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Electrodeposition of CdSe Thin Films from Aqueous Solution

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Abstract: *CdSe thin film was electrodeposited from an aqueous solution of $CdSO_4$ and H_2SeO_3 at 75^oC on indium tin oxide (ITO)-covered glass substrates. The deposition films were characterized with X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive analysis by X-rays (EDAX), photoluminescence (PL) and UV spectrometry, respectively. XRD analysis shows that the films are exhibit in polycrystalline nature with hexagonal structure. The various mircrostructural parameters such as crystallite size, micro strain, dislocation density and texture coefficient were calculated. SEM study shows that the total substrate surface is well covered by uniformly distributed spherical shaped grains with stoichiometry compositions. Optical transmittance study shows the presence of direct transition with band gap energy 1.75 eV. A Photoluminescence spectrum of films was recorded and the results are discussed.*

Keywords: Electrodeposition, optical properties, microstructural properties, morphological studies

1. INTRODUCTION

Semiconducting chalcogenides are promising materials due to their wide range of applications in photovoltaic, photo detection and optoelectronic devices [1-4]. Extensive research has been carried out in the last decade to study the preparation and properties of semiconducting chalcogenides. The CdSe usually exhibits n-type conduction and is reported to have a direct band gap of about 1.7 eV [5]. An n-type material is considered to be important for photovoltaic applications, because of its high absorption coefficient and nearly optimum band gap energy for efficient absorption of light and conversion into electrical power. It can be used as an absorber layer in the top cell of a tandem solar cell. CdSe triggered in the last decade due to its tailored properties and potential applications in solar energy conversion.

Prospective semiconducting materials for possible photoelectrochemical solar cell fabrication include the Cd-chalcogenides which incidentally satisfy most of the requirements for several new electronic and opto-electronic devices such as light emitting diodes, photodiodes, blue green lasers etc., [5,6]. Numerous methods have been adopted to prepare CdSe thin films with both cubic and hexagonal structures: (i) pulsed laser deposition [3] (ii) thermal evaporation [7], (iii) vacuum evaporation [8], (iv) sputtering [9] (v) chemical deposition technique [10]. Among the above mentioned deposition techniques, electrodeposition has emerged as a simple, economical and viable technique to synthesize good quality films for device applications [5,11,12]. Development of the electrodeposition is widely used because it is a simple and economic and viable technique, which produces films of good quality for device application. XRD studies of CdSe thin films have been either a cubic or hexagonal or mixed phase depending on the preparation technique as well as preparation conditions. Optical studies on CdSe thin films have been carried out by some researchers [10] and they have reported that CdSe thin films have an absorption edge approximately at 780 nm with direct band gap energy of 1.75 eV. Electrical measurements in a wide range of temperatures were reported by only a few works [11]. CdSe is found to be an excellent material with a direct band gap value 1.7 eV which make them interesting for photoelectrochemical solar cells because of its compatibility of band gap with the solar spectrum [7]. Pal et al [8] have investigated the variation of above parameters with respect to film thickness and substrate temperature for vacuum evaporated CdSe thin films. Velumani et al [13] have reported the variation of above parameters with quartz tube length for hot wall deposited CdSe thin films. But the variation of above parameters with deposition potential, solution pH and annealing temperature for electrodeposited CdSe thin films have not been investigated earlier.

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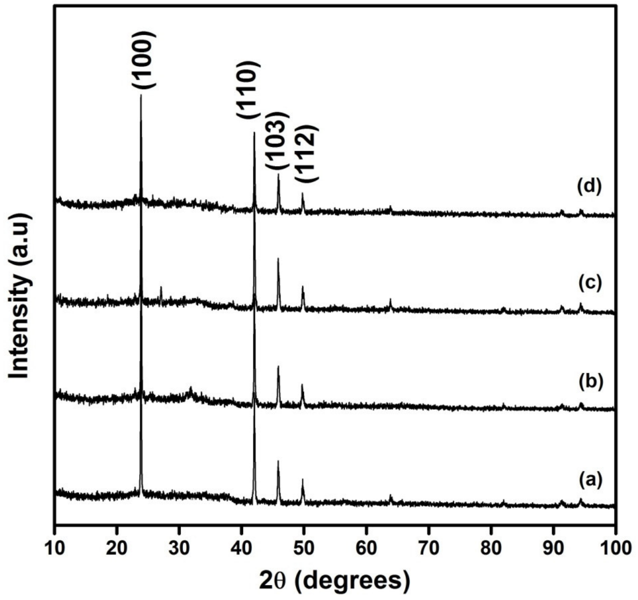

Figure 1. X-ray diffraction patterns of CdSe thin films prepared at various deposition potentials: (a) -600 (b) -700 (c) -800 and (d) -900 mV versus SCE

Therefore, we have planned to investigate the variation of above parameters with deposition potential, solution pH and annealing temperature. In the present work we report the CdSe thin films prepared by simple and low cost electrodeposition technique. The films have been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive analysis by X-rays (EDAX) and optical measurement techniques and the results have been discussed.

2. EXPERIMENTAL DETAILS

The study of the electrodeposition mechanism was performed using a PAR scanning potentiostat (Model 362, USA). A three-electrode system was adopted to deposit CdSe thin films. A magnetic stirrer cum heater set-up was used to deposit the films by stirring the bath as well as raising the temperature. A saturated calomel electrode (SCE) was immersed into the bath very near to the cathode, in order to measure the potential of the working electrode. Both working and counter electrodes are kept close to each other to obtain good results. The two surfaces facing each other were kept parallel, so that the released ions will be attracted and deposited exactly perpendicular to the cathode surface. The deposition of CdSe thin films was carried out from an aqueous electrolyte containing 0.3 M and 0.005M concentrations of $CdSO_4$, and SeO_2 at a deposition potential are from -500 mV to -800mV vs SCE. The deposition bath temperature was maintained at 75°C.

Electrodeposition was carried out using an electrochemical system consisting of PAR (EG&G Princeton Applied Research, USA Model 362A) potentiostat/galvanostat unit. Cyclic voltammetric studies were carried out in a standard three compartment cell using BAS 200A electrochemical analyzer. An X-ray diffractometer system [X'PERT PRO PANalytical, Netherlands] with Cuk$_{\alpha}$ radiation (λ = 0.1540) nm was used to identify the crystal structure of the films. 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 properties of the samples were analyzed using a UV- Vis- NIR double beam spectrophotometer (HR - 2000, M/S ocean optics, USA).

3. RESULTS AND DISCUSSION

The electrochemical deposition of CdSe thin films is carried out potentiostatically from an aqueous acidic bath containing $CdSO_4$ and SeO_2. The electrochemical Eq.'s involving the co-deposition of Cd and Se are described as follows:

$$\left.\begin{aligned} & Cd^{2+} + 2e^- \rightarrow Cd\left(E^0 = -0.403V\right) \\ & E_{Cd} = E^0 + \frac{RT}{2F}\log\left[\frac{a_{Cd^{2+}}}{a_{Cd}}\right] \\ & E_{Cd} = -0.403 + \frac{0.591}{2}\log\left[\frac{a_{Cd^{2+}}}{a_{Cd}}\right] \end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned} & SeO_2 + H_2O + 4H^+ + 4e^- = Se + H_2O\left(E^0 = 0.740V\right) \\ & E_{Se} = E^0 + \frac{RT}{4F}\ln\left[\frac{a_{SeO_2}}{a_{Se}}\right] + \frac{RT}{4F}\ln\left(a_{H+}\right)^4 \\ & E_{Se} = 0.740 + \frac{0.591}{4}\ln\left[\frac{a_{SeO_2}}{a_{Se}}\right] + \frac{0.591}{4}\ln\left(a_{H+}\right)^4 \end{aligned}\right\} \quad (2)$$

where E^0_{Cd} and E^0_{Se} are the standard electrode potential for Cd and Se respectively, with respect to SCE and a^{2+}_{Cd} is the activities of Cd ion in the electrolyte and a_{Cd} is the activities of the respective atom in the deposited film. The deposition of Cd occur at potentials more positive than their standard reduction potential by gaining free energy in compound formation [14–16] and films of CdSe are formed via the Eq. (3)

$$Cd^{2+} + Se + 2e^- = CdSe \qquad (3)$$

It has been reported by Shen [17] that under potential deposition of less noble constituent (here Cd) of a compound (CdSe) is brought about by the gain of free energy by its formation. Hence, it is essential to obtain the co-deposition of Cd and Se, we used a higher concentration of Cd and lower concentration of Se, to bring the electrode potentials of the deposits closer. Furthermore, different deposition potentials of selenium, –0.5 V vs. SCE [18] and –0.40 V vs. SCE [19] have been reported. These differences may be attributed to different substrates and other condition of experiments such as stirring solution, pH, temperature and concentration.

X-ray diffraction patterns recorded for CdSe thin films prepared on ITO substrates at various deposition potentials ranging from -600 to -900 mV versus SCE is shown in figure 1. XRD results represent that the deposited films are found to exhibit hexagonal structure with lattice constants (a = 4.299 Å; c = 7.010 Å). All the peaks identified are from CdSe alloy phase and hence no peaks corre-

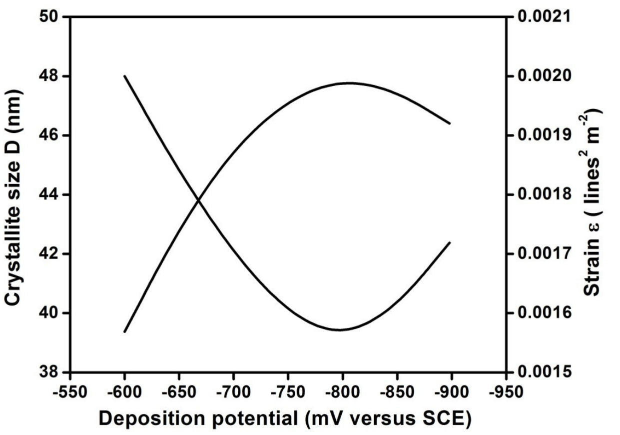

Figure 2. Variation of crystallite size and strain with various deposition potentials for CdSe thin films

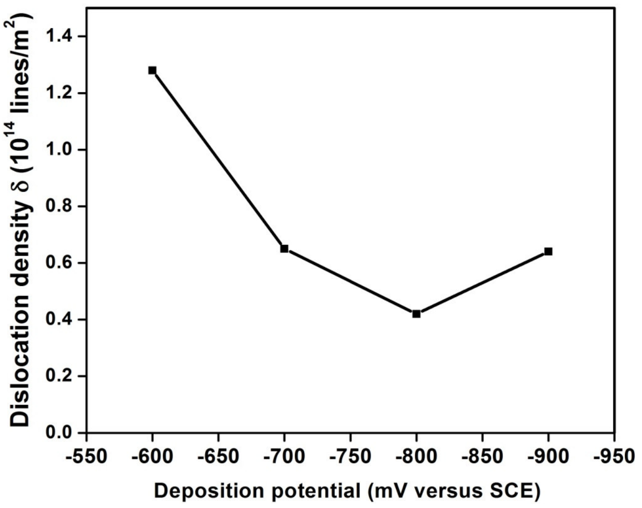

Figure 3. Variation of dislocation density with various deposition potentials for CdSe thin films

sponding to individual elements of Cd and Se are present. The different peaks in the diffractogram are indexed and the corresponding values of interplanar 'd' are calculated and compared with standard JCPDS-ICDD file for hexagonal CdSe [20]. It is observed from the diffractogram (Fig.1) that the height of the prominent peaks are found to increase while increasing the deposition potential from -600 to -800 mV versus SCE, thereafter the intensity of all the peaks are found to decrease in -900 mV vs SCE as shown in figure 1d. The intensity of (100) peak is found to be more than all other peaks in the diffractogram indicate that the crystallites are preferentially oriented along (100) plane. The presence of sharp and more intense diffraction lines at a deposition potential -800 mV versus SCE represent the formation of polycrystalline morphology of good quality films. The effect of deposition potential on structural studies shows that the deposition potential does not change the structural phase of the deposited films, however an increase in crystallinity with deposition potential for CdSe thin films are represented by XRD peak position.

The sizes of the crystallites are determined using FWHM data and Debye-Scherrer formula given by Eq.(4) [21].

$$D = {}^{0.9\lambda}\!\Big/_{\beta\cos\theta} \qquad (4)$$

where D is crystallite size and β is the FWHM. For the calculation of crystallite size and micro strain the line profiles are subjected to variance analysis method given by Mitra [22]. An aggregate of distorted crystallites as a measure of crystallite size and strain could affect the variation of X-ray diffraction line profiles. Since, the method is sensitive to the variation near the tails of the peaks a careful adjustment of the background has been carried out using the method given by Mitra and Misra [23]. . The micro strain ε is calculated using the relation,

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{D} + \frac{\varepsilon\sin\theta}{\lambda} \qquad (5)$$

where λ is wavelength, D is crystallite size, β is FWHM of the predominant orientation and θ is Bragg's angle. The variation of crystallite size and micro strain with bath temperature for CdSe film is shown in figure 2. X-ray line profile analysis revealed that the crystallite size increases with deposition potential and the films deposited at -800 mV vs SCE are found to have maximum value of crystallite size. Due to the removal of defects in the lattice with increase in deposition potential the micro strain in the films get released and attained a minimum value at -800 mV vs SCE. A sharp increase in crystallite size and decrease in micro strain with potential is as shown in XRD patterns.

The dislocation density δ defined as the length of dislocation lines per unit volume of the crystal and can be evaluated from the particle size D by the relation:

$$\delta = \frac{n}{D^2} \qquad (6)$$

where n is a factor, when equal unity giving minimum dislocation density. CdSe films with lower micro strain and dislocation density improves the stoichiometry of the films which in turn causes the volumetric expansion of thin films. The lower value of dislocation density 4 x 10^{13} lines/m^2 is obtained at -800 mV vs SCE is as shown in figure 3. Crystallinity improvements with deposition potential enhance the concentration and mobility of Se ion vacancies within the lattice and hence reduce the resistivity of the films. The studies on functional dependency of microstructural parameters on potential indicate that the micro strain and dislocation density decreases with deposition potential whereas the crystallite size increases upto -800 mV vs SCE. From the above discussion we have concluded the -800 mV vs SCE potential is optimized condition for its crystallinity, polycrystalline nature and stoichiometry of the film.

The effect of deposition condition such as deposition potential on the orientation of polycrystalline thin films are determined by evaluating the texture coefficient of the *(hkl)* plane using the following Eq.(6)[24].

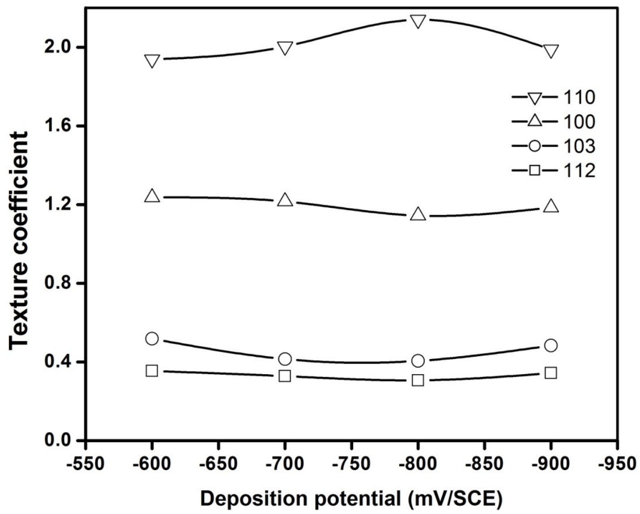

Figure 4. Variation of texture coefficient along (110) (100) (103) and (112) plane for CdSe thin films obtained at various deposition potentials

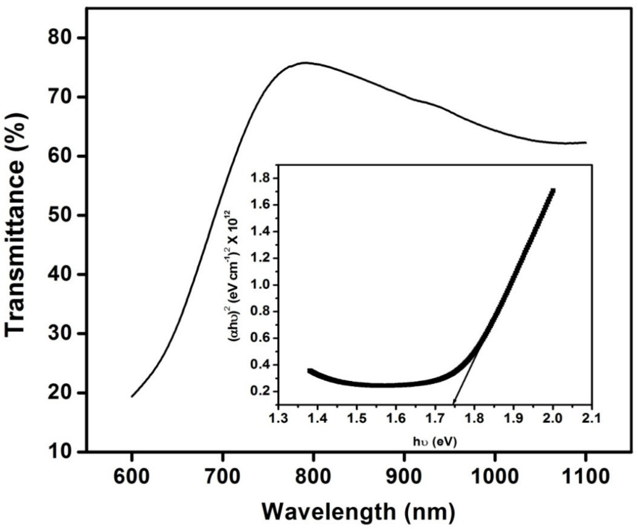

Figure 5. Optical transmittance spectrum of CdSe thin film deposited at -800 mV vs SCE. Inset:

$$P(h_ik_il_i)=\frac{I(h_ik_il_i)}{I_0(h_ik_il_i)}\left[\frac{1}{n}\Sigma\frac{I(h_ik_il_i)}{I_0(h_ik_il_i)}\right]^{-1} \tag{7}$$

where $T_c(hkl)$ is the texture coefficient of the (*hkl*) plane, *I* is the measured intensity, I_0 is the JCPDS standard intensity and *N* is the number of diffraction peaks. It is observed from Eq.(6) that the value of texture coefficient approaches unity for a randomly distributed powder sample, while $T_c(hkl)$ is greater than unity when the *(hkl)* plane is preferentially oriented. Figure 4 shows the variation of texture coefficient with *(hkl)* plane for CdSe thin films prepared at various deposition potentials in the range between -600 and -900 mV versus SCE. It is observed that the texture coefficient increases while increasing the deposition potential from -600 to -800 mV versus SCE, thereafter it decreases slightly as shown in Fig.4. The films prepared at a deposition potential -800 mV versus SCE have better crystallinity and well adherent to the substrate.

Figure 5 shows the optical transmittance of the CdSe thin film prepared at optimized deposition potential -800 mV vs SCE. It is shows the spectral distribution of the transmission T at normal incidence. The spectrum shows interference pattern with sharp fall of transmittance at the band edge, which is an indication of good crystallinity. A transmission spectrum is decrease in the near infrared spectral region due to the substrate property of the film. In addition, the interferential phenomena in the near-infrared spectral region could be an indication that neither thickness nor surface effects are at the origin of the decrease of the transmission, although the detailed mechanism to explain the higher wavelength spectra could not transmit through glass medium. But in these film transmission spectra has slight changes occur it may be due to the good crystalline formation of the film to transmit in higher wave length region.

The optical parameters such as absorption coefficient and band gap are determined from optical absorption measurements. The value of absorption coefficient for strong absorption region of thin film is calculated using the following Eq. (7) [25].

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

where α is the absorption coefficient in cm^{-1}, t is the thickness of the films, A is absorbance and T is transmittance. The nature of transition is determined using the following Eq. (8) [25].

$$\alpha h\nu=A\left(h\nu-E_g\right)^n \tag{9}$$

where α is absorption coefficient in cm^{-1} , hν is photon energy, E_g is an energy gap, A is energy dependent constant and n is an integer. An energy gap of 1.75 eV is obtained for as-deposited film by extrapolating the linear portion of the curves *hυ* versus $(\alpha h\upsilon)^2$ as shown in inset figure 5. The deviation in band gap for as-deposited films may due to an excess amount of Se present in the deposited films. The presence of Se introduces a significant fraction of electronic levels in the band gap close to the valence band edge of CdSe, with a consequent reduction of the energy associated with the direct transition. Photoluminescence measurement is a powerful and sensitive tool for studying the effects of purification and contamination on the film in the growth process [26]. A typical PL spectrum of CdSe thin film deposited at 75ºC and -800 mV versus SCE in shown in figure 6. The PL spectrum of CdSe thin film shows strong emission bands centered at 691nm (blue emission), in comparison with that of bulk CdSe at 730 nm [27]. The excitation wavelength was 455 nm. This effect may be related to the quantum effects.

Figure 7 shows scanning electron micrographs of the film deposited at 55ºC and -800 mV versus SCE. The surface morphology of as-deposited films shows uniform distribution of spherical grains

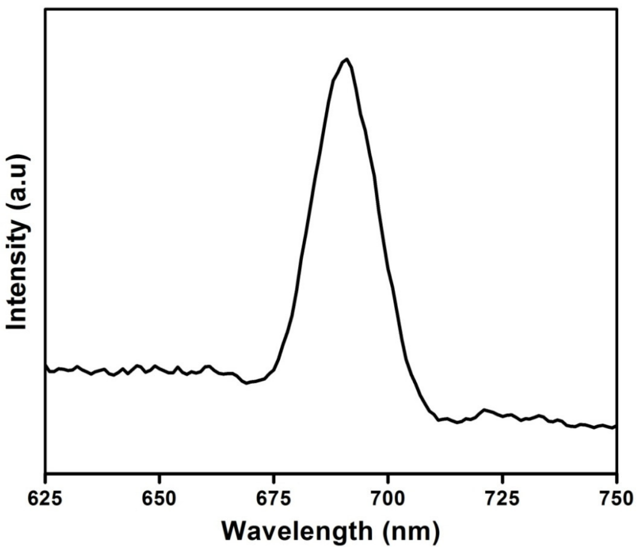

Figure 6. Photo luminescence spectra for CdSe thin films deposited at -800 mV vs SCE

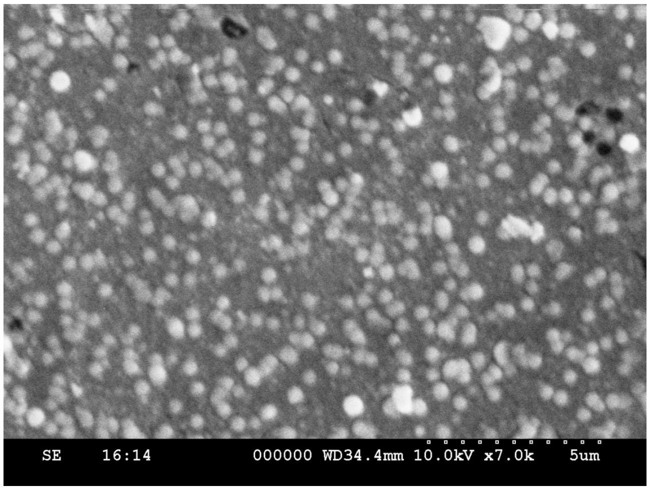

Figure 7. SEM picture of CdSe thin film prepared at deposition potential -700 mV vs SCE

over total coverage of the substrate with a compact and fine grained morphology. At potential -800 mV versus SCE there is increase in cathodic polarization. This increase in polarization resulted in an increase in nucleation over growth and the film surface is covered with uniform spherically shaped grain as shown in figure. The composition of the CdSe film was investigated using an energy dispersive analysis by X-rays (EDAX) and shown in the inset in figure 8. EDAX analysis the average atomic percentage of Cd and Se is 50.70 and 49.30 in the CdSe thin film showing that the electrodeposited CdSe film is almost stoichiometry. CdSe films prepared at different potentials show different compositional values indicating that nearly stoichiometry CdSe film from aqueous medium can be formed at bath temperature 75°C and potential -800 mV versus SCE.

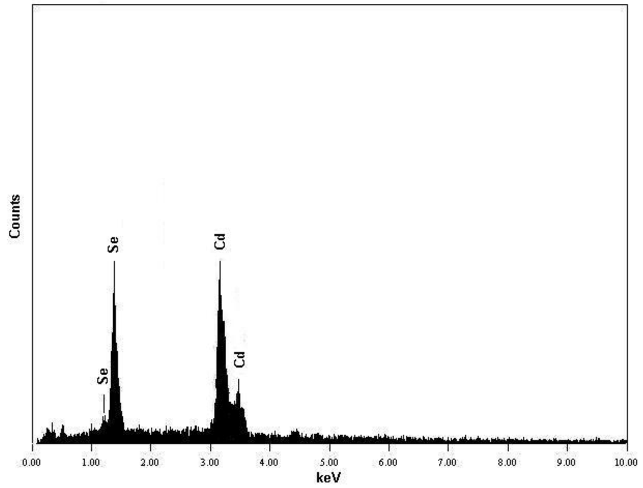

Figure 8. Typical EDX spectrum of CdSe thin film prepared at deposition potential -700 mV vs SCE

4. CONCLUSIONS

Polycrystalline CdSe thin films have been prepared on ITO substrates using potentiostatic cathodic electrodeposition technique. X-ray diffraction results reveals the formation of films with hexagonal structure with preferential orientation along (100) plane. Microstructural parameters such as crystallite size, strain and dislocation density are calculated using line profile analysis and their dependency with deposition potential are investigated. Morphological studies shows that smooth surface with fine grains are obtained for films prepared at a deposition potential -800 mV versus SCE. Stoichiometry good quality films are obtained at a potential -800 mV versus SCE. The presence of elemental constituents was confirmed from EDAX analysis. The average atomic percentage ratio of CdSe was found to be (50.70)Cd; (49.30)Se. Photoluminescence spectra were taken for CdSe film to study their emission property. Optical data analysis showed direct type of band gap at 1.75 eV.

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