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CHARACTERIZATION OF ELECTRODEPOSITED INDIUM DOPED CdSe THIN FILMS

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Thin films of CdSe and In:CdSe were deposited onto indium doped tin oxide coated conducting glass (ITO) substrates by electrodeposition technique. The appropriate potential region for the formation of stoichiometric CdSe and In-doped CdSe thin films occurs was found to be -700 mV versus SCE. The structural investigations performed by means of X-ray diffraction (XRD) technique, Scanning electron microscopy (SEM), energy dispersive analysis by x-rays (EDS), and optical studies for the determination of structural, morphological, compositional and optical properties. X-ray diffraction shows development of well-crystallized film with hexagonal structure. The parameters such as crystallite size, strain, and dislocation density are calculated from X-ray diffraction studies. SEM studies reveal that the films with uniformly distributed grains over the entire surface of the substrate. The surface morphology is found to be modified due to doping. The energy dispersive X-rays analysis indicates that the atomic percentage. The films show good optical properties and transmittance study shows the presence of direct transition and a considerable decrease in band gap, Eg 1.7 eV to 1.63 eV.

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1. Introduction

In recent years, electrodeposited thin film semiconductors are popular in the field of solar cells, opto-electric devices, solar selective coating, IR detectors, lasers and light emitting diodes [1-8]. Among II-IV group, cadmium selenide (CdSe) having cubic and hexagonal crystal structure is considered to be a potential candidate for photo electrochemical conversion because of the compatibility of its band gap (1.7 eV) with the solar spectrum [9]. Major attention has been given to the investigation of the electric and optical properties of CdSe thin films in order to improve the performance of the devices and also to find new applications [10,11]. A variety of methods have been used to prepare CdSe and In:CdSe thin films including vacuum evaporation [12], sputtering, chemical bath deposition , chemical vapour deposition, spray pyrolysis, and electrodeposition[13] , etc.,

In this work, the preparation and characterization of CdSe and In:CdSe thin films in terms of structural, optical, photoluminescence properties along with morphological and compositional analyses of the films were carried out. The effects of bath temperature and various concentrations of indium on the structural, morphological, compositional, optical and photoluminescence properties of CdSe and In-doped CdSe thin films are studies and reported.

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2. Experimental details

Electrodeposition technique was adopted for the preparation of cadmium selenide (CdSe) and In-doped cadmium selenide (In:CdSe) thin films. The chemicals used for the preparation were analytical reagent grade (99 % purity, E-Merck). The electrochemical experiments were performed using a PAR scanning potentiostat (Model 362, EG&G, Princeton Applied Research, USA) employing a three- electrode configuration, with the indium doped tin oxide coated conducting class substrate as cathode, graphite plate as anode and saturated calomel electrode (SCE) as reference electrode. Before use, indium doped tin oxide substrates were treated for 15 min with ultrasonic waves in a bath of isopropanol and then rinsed with acetone. The saturated calomel electrode was introduced into the solution by luggin capillary whose tip was placed as close as possible to the working electrode. All the experimental potentials are referred to this electrode. An aqueous electrolytic bath containing 250 mM of $CdSO_4$ and 2.5 mM of SeO_2 are nearly stoichiometric. When the $CdSO_4$ concentration is kept below 200 mM there is no incorporation of Cd ions in the film. If the concentration of $CdSO_4$ is increase above 250 mM there is an excess of Cd content in the films. It was observed that a very low pH<2.5 value the films grow spontaneously at high current densities making the process uncontrollable. The rapid growth of films followed by its peeling out from the substrate is observed. At pH>3.0, precipitation of $CdSO_4$ occurs in the deposition bath. At pH value around 2.5±0.1, there is controllable growth of films with current density around 10mA cm^{-2}. Hence, the optimum value of pH for all depositions was fixed at 2.5±0.1. Deposition period was 30 minutes, as which uniform and adherent films were obtained. After 30 minutes there is a rapid growth of films followed by peeling out from the substrate. The potential of the electrolytic bath was increased or decreased from -750 mV to -650 mV. When the potential is increased -750 mV and decreased below -650 mV, there is a rapid growth of the film followed by feeling out from the substrate itself. The potential was fixed at -700 mV versus SCE for all depositions. The optimum condition to synthesize In:CdSe thin films are identified as: (i) electrolyte concentration: 250 mM of $CdSO_4$, 2.5 mM of SeO_2 and various concentrations of $InCl_3$; (ii) solution pH: 2.5±0.1; (iii) deposition potential:-700 mV versus SCE; (iv) bath temperature: 75 ºC; (v) deposition time: 30 min.

Thickness of the deposited films was estimated using ‘stylus profilometer’. X-ray diffraction data of the electrodeposited undoped CdSe and In-doped CdSe samples were recorded with the help of Philips Model PW 1710 diffractometer with Cu Kα radiation (λ=0.1542 nm). Surface morphological and compositional analyses were carried out using a scanning electron microscope and energy dispersive X-ray analysis setup (EDAX) attached with SEM (Philips Model XL 30), respectively. Optical transmittance spectrum was recorded using a JASCO-V-570 spectrophotometer.

3. Results and Discussion

Growth Kinetics

Deposition of CdSe thin film occurs when the ionic product of Cd^{2+} and Se^{2-} ions exceeds the solubility product of CdSe, and same is the case in the deposition of Indium doped CdSe thin film. The control of Cd^{2+} and Se^{2-} ions along with In^{3+} ions in the case of In-doped CdSe film on indium doped tin oxide (ITO) substrate may be expressed as follows,

$$3CdSO_4.8H_2O + H_2O \longleftrightarrow Cd^{2+} + SO_4^{2-} + 9H_20$$

$$SeO_2 + H_2O \longleftrightarrow H_2SeO_3$$

On reduction of H_2SeO_3

$$H_2SeO_3 + 4H^+ + 6e^- \longleftrightarrow Se^{2-} + 3H_2O$$

And the formation of CdSe takes place according to the chemical reaction.

$$Cd^{2+} + Se^{2-} \longleftrightarrow CdSe$$

When indium trichloride is added in the electrolyte, In:CdSe thin film formation occurs due to the following reaction;

$$Cd^{2+} + In^{3+} + Se^{2-} \longleftrightarrow Cd(In)Se$$

The deposition of CdSe and In:CdSe thin films were controlled by two independent variables such as: (i) film thickness and its uniformity and (ii) surface morphology [14]. Thickness of the CdSe and In:CdSe were measured using 'stylus profilometer'. Figure 1(a), (b), (c) and (d) shows the variation of film thickness with deposition time of CdSe and In:CdSe thin films growth. The film thickness increases with deposition time and reaches a maximum value of 825.97 nm in 30 min for the deposition temperature of 55 ºC and indium concentration 0.02 mM. Cadmium dendrites were also observed on films deposited at bath temperature 55 ºC. Above 55 ºC, the decomposition of water with the subsequent hydrogen evolution was observed. This may be due to the fasted release of ions. It is observed from figure 1c that the film thickness increases linearly with deposition time 40 min and tends to attain saturation. The bath temperature is expected to influence the deposition rate by (i) increase of precursor solubility and (ii) increase of the diffusion coefficient and the decrease of viscosity. Due to the increase in solubility of precursor with bath temperature, higher thickness was obtained at bath temperature of 55 ºC and indium concentration 0.02 mM.

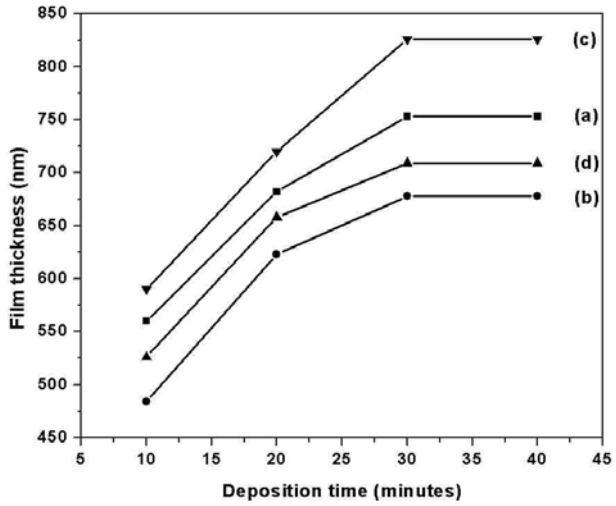

Figure 1 Variation of film thickness with deposition time for : (a) CdSe thin film and In:CdSe thin films at various indium concentrations in the solution ratios: (b)0.01 mM, (c)0.02 mM and (d)0.03 mM.

XRD patterns of the electrodeposited thin films prepared on indium doped tin oxide (ITO) substrates with bath composition 250 mM $CdSO_4$, 2.5 mM SeO_2 and various indium concentrations at bath temperature 55 ºC are shown in Figure.2 (a), (b), (c) and (d). The XRD patterns revealed that the deposited films are found to be hexagonal crystal structure is highest peak corresponds to the (001), (002), (102) and (103) phase of hexagonal CdSe. The different peaks in the diffractogram were indexed and the corresponding values of interplanar spacing "d" were calculated and compared with standard values of JCPDS data [15]. To get quality film, In:CdSe film was deposited 55 ºC and indium concentration 0.01 mM it is found to be poorly crystallized. This is indicated by broad XRD peaks in Figure 2 (b). It is found that deposition bath temperature 55 ºC and indium concentration 0.02 mM led to the formation of well-crystallized films. Figure 2 (b), (c) and (d), the addition of In^{3+} ions in CdSe was found to increase the intensity of peaks, addition peaks and shifting of peak positions. It is observed from Figure 2 (c) deposition bath temperature 55 ºC and indium concentration 0.02 mM resulted in good quality films with improved crystallinity as evidenced by intense diffraction peaks indicated in Figure 2 (c).

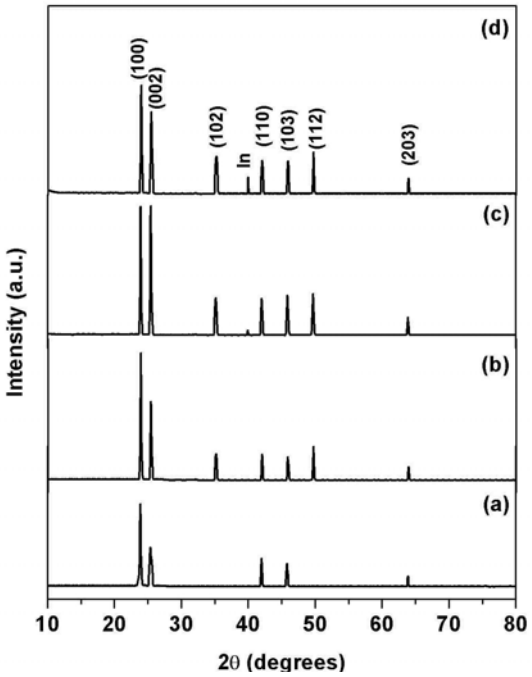

Figure 2. XRD patterns of: (a) CdSe thin film and In:CdSe thin films at various indium concentrations in the bath: (b) 0.01 mM, (c) 0.02 mM and (c) 0.03 mM.

X-ray diffraction patterns of In:CdSe thin films deposited bath temperature 55 ºC and various indium concentrations from 0.01 mM, 0.02 mM and 0.03 mM are recorded. Using FWHM data and Debye-Scherrer formula, the crystallite size of the films was calculated. The strain ε was calculated from the slope of βcosθ versus sinθ. The variation of crystallite size and strain with indium concentration for In:CdSe thin films deposited at bath temperature 55 ºC and various indium concentrations from 0.01 mM, 0.02 mM and 0.03 mM is shown in Figure 3 (a). It is observed from Figure 3 (a), that the crystallite size increases with indium concentration and films deposited at bath temperature 55 ºC and indium concentration 0.02 mM are found to have maximum value of crystallite size and decreases strain, thereafter increase indium concentration 0.03 mM crystallite size slightly decreases. The dislocation density (δ) can be evaluated from Williamson and Smallman's formula, Figure 3 (b) represents the variation of dislocation density with indium concentration for In:CdSe thin films. It is observed from Figure 3 (b) the dislocation density is found to decrease while increasing indium concentrations from 0.01 mM, 0.02 mM and 0.03 mM, thereafter it is slightly increases. A sharp increase in crystallite size and decrease in strain with indium concentration indicated in Figure 3 (a). Such a release in strain reduced the variation of interplanar spacing and thus leads to decrease in dislocation density of In:CdSe thin films and minimum values are obtained for films deposited at temperature 55 ºC and indium concentration 0.02 mM. Crystallinity improvement with indium concentration enhances the

concentration and mobility of Cd ion vacancies within the lattice and hence reduces the resistivity of the films. The studies on functional dependency of strain, dislocation density with indium concentration indicate that the strain, dislocation density decrease with indium concentration whereas the crystallite size increases.

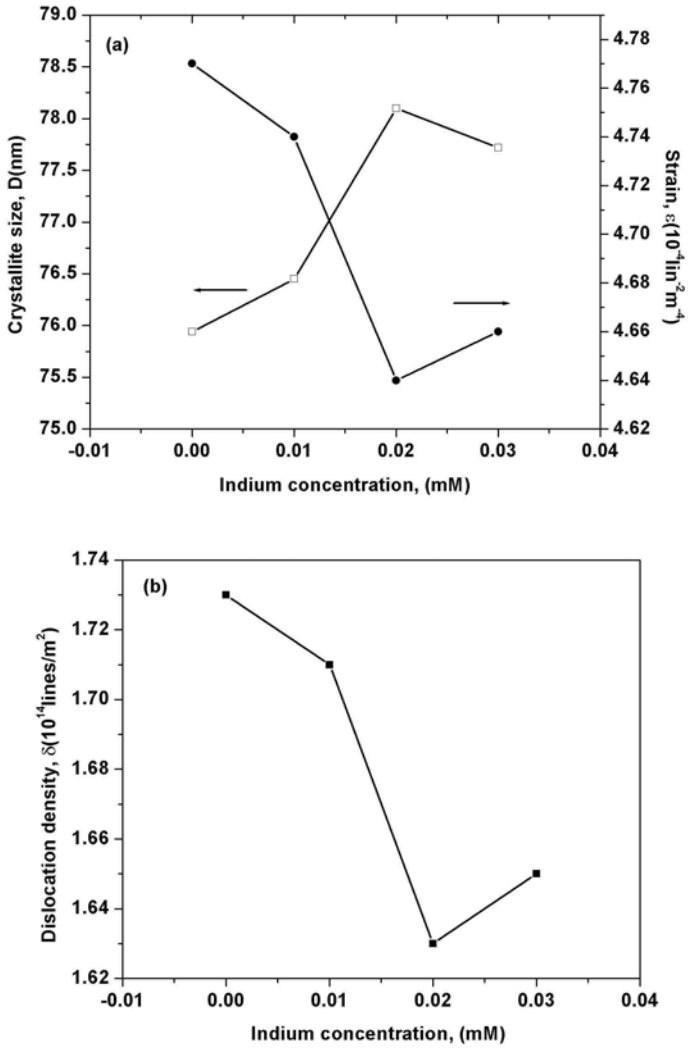

Fig. 3 (a). Variation of crystalline size and strain with various indium concentrations in the solution bath for In:CdSe thin films. (b) Variation of dislocation density with various concentrations in the solution bath for In:CdSe thin films.

The surface morphology of CdSe and In:CdSe films electrodeposited at bath temperature 55 ºC for deposition time 30 min is shown Figure 4(a) and (b). Surface morphological studies of the CdSe and In:CdSe films have been carried out using scanning electron micrographs. Figure 4 (a) and (b) shows the SEM of CdSe and In:CdSe films respectively. Comparison of Figure 4 (a) and (b) clearly shows that the morphologies of the CdSe and In:CdSe. From the micrographs one can see the uniform distribution of grains over total coverage of the substrate with a compact and fine grained morphology. At bath temperature of 55 ºC there is an increase in cathodic polarization. This increase in polarization resulted in an increase in nucleation over growth and the films surface is covered with uniform grain which is represented in Figure 4 (a). The grains visible in SEM picture Figure 4(a) thus represent the aggregation of very many small crystallites. After addition of indium in the electrolytic bath, the increase in grain density favours coalescence between individual grains during lateral growth and explains an increase of the compactness of the deposits. Coalescence between grains is clearly seen Figure 4 (b). The larger grains appeared to grow by coalescence of smaller ones. It is evident that the growth has been taken place by nucleation and coalescence process. The average sizes of the grains are found to be 162.98 nm.

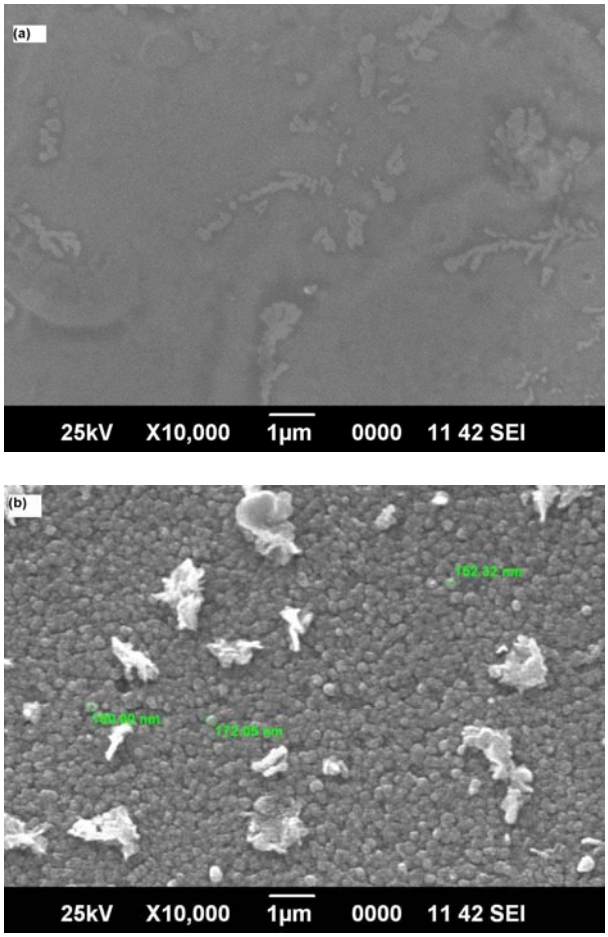

Fig. 4. Typical SEM pictures of (a) CdSe thin film (b) In:CdSe thin film.

The composition of the films was investigated using an energy dispersive analysis by X-ray analysis set up attached with scanning electron microscope. Figure 5 (a) and (b) shows the elemental analysis was carried out only for Cd and Se, the average atomic percentage of Cd:Se and In:CdSe was (54.28)Se; (45.68)Cd and (1.22)In; (54.28)Se; (44.50)Cd showing that the sample was slightly selenium rich, which is in good agreement with the reports of Tomkiewicz et al [16] and Skyllas Kazcos and Miller [17].

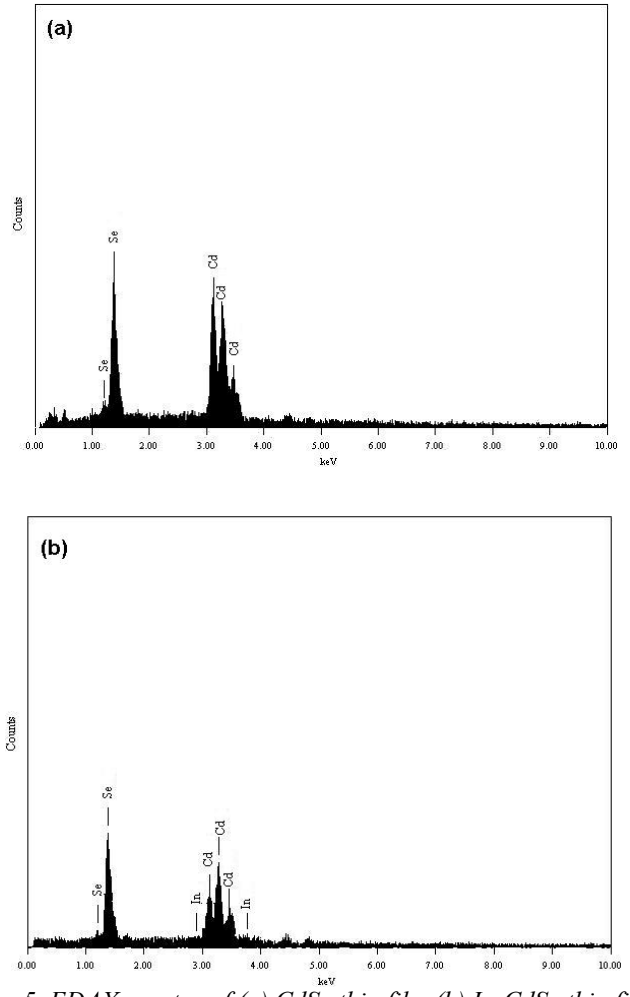

Fig. 5. EDAX spectra of (a) CdSe thin film (b) In:CdSe thin film.

The optical absorption of the films has been studied in the wavelength range between 300 and 1100 nm. The variation of optical density with wavelength is analyzed to find out the nature of transition involved and the optical band gap. From the calculated value of the absorption coefficients a plot of $(\alpha hv)^2$ against hv plot is extrapolated to the point at $\alpha=0$. The plots of of $(\alpha hv)^2$ versus hv (Tauc's plot) of the CdSe and In:CdSe films are shown in Figure 6 (a), (b), (c) and (d). It is seen that the band gap of CdSe is 1.7 eV (Figure 6 (a)). This may be due to the crystalline nature of the CdSe thin film, where charges are localized in individual crystals which results in an increase in band gap [18]. The band gap is found to decrease to 1.63 eV for In:CdSe (Figure 6(c)). This may be due to the **In** defect states originated within the forbidden gap, which may lead to absorption of incident photons and a substitutional dissolution which yield an improvement in grain structure of the film [20]. It was noticed that the band gap energy of bulk CdSe material was 1.7 eV and 1.92 eV respectively [20, 21]. The reason for variation with other reported values are attributed to the crystal nature and deposition conditions of the films.

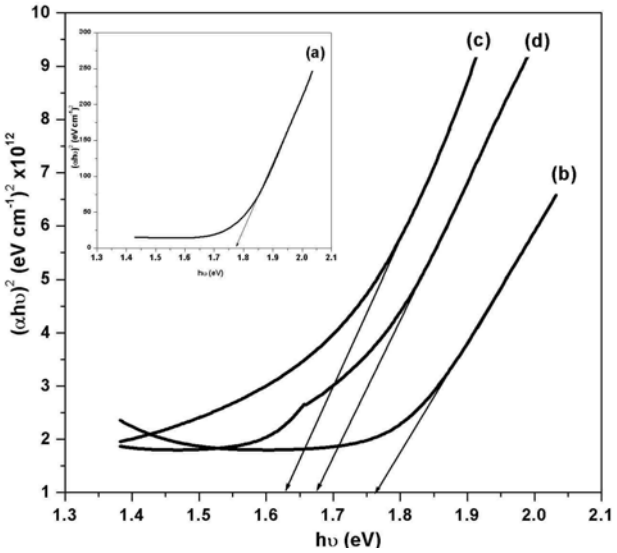

Fig. 6. Plot of hv vs. $(\alpha hv)^2$ for: (a) CdSe thin film and In:CdSe thin films at various indium concentrations in the solution ratios: (b)0.01 mM, (c)0.02 mM and (d)0.03 mM.

4. Conclusions

The CdSe and In:CdSe thin films are potential candidates used in various application like solar cells and hence they were taken for the present work. The CdSe and In:CdSe thin films were deposited on indium tin oxide coated conducting glass (ITO) substrates at bath temperature 55 ºC and various indium concentrations using an electrodepostion technique. X-ray diffraction analysis confirmed that the deposition CdSe films are polycrystalline in nature with hexagonal structure and there is chance in the intensity, addition peaks and peak position (2θ) of the In:CdSe film. Various structural parameters such as crystallite size, strain, dislocation density are calculated and are found to depend upon various indium concentrations. SEM studies reveal that the films with uniformly distributed grains over the entire surface of the substrate. The average sizes of the grains are found to be 162.98 nm are reported. The presence of elemental constituents was confirmed from EDX analysis. The average atomic percentage ratio of CdSe and In:CdSe was found to be (54.28)Se; (45.68)Cd and (1.22)In; (54.28)Se; (44.50)Cd. Optical transmittance measurements indicate that the deposited films have a direct band gap of 1.78 eV which confirm the formation of well-crystallized CdSe films. The band gap is found to decreases to 1.63 eV for In:CdSe thin films.

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