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ELECTROSYNTHESIS AND CHARACTERIZATION OF $Zn_{1-x}Cd_xSe$ THIN FILMS

R CHANDRAMOHAN, C SANJEEVIRAJA, S RAJENDRAN, T MAHALINGAM, M JAYACHANDRAN* AND MARY JULIANA CHOCKALINGAM*

Department of Physics, Alagappa University, Karaikudi 630 003, INDIA

*Central Electrochemical Research Institute, Karaikudi 630 006, INDIA

Electrosynthesis is a cost effective and viable technique for the synthesis of polycrystalline materials. In this study, thin films of (ZnCd)Se ternary semiconductor belong to II-VI group were cathodically deposited onto SnO_2 conducting glass and titanium substrates. XRD results show the polycrystalline wurtzite structure for the films deposited under the proposed conditions for all composition. Optical studies show a band gap value in the range of 2.78 to 1.71 eV as the film composition changes from ZnSe to CdSe. SEM pictures show well defined particulate grains. The ESCA studies revealed the presence of carbon and oxygen in the films. The photoelectrochemical (PEC) studies have been conducted and the results are presented.

Keywords: Photoelectrochemical solar cells, zinc cadmium selenide, thin films, II-VI semiconductors, cadmium chalcogenide films

INTRODUCTION

Zinc selenide is a non-degenerate, II-VI semiconducting compound used in the fabrication of blue light emitting diodes, blue lasers and solar cells. Cadmium selenide is another interesting material belonging to this family of semiconductors used in the fabrication of thin film transistors, photoelectrochemical solar cells, etc. By alloying these two semiconductors, a series of compounds of (ZnCd)Se, which can be tailored to the need of the devices in the entire UV-VIS-NIR spectra, can be obtained. Development of semiconductors with tailored band gap is of immense interest in modern scientific research. The growth of ternary Zn/Cd selenides opens up the possibility of their applications for novel optoelectronic devices in the visible region of electromagnetic radiation [1]. The (ZnCd)Se system which enables a tunable band gap region between 1.7 and 2.7 eV at normal temperature facilitates the development of several new electronic and optoelectronic devices such as light emitting diodes, photodetectors blue green lasers, etc. [2]. Thin films of these materials are usually synthesized by molecular beam epitaxy [3], electron beam evaporation [4] and chemical formation [5]. However, it has been shown [6] that electrodeposition is a simple and viable alternative to these cost intensive methods. Electrosynthesis of (ZnCd)Se thin films is difficult due to the wide difference in the reduction potentials of the different species present in the solution bath [7,8]. In this report, the fabrication of composition modulated thin film structures in the (ZnCd)Se systems and the characterisation studies related to structural and optical behaviour are reported. Photoelectrochemical solar cells have been fabricated by dipping the electrosynthesised (ZnCd)Se electrodes in polysulphide electrolyte and the results are discussed.

EXPERIMENTAL

The cell configuration was a conventional three electrode system. A platinum flag served as a counter electrode, the reference electrode was saturated calomel electrode and the working electrode comprises either precleaned titanium or tin oxide coated transparent conducting glass substrate with sheet resistance ohms/square. The starting chemicals were GR grade $ZnSO_4$, $CdSO_4$ and SeO_2 available from commercial sources and used as received (E Merck). All experiments were performed on carefully deaerated solution. The depositions were carried out potentiostatically

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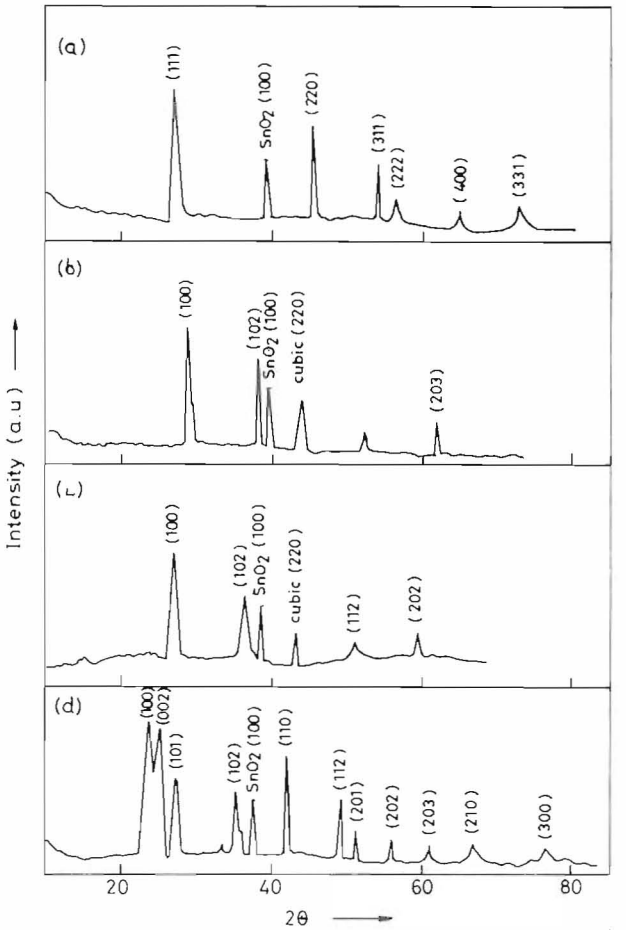


Fig. 1: X-ray diffractograms obtained for a) ZnSe, b) $Zn_{0.4}Cd_{0.6}Se$ *, c)* $Zn_{0.2}Cd_{0.8}Se$ *and d) CdSe*

employing a potential range of 0.6 to -1.1 V with respect to SCE. The deposition parameters were optimised after series of experiments in cyclic voltammetry and after undertaking several depositions.

The deposition bath comprised 250 mM $ZnSO_4$, 2 mM SeO_2 with various concentrations of $CdSO_4$ (0.5 to 9.5 mM) in triple distilled water. The *p*H was adjusted to 1.9 ± 0.1. The films deposited at a bath temperature of 348 K were found to be uniform, shining and well adherent. It is found that the formation of middle composition of zinc cadmium selenide thin films are favoured when the ratio of Cd:Se ions are 2:1 in the solutions bath. The deposited films are annealed in air at 673 K for 15 minutes before characterization.

Structural studies were carried out on these films of thickness 1.0 micron using and X-ray diffractometer (JEOL JDX 100) and the thickness of the films were estimated using multiple beam interferrometry and weight loss methods in the

TABLE I: The variation of band gap with cadmium content 'x' in $Zn_{1-x}Cd_xSe$ thin films and the respective solution composition and band gap

Concentration of			Cd content in film from EDAX	Band Gap(E_g)
$ZnSO_4$ mM	$CdSO_4$ mM	SeO_2 mM		eV
250	0	2.5	0.0	2.82
250	2	2.5	0.2	2.52
250	5	2.5	0.5	2.25
250	8	2.5	0.8	1.94
250	9	2.5	0.9	1.82
250	10	2.5	1.0	1.72

appropriate ranges. The multiple beam interferrometer is used to measure the film thickness up to 0.5 micron. The transmission and reflectance spectra were recorded using a double beam UV-VIS-NIR spectrophotometer (Hitachi U-3400). The surface morphology studies were performed using a scanning electron microscope (JEOL, JSM 35).

Photoelectrochemical solar cells have been fabricated by dipping the thin film (ZnCd)Se electrodes in an electrolyte comprising Na_2S, S and NaOH (1 molar each). The current and voltages are measured in dark and under illumination. A platinum flag acted as counter electrode. About 0.5 square cm of the electrode surface was illuminated with 550 mW radiation. Thin films deposited onto titanium to a thickness in the range of 1.2 to 2.0 microns were used for the PEC studies. The films were subjected to etching (chemical and photo etch) and the PEC performance were studied.

RESULTS AND DISCUSSION

The XRD patterns recorded for the electrodeposited thin films for various compositions onto tin oxide coated

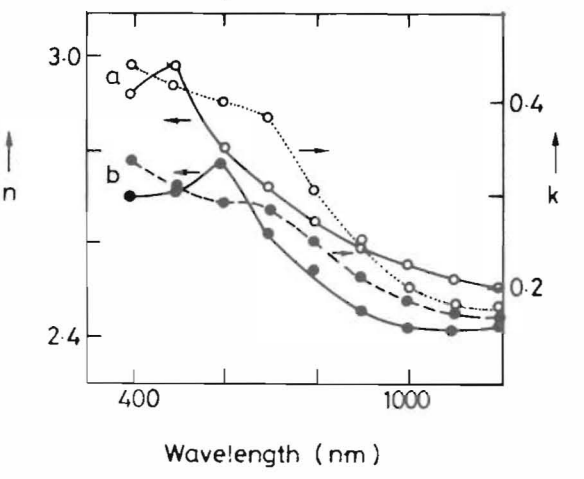
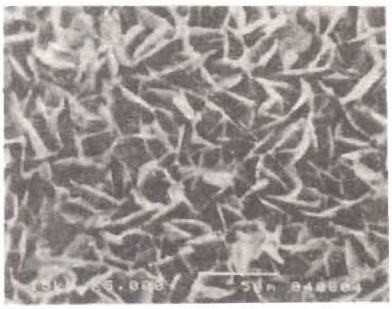


Fig. 2: Variation of refractive index and extinction coefficient 'k' for a) $Zn_{0.7}Cd_{0.3}Se$ *and b)* $Zn_{0.3}Cd_{0.7}Se$ *thin films*



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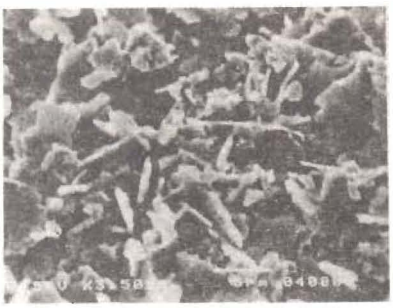

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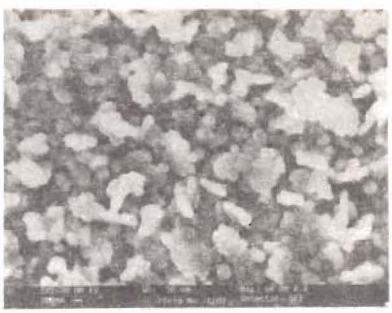

(3c)

Fig. 3: The SEM pictures obtained for typical a) ZnSe, b) $Zn_{0.2}Cd_{0.8}Se$ *and c)* $Zn_{0.8}Cd_{0.2}Se$

substrates show that the films are polycrystalline in nature with a hexagonal structure. Some peaks corresponding to cubic phase were also present. Fig. 1 shows XRD pattern obtained for typical ZnSe, CdSe and ZnCdSe thin films coated onto tin oxide coated transparent conducting glass substrates. The d values obtained for compound films compare well with the available standards. It is observed that CdSe and ZnCdSe thin films exhibited a predominant wurtzite structure. However, the ZnSe films exhibited a predominant cubic phase.

The absorption studies were carried out using the transmission spectra which reveal an absorption edge at 700 nm for x = 0 corresponding to the band gap of the cadmium selenide thin film and the spectra obtained for x = 0.2, 0.6 and 1.0 indicated the shift of absorption edge towards the shorter wavelength side. The variation of band gap with the cadmium content 'x' is found to be linear and indicate the formation of a continuous series of solid solution. The variation of band gap for electrodeposited ZnCdSe thin films is found to obey Vegard's law.

TABLE II: Important semiconductor parameters evaluated for CdSe and ZnCdSe thin film

Semiconductor parameters	Estimated values	
	CdSe	ZnCdSe
Flat band potentials Vfb	-1.07 V	-1.19 V
Band bending Vb	0.41 V	0.43 V
Doping density ND	1E16	2.9E16
Depletion layer width	0.2 μm	0.15 μm

$$xE_1 + b(1 - x) \times E_2 = E_g x$$

where E_1 is the band gap of CdSe. The value of b was found by fit of the experimental data and estimated to be 1.06. However, the value of 'b' tend to decrease below 1.0 for cadmium concentration x greater than 0.8. Similar variation of 'x' with E_g with b = 1 has been reported by Bassam et al for ZnCdSe crystals [9]. The variation of band gap with film composition is shown in Table I. The refractive index 'n' and extinction coefficient 'k' obtained using a continuous differential descent method for x = 0.3 and 0.7 are illustrated in Fig. 2. The refractive index 'n' is found to be maximum at a wavelength near 700 nm for x = 0 corresponding to the absorption edge. The addition of Zn to the deposit results in an increase of refractive index 'n' and the extinction coefficient 'k'. The dispersion of refractive index 'n' and extinction coefficient 'k' with wavelength for x = 0.2 and 0.6 shows a maximum value of 'n' which corresponds to the onset of absorption edge which is in conformity with earlier reports for CdS thin films [10].

The grain size of the electrodeposited films was found to be 0.01 microm using the full width at half maximum data obtained from XRD studies. The SEM pictures obtained for typical ZnSe, $Zn_{0.2}Cd_{0.8}Se$ and $Zn_{0.8}Cd_{0.2}Se$ are shown in Figs. 3(a), (b) and (c) respectively. The surface micrographs from the scanning electron microscope revealed a combination of needles and cauli flower shaped structure for a typical ZnCdSe film. The average grain sizes are found to be in the range of 0.5 to 2.0 microns.

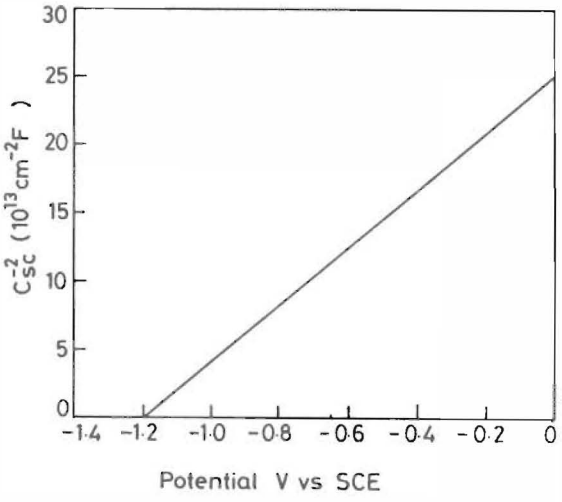

Fig. 4: Mott-Schottky plot for a typical thin film

EDAX studies revealed a small percentage of excess cadmium in all electrodeposited alloy films. The EDAX studies on films electrodeposited by employing the concentration of $CdSO_4$ as 10 mM or greater do not show any zinc incorporation. The possible mechanism for the formation of ZnCdSe may be that selenous acid reduction to Se^4 precedes the reduction of $CdSO_4$ to Cd^{2+} followed by $ZnSO_4$ to Zn^{2+} reduction. When the cadmium concentration in the deposition bath is greater, cadmium reduction is found to be dominant. ESCA studies reveal the presence of oxygen and carbon contamination in all these films. The relative compositions of Zn, Cd and Se obtained for various solution composition are shown in Table I.

The electrosynthesised films were used as photoelectrodes in polysulphide electrolyte. The films of ZnCdSe and CdSe are found to exhibit photoanodic behaviour and the films of ZnSe behaved as a photocathode. It is observed that the efficiency of the electrodes subjected to photoetching followed by chemical etching is maximum. The

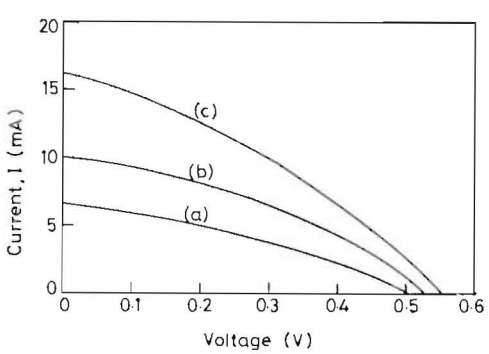

Fig. 5: I-V behaviour of CdSe photoelectrodes annealed in vacuum at 723 K a) without etching b) chemical etching c) photoetch followed by chemical etching

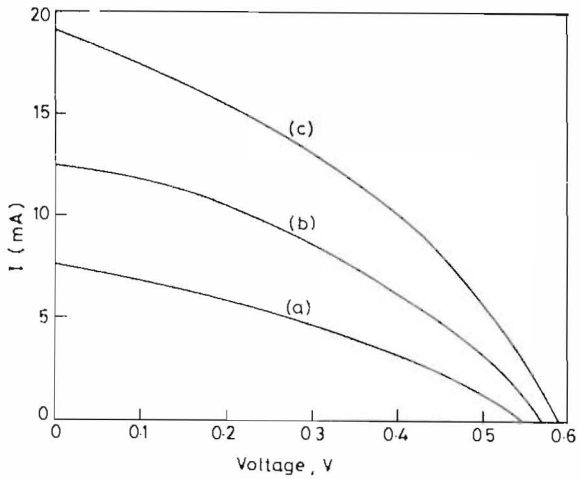

Fig. 6: I-V behaviour of photo electrodes annealed at 723 K in vacuum a) without etching b) chemical etching and c) photoetch followed by chemical etching

$Zn_{0.2}Cd_{0.8}Se$ electrode showed the maximum efficiency under unetched and etched conditions. Mott-Schottky plot for typical CdSe and $Zn_{0.2}Cd_{0.8}Se$ are drawn and the various PEC parameters evaluated are shown in Table II. Fig. 4 shows the Mott-Schottky plot obtained for a typical $Zn_{0.2}Cd_{0.8}Se$ thin film. Fig. 5 shows the I-V characteristics obtained for a typical CdSe electrode under photoetch followed by chemical etched conditions. It is observed from Figs. 5 and 6 that the zinc incorporation in CdSe thin film electrode has improved the photoelectrochemical behaviour of the electrodes to an extent in all the cases [12]. However, it is observed that Zn incorporated films with $Zn_{0.4}Cd_{0.6}Se$ and $Zn_{0.6}Cd_{0.4}Se$ exhibited a poor photoelectrochemical response when compared to CdSe thin films. Further studies on the estimation of optimal mixing ratios of Zn:Cd for the best photoelectrochemical results from this ternary system are under progress.

CONCLUSIONS

The synthesis of (ZnCd)Se solid solution thin films have been reported. The structure, microstructure and optical properties of the films are studied and reported. Photoelectrochemical solar cell studies have carried out on these films with polysulphide electrolyte as the redox system. The incorporation of Zn into cadmium selenide to an extent has been reported to have resulted in an enhancement of the photoelectrochemical properties.

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