

CHEMICAL AND STRUCTURAL CHARACTERIZATION OF CdSe THIN FILMS

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Since the last two decades, in the area of electronics, group II-VI compounds have drawn considerable interest due to their various applications. Cadmium Selenide (CdSe), a member of this group, is one of the promising semi conducting material from its applications point of view. The present investigations have been in the direction of the preparation and structural characterization of CdSe thin films. The chemical composition of the deposited CdSe thin films has been confirmed using EDAX technique. It has been found that the material in thin film form possesses nearly desired stoichiometry. The structural characterization of these films has been carried out using X-ray diffraction and electron microscopy and the data have been analyzed. The transmission electron microscopy of the CdSe thin films was also investigated and the effect of film thicknesses on the grain size has been analyzed.

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1. Introduction

The group A^{II} B^{VI} compounds have been found to be interesting for the technical applications because of their wide range of chemical, structural, electrical and optical properties [1-7]. Therefore, intensive investigations have been carried out to form this compound in single crystal [8] and thin film form. Several methods have been employed for the preparation of thin films of these compounds [9-18]. The thermal evaporation carried out in vacuum is one of the most known methods for the same. However, experiments have revealed that it is always a little difficult to prepare thin films using this technique where the repeatable structural and chemical properties could be achieved. This is primarily attributed to the fact that these compounds crystallize in either hexagonal structure or a cubic zinc blende structure. It is therefore, always difficult to form thin films having crystallites of only one phase. Besides, the thermal evaporation of these compounds may result into the small non-stoichiometric growth of the films. All these aspects also prevail with CdSe compound when prepared in thin film form using the thermal evaporation technique.

In light of this, the present investigations have been carried out to study the effect of thickness on the chemical and structural properties of CdSe deposited in thin film form using the well known thermal evaporation technique. Also, the micro structure of the thin films deposited on glass substrates has been studied and these results are used to evaluate the grain size in such films. The comments have been incorporated in present paper regarding the effect of thickness on the grain size involved in the formation of CdSe thin films.

2. Experimental

CdSe thin films of different thicknesses have been deposited by thermal evaporation technique using stoichiometric powder (99.99% pure) of CdSe compound from molybdenum boat on ultrasonically and chemically cleaned glass substrates. The films have been deposited at a pressure less than 10^{-5} Torr in a vacuum

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coating unit (Hind high vac, Bangalore, India). The thicknesses of the films have been controlled during deposition process and measured using a quartz crystal thickness monitor.

The chemical compositions of the deposited films have been confirmed using the standard Energy Dispersive Analysis of X-rays technique. The X-ray powder diffraction technique has been used for structural characterization. The d-values were calculated and the data has been analyzed to confirm the structure of CdSe.

To observe the microstructure of CdSe thin films, thin film samples were prepared on freshly cleaved crystals of NaCl substrates using CdSe powder. These thin film samples were floated on distilled water to dissolve the NaCl substrates and the films were transferred on the grid of the Philips, Netherlands (Model: Tecnai 20) electron microscope for further experiments.

3. Results and discussion

CdSe thin films having various thicknesses ($t = 3000 \text{ \AA}$, 6000 \AA , 9000 \AA and 12000 \AA) were deposited on pre-cleaned glass slides (used as substrate) at a room temperature. These films were characterized for their chemical and structural behavior using Energy Dispersive Analysis of X-rays, X-rays diffraction and Transmission Electron Microscopy.

The results of EDAX have been shown in Fig. 1 for the films having four different thicknesses (3000 \AA , 6000 \AA , 9000 \AA and 12000 \AA).

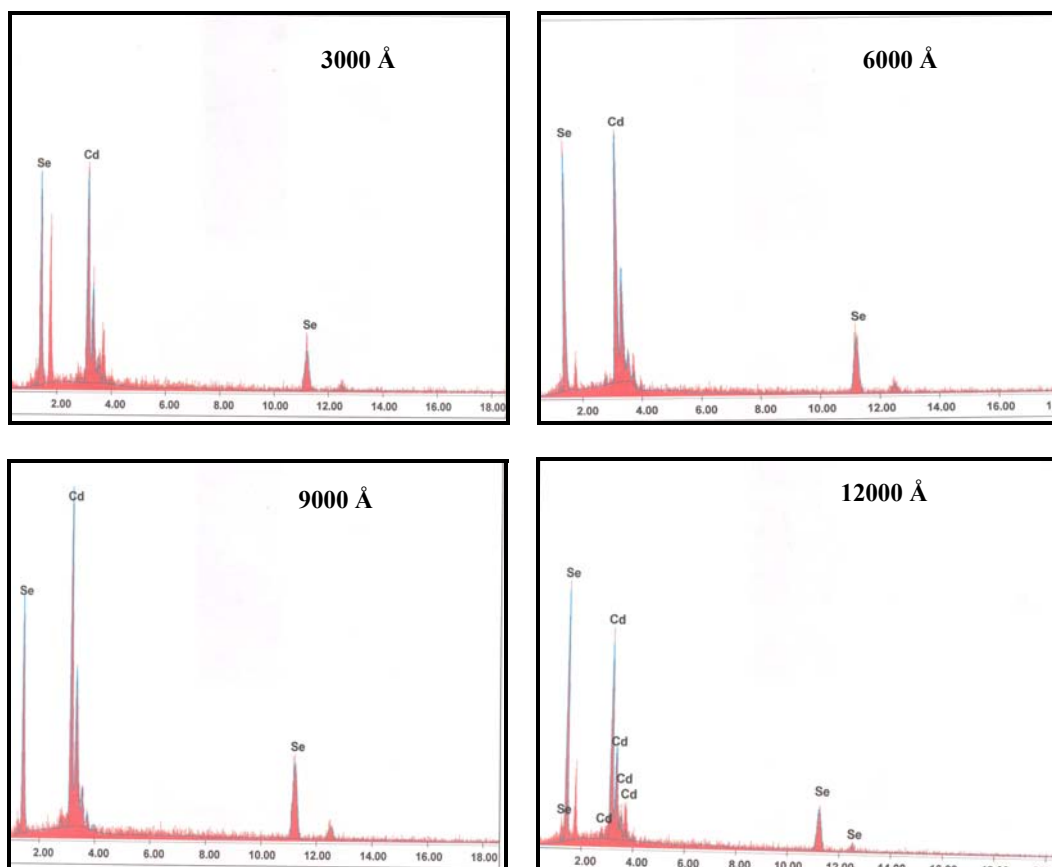


Fig.1. Typical EDAX for CdSe thin films having thicknesses 3000 \AA , 6000 \AA , 9000 \AA and 12000 \AA

These results were used to calculate the weight percentage of Cadmium & Selenium in CdSe films for all the four thicknesses, which have been summarized in Table 1.

Table 1. Atomic and Weight percentage of Cd and Se in thin CdSe films for four thicknesses

Elements	Standard		Thickness 3000 Å		Thickness 6000 Å		Thickness 9000 Å		Thickness 12000 Å	
	Cd	Se	Cd	Se	Cd	Se	Cd	Se	Cd	Se
Wt %	58.73	41.27	63.43	36.57	59.20	40.80	59.68	40.32	61.00	39.00
At %	—	—	54.93	45.07	50.48	49.52	50.97	49.03	52.35	47.65

Table 1 also contains the weight percentage of Cadmium and Selenium evaluated using the standard atomic weights. From this table, it can be seen that the composition of CdSe in all the films reveal nearly desired stoichiometry. The table also shows that there is a presence of excess Cadmium in all these films. This is quite obvious because CdSe, being a compound semiconductor, disintegrates a little during the thermal evaporation process. This leads to the presence of excess Cadmium and deficiency of selenium.

After confirmation of the stoichiometry of CdSe in all these films, the structural characterization was carried out to find out various structural parameters as well as the exact type of structure. The X-ray diffractogram of CdSe obtained through X-ray powder diffraction technique for all thicknesses have been shown in fig. 2. From this figure it is quite evident that there is one peak having very high intensity which appears around angle 25° . The same graphs with magnification of scale have been shown in fig. 3. The details of the peaks observed in all these magnified X-ray diffractogram have been used to calculate the d-spacings. Also the structure of CdSe in all these films has been confirmed from the same data.

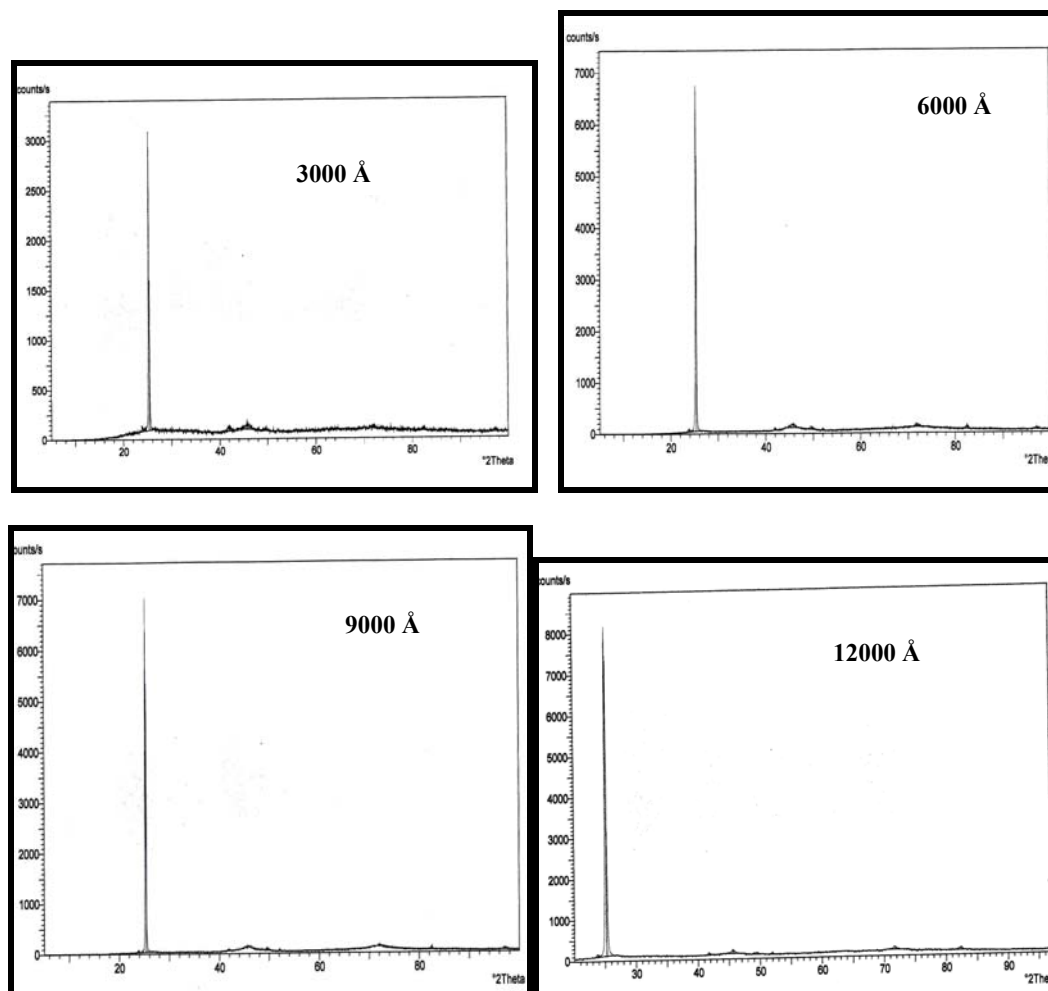


Fig. 2. Typical X-ray diffractograms for CdSe thin films of thicknesses 3000 Å, 6000 Å, 9000 Å and 12000 Å.

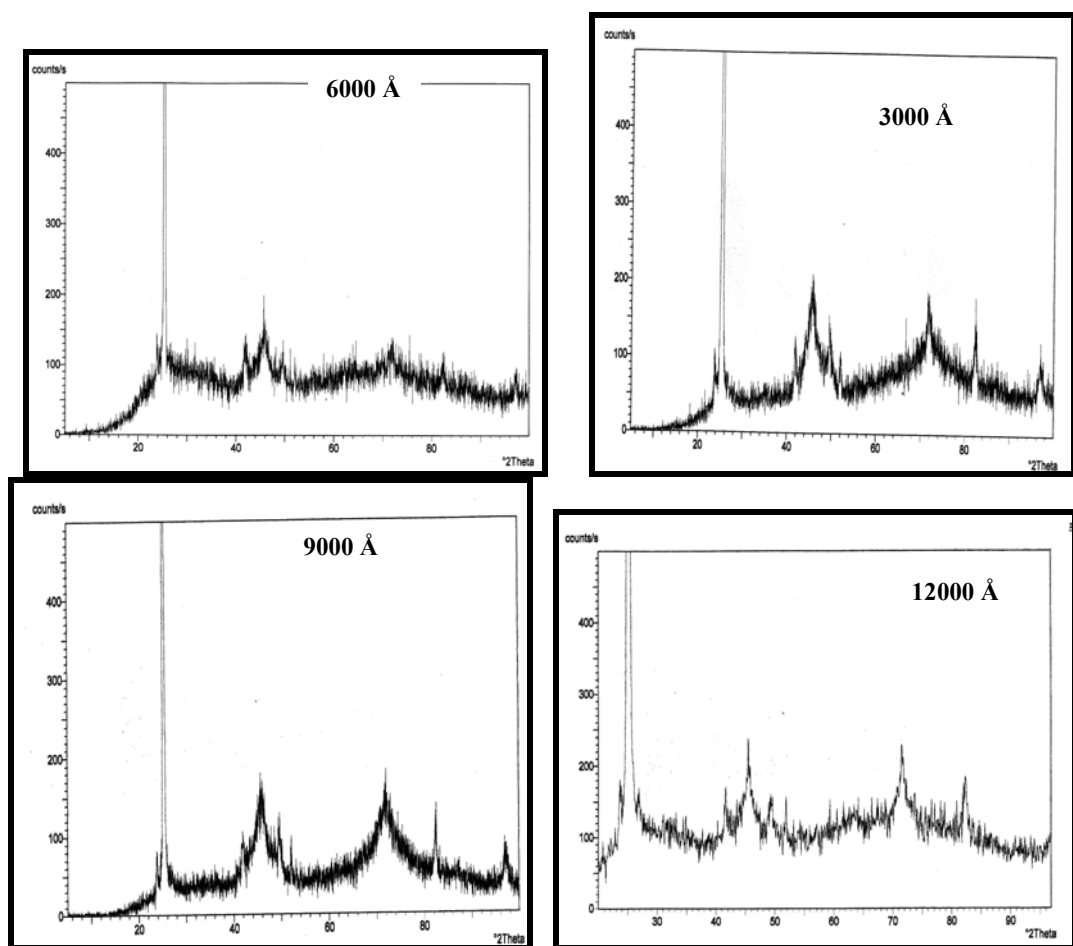


Fig.3 Typical X-ray diffractograms for CdSe thin film with magnified scale for thicknesses 3000 Å, 6000 Å, 9000 Å and 12000 Å

Table 2, 3, 4 and 5 contains the details of the d-spacings, the angle at which the peaks have been observed, relative intensity of all these peaks etc. in case CdSe thin films of all the four thicknesses.

Table 2. XRD data of CdSe thin film ($t = 3000 \text{ \AA}$)

d-spacing (Å)	Relative Intensity (%)	Angle ($^{\circ}2\theta$)	Peak Height (counts/s)	Background (counts/s)	Tip Width ($^{\circ}2\theta$)	Significance
3.70983	2.52	23.96726	37.99	79.90	0.30000	1.03
3.50329	100.00	25.40322	1510.47	91.13	0.48000	2.88
2.15012	2.81	41.98555	42.40	79.89	0.60000	1.63
1.97764	3.42	45.84603	51.66	98.48	0.96000	1.28
1.83689	1.55	49.58566	23.43	82.17	0.96000	1.28
1.31096	1.62	71.96922	24.44	95.72	0.96000	1.22
1.16881	1.62	82.45144	24.48	70.16	0.72000	1.41
1.02594	1.52	97.31967	22.91	53.77	0.60000	1.31
1.00985	1.04	99.41786	15.77	53.77	0.42000	1.01

Table 3. XRD data of CdSe thin film ($t = 6000 \text{ \AA}$)

d-spacing (\AA)	Relative Intensity (%)	Angle ($^{\circ}2\theta$)	Peak Height (counts/s)	Background (counts/s)	Tip Width ($^{\circ}2\theta$)	Significance
3.71853	0.95	23.91033	50.65	39.63	0.36000	3.55
3.51042	100.00	25.35075	5338.73	51.54	0.36000	19.08
2.14937	0.82	42.00088	43.64	64.88	0.48000	1.56
1.97935	1.39	45.80425	74.22	114.00	0.60000	1.49
1.83369	1.07	49.67800	56.92	78.66	0.36000	2.03
1.75280	0.77	52.13842	41.16	57.89	0.48000	1.69
1.31207	1.07	71.89880	57.10	113.08	0.48000	1.01
1.16825	1.12	82.49985	59.83	70.82	0.42000	1.42
1.02690	0.71	97.19851	37.97	54.30	0.96000	1.80

Table 4. XRD data of CdSe thin film ($t = 9000 \text{ \AA}$)

d-spacing (\AA)	Relative Intensity (%)	Angle ($^{\circ}2\theta$)	Peak Height (counts/s)	Background (counts/s)	Tip Width ($^{\circ}2\theta$)	Significance
3.72092	0.76	23.89473	40.37	29.13	0.30000	1.45
3.50461	100.00	25.39343	5303.38	38.41	0.36000	18.60
2.15194	0.59	41.94825	31.52	58.00	0.48000	1.23
1.83433	0.67	49.65964	35.57	64.01	0.48000	1.60
1.75286	0.62	52.13662	33.06	45.97	0.36000	2.23
1.16781	1.05	82.53779	55.84	52.66	0.48000	1.80
1.02727	0.61	97.15229	32.21	36.90	0.60000	1.27

Table 5. XRD data of CdSe thin film ($t = 12000 \text{ \AA}$)

d-spacing (\AA)	Relative Intensity (%)	Angle ($^{\circ}2\theta$)	Peak Height (counts/s)	Background (counts/s)	Tip Width ($^{\circ}2\theta$)	Significance
3.72989	0.82	23.83645	59.33	104.75	0.42000	1.65
3.52451	100.00	25.24772	7227.19	125.78	0.42000	17.07
2.16095	0.74	41.76524	53.74	105.63	0.56000	1.06
1.98581	1.24	45.64681	89.29	131.93	0.56000	1.20
1.84274	0.64	49.41768	46.20	102.56	0.84000	2.20
1.75839	0.57	45.96036	41.40	95.88	0.42000	1.53
1.31428	1.08	71.75926	78.01	144.41	0.42000	1.61
1.16919	0.97	82.41886	70.01	109.29	0.56000	1.19

From these tables and Fig. 2, it is quite apparent that at angle around 25° , we get the highest intensity of peak, which is very prominent. It reflects that the orientation of plane along this angle is observed to be highly preferable in CdSe thin film investigated here. The above results have been used to find out the h,k,l values in all the cases. These results have been summarized in Table 6, 7, 8 and 9. The values of h,k,l and d-spacing have been matched with the standard ASTM data [19]. From the comparison of the observed d-spacing values and the ASTM data, it was inferred that CdSe possesses hexagonal structure in present investigation which match with the reports observed in literature [20-22]. Once the structure is confirmed, the lattice parameters a and c have been calculated using the following formula.

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

These values are also presented in Table 6, 7, 8 and 9.

Table 6. Indexing of X-ray diffraction peaks for CdSe thin films ($t = 3000 \text{ \AA}$)

Obs. No.	d-spacing (\AA) observed	d-spacing (\AA) ASTM data	hkl
1.	3.7098	3.720	100
2.	3.5033	3.510	002
3.	2.1501	2.151	110
4.	1.9776	1.980	103
5.	1.8369	1.834	112
6.	1.3110	1.312	105
7.	1.1688	1.170	302
8.	1.0259	1.0267	116
9.	1.0099	—	—
a = 4.292 \AA		c = 7.007 \AA	

Table 7. Indexing of X-ray diffraction peaks for CdSe thin films ($t = 6000 \text{ \AA}$)

Obs. No.	d-spacing (\AA) observed	d-spacing (\AA) ASTM data	hkl
1.	3.7185	3.720	100
2.	3.5104	3.510	002
3.	2.1494	2.151	110
4.	1.9794	1.980	103
5.	1.8337	1.834	112
6.	1.7528	—	—
7.	1.3121	1.312	105
8.	1.1683	1.17	302
9.	1.0269	1.0273	222
a = 4.297 \AA		c = 7.021 \AA	

Table 8. Indexing of X-ray diffraction peaks for CdSe thin films ($t = 9000 \text{ \AA}$)

Obs. No.	d-spacing (\AA) observed	d-spacing (\AA) ASTM data	hkl
1.	3.7209	3.720	100
2.	3.5046	3.510	002
3.	2.1519	2.151	110
4.	1.8343	1.834	112
5.	1.7529	—	—
6.	1.1678	1.17	302
7.	1.0273	1.0273	222
a = 4.301 \AA		c = 7.009 \AA	

Table 9. Indexing of X-ray diffraction peaks for CdSe thin films ($t = 12000 \text{ \AA}$)

Obs. No.	d-spacing (\AA) observed	d-spacing (\AA) ASTM data	hkl
1.	3.7299	3.720	100
2.	3.5245	3.510	002
3.	2.1610	2.151	110
4.	1.9858	1.98	103
5.	1.8427	1.834	112
6.	1.7584	—	—
7.	1.3143	1.312	105
8.	1.1692	1.17	302
a = 4.292 \AA		c = 7.049 \AA	

From all the above results, it can be inferred that the (002) plane of orientation is observed to be highly preferred plane of orientation in CdSe thin films which also match with earlier reports [23, 24]. The dominance of (002) hexagonal reflection indicates that the preferential growth of crystallites is along this particular direction in case of present investigations. The strong X-ray peak along (002) plane indicates that the preferred orientation of the crystallite grains with c-axis perpendicular to the plane of the substrate that makes (002) peak very strong as compared to the other peaks. The X-ray diffractogram also reveal the fact that CdSe possesses a polycrystalline nature in present investigation.

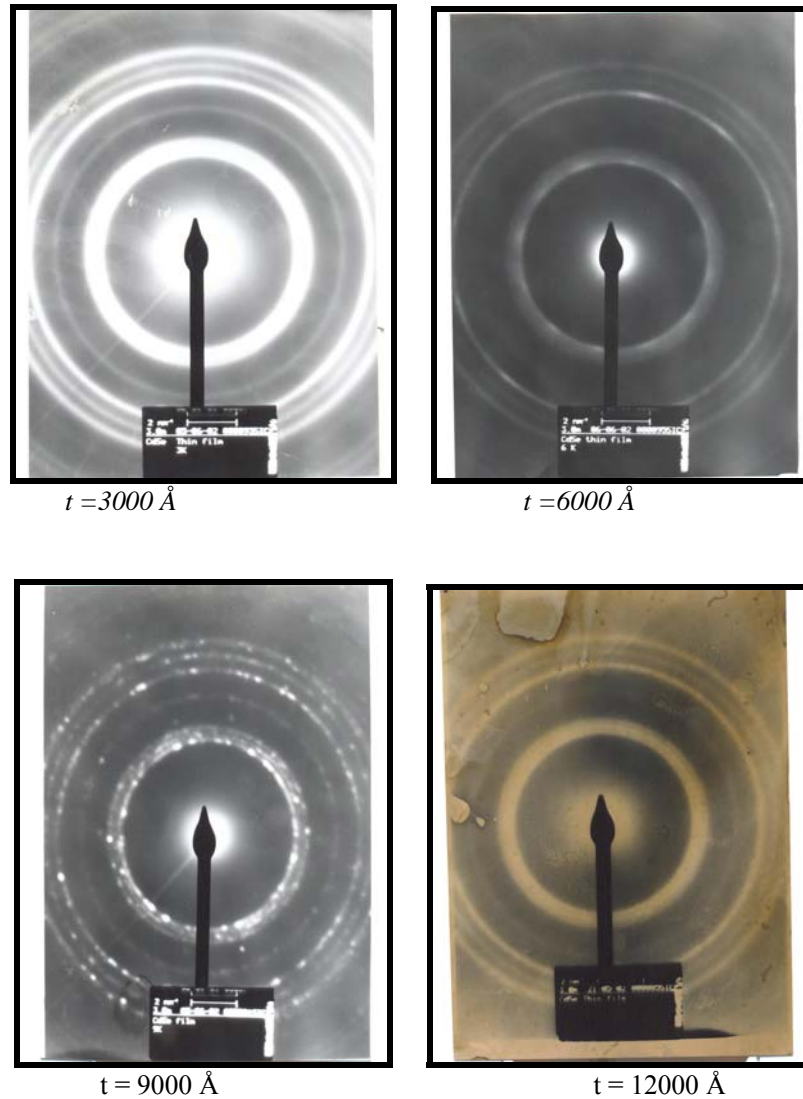


Fig 4. Electron diffraction pattern for CdSe thin film having thicknesses 3000 Å, 6000 Å, 9000Å and 12000 Å.

Since CdSe has been investigated in thin film form, it is extremely difficult to carry out the X-ray diffraction analysis because the penetration depth of the X-ray beam when incident perpendicular to the surface of the sample becomes very small due to small thickness. As a result the intensity of peaks observed becomes weak. The X-ray diffraction patterns shown in Fig. 3 clearly indicate that the intensity of the peak is not very high as compared to the background noise even though. This X-ray diffractogram have been taken by adjusting the sample using Seeman-Sboblín geometry (specially used to analyze thin samples by adjusting the grazing angle).

The electron diffraction patterns for Cadmium Selenide thin films are shown in Fig.4. The nature of these diffraction patterns (observed rings) confirms that the CdSe thin films deposited in present investigations using thermal evaporation technique are polycrystalline in nature.

These diffraction patterns were chosen for the calculations of the d-values (distance between adjacent planes) and the indexing of reflections. For this determination, the normal constant λL , which is also referred to as area constant, was determined by knowing the value of λ (the wavelength of the electron beam) and L (the distance between photographic film and the specimen). The electron beam wavelength λ was calculated from the equation

$$\lambda = \sqrt{\frac{1.50}{U(V)}} \text{ nm} \quad (2)$$

where U (V) is the accelerating potential in volts.

The accelerating potential of the electron beam used for these measurements was 200 kV. Substitution of this value in equation (2) yield λ around 0.0274 Å. Using the value of L (3 m) and the value of λ , the product λL was calculated and found to be $822 \times 10^{-10} \text{ cm}^2$.

After this exercise, the patterns were placed on the platform of a comparator for the measurement of diameters of the rings. Substituting the value of diameters of the rings and λL in equation (3), the d-values corresponding to all these rings have been calculated and are given in Table 10, 11, 12 and 13.

$$d = \frac{2 \lambda L}{\text{diameter}} \quad (3)$$

These tables also contain the d-values obtained from standard ASTM data. It is seen that there is a good matching between the calculated d-values and the standard ones [19]. This confirms that the deposited CdSe films possess the hexagonal structure.

Thus, it can be broadly concluded that CdSe films having hexagonal structures can be prepared by thermal evaporation method (resistive heating technique).

Table 10. Results of TEM analysis for CdSe thin films ($t = 3000 \text{ \AA}$)

Ring No.	Diameter of ring D cm	Interplanar spacing $d = 2\lambda L/D \text{ \AA}$	ASTM data d-values \AA	hkl
1.	4.421	3.716	3.72	100
2.	6.423	2.558	2.554	102
3.	7.532	2.181	2.151	110
4.	8.269	1.987	1.980	103
5.	8.821	1.863	1.863	200
6.	11.303	1.453	1.456	203

Table 11. Results of TEM analysis for CdSe thin films ($t = 6000 \text{ \AA}$)

Ring No.	Diameter of ring D cm	Interplanar spacing $d = 2\lambda L/D \text{ \AA}$	ASTM data d-values \AA	hkl
1.	4.433	3.707	3.72	100
2.	4.689	3.504	3.51	002
3.	7.206	2.280	—	—
4.	7.652	2.147	2.151	110
5.	8.311	1.977	1.980	103

Table 12. Results of TEM analysis for CdSe thin films ($t= 9000 \text{ \AA}$)

Ring No.	Diameter of ring D cm	Interplanar spacing $d = 2\lambda L/D \text{ \AA}$	ASTM data d-values \AA	hkl
1.	4.422	3.715	3.72	100
2.	4.683	3.508	3.51	002
3.	7.055	2.329	—	—
4.	7.640	2.151	2.151	110
5.	8.305	1.978	1.980	103

Table 13. Results of TEM analysis for CdSe thin films ($t = 12000 \text{ \AA}$)

Ring No.	Diameter of ring D cm	Interplanar spacing $d = 2\lambda L/D \text{ \AA}$	ASTM data d-values \AA	hkl
1.	4.422	3.716	3.72	100
2.	4.681	3.51	3.51	002
3.	7.103	2.313	—	—
4.	7.640	2.151	2.151	110
5.	8.298	1.98	1.98	103

Using the electron microscope, the micrographs of the CdSe thin films of the above four thicknesses deposited on glass substrates in present investigations have been taken at magnification 260000 X and are shown in Fig.5.

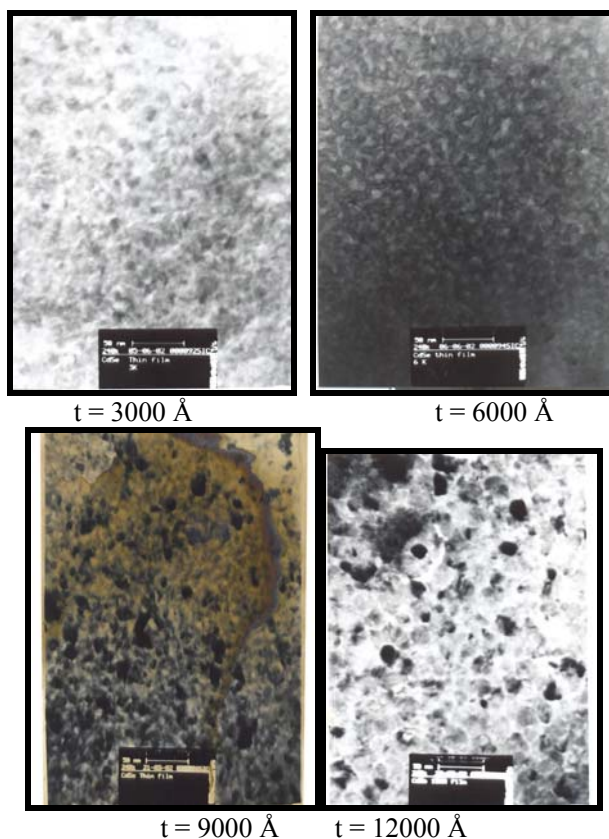


Fig. 5 Micrographs of the CdSe thin films having different thicknesses

The average grain size observed from the micrographs for different film thicknesses are given in Table 14. The micrographs and the Table 14 apparently indicate that the average value of grain size of the CdSe films having thickness between 3000 Å to 12000 Å has been found to be in the nanometer range. This result is in good matching with the results reported by previous workers [25]. Besides the micrographs and Table 14 it is quite apparent that the average grain size increases with thickness. This observation is also in good agreement with the results reported by previous workers [23-26].

Table 14 Values of grain size for different film thickness

Thickness of the film	Grain size
3000 Å	7.7 nm
6000 Å	11.55 nm
9000 Å	15.4 nm
12000 Å	19.25 nm

4. Conclusion

The present study indicates that CdSe thin films deposited by thermal evaporation technique having different thicknesses are found to have preferred orientation along (002) plane. In present investigations, CdSe thin films possess hexagonal structure. The X-ray diffractograms reveals the fact that CdSe possesses a polycrystalline nature in present investigations. The average grain size increases with film thickness.

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