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Investigation on CdSe Thin Film deposited by Electron Beam Evaporation Technique

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Abstract : Cadmium selenide (CdSe) thin films were deposited at room temperature on the microslide glass substrates by electron beam evaporation technique at various source – substrate distances. X-ray diffraction analysis indicates the formation of mixed phase cadmium selenide thin films possessing hexagonal and cubic phases when the coating distance is 12 and 15 cm. The film deposited at a distance of 8cm exhibits the single phase of hexagonal system. Crystallite size, strain and dislocation density of the films were evaluated. The surface morphology and elemental composition of the deposited cadmium selenide thin films were analyzed by scanning electron microscopic and Energy Dispersive X-ray studies respectively. The film deposited at 12 cm is selenium rich when compared to that of the films prepared at 8cm and 15cm distances. The fluorescence study of the CdSe films deposited at 12 and 15 cm distances shows emission band centered at 589 nm and the film deposited at 8 cm shows the emission band centered at 590 nm.
Keywords: Electron beam evaporation, Powder XRD, Morphology, Elemental Analysis, Fluorescence

Introduction

Semiconducting chalcogenides belonging to II-VI groups are considered to be the important materials because of their tunable electrical and optical properties. CdSe is one among the semiconducting chalcogenides with a band gap of 1.7eV. CdSe has n-type conductivity, high photosensitivity and high absorption coefficient which make CdSe to find applications in the light emitting diodes, photovoltaic and photodetection devices, thin film transistors and gamma ray detectors[1,2,3]. CdSe thin films exhibit both the hexagonal (wurtzite) and cubic (zinc blende) structures depending upon the deposition conditions[4]. Electrodeposition[5], chemical bath deposition[6,7,8], spray pyrolysis[9,10], hotwall deposition[11], electron beam evaporation[12,13] and thermal evaporation[14,15] methods have been employed to deposit the CdSe thin films.

Influence of the deposition conditions in particular the influence of substrate temperature on the photoluminescence (PL) properties of CdSe thin film deposited using closed space vacuum sublimation technique was investigated[16]. Structural and optical properties of chemical bath deposited $Cd_{0.4}Se_{0.6}$ films were reported[17]. CdSe thin films with thicknesses of 50, 75 and 100 nm were prepared by thermal vacuum evaporation method and its electrical properties were studied[18]. Effect of substrate temperature on the structural properties of the CdSe thin film deposited by thermal evaporation technique was reported[19]. Structural, optical and electrical properties of the electron beam evaporated CdSe thin films prepared at different substrate temperature (RT to 300°C) were investigated[20]. AC photoconductivity behavior of the CdSe films deposited at different substrate temperature (30 to 300°C) using electron beam evaporation method was investigated[21]. Effect of substrate temperature on the structural, optical and morphological properties of CdSe thin film deposited on the glass substrates by electron beam evaporation technique was reported[22]. Electrical, photo-electrical, optical and structural properties of CdSe thin films deposited by thermal and electron beam evaporation techniques were investigated[23]. In the present study, we have reported the deposition of CdSe thin films at different source - substrate distances (8 cm, 12 cm and 15 cm) by electron beam evaporation method and the influence of different coating distances on the structural, optical and surface morphological properties of cadmium selenide thin films are reported.

Experimental

CdSe thin films were deposited by electron beam evaporation technique using a V. R. Technology coating unit model-VRT-ERF PS-3KW. Well cleaned microslide glass substrates were used for the deposition of CdSe thin film at room temperature. The CdSe powder sample (0.025g; Alfa Aesar) was taken in the graphite crucible and evaporated to coat the film by deflecting the electron beam by 270˚ with 3KW electron beam gun power supply. The vacuum level maintained was 5×10^{-5} mbar. CdSe thin films were deposited at three different distances of 8 cm, 12 cm and 15 cm by keeping the other parameters constant. The deposited CdSe thin films were characterized for their structural, surface morphological and fluorescence properties. The structural properties were studied by the X - pert proanalytical powder X-ray diffraction system using CuKα radiation (λ = 1.5405Å) in Bragg – Brentano geometry (θ/2θ coupled) in the 2θ range 20-90˚. Surface morphology of the prepared CdSe films was studied using the model FEI Quanta FEG200 scanning electron microscope (SEM). The elemental analysis of CdSe thin films was carried out by Energy Dispersive X-ray Analysis (EDAX) technique (model FEI Quanta FEG200). The fluorescence spectra were recorded using JASCO FP-6300 spectrofluorometer with 150 watt Xe lamp.

Results and Discussion

Structural analysis

CdSe crystallizes in hexagonal (wurtzite) and cubic (zinc blende) crystal structures. Cubic structure of CdSe, a low temperature phase, is transformed into hexagonal phase at higher temperature (350 - 400°C)[4]. Thus the deposition technique and parameters play a vital role in the formation of the CdSe either in cubic (or) hexagonal (or) mixed phase. In the present work the deposited CdSe film changes from hexagonal phase to cubic and hexagonal mixed phase when the distance between source and substrate varies. Fig. 1 shows the X-ray diffraction (XRD) pattern of CdSe thin films deposited by e-beam method at three different source - substrate distances (8 cm, 12 cm and 15 cm). XRD pattern of the CdSe film deposited at 8 cm distance corresponds to the hexagonal phase and shows preferred growth orientation along (002) direction and the XRD peaks agree well with the corresponding JCPDS card no. 772307. When the distance between the source and substrate is increased to 12 cm and then to 15 cm the XRD peaks recorded for the films revealed the formation of cubic and hexagonal mixed phases. The sharp peak observed at 2θ = 25.50° corresponds to $(111)^{\#}$ plane of cubic phase, whereas 2θ = 45.81° corresponds to (103) plane of hexagonal phase (Fig. 1).

CdSe thin film deposited by closed spaced vacuum sublimation method at different substrate temperatures in the range from 373K to 873K was investigated[16]. The films deposited at low substrate temperature T_s<473K are bi-phase (cubic and hexagonal phases) and above this temperature formation of the hexagonal phase is observed. CdSe thin film deposited by cathodic electrodeposition method shows cubic zinc blende structure with preferred XRD peak oriented along $(111)^{\#}$[5] (cubic phase). Effect of bath temperature on cathodic electrodeposited CdSe thin film on Ni substrate was investigated[24]. Electrodeposited film has cubic structure and it exhibits a more or less pronounced $(111)^{\#}$ (cubic phase) preferred growth orientation. CdSe thin film irradiated with γ – rays of 100 rad and 150 rad transformed the CdSe film from cubic structure to cubic and hexagonal mixed structure[25]. The lattice constants of cubic *(a)* and hexagonal *(a and c)* phases of the CdSe thin films deposited in the present work were evaluated using the equations,

$$a = d(h^2 + hk + l^2)^{1/2} \quad (1)$$

$$1/d^2 = [4/3 \{(h^2 + hk + k^2)/a^2\} + l^2/c^2] \quad (2)$$

The crystallite size (D) of CdSe thin film was evaluated using Debye – Scherrer formula[26],

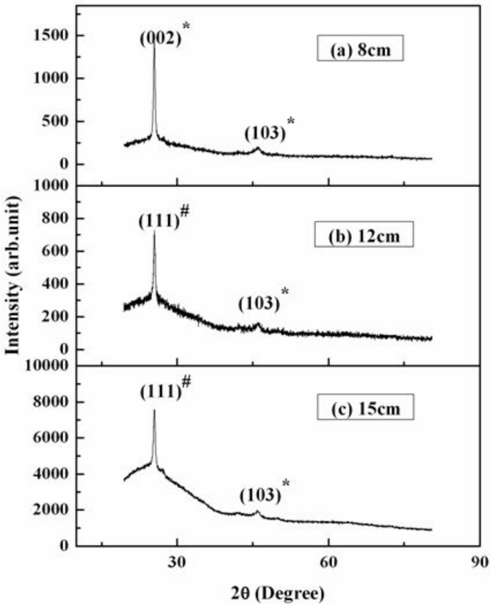
$$D = 0.9\lambda /(\beta cos\theta) \quad (3)$$

where λ is the wavelength of the X-ray radiation (λ = 1.5405), β is the full width at half maximum of the diffraction peak (radian), d is the interplanar distance and θ is the Bragg angle. The dislocation density (δ) was determined for the CdSe films using Williamson and Smallman's formula[27].

$$\delta = 1/D^2 \quad (4)$$

The strain (ε) in the deposited film was calculated using the formula[28]

$$\varepsilon = \beta cos\theta/4 \quad (5)$$



Figs .1a-c XRD pattern of CdSe thin film coated at the distance of (a) 8cm (b) 12cm and (c) 15cm ((#) indicates the cubic phase and (*) indicates the hexagonal phase)

The lattice constants, grain size, dislocation density and strain, calculated from XRD peaks (111)# and (002) of CdSe films are listed in Table 1. It is observed from the Table 1 that crystallite size slightly increases for the film coated at 12 cm source and substrate distance. The crystallite size decreases for the film coated at the distance of 15 cm. The strain and dislocation density varies from 14.9 $lin^{-2}m^{-4}$ to 15.6 $lin^{-2}m^{-4}$ and from 1.8 line m^{-2} to 2.06 line m^{-2} respectively as the distance increases from 8 cm to 15 cm. Thus the results show that mixed phase CdSe film deposited at the distance of 12 cm has the low strain and dislocation density.

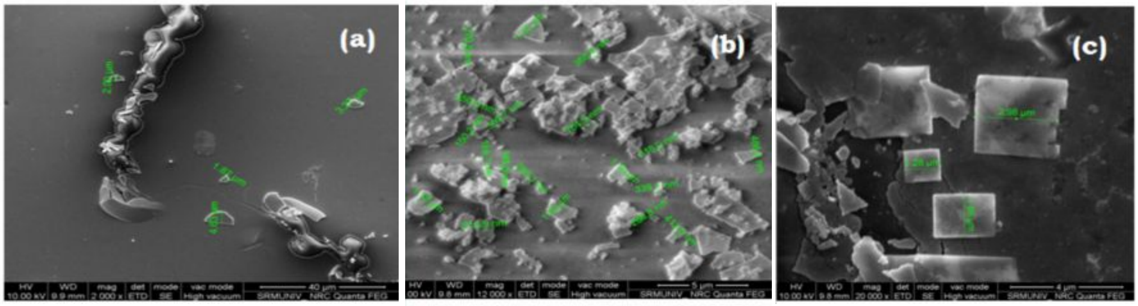
Table 1 Structural parameters of CdSe thin films deposited at different distance.

Source – Substrate distance	XRD peak (hkl)	2θ (°)	β (°)	d-spacing (Å)	D(nm)	$\delta\times10^{15}$ lin/m^2	$\varepsilon\times10^{-4}$ lin^{-2} m^{-4}	Lattice Constant (Å)
15cm (mixed phase)	(111)#	25.50	0.36643	3.489216	22.02	2.06	15.58	a = 6.0434
12cm (mixed phase)	(111)#	25.50	0.3522	3.489216	23.13	1.86	14.98	a = 6.0434
8cm (hexagonal phase)	(002)*	25.47	0.36828	3.493796	22.13	2.04	15.66	a = 4.3441 c = 6.9784

(#) refers the cubic phase and (*) refers the hexagonal phase

Morphological Properties

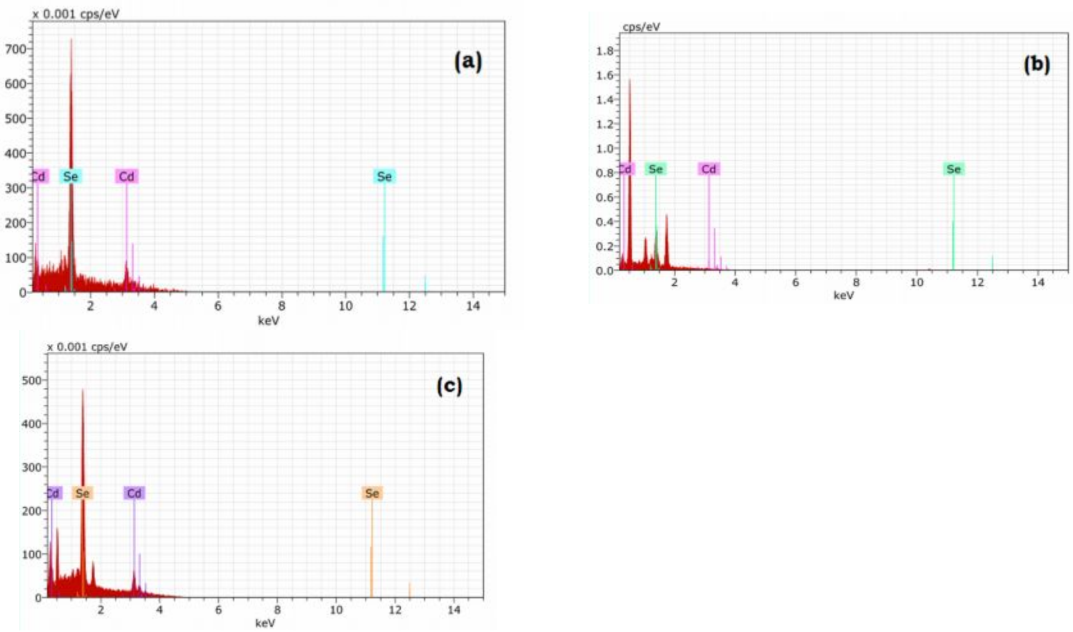
Figs. 2a-c show the scanning electron micrographs of electron beam deposited CdSe thin film coated at the distance of 8 cm, 12 cm and 15cm respectively. The Fig. 2a shows that the film deposited at 8cm distance possesses homogenous growth over the substrate with observable cracks in the film. The surface morphology of the film deposited at 12 cm given in Fig. 2b shows the accumulated grains with various sizes and shapes in nanometer scale on the surface of the film. The film deposited at 15 cm shown in Fig. 2c exhibits square (size ~3µm), rectangular and triangular shaped grains on the surface. Thus the results indicate that deposition distance influences the phase of the cadmium selenide thin films which in turn effectively influences the surface morphology of the film.



Figs. 2a-c Surface Morphology of the CdSe Thin Film deposited at different distance: (a) 8cm, (b) 12cm and (c) 15 cm

Compositional analysis

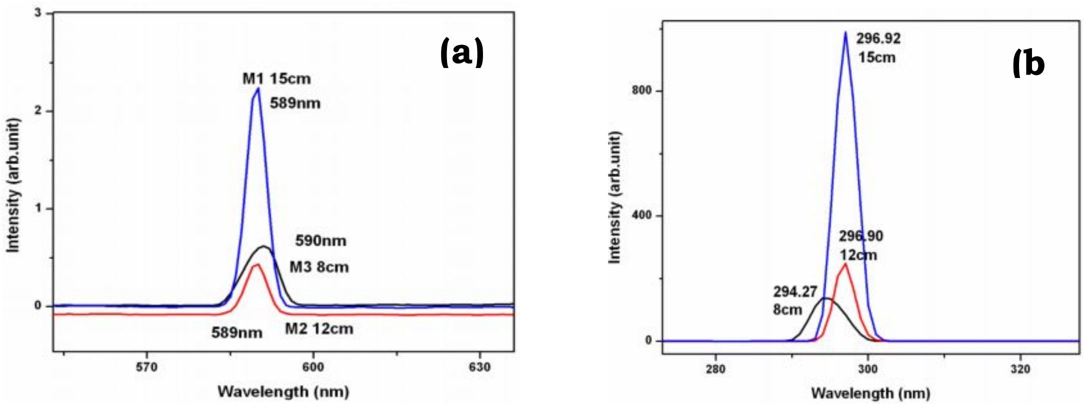
The presence of Cd and Se elements in the films deposited at various distances was studied by using EDAX technique and results are presented in Figs. 3a-c. The average atomic percentage ratio of Cd : Se film deposited at 15 cm distance is ~ 37.2: 62.8, thus showing the film is rich in selenium. The average atomic percentage of Cd : Se in the film deposited at 12 cm distance is ~ 8.9: 91.1, showing the film is highly selenium rich. In the CdSe film deposited at a distance of 8cm the atomic percentage of Cd : Se is ~ 37.1: 62.9. Thus the deposited films are rich in selenium which suggests the presence of cadmium vacancies. Cadmium vacancies in the deposited film lead to p-type conductivity. The fact that non-stoichiometry of the films leads to p-type semiconductivity if it is rich in selenium or n-type semiconductivity if it is rich in cadmium was reported earlier[13].



Figs. 3a-c EDAX spectrum of the CdSe thin film deposited at different distance: (a) 8cm, (b) 12cm and (c) 15 cm

Fluorescence

Figs. 4a, b show the fluorescence excitation and emission spectra of electron beam evaporated CdSe thin films prepared at different distances. The emission spectra show that films deposited at 12 cm and 15 cm distance have emission band centered at 589 nm whereas the film deposited at 8 cm has emission band at 590 nm. The excitation spectra show that the CdSe films deposited at 12 cm and 15 cm have excitation at ~297 nm whereas the film deposited at 8 cm has excitation at ~294 nm. CdSe film deposited by electrodeposition method shows a strong photoluminescence (PL) emission band centered at 690 nm for the excitation at 455 nm[4]. Thermally evaporated CdSe films at different substrate temperature show sharp PL emission band centered at 534 nm[15].



Figs. 4a, b Fluorescence spectra of CdSe thin film: (a) Emission and (b) Excitation spectrum

Conclusion

CdSe thin films were deposited on glass substrate at different source and substrate distances (8 cm, 12 cm and 15 cm) using electron beam evaporation technique. The CdSe film prepared at 8 cm distance consists of hexagonal phase whereas the films prepared at the distance of 12 cm and 15 cm show the mixed phase of cubic and hexagonal structure. Microstructural parameters such as crystallize size, lattice constant and dislocation density are influenced by the deposition distance. Morphological analysis shows that surface of the film deposited at 8 cm contains particles of various size whereas the film deposited at 12 cm distance shows randomly arranged dense platelet structures. The surface of the CdSe film coated at the distance of 15 cm contains square, rectangular and triangular shaped structures. Thus the source to substrate distance influences the surface morphology of the CdSe film. Compositional analysis shows that film deposited at the distance of 12 cm is highly rich in selenium. Fluorescence results reveal that the mixed phase CdSe films coated at 12 cm and 15 cm distance have emission at 589 nm for the excitation at 296 nm. The cubic phase CdSe film deposited at 8cm distance has emission at 590 nm for excitation at 294 nm. The fluorescence results show that the intensity of the fluorescence peak in the mixed phase CdSe film prepared at 15 cm distance is relatively high.

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