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Effect of indium doping on the structural and morphological properties of CdSe thin films

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Abstract

Semiconductiong CdSe and indium doped CdSe (In:CdSe) thin films have been synthesized on stainless steel and fluorine doped tin oxide coated glass substrates in an aqueous medium using potentiostatic mode of electrodeposition. The doping concentration of indium has been optimized to 0.15vol% using reliable photoelectrochemical technique. The structural and morphological studies of undoped CdSe and 0.15vol%In:CdSe thin film were carried out using X-ray diffraction and field emisssion scanning electron microscopy.

Keywords: CdSe, Photoelectrochemical, Indium doping, Morphology, XRD.

1. Introduction:

CdSe is a one of the most versatile II-VI semiconductors with band gap (1.7eV) near to visible spectrum maxima. Because of high absorption coefficient, direct band gap, size dependant physical and chemical properties, intrinsic birefringence and luminescent properties it has earned recognizable attention of researchers. These properties promote use of CdSe in various applications as solar cell [1-3], thin film transistor [4], light emitting diode [5], γ-ray detector [6] etc. CdSe thin films have been grown by diverse physical and chemical techniques

Researchers have been trying to alter chemical and physical properties of CdSe material using different techniques to explore its further potential. Doping is one of the ways to alter the optical as well as electrical properties in semiconductor materials [7]. Especially in Photo electrochemical (PEC) cell lower performance of photoanode is attributed to higher values of band gap and electrical resistivity that could be efficiently reduced by doping it with suitable impurity. The performance of CdSe thin film has been enhanced in various applications via doping it with suitable dopant materials.

As doping with trivalent indium is found to enhance conductivity, decrease band gap and also to improve performance of PEC cell significantly thus we have chosen indium as a dopant in synthesis of cadmium selenide thin films. Amongst the various deposition techniques, electrodeposition is simple, economic and low cost technique. By this technique, films can be grown over large area with high scalability, without vacuum and at room temperature [8]. Thus electrodeposition technique was selected for thin film deposition purpose.

The aim of current study is to inspect the influence of volumetric indium doping on structural properties and morphology of electro synthesized CdSe thin film.

2. Experimental details:

2.1 Deposition of CdSe and In:CdSe thin films.

Thin film synthesis was carried out using a three electrode cell with graphite bar (60mm×13mm×4mm) as a counter electrode, saturated calomel electrode (SCE) as a reference electrode and substrate as a working electrode.

All the chemicals used for synthesis ($3CdSO_4.8H_2O$, SeO_2 and $InCl_3$) were analytical reagent grade. Double distilled water was used for preparation of all precursor solutions. With the intention to obtain more photosensitive electrodeposit, a PEC method is used to optimize preparative parameters of CdSe thin film[9]. For this purpose, the PEC cell was fabricated using two electrode configuration, with CdSe as photoanode and graphite as counter electrode. 1M polysulfide (1M NaOH- 1M Na_2S- 1 MS) was used as redox electrolyte. The performance of PEC cell was studied in dark and under illumination intensity $50mW/cm^2$.

2.1.1 Deposition of CdSe thin film.

During preparation of CdSe thin film, initially the selenium precursor concentration was varied from 0.1 to 0.0005M keeping the cadmium concentration fixed to 0.05M. Fig. 1 shows variation in Jsc and Voc as a function of selenium precursor concentration at fixed cadmium precursor concentration (0.05M). It is seen that values of Jsc and Voc are increases with increase in Cd:Se precursor concentration and attains maximum value at 0.01M selenium precursor concentration that is when Cd:Se concentration ratio is 5:1 . For further decrease in selenium precursor both Jsc and voc drops. This may be due to stiochiometric CdSe formation taking place at 5:1 Cd:Se precursor concentration ratio[10]. At other selenium precursor concentration deviation from stoichiometry taking place.

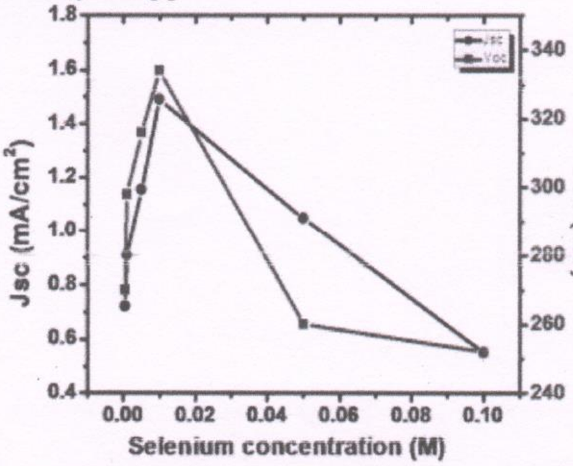

Fig.1 Variation of Jsc and Voc with selenium precursor concentration for CdSe/1M Polysulfide/C PEC cell.

Polarization curves were recorded using linear sweep voltammetry technique for this optimized concentrations using scanning potentiostat for Cd, Se and undoped CdSe thin films from their respective baths. The polarization curves for Cd, Se and undoped CdSe (on substrate area 1.5cm^2, at pH= 3) are plotted to estimate deposition potentials are shown in Fig.2 (polarization curve for 0.15vol%In:CdSe is also included in Fig.2)

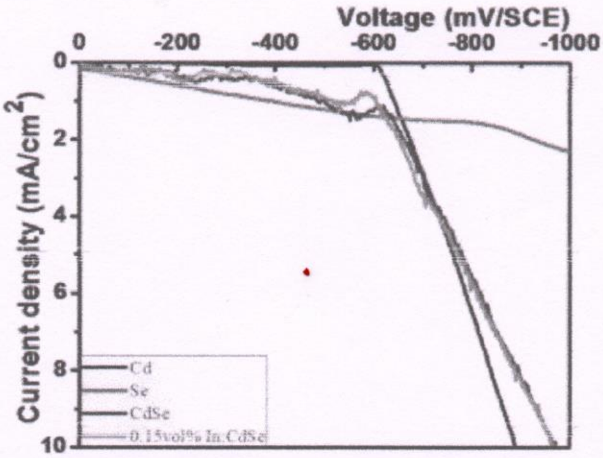

Fig.2 Cathodic polarization curves for Cd, Se, CdSe and 0.15vol%In:CdSe thin films on stainless steel substrate.

The estimated deposition potentials obtained from polarization curves are listed in the Table. 1. It reveals that the deposition potential of CdSe lies among reduction potential of cadmium and selenium.[11]. The CdSe thin film of brown color was found to be deposited at deposition potential -590(±10)mV/SCE. Room temperature electrodepostion of CdSe thin films was carried out by employing potentiostatic mode at -590mV/SCE from electrolytic bath (pH=3) containing 0.05M $CdSO_4$ and 0.01M SeO_2 in 1:1 proportion.

Table 1 Estimated deposition potentials for Cd, Se, undoped CdSe and 0.15vol.%In:CdSe thin films for stainless steel substrate.

Sample	Cd	Se	CdSe	0.15vol% In:CdSe
Deposition potential (mV/SCE)	-610	-470	-590	-580

Deposition time was optimized using PEC method. Fig. 3 shows variation in Jsc and Voc as a function of deposition time. The values of Jsc and Voc are found to be maximum corresponding to deposition period 40 minutes which is attributed to maximum film thickness 490nm attained by CdSe thin film. After 40 minutes film starts to redissolve in bath.

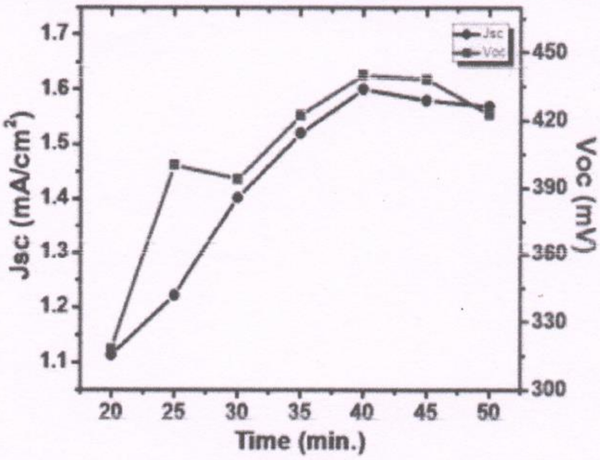

Fig.3 Variation of Jsc and Voc with deposition time for CdSe/1M Polysulfide/C PEC cell.

2.1.2 Deposition of In:CdSe thin films.

For deposition of indium doped Cadmium selenide (In:CdSe) thin films an indium trichloride ($InCl_3$) was used as source material . The doping percentage of indium was varied by adding appropriate volume of 0.05M InCl3 solution to electrodepositon bath using micropipette so as to maintain volumetric doping percentages 0.025, 0.050, 0.075, 0.1, 0.15, 0.25, 0.5. For indium doping percentage higher than 0.5vol%, electrolyte bath becomes turbid, milky precipitate settles down in bath which constrains film formation. All In:CdSe thin films were deposited without aid of any complexing agent. The doping percentage of indium was optimized using PEC method. The variation in Jsc and Voc with indium volumetric doping percentage is shown in Fig. 4.

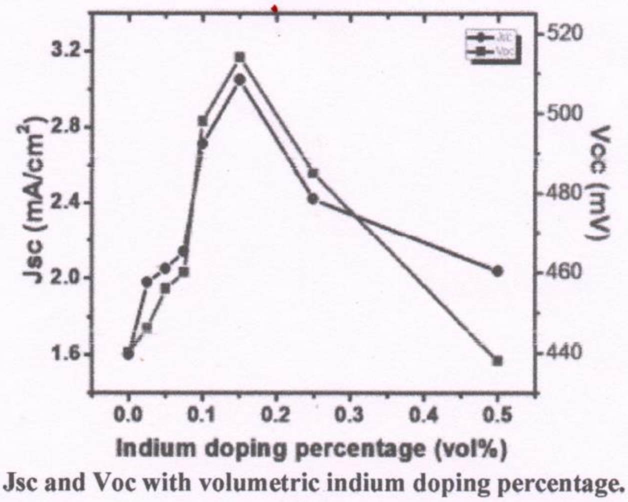

Fig.4 Variation of Jsc and Voc with volumetric indium doping percentage.

It is found that Jsc and Voc both increases with increase in indium doping percentage, reaches highest values corresponding to 0.15 vol% doping percentage and then drop off. This drop off in Jsc and Voc may be due to stoichiometric deviation and increased resistivity of In:CdSe thin films[12]. The optimized doping percentage of indium in CdSe thin film found to be 0.15vol%. A careful look at Fig. 2 shows that, deposition of In:CdSe film occurs at more positive potential than CdSe. Since no significant difference observed in deposition potential of CdSe and 0.15vol%In:CdSe thin films as in Table 1. Thus both films deposited under same optimized preparative conditions and used for further studies.

2.2 Characterizations

The structural investigation of the films was carried out by using Philips X-ray diffractometer PW-3710. The source of radiation was Cu Kα with λ=1.54A^0. Surface morphological study was carried out using FESEM (S-4700, Hitachi).

3. Results and Discussion

3.1 X-ray diffraction (XRD) studies

XRD patterns of undoped CdSe and 0.15vol%In: CdSe thin film are shown in Fig.5 The comparison of the observed XRD patterns with Standard JCPDS data (card no. 00-019-0191) confirms the formation of CdSe with cubic crystal structure.

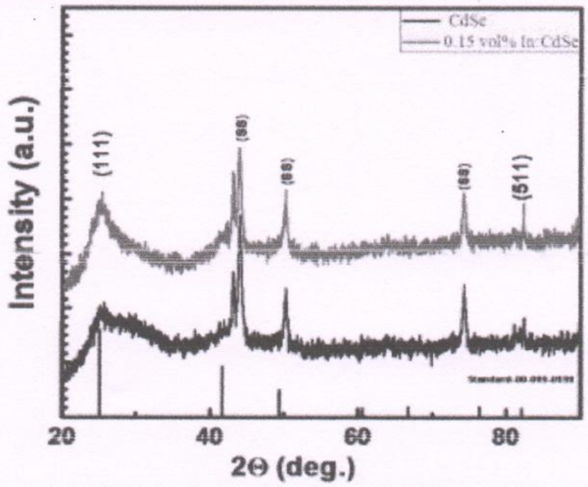

Fig.5 XRD patterns of potentiostatically electrodeposited undoped CdSe and 0.15vol%In: CdSe thin films. Vertical lines at bottom show standard JCPDS peaks (card No. 00-019-0191) of a cubic phase.

Both CdSe and In:CdSe thin films are amorphous in nature with broad humps observed in XRD patterns. The diffraction peaks observed close to 2θ values 25.24^0 and 82.36^0 are indexed to (111) (511) planes of cubic CdSe respectively which are in good agreement with nanocrystalline CdSe thin films electrodeposited by Sarangi [13]. XRD pattern shows, with indium doping, broadening of (111) peak decreases and also its intensity enhance. The (111) plane diffraction peak becomes more intense and narrower corresponding to 0.15vol%Indium doped CdSe thin film indicating improvement in quality of electrodeposit.

3.2 Field emission scanning electron microscopy

The morphological modulation induced in CdSe thin film via indium doping was studied using FESEM. FESEM images of undoped CdSe and 0.15vol%In:CdSe thin films at lower and higher magnification are shown in Fig.6. Undoped CdSe thin film shows fiberlike morphology. Web like interconnected fibers of diameter ranging between 52nm to 150nm and length from 4 to 7 nm are found to be dispersed all over the substrate shown in upper row of Fig.6. Min [14] reported analogous morphology for galvanostatically electrodeposited CdSe thin films grown on ITO substrate. Further indium doping showed significant modulation in morphology FE-SEM images of 0.15vol%In:CdSe thin film show a compact and crowded web of nanofibers.

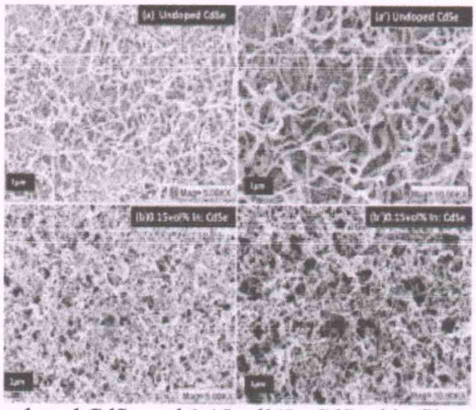

Fig.6 FESEM images of undoped CdSe and 0.15vol%In:CdSe thin films at lower and higher magnification.

4. Conclusions

In conclusion, the synthesis of undoped and indium doped CdSe thin films is possible using facile potentiostatic electrodeposition technique. Undoped and all indium doped CdSe thin films are photoactive in nature and superior PEC performance observed corresponding to indium doping percentage 0.15vol%. Indium doping found to be induced structural and morphological modulations in CdSe thin film. XRD studies reveals that both CdSe and 0.15vol%In:CdSe thin films are amorphous in nature with cubic crystal structure. Considerable improvement in intensity of (111) plane observed upon indium doping. Morphological modulation observed from CdSe fibers to bloomed buds grown on web of interconnected nanofibers corresponding to 0.15vol% Indium doping.

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