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STRUCTURAL CHARACTERIZATION OF THERMALLY EVAPORATED CdSe THIN FILMS

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Cadmium Selenide thin films of different thickness, (1530-2230 Å) deposited by thermal evaporation on suitably cleaned glass substrates at different substrate temperatures (473-623K) are of polycrystalline nature having hexagonal structure. For all deposited films the preferential orientation is [002]. Some other orientations like [100], [110] and [112] are also observed in the films depending upon the substrate temperature of deposition. The values of lattice constant, grain size, microstrain and dislocation density of the deposited films are calculated and their variations with substrate temperature and film thickness are studied.

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Keywords. CdSe thin films, Lattice constant, Grain size, Microstrain, Dislocation density

1. Introduction

CdSe is a binary II-VI semiconductor and among this group of semiconductor compounds, it is considered as an important material for the development of different optoelectronic devices [1,2,3] because of its high photosensitivity and suitable intrinsic band gap, 1.74eV [4]. In recent years special attention has been given to the investigation of optoelectronic properties of CdSe thin films in order to improve the performance of devices made of it and also for finding new applications [5,6]. For preparation of CdSe thin films, different growing methods have been reported [7,8]. Out of these, physical vapour deposition in its variants is often used as it offers many possibilities to modify the deposition parameters and to obtain films with pre-determined structure and suitable phototransport properties. Electrical and optical properties of semiconducting films are essential requirement for proper application in various optoelectronic devices. These properties of the films are sufficiently structure sensitive. Therefore appropriate structural characterization of the films is necessary. It may be noted that the structural parameters such as crystallinity, crystal phase, lattice constant, grain size etc are strongly dependent on the deposition conditions. The structure of thermally deposited CdSe thin films is likely to be governed by the degree of vacuum, rate of deposition, substrate temperature, film thickness etc. An experimental study has been undertaken in order to structurally characterize thermally evaporated CdSe thin films and in this paper some correlative results of different structural parameters with substrate temperature and film thickness has been reported.

2. Experimental

Thin films of CdSe of different thickness, t, (1530-2230Å), were deposited at different substrate temperatures, T_s ,(473-623K), on chemically and ultrasonically cleaned glass substrates with the help of a Hind High Vacuum Coating unit at a vacuum better than 10^{-5} Torr. The source to

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substrate distance was maintained at 6.5 cm for all the cases. The prepared films were annealed in vacuum at elevated temperature for an hour. Pure (99.999%) bulk CdSe sample was used as the source material. Thin tantalum boats of proper size and shape were used as the source heater. A suitably designed and assembled multiple beam interferometer was used to measure the thickness of the films with an accuracy of ±15 Å. X-ray diffractogram of CdSe thin films were taken by using Philips X-ray diffractometer (Philips X'Pert Pro) with CuKα radiations of wavelength 1.54 Å. The diffractrometer was operated at 40 keV and 30 mA. The line profile was chart recorded at a scanning rate of $(0.01^0–0.07^0)s^{-1}$ with a Phillips automatic recorder. X-ray diffractogram analysis including the peak search was done by computer programming (Philips X'pert software) with minimum peak significance 0.65. XRD pattern of all the CdSe films were taken from 10^0 to 70^0.

Surface morphology of the CdSe films were investigated by using scanning electron microscope with an accelerating potential of 18 kV and the qualitative analysis were carried out with the help of WDXRF (Wavelength Dispersive X-ray Fluorescence) spectrometer with atomic number 9 (Fluorine) to 92 (Uranium).

3. Structural parameters

3.1 *Determination of lattice constant*

The lattice parameter, a, for cubic phase structure [hkl] is determined by the relation

$$d_{hkl} = a/(h^2+k^2+l^2)^{1/2} \tag{1}$$

where $N = h^2+k^2+l^2$ is a number. Observing the distribution of N values, the type of the cubic lattice may be determined [9]
From the Bragg's law,

$$\lambda = 2a \sin\theta / (h^2+k^2+l^2)^{1/2}$$

or

$$\sin^2\theta = (\lambda^2/4a^2)(h^2+k^2+l^2) = \lambda^2 N / 4a^2 \tag{2}$$

For hexagonal crystals; the lattice constants, a, and, c, are evaluated from the following relations

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

From Bragg's law

$$\sin^2\theta = [(\lambda^2/3)\ \{(h^2+hk+k^2)/a^2\}] + (\lambda^2 l^2/4c^2) \tag{4}$$

According to Vegards law, the lattice parameters of hexagonal unit cell are nearly related to cubic lattice parameters of same material by [10]

$$a_{hex}= (1/2)^{1/2}a_{cubic} \qquad c_{hex}= (4/3)^{1/2}a_{cubic} \tag{5}$$

Hence for 'ideal' Wurtzite lattice, the relation between the two lattice parameters is [11]

$$c_{hex}= (1.633)a_{hex} \tag{6}$$

which can be used for the calculation of lattice parameters of CdSe thin films.

There are several possible sources of error like divergences of X-ray beams, refraction and absorption of X-rays by the specimen etc in the

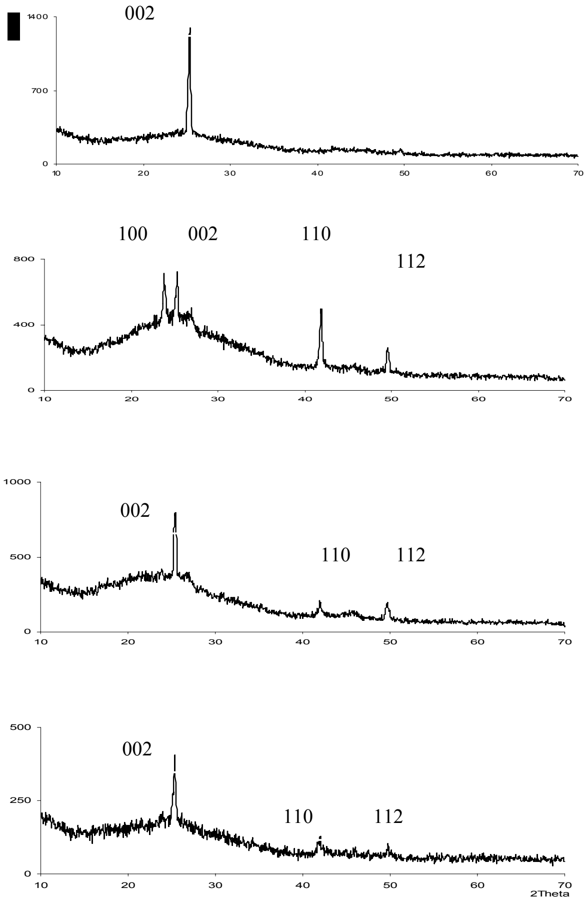

Fig. 1. XRD patterns of CdSe thin films of same, t = 2000 Å and deposited at different T_S.

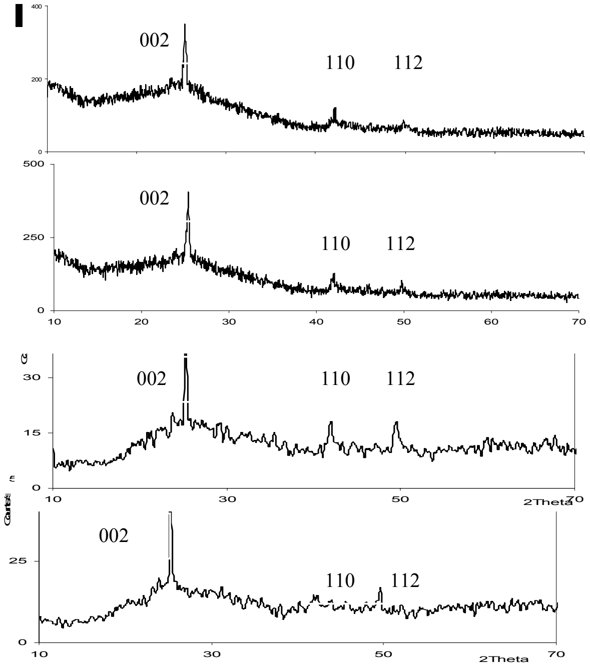

Fig. 2. XRD patterns of CdSe thin films of different, t, and deposited at same T_S = 473K.

measurement of θ and d values. So accuracy in the determination of lattice constant is dependent upon the accuracy of their measurements. We have

$$d = (\lambda/2)\ \mathrm{cosec}\theta \tag{7}$$

So $\delta d = -\ (\lambda/2)\ (\mathrm{cosec}\theta\ \cot\theta)\ \delta\theta$

For $\theta = 90^o$, $\delta d/d=0$

The most accurate value of lattice parameters are estimated from the Nelson-Riley plot [12] when $\theta = 90^o$. It is plotted between calculated lattice constant values (a and c) for different planes and the error function

$$f(\theta) = (1/2)\{(\cos^2\theta/\sin\theta)+(\cos^2\theta/\theta)\} \tag{8}$$

3.2 *Grain size*

The grain size (D_{hkl}) for the thermally evaporated CdSe thin films are evaluated for the preferred planes [hkl] using the Scherrer formula [13]

$$D_{hkl} = k\lambda / \beta_{2\theta}\mathrm{Cos}\theta \tag{9}$$

with k = 0.94, where θ is the Bragg's angle, λ is the wavelength of X-rays used, $\beta_{2\theta}$ is the width of the peak at the half of the maximum peak intensity.

3.3 *Average strain*

The origin of strain is related to lattice 'misfit' which in turn depends upon the growing conditions of the films. The microstrain (ε) developed in the thin films can be calculated from the relation [14]

$$\varepsilon = (\beta_{2\theta}\cot\theta)/4 \tag{10}$$

where θ and $\beta_{2\theta}$ has their usual significances.

3.4 Dislocation density

Dislocations are an imperfection in a crystal associated with misregistry of the lattice in one part of the crystal with respect to another part. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections. In fact growth mechanism involving dislocation is a matter of importance. The dislocation density of thin films are given by the Williamson and Smallman's relation [15]

$$\delta = n / D^2 \tag{11}$$

where n is a factor, which equals unity giving minimum dislocation density and D is the grain size.

4. Results and discussion

4.1 Structural analysis

The X-ray diffraction profiles of CdSe thin films (Figs 1 & 2) of different t, (1530-2230Å) reveal that films grown at room temperature are amorphous (not shown in figure) and those grown at elevated, T_s ,(473-623K) are polycrystalline having hexagonal ZnS type structure. This is confirmed by comparing the observed 'd' values of the XRD patterns of the films with the standard 'd' values of JCPDS X-ray powder file data [16]. In these films [002] plane is very clear and abundant. However small percentage of orientations of [110], [112] & [100] planes are also observed depending upon T_s of deposition. For the film deposited at 573K diffracted intensity from [100] and [110] is comparable to the corresponding intensity for [002] plane. The dominance of [002] hexagonal reflection indicates that the preferential growth of crystallite is in this particular direction. The broad hump that is observed in the background of XRD is due to the amorphous glass substrate and also possibly due to some amorphous phase present in the CdSe thin film.

Different structural parameters of the CdSe thin films having different, t and grown at different T_s are calculated by using relevant formulae and are systematically presented in Table 1.

The data of the table show variations in the structural parameters with T_s, t and also along different orientations. The corrected values of lattice constants are estimated from Nelson-Riley plots (not shown here) which are found to be in the range (4.286-4.304 Å) for, a, and (6.992-7.020 Å) for, c. The values of lattice parameters (a and c), grain size, microstrain and dislocation density are correlated with T_s as well as with t and are depicted in figures from 3 to 10. The correlation with T_s (figure 3) shows that with increase of T_s the lattice constants (a and c) initially increase, reach a maximum at around 560 K and then shows a decreasing trend. There is a change in lattice constants for the deposited thin films over the bulk values, which suggest that film grains are strained. This may be due to change of nature and concentration of the native defects. The density of the films is therefore expected to change in accordance with the change of lattice constant [17]. The standard values of, a, and, c, for strain free bulk CdSe sample are 4.299 Å and 7.010 Å respectively [16]. Thus it is observed that value of, a, and, c, are slightly greater for films deposited at T_s = 523 K and 573K than their bulk counterparts whereas the values nearly coincide for film deposited at 623 K and t = 2000 Å. The values of, a, and, c, are less than the lattice parameters of the bulk CdSe for films deposited at T_s = 473K with t = 2000 Å.

Table 1. Calculated values of the structural parameters of CdSe thin films, having different thickness, t and also deposited at different T_s.

t (Å)	T_s (K)	hkl	a (Å)	Corr-ected a (Å)	c (Å)	Corr-ected c (Å)	D_{hkl} (Å)	ε in 10^{-3}	δ in 10^{11} cm^{-2}
2000	623	002	4.298	-	7.011	-	350	4.70	0.81
	573	100	4.307	4.304	7.025	7.020	268	6.52	1.39
		002	4.310		7.029		308	5.35	1.05
		110	4.306		7.024		295	3.42	1.14
		112	4.306		7.023		253	3.40	1.56
	523	002	4.296	4.302	7.006	7.017	283	5.80	1.24
		110	4.297		7.008		301	3.34	1.10
		112	4.301		7.015		201	4.26	2.47
	473	002	4.303	4.286	7.018	6.992	280	5.90	1.27
		110	4.297		7.008		253	3.97	1.56
		112	4.293		7.003		221	4.17	2.04
2230	473	002	4.301	4.281	7.016	6.981	323	5.10	0.95
		110	4.291		6.999		341	2.95	0.85
		112	4.290		6.997		326	2.63	0.94
2000		002	4.303	4.286	7.018	6.992	280	5.90	1.27
		110	4.297		7.008		253	3.97	1.56
		112	4.293		7.003		221	4.17	2.04
1750		002	4.323	4.293	7.052	7.005	275	6.20	1.32
		110	4.301		7.015		185	5.46	2.92
		112	4.312		7.032		145	5.95	4.75
1530		002	4.320	4.295	7.046	7.007	171	9.67	3.41
		110	4.297		7.009		167	6.01	3.58
		112	4.314		7.037		228	3.78	1.92

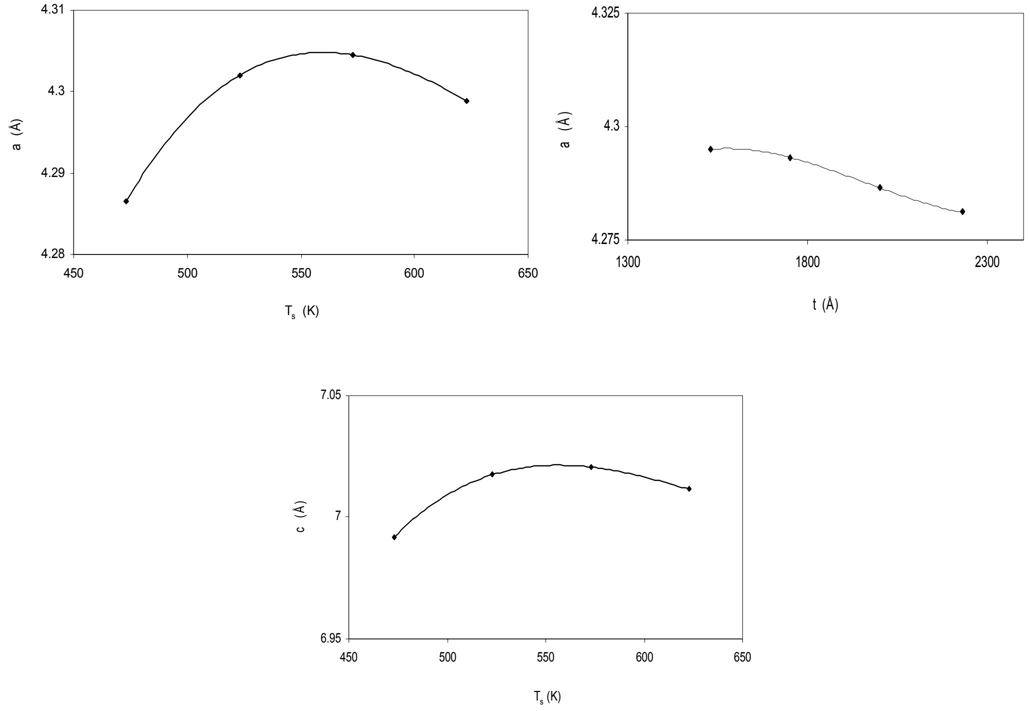

Fig. 3. Variation of lattice constants (a and c), with T_s of CdSe thin films of same t = 2000 Å.

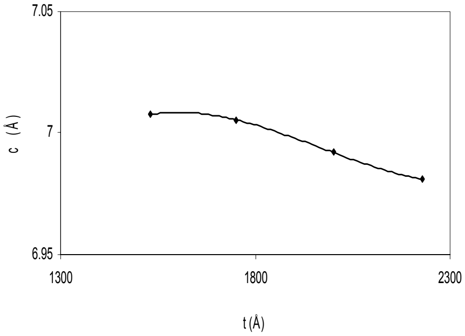

Fig. 4. Variation of lattice constants (a & c), with t of CdSe films deposited at T_s= 473K. 2000Å. This is also true for the other films deposited at T_s = 473K and within the thickness range (1530-2230Å), as observed from table 1, which indicates that deposited films are under compressive strain [18].

The grain sizes of the films corresponding to [002] hexagonal reflection have been found to increase with T_s (figure 5). For the same plane the grain sizes are also found to increase with, t, as seen for the films grown at T_s = 473K (figure 6). But the variation in grain size within the thickness range (1750-2230Å) is not very significant. With increase of T_s the crystallinity of the films improves substantially. At higher T_s in the formation process of the films, ad-atoms possess greater mobility along direction parallel to the substrate surface, thus contributing to the improvement of the crystallization process.

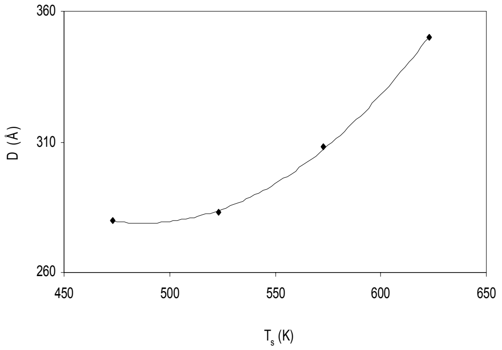

Fig. 5. Variation of grain size (D_{hkl}) with T_s of CdSe thin films of same t = 2000Å.

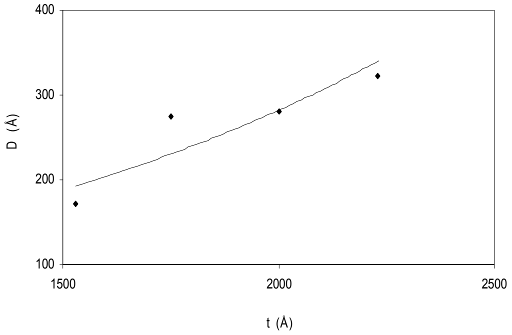

Fig. 6. Variation of grain size (D_{hkl}) with t of CdSe thin films deposited at same T_s= 473K.

The variation of strain with the T_s and t are respectively shown in figures 7 and 8. It is seen that there is a decrease of strain with deposition temperature and thickness of film. Figures 9 and 10 show the variation of dislocation density of CdSe thin films with T_s and t, for films of constant t and constant T_s respectively.

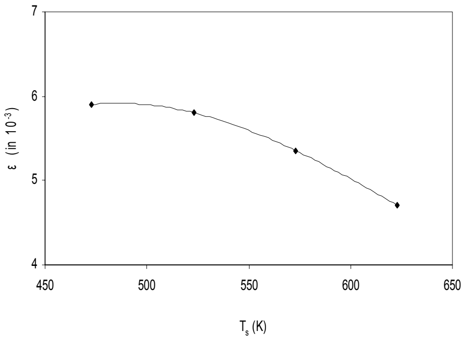

Fig. 7. Variation of strain (ε) with T_s of CdSe thin films of same t = 2000Å.

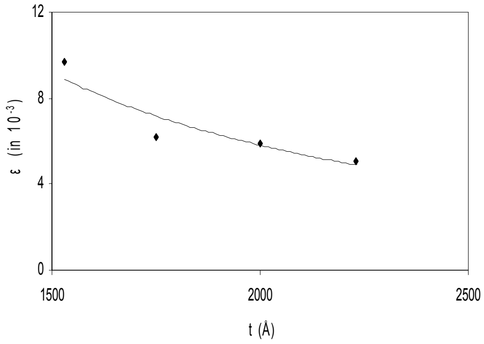

Fig. 8. Variation strain (ε) with t of CdSe thin films deposited at same T_s= 473K.

In polycrystalline samples dislocated atoms occupy the regions near the grain boundaries and from the plots it is observed that dislocation density decreases with t and T_s.

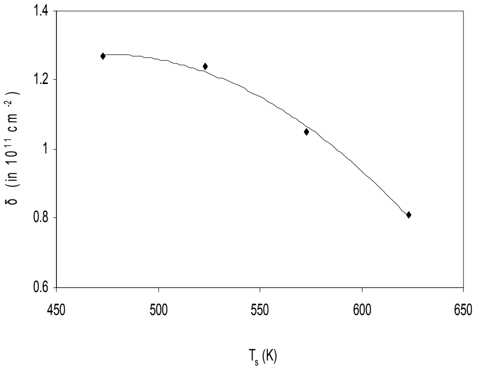

Fig. 9. Variation dislocation density with T_s of CdSe thin films of same t = 2000Å.

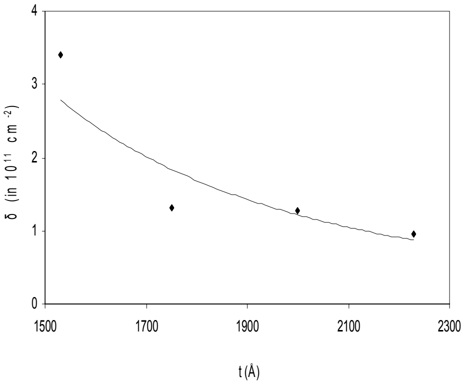

Fig. 10. Variation of dislocation density with t of CdSe films deposited at same T_s= 473K.

But the decrease in dislocation density with film thickness is not very significant. It is therefore confirmed that in thin films containing smaller grain size the number of dislocation density is more.

4.2 Morphological Study

The film morphology under SEM studies show that the films deposited at higher substrate temperatures (below 623K) are fairly uniform, polycrystalline and free from macroscopic defects like cracks or peeling. So for the optoelectronic observations the qualities of such grown films are quite suitable.

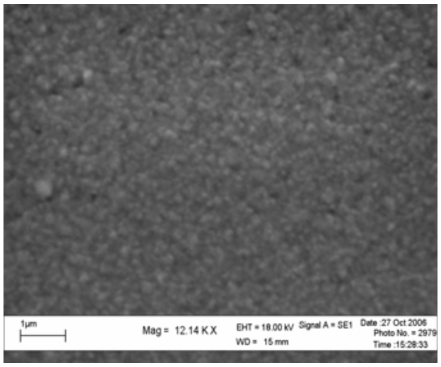

Fig. 11. SEM of a CdSe thin film (t = 2000Å, T_S = 473K) Magnification 12.14 KX.

4.3 Elemental study

Figs 12(a to d) show the XRF spectra of an 'as-deposited' CdSe thin film grown at T_s = 473K. The spectrum in Fig 12(a) shows two peaks of SeK_β and $SeK_{\alpha 1}$ lines, which indicates the presence of Se in the sample film, along with two unknown peaks. The spectrum in Fig 12(b) shows, single peak of $CdK_{\alpha 1}$ lines along with $SbK_{\alpha 1}$ lines. Fig 12(c) shows the presence of $ZrK_{\alpha 1}$ and SeK_β lines where as Fig 12(d) shows the peak of SeL_α lines along with MgK_α and NaK_α lines. Peaks for Zr, Mg and Na appear from the target used and probable impurities present in glass substrate. The unknown peaks were not identified as the supporting peaks were not found.

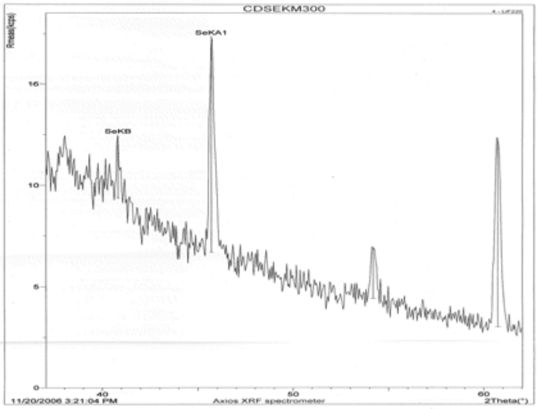

Fig. 12(a) XRF spectra of an 'as-deposited' CdSe thin film showing SeK_β and $SeK_{\alpha 1}$ lines along with two unknown peaks.

Fig. 12(b) XRF spectra of an 'as-deposited' film showing peaks for Sb$K_{\alpha 1}$ and Cd$K_{\alpha 1}$ lines.

Fig. 12(c) XRF spectra of an 'as-deposited' CdSe thin film showing Zr$K_{\alpha 1}$ and SeK_{β} lines.

The presence of such peaks at the same positions for analyzed samples, other than CdSe, indicated that these were not related with experimental CdSe sample. The qualitative analysis of thermally deposited CdSe films by XRF spectrometer confirms the presence of Cd and Se elements without incorporation of any impurities.

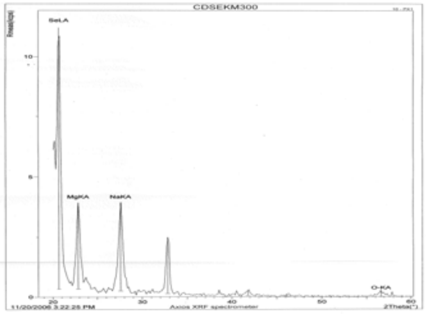

Fig. 12(d) XRF spectra of an 'as-deposited' film showing SeL_{α}, MgK_{α} & NaK_{α} lines along with a small O-K_{α} and an unknown peak.

5. Conclusions

CdSe thin films deposited by the technique of thermal evaporation within the thickness and substrate temperature range (1530-2230Å) and (473-623K) respectively are of polycrystalline nature having hexagonal ZnS type structure. The films are found to have preferred orientation along [002] plane and some small percentage of growth along [100], [110] & [112] are also observed depending upon the substrate temperature of deposition. The crystallinity of the films improves with the increase of substrate temperature of deposition. At any deposition temperature there is a variation in lattice constants of the grown thin films over the bulk suggesting that built-in strains are present in the film grains. The built-in microstrains and dislocation density of the deposited films are found to be dependent on the growth temperatures and the thickness of the films.

SEM observations show the polycrystalline growth for the films deposited at higher T_s and the results of XRF spectra show that 'as-deposited' CdSe thin films are free from impurity, contains Cd and Se elements in nearly in equal proportion. This indicates that the grown CdSe thin films are acceptably stochiometric.

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