OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 2, No. 6, June 2008, p. 342 - 348

Effect of substrate temperature on structural properties of thermally evaporated CdSe thin films of different thickness

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The CdSe, a narrow band gap semiconductor has potential use in optoelectronics and solar cell applications. The structural parameters of a thin film semiconductor largely depend on the preparation method and conditions. Cadmium Selenide thin films of different thickness (830Å - 3160Å) have been prepared by thermal evaporation on chemically cleaned glass substrates at different substrate temperatures ranging from 300K to 523K. The structural properties of these films were studied by X-ray diffraction technique and different micro structural parameters such as lattice constants, grain size, internal strain and dislocation density etc. were determined. The XRD spectra showed that the CdSe films prepared at higher substrate temperatures are of polycrystalline nature having hexagonal structure. The average grain size and average internal strain of the polycrystalline CdSe films were calculated from the broadening of the XRD line spectra by plotting Williamson and Hall plots. The average grain size are found to increase while the internal strain and dislocation density of these films are found to decrease with increase of substrate temperature at the time of deposition and also with film thickness. The substrate temperature about 473K has been found to be suitable for depositing good quality CdSe thin films of thickness 2000Å and above with less number of defects and with bulk values of lattice constants.

(Received April 19, 2008; accepted May 18, 2008)

Keywords: Polycrystalline thin film, CdSe, substrate temperature, thickness, structural parameters

1. Introduction

CdSe, a direct gap II-VI semiconductor with band gap energy of 1.74 eV, has long been found as promising material for optoelectronic devices such as solar cells, high efficiency thin-film transistors, electron-beam pumped lasers, LED, electroluminescent devices, etc [1-5]. In addition, CdSe has large absorption coeffient to visible light. This property is useful for a good theoretical conversion efficiency and has led to the investigations for obtaining efficient solar cells. There are a number of reports on the different structural, optical and electrical properties of CdSe polycrystalline thin films prepared by various techniques such as vacuum evaporation [6-8], quasi-closed volume technique[9], electrodeposition [10-13], chemical bath deposition (CBD) [14-15], spray pyrolysis [16], sputtering [17] etc. It is seen that different parameters of a film are structural dependent which is also depends on the method of preparation, its thickness and other factors. Earlier we have reported the effect of substrate temperature on structural properties of ZnSe thin films prepared by thermal evaporation [18]. In this work we have studied the effect of substrate temperature on the structural properties of thermally evaporated CdSe thin films of different thicknesses. Structural parameters such as grain size, internal strain and dislocation density measured from XRD spectra are found to depend on the substrate temperature and also on the film thickness. The details have been reported in this paper.

2. Experimental

CdSe films were prepared by vacuum evaporation under the pressure better than 10^{-5} Torr on chemically cleaned glass substrates from 99.99% pure CdSe powder (Aldrich) using molybdenum boat. The substrates were kept a distance 8 cm from the material boat. The CdSe films of different thicknesses in the range 830Å – 3160Å were deposited at a nearly same deposition rate at different substrate temperatures from 300K to 523K for different sets of films. After deposition, films were vacuum annealed in-situ at 523K for 30 minutes. The thickness of all the films was measured by multiple beam interferometer technique. The XRD patterns of the films were analyzed by the Bruker X-ray diffractometer using CuKα radiation with wave length (λ) 1.5406 Å in the 2θ range from 10^0 to 70^0. Surface morphological studies of the thermally deposited CdSe thin films were done using the Scanning Electron Microscope (LEO 1430 VP) operating with an accelerating voltage 15 kV. The quantitative compositional analysis of the CdSe films were carried out by EDAX (Energy dispersive X-ray Analyzer) technique attached with the SEM.

3. Results and discussion

3.1 Structural analysis

3.1.1: X-ray diffractograms

X-ray diffractograms of the CdSe films of thickness of about 3000Å deposited at different substrate temperatures (300K to 523K) are shown in the figure 1. From the XRD patterns it is found that the CdSe films prepared at higher substrate temperatures 423K, 443K, 473K, 493K, 523K are polycrystalline, however, the film prepared at room temperature is amorphous in nature. The main features of the diffraction patterns are same but only the peak intensity is found to vary. The XRD spectrums of films of lower thicknesses show almost featureless spectra with weak peaks. As the substrate temperature increases (from 423K to 523K), more number of X-ray peaks appear, showing formation of the polycrystalline films. The peaks become sharper at elevated substrate temperature indicating larger crystallite size *D*. The diffraction spectra display the typical lines corresponding to hexagonal phase of CdSe. The observed d-values are in good agreement with the standard JCPDS d-values for the hexagonal structure [19].

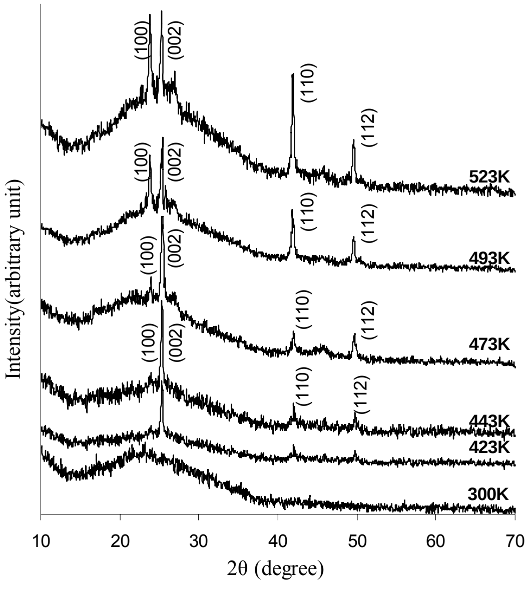


Fig. 1. XRD spectra of five typical CdSe thin films (thickness~3000Å) thermally deposited at different substrate temperatures (300K, 423K, 443K, 473K, 493K, 523K).

In all the cases the intensities of the (100), (110) and (112) peaks are low in comparison with the (002) one indicating the dominant orientation of the grains along [002] direction.

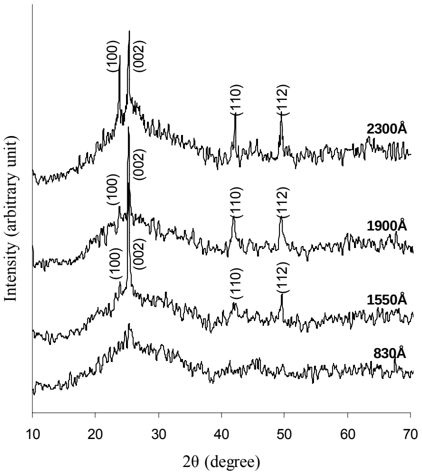


Fig. 2. XRD spectra of three typical CdSe thin films deposited at substrate temperature 473K but having different thicknesses (830 Å, 1550 Å, 1900 Å and 2300 Å).

The preferential orientation in the [002] direction has also been reported for sprayed [20], vacuum deposited [6, 21] and the annealed CdSe thin films prepared by chemical bath deposition [22]. As expected, the crystallinity is improved with increase of substrate temperature of deposition and on heat treatment (a vacuum annealing of films at 523K for 30 min). From these results it can be concluded that the elevated substrate temperatures (473K to 523K) are the suitable optimum growth conditions to prepare good quality polycrystalline CdSe thin films by thermal evaporation.

The thickness dependence of XRD spectra of CdSe thin films prepared at substrate temperature 473K has been shown in figure 2. The (002) peak does not appear in the films of lower thickness but as the thickness increases from 830Å to 3160Å, the (002), (110) and (112) peaks appear and their intensity increase. The increase in grain size in the films with increase in film thickness is clearly exhibited by the sharp intense peaks in the diffractograms. As the film thickness increases, the diffraction intensity increases due to the growth of the materials incorporated in the diffraction process [23].

3.1.2: Lattice Parameters

Lattice constants '*a*' and '*c*' of CdSe thin films of different thicknesses prepared at different substrate temperatures on glass substrates were determined from the following relations [24]:

$$\frac{1}{d^2}=\frac{4}{3}\left[\frac{h^2+hk+k^2}{a^2}\right]+\frac{1}{c^2} \quad \text{and}$$

Bragg's law: $\sin^2\theta=\frac{\lambda^2}{3a^2}\left(h^2+hk+k^2\right)+\frac{\lambda^2}{4c^2}l^2$

and have been tabulated in table1. The lattice constants evaluated from highest angle reflection data are reliable but are found to be slightly different for different orientations of the same film.

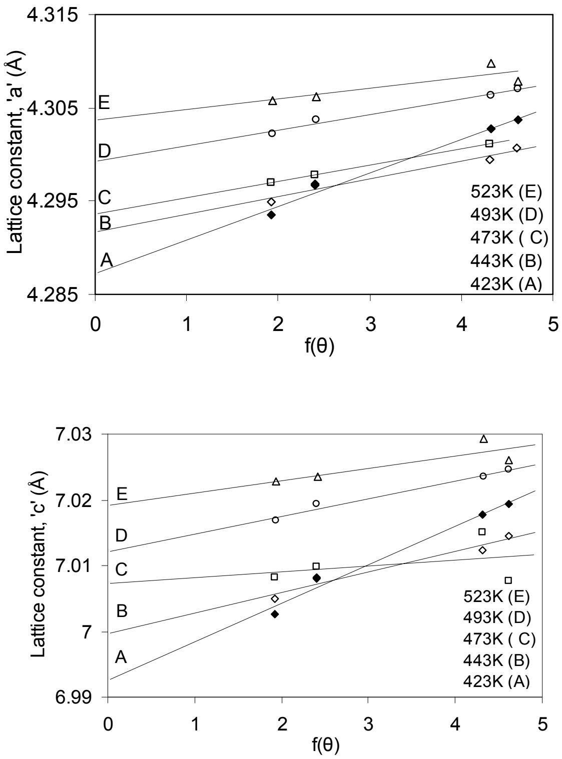


Fig. 3. Nelson-Riley plots for calculation of corrected value of lattice constants (a & c) of CdSe films (thickness ~3000 Å) deposited at different substrate temperatures.

This is due to the divergence of the X-ray beams, refraction and absorption of X-rays by the specimens etc., which involve a number of systematic errors in the measurement of θ and hence d values. Therefore corrected value of lattice constants are estimated from the intercept of the Nelson-Riley plots [25] as shown in figures 3 and 4 for CdSe films. These are plots of the error function $f(\theta)=\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ versus calculated values of lattice constant for different planes. The plots are found to be straight lines intersecting Y-axis as shown in the figures for films grown at different substrate temperatures (Fig.3) and with different thicknesses (Fig.4). The values obtained from N-R plots are more or less free from systematic errors and are tabulated in table 1. Fig. 5(a) shows the variation of lattice constants '*a*' and '*c*' (corrected) with substrate temperature and Fig. 5 (b) shows that with thickness of the films. Form the plots it is seen that the lattice constants increase with substrate temperature and also with thickness and reaches nearer to the bulk values (a = 4.299Å & c =7.010Å (Card No. 8-459)) for thickness above 2000Å and at substrate temperature between 473K and 523K.

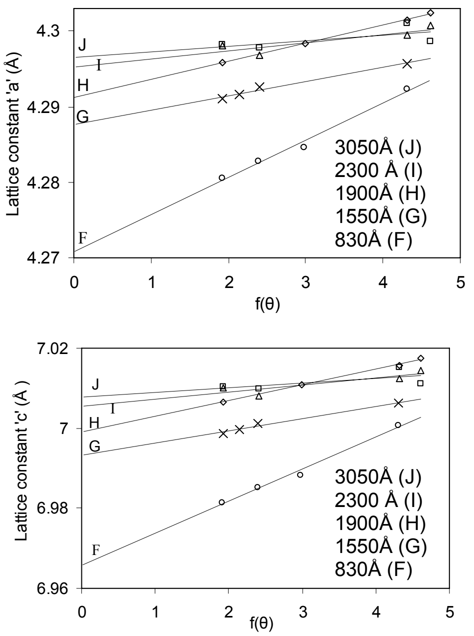


Fig. 4. Nelson–Relay plots for calculation of corrected value of lattice constants (a & c) of CdSe thin films of different thicknesses but deposited at same substrate temperature 473 K.

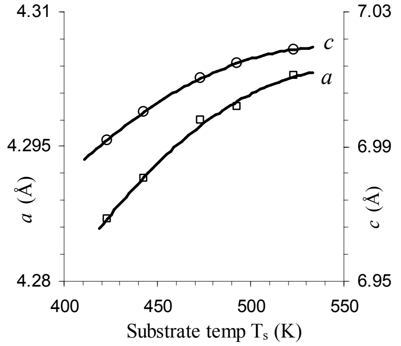


Fig.5(a). Variation of lattice constants 'a' & 'c' (corrected) with substrate temperature of CdSe films of thickness about 3000 Å.

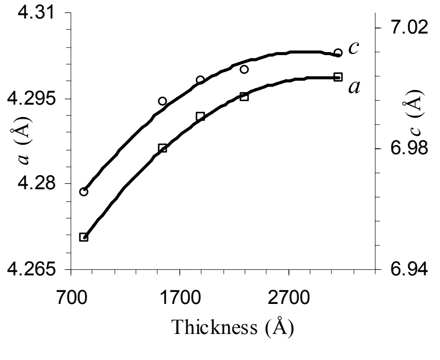


Fig.5(b). Variation of lattice constants 'a' & 'c' (corrected) with thickness (substrate temperature 473K).

3.1.3 Average grain size and internal strain measured from W-H plot:

The FWHM (full width at half maximum) was found to decrease markedly with the increase of film thickness and substrate temperature. Such a decrease reflects the decrease in the concentration of lattice imperfections due to the decrease in the internal micro-strain within the films and an increase in the crystallite size [23]. Considering the entire broadening of diffraction profile to be due to simultaneous contributions from both particle size and strain and using the Williamson and Hall method [26] for Cauchy nature of broadened profile, we have the relation [27] for β as:

$$\beta = \frac{\lambda}{D\cos\theta} + 4\varepsilon\tan\theta$$

or,

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{D} + 4\varepsilon\frac{\sin\theta}{\lambda}$$

where ε is the average internal strain. For multiple ordered diffraction pattern a plot of $\beta\cos\theta / \lambda$ versus $2\sin\theta / \lambda$ will give a straight line and intercept and slope of this plot (Williamson and Hall plot) will give the average grain size D and average strain ε respectively.

In this study the FWHM (β) for each diffraction peak of all the films prepared at different substrate temperatures were measured. Using the corrected value of β of the fitted diffraction peak by subtracting instrumental broadening from the experimental integral width, $\beta\cos\theta / \lambda$ versus $2\sin\theta / \lambda$ plots were drawn for each film (as shown in figure 6 and 7). The average grain sizes D and average strains ε calculated from the intercepts and slopes of these linear plots for different films are tabulated in table 1. Figure 8(a) shows the variation of average grain size D with substrate temperature and thickness while figure 8(b) shows the variation of average strain ε with substrate temperature and thickness.

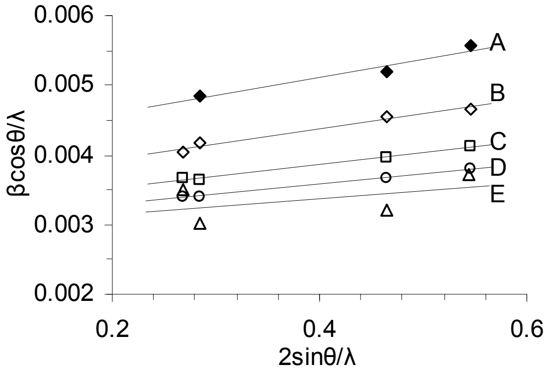


Fig.6. W-H plots of CdSe films of thickness about 3000 Å deposited at different substrate temperatures 423K (A), 443K (B), 473K (C), 493K (D) and 523K (E).

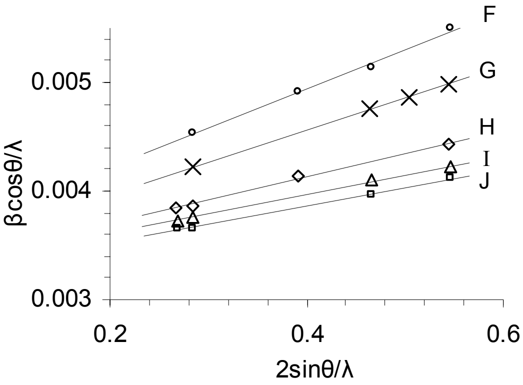


Fig. 7. W-H plots of CdSe films of different thicknesses 830Å (F), 1550Å (G), 1900Å (H), 2300 Å (I) and 3050 Å (J) but deposited at same substrate temperature (473K).

The average grain size was found to increase from 240 Å to 345 Å (Fig 8.a) with a decrease of internal strain from 2.6×10^{-3} to 1.1×10^{-3} (Fig 8.b) with increase of substrate temperature from 423K to 523K for films of thickness about 3000 Å. Similar variation of grain size and strain with thickness also observed for films deposited at substrate temperature 473K as shown in figures 8(a) and (b).

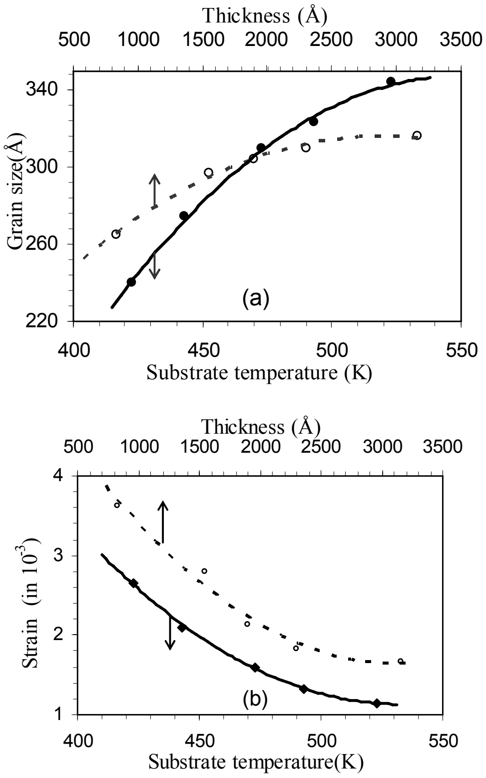


Fig. 8. Variation of average grain size and internal strain with substrate temperature and thickness.

3.1.4: Dislocation density:

The dislocation density δ, defined as the length of dislocation lines per unit volume of the crystal has been determined for CdSe thin films by making use of the values of average grain size D in Williamson and Smallman's formula [28] $\delta = \frac{n}{D^2}$, where n is a factor, which equals unity giving minimum dislocation density. The estimated dislocation densities for the films of different thicknesses prepared at different substrate temperatures are tabulated in table1. The dislocation density has been observed to decrease with increase of substrate temperature and also with film thickness. The nature of variation has been shown in figure figure 9.

It is seen that the dislocation density decreases abruptly from 1.736×10^{14} line/m^2 to 0.84×10^{14} line/m^2 with increase of substrate temperature up to 473K for films of thickness about 3000 Å and from 1.231×10^{14} line/m^2 to 1.027×10^{14} line/m^2 with increase of film thickness for films deposited at substrate temperature 473K and then decreases very slowly.

Comparison of plots in figures 8 (a), 8(b) and 9 shows that the crystallite size increases but the internal strain and dislocation density decreases with increase of film thickness and the substrate temperature at the time of deposition. When thickness increases the average grain size increases and for the film with higher thicknesses the size of the grains does not increase considerably. Since the dislocation density and strain are the manifestation of dislocation network in the films, the decrease in the strain and dislocation density indicates the formation of higher quality films at higher substrate temperatures. When the substrate temperature increases the line width narrows due to the increase in crystallite size. The adatom mobility also increases as the substrate temperature increases which also results in the crystalline size and crystallinity of the films [29].

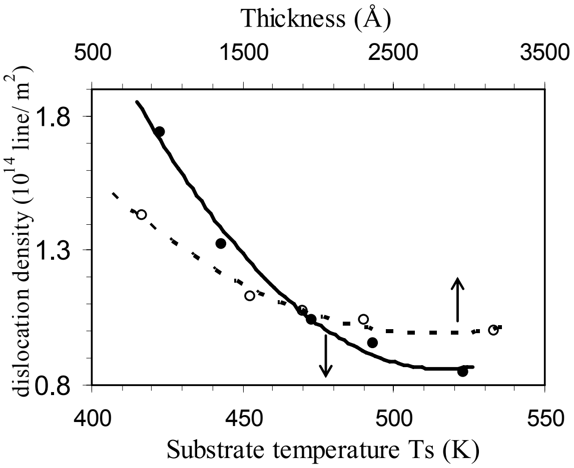


Fig.9.Variation of dislocation density (δ) with substrate temperature and thickness.

Table 1. Micro-structural parameters of CdSe films of different thicknesses prepared on glass substrate at different substrate temperatures.

Substrate temperature (K)	Thickness (Å)	Plane (*hkl*)	Interplaner spacing *d* (Å)	Corrected Lattice constant *a* (Å)	Corrected Lattice constant *c* (Å)	Average grain size *D* (Å)	Average internal strain (ε) 10^{-3}	Dislocation Density (δ) 10^{14} line/m^2
423	3130	(002) (110) (112)	3.510 2.149 1.831	4.286	6.992	240	2.65	1.736
443	3090	(100) (002) (110) (112)	3.732 3.512 2.150 1.832	4.291	7.000	274	2.10	1.332
473	3160	(100) (002) (110) (112)	3.729 3.504 2.149 1.833	4.298	7.010	316	1.66	1.027
493	3050	(100) (002) (110) (112)	3.732 3.516 2.151 1.834	4.299	7.012	323	1.33	0.958
523	3000	(100) (002) (110) (112)	3.731 3.516 2.154 1.836	4.302	7.015	345	1.10	0.840

Substrate temperature (K)	Thickness (Å)	Plane (*hkl*)	Interplaner spacing *d* (Å)	Corrected Lattice constant *a* (Å)	Corrected Lattice constant *c* (Å)	Average grain size *D* (Å)	Average internal strain (ε) 10^{-3}	Dislocation Density (δ) 10^{14} line/m^2
473	830	(002) (102) (110) (112)	3.521 2.364 2.149 1.839	4.270	6.965	264	3.63	1.427
473	1550	(002) (110) (103) (112)	3.527 2.151 2.032 1.838	4.289	6.996	297	2.80	1.131
473	1900	(100) (002) (102) (112)	3.734 3.517 2.426 1.837	4.293	7.002	303	1.90	1.077
473	2300	(100) (002) (110) (112)	3.731 3.508 2.147 1.834	4.295	7.007	310	1.81	1.040
473	3160	(100) (002) (110) (112)	3.729 3.504 2.149 1.833	4.298	7.010	316	1.66	1.027

3.2 Morphological and quantitative study

3.2.1 Scanning electron microscope (SEM)

Fig. 10 shows the scanning electron micrograph of a typical CdSe thin film of thickness about 3050Å deposited at a substrate temperature of 473K. Figure shows the presence of a homogeneous, adherent, fine grained polycrystalline surface morphology. The grains in the films are densely packed, well defined and having almost similar size. There are no macroscopic defects like void, pinhole, peeling or cracks. From the featureless surface morphology we can anticipate that this film will exhibit very low optical scattering losses and should therefore be suitable for optoelectronic applications.

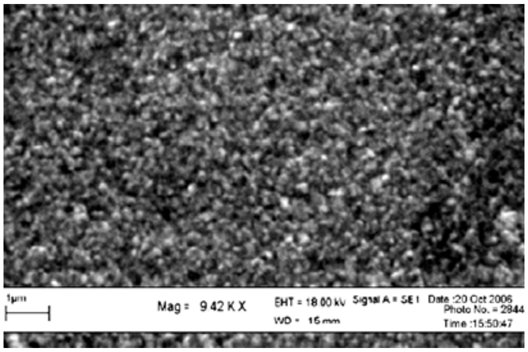
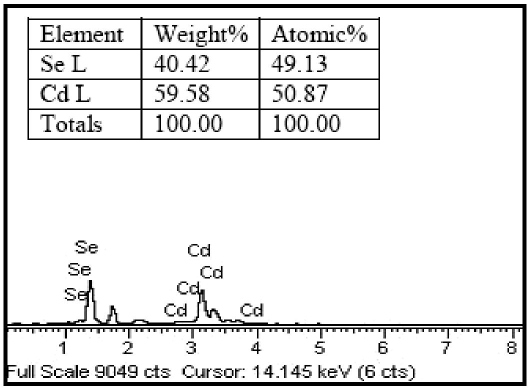


Fig. 10. SEM photograph of a CdSe thin film of thickness ~ 3050Å deposited at Ts = 473K (Magnification 9.42kX).

3.2.2 Composition analysis



Element	Weight%	Atomic%
Se L	40.42	49.13
Cd L	59.58	50.87
Totals	100.00	100.00

Fig. 11. The EDAX spectrum giving the compositional information of CdSe film deposited at 473 K.

The quantitative analysis of the CdSe films thermally deposited on glass substrates at substrate temperature 473K were carried out by using EDAX technique, at different points to study the stoichiometry of the film. Figure 11 shows a typical EDAX pattern and details of relative analysis. The elemental analysis was carried out only for Cd and Se; the average atomic percentage of Cd:Se was 50.87:49.13, showing that the sample was slightly Se deficient (showing that the film was in good stoichiometric ratio).

4. Conclusions

CdSe thin films of different thicknesses have been prepared by thermal evaporation method at different substrate temperatures. From the XRD spectra it is found that the CdSe films prepared at higher substrate temperature are polycrystalline in nature and have hexagonal (wurtzite) structure. The structural parameters such as lattice constants, average grain size, internal strain and dislocation density were calculated. With the increase of substrate temperature at the time of deposition and thickness of the films the average grain size is found to increase, however, the internal strain and dislocation density decrease. The substrate temperature of about 473K has been found to be suitable for depositing good quality polycrystalline thin films of CdSe of thickness about 2000Å and above with less number of defects and with lattice constants nearer to the bulk values of CdSe.

Acknowledgement

The authors sincerely thank M. Kar, Scietific Officer, Nanotechnology Centre, IIT Guwahati, for providing the XRD facility. Two of the authors (M N B and S C) are grateful to the UGC, Govt. of India for awarding Teachers Fellowship for these research works.

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