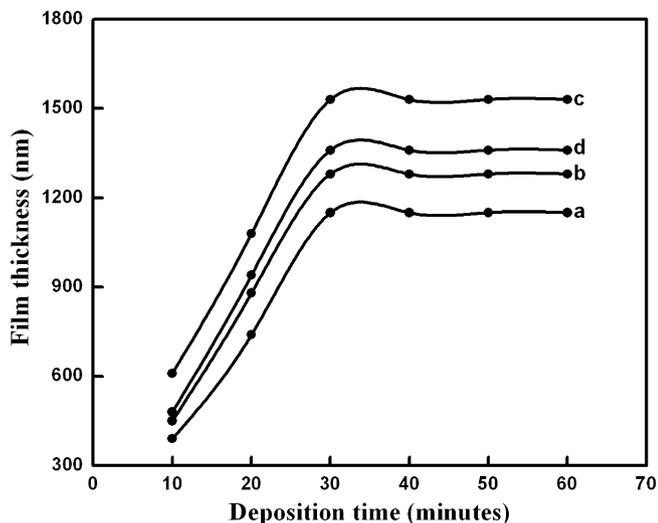


Fig. 2. Variation of film thickness with deposition time for CdIn₂Se₄ thin films obtained at various deposition potentials: (a) –750 (b) –850 (c) –950 (d) –1050 mV versus SCE.

conductor depending upon the deposition potential. No unique element is formed, but sequence of layers corresponding to different compositions are obtained in the potential range between –750 and –1050 mV versus SCE. The results of the cyclic voltammetry on CdIn₂Se₄ system represent that the potential range of –750 and –1050 mV versus SCE may be used for the preparation of CdIn₂Se₄ thin films [12].

3.2. Thickness and rate of deposition

Thickness of the deposited films is controlled by two independent variables such as (i) uniform growth (ii) surface morphology. The film thickness is measured using stylus profilometer. By controlling the deposition potential and plating time thickness of the deposited films could be controlled. Fig. 2 shows the variation of film thickness with deposition time for CdIn₂Se₄ thin films obtained at various deposition potentials ranging from –750 to –1050 mV versus SCE. It is observed from Fig. 2 that the films with lower thickness with irregular growth is obtained at lower deposition potential such as below –750 mV versus SCE. The films prepared at higher deposition potential such as above –950 mV versus SCE, thickness of the film decreases due to hydrogen evolution [9]. Hence the films obtained in the potential region between –750 and –1050 mV versus SCE are found to be uniform and dense. It is observed from Fig. 2a, that the film thickness increases linearly with deposition time and tend to attain saturation after 30 minutes of deposition. Further increasing deposition time above 30 minutes thickness of the film remains constant up to 60 minutes, thereafter thickness of the film decreases slightly not shown in Fig. For this reason the deposition time is fixed as 30 minutes in order to get films with higher thickness. Similar trend is observed for films obtained at different deposition potentials such as –850, 950 and –1050 mV versus SCE. The maximum value of film thickness is obtained for films prepared at a deposition time of 30 minutes and at a deposition potential of –950 mV versus SCE.

3.3. Structural studies

X-ray diffraction pattern recorded for CdIn₂Se₄ thin films prepared on ITO substrates with bath composition of 0.025 M CdSO₄, 0.05 M In₂(SO₄)₃ and 0.005 M SeO₂ at various deposition potentials ranging from –750 to –1050 mV versus SCE is shown in Fig. 3. X-ray diffraction patterns revealed that the deposited films possess

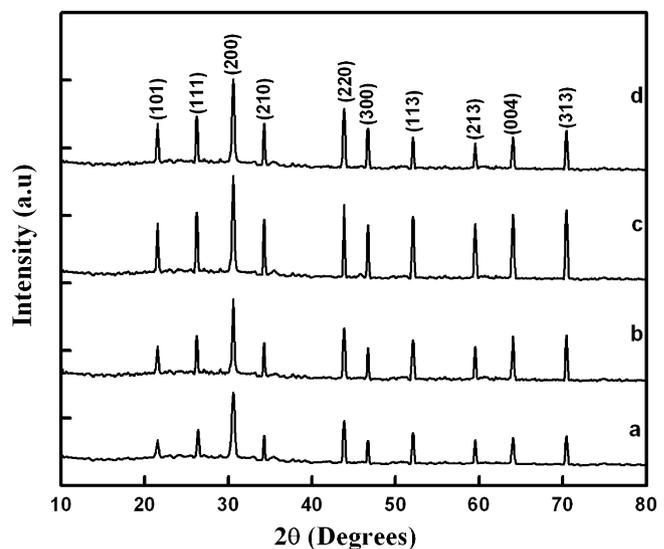


Fig. 3. X-ray diffraction pattern obtained for CdIn₂Se₄ thin films obtained at various deposition potentials: (a) –750 (b) –850 mV (c) –950 (d) –1050 mV versus SCE.

polycrystalline nature with tetragonal structure with lattice constants ($a = 5.820 \text{ \AA}$; $c = 5.8125 \text{ \AA}$). The diffraction peaks of tetragonal CdIn₂Se₄ are found at 2θ values of angles 21.52, 26.22, 30.57, 34.27, 43.82, 46.67, 52.07, 59.52, 64.02, 70.42 corresponding to the lattice planes (101), (111), (200), (210), (220), (300), (113), (213), (004) and (313), respectively. The different peaks in the diffractogram are indexed and the corresponding values of interplanar spacing 'd' are calculated and compared with standard values [13]. All the peaks identified are from CdIn₂Se₄ and no additional lines corresponding to Cd, In and Se are present. Fig. 3 represents that the degree of crystallinity of the deposited films increased while increasing the deposition potential from –750 to –950 mV versus SCE, thereafter the degree of crystallinity decreases slightly. The height of (200) plane is found to be higher than all other planes in X-ray diffraction pattern indicates that the deposited films exhibits preferential orientation along (200) planes. It is also observed from Fig. 3 that the height of preferential peak is found to increase while increasing the deposition potential from –750 to –950 mV versus, afterwards it decreases slightly. The decrease in peak height for films obtained at potential above –950 mV versus SCE which may be due to the process of hydrogen evolution. The process of hydrogen evolution apparently reduces the plating efficiency by ejecting the already deposited materials into the solution [14]. The films obtained at a potential –950 mV versus SCE has sharper peaks with small FWHM data results higher value of crystallite size than films obtained at other potentials. The crystallite size of the deposited films are calculated using FWHM data and Debye Scherrer formula given below [10].

$$D = \frac{0.9\lambda}{\beta \cos \theta_B} \quad (5)$$

where λ is the wavelength of CuK α target used ($\lambda = 1.540 \text{ \AA}$), θ_B is Bragg's diffraction angle at peak position in degrees and β is Full Width at Half Maximum of the peak in radian. The strain in the deposited films are calculated from the slope of $\beta \cos \theta$ versus $\sin \theta$ plot by using the formula given below [9]

$$\beta = \left[\frac{\lambda}{D \cos \theta} \right] - [\varepsilon \tan \theta] \quad (6)$$

Dislocation density is defined as the length of dislocation lines per unit volume of the crystal [15]. The dislocation density is cal-

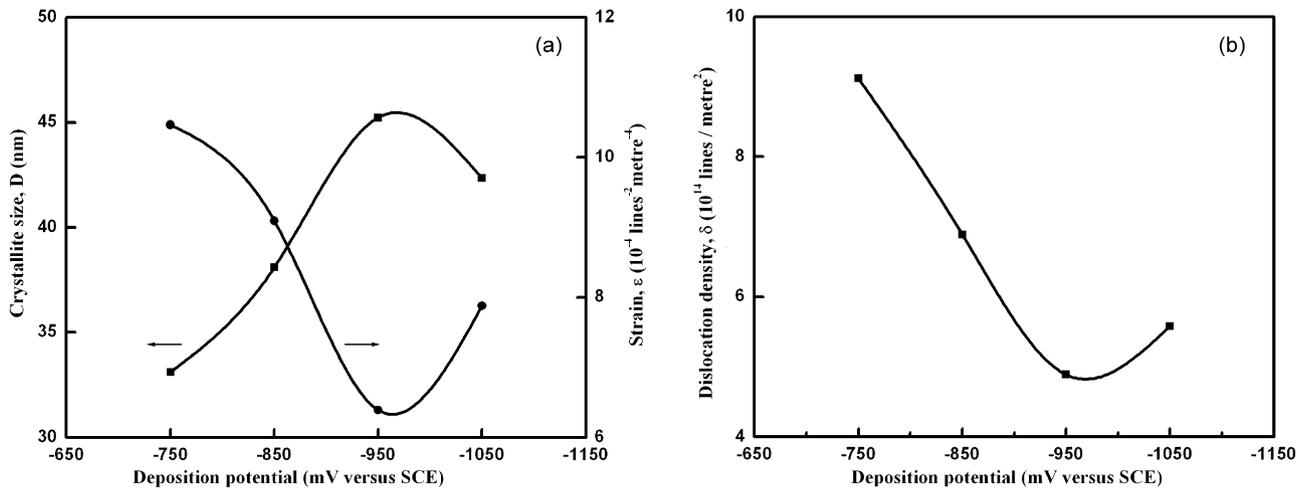


Fig. 4. (a) Variation of crystallite size and strain with deposition potential for films obtained under different deposition potentials; (b) Variation of dislocation density with deposition potential for films obtained under different deposition potentials.

culated using the formula given below [10]

$$\delta = \frac{1}{D^2} \quad (7)$$

Fig. 4a shows the variation of crystallite size and strain with deposition potential for CdIn_2Se_4 thin films obtained at various deposition potentials ranging from -750 to -1050 mV versus SCE. It is observed from Fig. 4a that the crystallite size increases with deposition potential and the films prepared at a deposition potential -950 mV versus SCE are found to have maximum value of crystallite size, thereafter the crystallite size slightly decreases. Due to the release defects in the lattice, the strain in the films gets released and minimum value of strain is obtained for films prepared at a deposition potential -950 mV versus SCE. A sharp increase in crystallite size and decrease in strain with deposition potential is observed in Fig. 4a. Decrease in value of strain with deposition potential results decrease in value of interplanar spacing which leads to decrease in value of dislocation density which is calculated using Eq. (7) and shown in Fig. 4b. It is also observed from Fig. 4a and b minimum value of strain and dislocation density are obtained for films prepared at a deposition potential of -950 mV versus SCE. CdIn_2Se_4 thin films with lower strain and dislocation density improves 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 deposition potential represents that the strain and dislocation density decreases whereas the crystallite size increases. Similar behaviour of variation of above parameters with respect to bath temperature and deposition potential has been reported earlier [9,10].

3.4. Surface morphology and film composition

The surface morphology of CdIn_2Se_4 thin films has been analyzed using scanning electron microscope. The SEM picture of CdIn_2Se_4 thin films obtained at optimized deposition potential of -950 mV versus SCE is shown in Fig. 5. Fig. 5 represents that the surface is observed to be rough with evenly distributed grains. The grains are dull grey in appearance with low specular reflectivity. The sizes of the grains are found to be in the range between 0.20 and $0.38 \mu\text{m}$. The average size of the grains is found to be $0.29 \mu\text{m}$. 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 the relationship between deposition potential and film composition. The variation of Cd, In and Se content with deposition potential

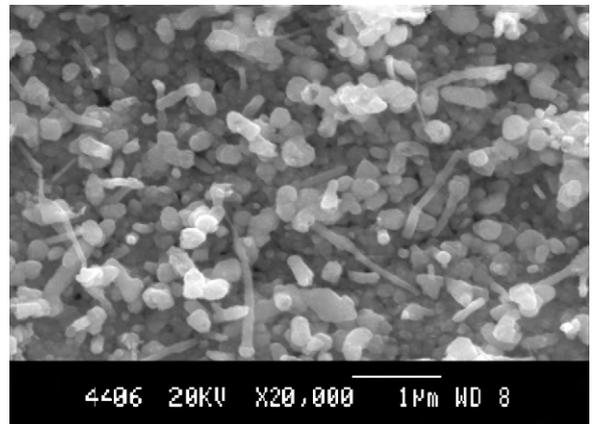


Fig. 5. SEM image of CdIn_2Se_4 thin films obtained at deposition potential -950 mV versus SCE.

for CdIn_2Se_4 thin films obtained at different deposition potential is shown in Fig. 6. The atomic molar ratio (Cd:In:Se) for CdIn_2Se_4 thin films prepared at a deposition potential -950 mV versus SCE is found to be 1.04:1.90:4.06 indicates the stoichiometric formation

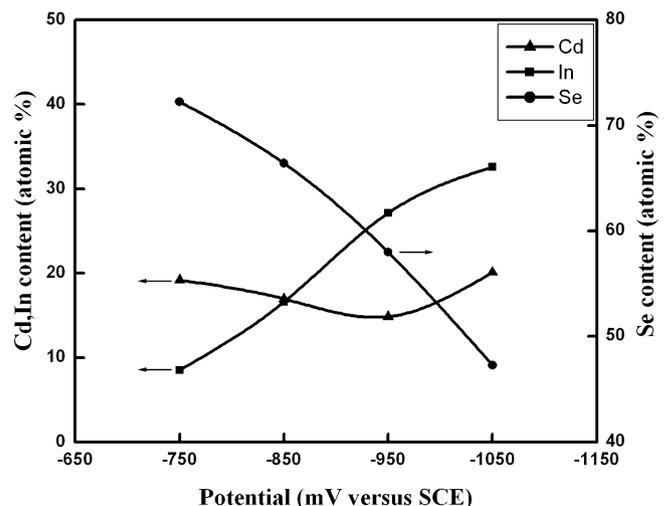


Fig. 6. Variation of Cd, In and Se content with deposition potential for films obtained at various deposition potentials.

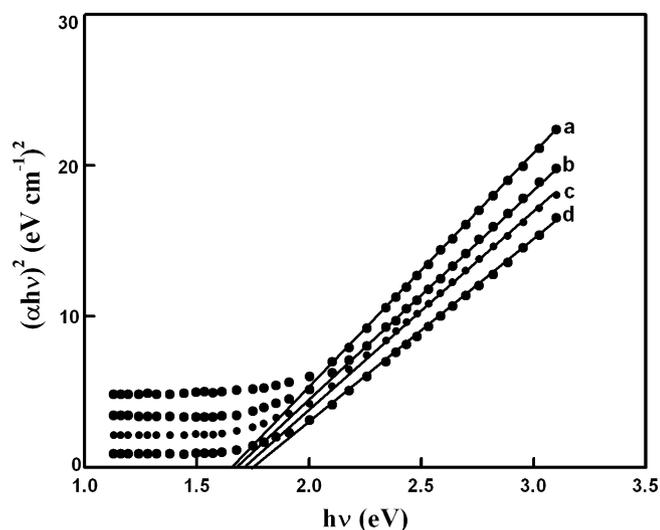


Fig. 7. Plot of $(\alpha h\nu)^2$ versus $(\alpha h\nu)^2$ for CdIn_2Se_4 thin films obtained at a deposition potential in the range between -750 and -1050 mV versus SCE.

of CdIn_2Se_4 thin films. Similar result has been reported earlier for CdIn_2Se_4 thin films [7,8]. It is observed from Fig. 6 that the content of Cd and In increased and the content of Se decreased while increasing the deposition potential from -750 to -1050 mV versus SCE. The content of In for films obtained at more negative potential -1050 mV versus SCE is found to be higher than films obtained at other potentials which may be due to thermodynamic reduction potential given in Eq. (2)[7,12]. Similarly the content of Cd is found to be high for films obtained at -1050 mV versus SCE than films obtained at other potentials.

3.5. Optical properties

The absorbance and transmission measurements have been taken out using an UV-Vis-NIR spectrophotometer in order to determine the band gap value of the material. The absorption coefficient (α) of the deposited films is calculated from the observed absorbance and transmittance values using the following Eq. (8) [16,17].

$$\alpha = \frac{1}{t} \ln \left(\frac{A}{T} \right) \quad (8)$$

where α is the absorption coefficient in cm^{-1} , t is the film thickness, A is absorbance and T is transmittance. The nature of transition is determined using the following Eq. (9) [10].

$$\alpha h\nu = A(h\nu - E_g)^n \quad (9)$$

where A is an energy dependent constant, E_g is the band gap of the material, $h\nu$ is photon energy. Optical absorption and transmission spectra of CdIn_2Se_4 thin films have been recorded as a function of wavelength in the range between 350 and 1100 nm. Substrate absorption if any, was corrected by introducing an uncoated ITO substrate in the reference beam. The value of absorption coefficient (α) rises sharply owing to band-to-band transition and levels off later. An analysis of absorption spectrum in the energy range 1.0 eV and 3.5 eV indicates that α follows the relation. A plot of $(h\nu)$ versus $(\alpha h\nu)^2$ drawn for films obtained at various deposition potentials ranging from -750 to -1050 mV versus SCE (Fig. 7). The linear portion of the plot is extrapolated to the energy axis (X-axis) which is shown in Fig. 7. The intersection point gives the band gap energy of the material. The estimated value of band gap is found to be in the range between 1.66 and 1.75 eV [8,18,19]. The band gap value of the material obtained in the present work is found to be

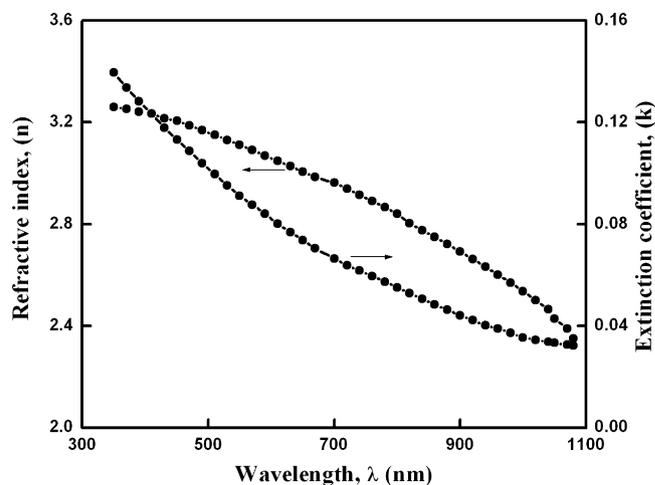


Fig. 8. Variation of refractive index (n) and extinction coefficient (k) with wavelength (λ) for CdIn_2Se_4 thin films obtained at a deposition potential -950 mV versus SCE.

in close agreement with the value reported earlier [8]. The variation of refractive index and extinction coefficient with wavelength for CdIn_2Se_4 thin films obtained at deposition potential -950 mV versus SCE is shown in Fig. 8. Fig. 8 represents that both refractive index and extinction coefficient decreases with respect to wavelength. The value of refractive index and extinction coefficient are found to be 2.86 and 0.03.

4. Conclusions

Thin films of CdIn_2Se_4 have been deposited on indium doped tin oxide coated conducting glass substrates at various deposition potentials using potentiostatic electrodeposition technique. Cyclic voltammetric study is used to fix the deposition potential in the range between -1500 and $+600$ mV versus SCE. X-ray diffraction pattern of the prepared films shows the formation of polycrystalline films with preferential orientation along (200) plane. The structural parameters such as crystallite size, strain and dislocation density are evaluated and their dependency with deposition potential is investigated. Stoichiometric films with well defined composition have been obtained at a deposition potential -950 mV versus SCE. Optical absorption measurements shows that the deposited films exhibit direct band gap value in the range between 1.66 and 1.75 eV for films obtained at various deposition potentials. The value of refractive index and extinction coefficient are found to be 2.86 and 0.03.

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