

Electrochemical deposition and characterization of Cd-Fe-Se thin films

S.Thanikaikarasan^{1, a}, T.Mahalingam^{1, b}, K.Sundaram^{1, c}, Taekyu Kim², Yong Deak Kim³ and S.Velumani⁴

¹ Department of Physics, Alagappa University, Karaikudi-630 003, Tamil Nadu, India.

² Center for Modeling and Simulation Studies, Security Management Institute, Kangnam-Ku, Seoul-135 871. Republic of Korea.

³ Department of Electrical and Computer Engineering, College of Information Technology, Ajou University, Suwon 443-749, Republic of Korea.

⁴ Department of Electrical Engineering (SEES), CINVESTAV-IPN, Col San Pedro Zacatenco, D.F.Mexico C.P.07360, Mexico.

^a s_thanikai@rediffmail.com, ^b maha51@rediffmail.com, ^c phd_sundaram@rediffmail.com

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Abstract: Cadmium iron selenide (Cd-Fe-Se) thin films were deposited onto tin oxide (SnO₂) coated conducting glass substrates from an aqueous electrolytic bath containing CdSO₄, FeSO₄ and SeO₂ by potentiostatic electrodeposition. The deposition potentials of Cadmium (Cd), Iron (Fe), Selenium (Se) and Cadmium-Iron-Selenide (Cd-Fe-Se) were determined from linear cathodic polarization curves. The deposited films were characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive analysis by x-rays (EDX) and optical absorption techniques, respectively. X-ray diffraction patterns shows that the deposited films are found to be hexagonal structure with preferential orientation along (100) plane. The effect of FeSO₄ concentration on structural, morphological, compositional and optical properties of the films are studied and discussed in detail.

1. Introduction

Alloys of II-VI group compounds are attracting candidates for opto-electronic device applications [1]. Recently, ternary/pseudo-binary semiconductor compounds have established much attention because of their potential applications in a wide spectrum of optoelectronic devices [2-4]. Among II-VI group ternary compounds CdHgSe, CdHgTe and CdFeS have been studied widely for solar cell and IR device applications [1, 5-6]. Even though CdHgSe and CdHgTe have been well studied in the past little work has been reported for thin films of cadmium iron selenide (Cd-Fe-Se). Electrodeposition of compound semiconductors from an aqueous solution was employed in the preparation of solar cells [7]. Cd-Fe-Se is an n-type semiconductor with an energy gap of 1.6 eV which make them quite interesting for the fabrication of photoelectrochemical solar cells [8]. Rajpure et al studied the growth of n-type CdFeSe thin films on stainless steel substrates and studied their structural and photoelectrochemical properties [9]. The photoconductivity measurements of Cd-Fe-Se single crystals were reported by Jolanta Stankiewicz and Maurico Di Lorenzo [10]. Electronic properties of CdSe and CdFeSe single crystals were investigated by Konior et al [11]. Jolanta Stankiewicz studied the temperature and composition dependence of the energy gap in Cd_{1-x}Fe_xSe single crystals grown by modified Bridgmann method [12]. An analysis of published data indicates that a huge amount of literature is available on the preparation and properties of bulk Cd_{1-x}Fe_xSe, but little is known regarding thin films. Cd-Fe-Se semiconducting thin films are usually crystallized in the hexagonal (FeSe) and hexagonal (CdSe) structures. Even though several sophisticated thin film deposition techniques are available, the electrodeposition technique seems to be attractive due to its low cost and low temperature processing and the possibility to control the film thickness and morphology and composition by readily adjusting the

electrical parameters as well as the composition of the electrolytic solution [13]. The electrodeposition of II-VI ternary compounds is more complex because they involve several deposition parameters which control the film properties such as film composition and structure. Hence, we carried out a systematic analysis in this work to analyze the deposition conditions to grow Cd-Fe-Se alloy thin films. The objective of the present work is to prepare Cd-Fe-Se thin films on tin oxide coated conducting glass substrates at various FeSO_4 concentrations. The deposition potential of elements Cadmium (Cd), Iron (Fe), Selenium (Se) and compound Cadmium-Iron-Selenium (Cd-Fe-Se) were determined using linear cathodic polarization curves. The deposited films were characterized by 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 FeSO_4 concentration on the above properties of the films are studied and discussed.

2. Experimental Details

All the chemicals used in this work were of analytical reagent grade (99.5% purity procured from S.d. Fine Chemicals, Mumbai, India). Thin films of Cd-Fe-Se were deposited onto tin oxide coated conducting glass substrates (sheet resistance $20\Omega/\square$) from an aqueous solution bath containing 0.25 M of CdSO_4 , 0.015 M to 0.03 M of FeSO_4 and 0.01 M of SeO_2 . The pH value of the solution is kept in the range between 1.5 and 3.5. The electrochemical experiments were performed using scanning potentiostat/galvostat (Model 362, EG&G, Princeton Applied Research, USA) employing three electrode configuration with tin oxide coated conducting glass substrate as cathode, graphite plate as anode and saturated calomel electrode (SCE) as reference electrode. Before use, tin conductive oxide substrates were treated for 15 minutes 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. The bath composition and solution pH was fixed after undertaking several depositions. When the FeSO_4 concentration is kept at 0.015 M there is a slight incorporation of Fe ions in the films. If the concentration of FeSO_4 is increased above 0.025 M there is an excess of Fe content in the films. Hence we fix the optimized bath composition of 0.25 M CdSO_4 , 0.025 M FeSO_4 and 0.01 M SeO_2 was optimized for all depositions. It was observed that at very low pH (<2.0) value the films grow spontaneously at higher current densities making the process uncontrollable. The rapid growth of films followed by its peeling out from the substrate is observed. At high pH (>3.0) value precipitation of FeSO_4 occurs in the deposition bath. At pH value around 2.5 ± 0.1 there is controllable growth of films with moderate current density around 10 mA/cm^2 . Hence, we choose the optimized pH value of 2.5 ± 0.1 for all depositions. The temperature of the bath was varied from 30 to 80°C with deposition time of 30 minutes for all depositions. The optimum deposition condition to synthesize Cd-Fe-Se thin films are identified as follows: (i) Electrolyte concentration: 0.25 M CdSO_4 , 0.015 M to 0.03 M of FeSO_4 and 0.01 M SeO_2 (ii) solution pH: 2.5 ± 0.1 (iii) Bath temperature: 75°C (iv) Deposition potential: -600 mV Vs SCE, (v) Deposition time: 30 minutes.

X-ray diffraction data of electrodeposited Cd-Fe-Se thin films were recorded using a JEOL-JDX 8030 diffractometer with CuK_α radiation ($\lambda=0.15418 \text{ nm}$). The film composition and surface morphology were analyzed using energy dispersive analysis by x-rays (EDX) set up attached with scanning electron microscope (Philips Model XL 30). Optical absorption measurements were carried out using a UV-Vis-NIR spectrophotometer (HR-2000, M/S Ocean Optics, USA).

3. Results and Discussion

3.1. Polarization curves: The linear cathodic polarization curves were plotted to determine the deposition potentials of selenium, iron, cadmium and cadmium iron selenide from their respective baths with tin oxide coated conducting glass substrates as working electrode, graphite plate as counter electrode and saturated calomel electrode as reference electrode. To estimate the deposition potentials from polarization curves the tangents were drawn at two linear portions of the curves a, b, c, d indicated in Fig. 1. The voltage corresponding to the point of intersection of the tangent defines the deposition potential of individual element selenium, iron, cadmium and compound cadmium iron selenide. The estimated deposition potential of selenium, iron, cadmium and cadmium iron selenide were -340, -280, -620 and -600 mV versus SCE, respectively. The deposition potential of cadmium iron selenide is found to be 600 mV versus SCE. This is due to the fact, that the under potential deposition of noble element (selenium) taking place first followed by iron and then cadmium iron selenide. Smooth, uniform and well adherent films of CdFeSe were prepared at various bath temperatures from 30 to 80°C employing a deposition potential of -600 mV Vs SCE.

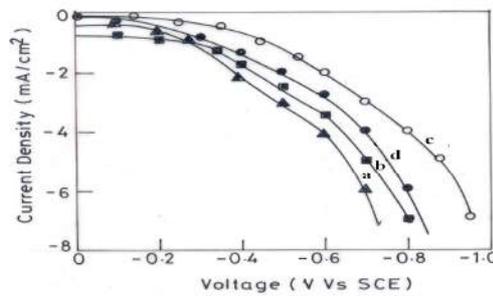
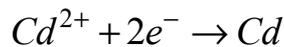


Fig.1. Linear cathodic polarization curves of Iron, Selenium, Cadmium and Cadmium Iron Selenide thin films obtained at room temperature condition.

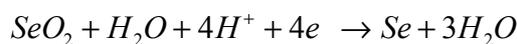
3.2. Growth kinetics: The electrodeposition of Cd-Fe-Se was carried out potentiostatically from an aqueous solution bath containing CdSO₄, FeSO₄ and SeO₂. The electrochemical equations involving the codeposition of Cd, Fe and Se are described below



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

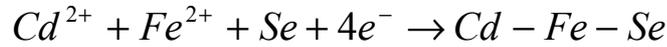


$$E_{\text{Fe}} = E_{\text{Fe}}^0 + \left[\frac{RT}{2F} \right] \ln \left[\frac{a_{\text{Fe}}^{2+}}{a_{\text{Fe}}} \right]$$



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

where E_{Cd}^0 , E_{Fe}^0 , E_{Se}^0 are the standard potentials of Cd, Fe and Se respectively, with respect to a saturated calomel electrode. a_{Cd}^{2+} , a_{Fe}^{2+} are the activities of respective atoms in the deposited films. The deposition of Cd and Fe occurs at potentials more than their standard reduction potentials by gaining free energy in the compound formation and ternary alloy films of Cd-Fe-Se are formed via the equation. Similar behaviour exhibited for ZnHgSe thin films reported earlier [14].



It has been observed that under potential deposition of less noble constituent (here Cd) of a compound is brought about by the gain of free energy by its formation [14]. Hence in order to attain the codeposition of Cd, Fe and Se we used a higher concentration of Cd and Fe, lower concentration of the noble element Se to bring the electrode potentials of three deposits closer.

3.3. Structural studies

Effect of bath temperature and pH: The structural properties of the deposited films using x-ray diffraction revealed that the bath temperature plays a vital role in the preparation of electrodeposited semiconducting alloy thin films. The bath temperature is expected to control the deposition rate by increasing the diffusion coefficient of the species and precursor solubility [15]. Cd-Fe-Se thin films deposited at bath temperature below 50°C are found to be poorly crystallized and the films deposited at a bath temperature of 75°C are found to exhibit well defined peaks in the diffractograms. The pH values between 1.5 and 3.5 were employed to deposit Cd-Fe-Se thin films. At pH value below 1.5 ± 0.1 , hydrogen evolution hindered the film growth and adherence of the films to the substrate was very poor. Hence, the bath temperature and solution pH were fixed as 75°C and 2.5 ± 0.1 respectively, for further deposition and characterization of Cd-Fe-Se thin films obtained in the present work.

Effect of FeSO₄ concentration: X-ray diffraction patterns of typical Cd-Fe-Se thin films electrodeposited at various FeSO₄ concentrations from 0.015 M to 0.03 M is shown in Fig. 2. X-ray diffraction patterns revealed that the deposited films of Cd-Fe-Se are crystallized mainly in the hexagonal (FeSe) and hexagonal (CdSe). The observed diffraction peaks of hexagonal (FeSe) are marked by [■] from various FeSO₄ concentrations are found at 2θ values of 28.40°, 41.86°, 54.78°, 60.97°, 67.40°, 82.84° corresponding to the lattice planes (100), (102), (103), (201), (202), (211) and hexagonal (CdSe) are marked by [*] are found at 2θ values of 25.34°, 35.09°, 48.86°, 55.87°, 63.96°, 72.34° and 79.48° corresponding to the lattice planes (002), (102), (200), (202), (203) and (212) respectively. The “d” values of semiconducting Cd-Fe-Se thin films confirm well to the available JCPDS standards [16-17]. Fig. 2 reveals that the appearance of new planes of hexagonal (FeSe) when the FeSO₄ concentration is increased from 0.015 M to 0.03 M. The preferred orientation of Cd-Fe-Se system is found to be predominant along (100) plane. When the FeSO₄ concentration is increased in the solution bath the intensity of preferred (100) plane also increases. The average crystallite sizes of Cd-Fe-Se thin films can be determined by Full Width at Half Maximum (FWHM) method using Debye-Scherrer’s formula.

$$P = \frac{0.9\lambda}{\beta \cos \theta_B}$$

where β is Full Width at Half Maximum of the peak position in radians, λ is the wavelength of x-rays used, θ_B is Bragg’s diffraction angle at peak position in degrees. The crystallite sizes of the films prepared at various FeSO₄ concentrations are found to be in the range between 12 and 36 nm. Here the crystallite size indicate the size of the individual crystallite.

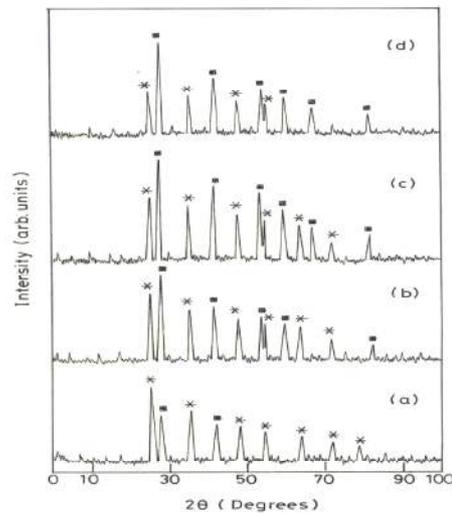
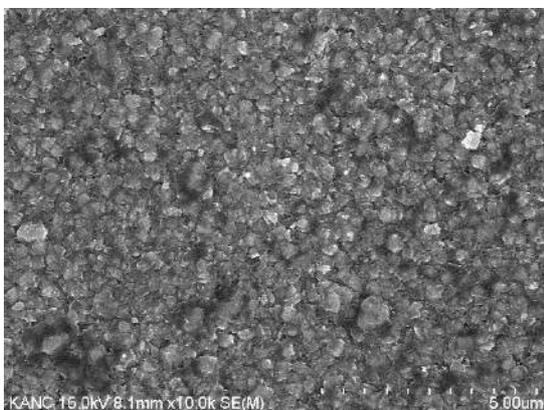


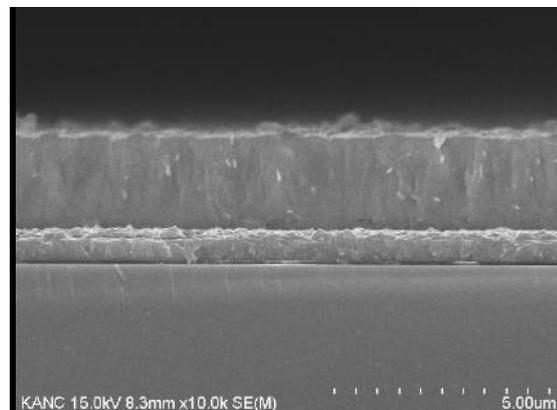
Fig. 2. X-ray diffraction patterns of Cd-Fe-Se thin films electrodeposited at various FeSO_4 concentrations. (a) 0.015 M, (b) 0.02 M, (c) 0.025 M, (d) 0.03 M

(*) CdSe (hexagonal) (■) FeSe (hexagonal).

3.4. Morphological and compositional analysis: The surface morphology of the electrodeposited Cd-Fe-Se films was analyzed by scanning electron microscopy. The scanning electron micrographs of Cd-Fe-Se films deposited at 0.025 M of FeSO_4 concentration is shown in Fig. 3a. The surface is observed to be uniform with compact structure. Some voids could be seen at few places in the SEM. Several smaller crystallites are grouped together to form a larger grains. The sizes of the grains are found to be in the range between 0.29 and 0.74 μm . The average size of the grains is found to be 0.46 μm . Fig. 3b shows the cross-sectional view of films obtained under 0.025 M FeSO_4 concentration. It is observed from Fig. 3b that the film surface is quite uniform. The non uniformity was estimated to be ± 100 nm for a magnification 10 K. This shows that films of various thicknesses could be prepared by this technique.



3a)



3b)

Fig. 3a. SEM picture of typical Cd-Fe-Se thin film electrodeposited at 0.025 M FeSO_4 concentration. Fig. 3b. Cross sectional view of typical Cd-Fe-Se thin film electrodeposited at 0.025 M FeSO_4 concentration.

The quantitative analysis of Cd-Fe-Se electrodeposits was performed with an aim to determine the relationship between various FeSO_4 concentrations and film composition (in atomic %). The quantitative determination of Cd-Fe-Se thin films was made by energy dispersive analysis by x-rays which shows the following composition (in atomic %): Cd (43.79); Fe (6.33); Se (49.88) for a film deposited with 0.015 M FeSO_4 concentration, Cd (38.34); Fe (13.42); Se (48.24) for a film deposited with 0.02 M FeSO_4 concentration, Cd(32.11); Fe (20.23); Se (47.66) for a film deposited with 0.025 M FeSO_4 concentration, Cd(30.24); Fe(23.32); Se(46.44) for film deposited with 0.03 M FeSO_4 concentration (Fig. 4).

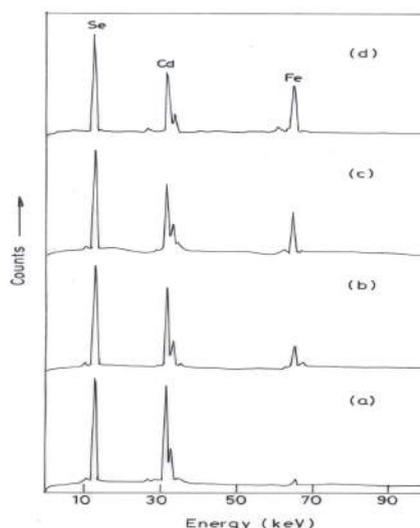


Fig. 4. EDAX patterns of electrodeposited Cd-Fe-Se thin films at various FeSO_4 concentrations. (a) 0.015 M, (b) 0.02 M, (c) 0.025 M, (d) 0.03 M.

The EDX results revealed that the content of Fe increased and the content of Cd and Se decreased while increasing the FeSO_4 concentration from 0.015 M to 0.03 M in Cd-Fe-Se electrolytic bath. This observation is also evidenced by the improvement of hexagonal phase of (FeSe) and reduction in the hexagonal phase of (CdSe) observed from x-ray diffraction analysis.

3.5. Optical properties: Optical absorption measurements of Cd-Fe-Se thin films have been studied without accounting for reflection and transmission losses. These measurements were used to estimate the band gap energy from the position of the absorption edge and it was found to change with alloy composition in Cd-Fe-Se thin films. The transmittance spectra obtained for Cd-Fe-Se thin films prepared at various FeSO_4 concentrations indicated a shift of absorption edge to shorter wavelengths. The optical absorption data were used to plot a graph of $(\alpha h\nu)^2$ versus $h\nu$, where α is the optical absorption coefficient of the material and $h\nu$ is the photon energy. Extrapolation of linear portion of plots to the x-axis gives the band gap energy of the films obtained at various FeSO_4 concentrations are shown by curves a,b,c,d in Fig. 5. The band gap of Cd-Fe-Se thin films obtained under optimized condition is found to be 1.61eV which is in close agreement with the value reported earlier [8]. It is observed from Fig. 4 the value of Fe content in the film increases the bandgap is shifted to lower values is due to the shift in position of absorption edge to longer wavelengths.

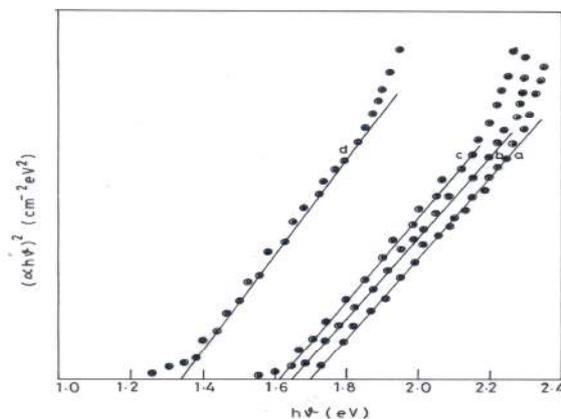


Fig. 5. Plot of $h\nu$ versus $(\alpha h\nu)^2$ of Cd-Fe-Se thin films electrodeposited at various FeSO_4 concentrations. (a) 0.015 M, (b) 0.02 M, (c) 0.025 M, (d) 0.03 M.

4. Conclusion

Cd-Fe-Se thin films were successfully electrodeposited on tin oxide coated conducting glass substrates at various FeSO_4 concentrations. The deposition potential of Se, Fe, Cd and Cd-Fe-Se were determined from linear cathodic polarization curves. X-ray diffraction patterns indicate the formation of polycrystalline Cd-Fe-Se films with preferential orientation along (100) plane. The sizes of the crystallites are found to be increase while increasing the FeSO_4 concentration from 0.015 M to 0.025 M afterwards it slightly decreases. The compositional analysis revealed that the content of Fe increases while increasing the FeSO_4 concentration in the electrolytic bath. The band gap energy of the films obtained in this work is found to be vary in the range between 1.32 and 1.7 eV for varying the FeSO_4 concentration s from 0.015 to 0.03 M. The surface morphology reveals uniform surface for films deposited at higher FeSO_4 concentration.

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