Chalcogenide Letters Vol. 6, No. 6, June 2009, p. 279 - 286

DEPOSITION OF CdSe THIN FILMS BY THERMAL EVAPORATION AND THEIR STRUCTURAL AND OPTICAL PROPERTIES

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CdSe, belonging to group II-VI semiconductors, is found to be promising material for its applications in the area of electronics and opto-electronics. The structural and optical properties of CdSe thin films have been investigated. CdSe thin films have been deposited on suitably cleaned glass substrates by thermal evaporation method. The pressure during evaporation was maintained at 10^{-5} Torr. The crystal structure and lattice parameter of these films were determined from X-ray diffractograms. It was observed that the films were polycrystalline in nature having wurtzite structure. The optical bandgap and phonon energy of these films were determined by UV-VIS-IR spectroscopy in the wavelength range 200-3200 nm. The variation of absorption, transmission and reflection parameters with wavelength was investigated. The relation of the extinction coefficient (K) and the refractive index (n) with wavelength have also been analysed and reported in this paper.

(Received May 30, 2009; accepted June 28, 2009)

Keywords: CdSe; Wurtzite; Structure; Bandgap; Phonon energy

1. Introduction

Several semiconducting films have been deposited for optoelectronic device applications. Group II-VI compounds, in general, and cadmium chalcogenides, in particular, have attracted intense scientific and technological interest. CdSe, is a binary II-VI semiconductor and is considered as an important material for the development of different optoelectronic devices [1]. CdSe is one of the prominent materials due to its near optimum direct energy gap and high absorption coefficient. It has become interesting because of its major contributions to light emitting diodes, solar cells, photodetectors, lasers and photo electrochemical cells [2-6]. For the preparation of CdSe thin films, different methods have been used and reported in literature [7]. Optical and electrical properties of semiconducting films are essential requirements for proper applications in various optoelectronic devices [8, 9]. These properties of the films are generally structure sensitive. The structural parameters such as lattice constant, grain size, etc. are dependent on the deposition conditions. The structure of CdSe thin films is dependent on the rate of deposition, substrate temperature, vacuum conditions, film thickness, etc. The optical absorption is known to arise through the interactions of the excited electrons with the lattice perturbed by vibrations or imperfections. In the present work, CdSe thin films were deposited by thermal evaporation method and the results have been analysed and presented.

2. Experimental

Thin films of CdSe having thickness around 2500Å were deposited on chemically and ultrasonically cleaned glass substrates with the help of vacuum coating unit. First of all, the gadgets of the vacuum chamber were cleaned by acetone. A clean evaporation source – molybdenum boat – was fixed in the filament holder inside the chamber. Stoichiometric CdSe powder having purity around 99.99 % was kept in a molybdenum boat. The substrates were cleaned first by acetone. Then they were put on the substrate stand and crystal monitor was placed near it. The chamber was evacuated at a pressure better than 10^{-5} Torr by the combination of rotary and diffusion pump. When 10^{-6} Torr vacuum was attained in vacuum chamber, the heater connected to the evaporation source was switched on which in turn slowly heated the source of CdSe to temperatures grater then the melting point. This allowed the evaporation of CdSe material. The thickness of the deposited films and the rate of evaporation were obtained from the thickness monitor.

The structural properties were determined by X-ray diffraction (XRD) using CuKα radiation of wave length 1.54Å at 300K. The optical absorption spectra of CdSe thin films were obtained by a UV-VIS-NIR spectrophotometer in the wavelength range of 200nm to 3200nm.

3. Results and Discussion

3.1 Structural Properties

The X-ray diffraction analysis of CdSe powder and CdSe thin film having thickness around 2500Å have been carried out and the X-ray diffractograms have been shown in Fig.-1.

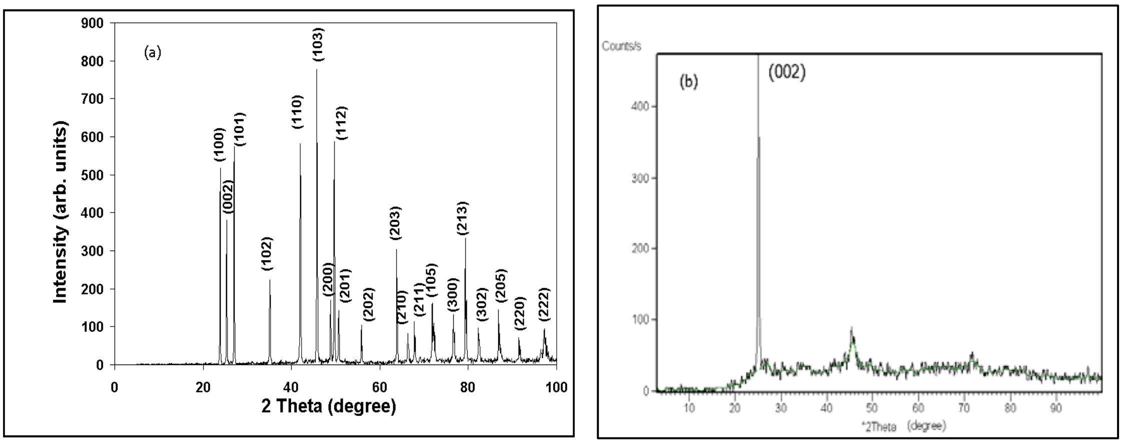


Fig.-1. X-ray diffractograms of (a) the CdSe powder and (b) the CdSe thin film of 2500Å

From this figure, it is quite apparent that the X-ray diffractogram of powder (which is used as a startup material) shows many peaks whereas only one prominent peak is observed in the X-ray diffractogram of CdSe thin films. The d-values for peaks in these diffractograms were calculated and have been given in Table-1 along with the standard JCPDS data [10]. It is good agreement between the calculated and the standard d-values for the hexagonal structure. In case of CdSe thin films, only one prominent peak is observed corresponding to which the d value has been calculated. The orientation corresponding to this value is (002) which is possible only in the hexagonal structure of CdSe, which confirms that the CdSe thin films deposited on glass substrate using thermal evaporation method possess hexagonal structure, in present case which agrees well with the reported data [1, 11, 12]. Since, the thickness of the film was not sufficiently enough, the intensity of other peaks is almost negligible (very near to the noise line). This can be rectified only after setting up of the grazing angle. Since the grown film possess hexagonal structure, the equation for calculation of ‘a’ and ‘c’ is,

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

The calculated values of the lattice parameters are a = 4.311Å and c = 7.025Å. These values are in good agreement with the desired one as well as the reported data [8, 10].

Table 1(a) Indexing of X-Ray Peaks for CdSe Powder.

Obs. No.	Observed d-spacing (Å)	Standard d-spacing (Å)	h k l
1	3.7082	3.7292	1 0 0
2	3.4899	3.5125	0 0 2
3	3.2776	3.2929	1 0 1
4	2.5459	2.5536	1 0 2
5	2.1443	2.1504	1 1 0
6	1.9757	1.9794	1 0 3
7	1.8582	1.8613	2 0 0
8	1.8295	1.8326	1 1 2
9	1.7972	1.7993	2 0 1
10	1.6438	1.6441	2 0 2
11	1.4552	1.4560	2 0 3
12	1.4049	1.4076	2 1 0
13	1.3798	1.3794	2 1 1
14	1.3117	1.3130	1 0 5
15	1.2395	1.2421	3 0 0
16	1.2053	1.2064	2 1 3
17	1.1685	1.1703	3 0 2
18	1.1183	1.1206	2 0 5

Table 1(b) Indexing of X-Ray Peaks for CdSe Thin Film of 2500Å.

Obs. No.	Observed d-spacing (Å)	Standard d-spacing (Å)	h k l
1	3.5477	3.5125	0 0 2

The electron diffraction patterns for CdSe thin film is shown in Fig.-2. The nature of this diffraction pattern confirms that CdSe thin films investigated in our case are polycrystalline in nature.

The d-values corresponding to all these rings have been calculated and presented along with the standard JCPDS data in Table-2. The table shows good matching of the calculated data with the standard one [10]. This confirms that the deposited CdSe thin films possess the hexagonal structure.

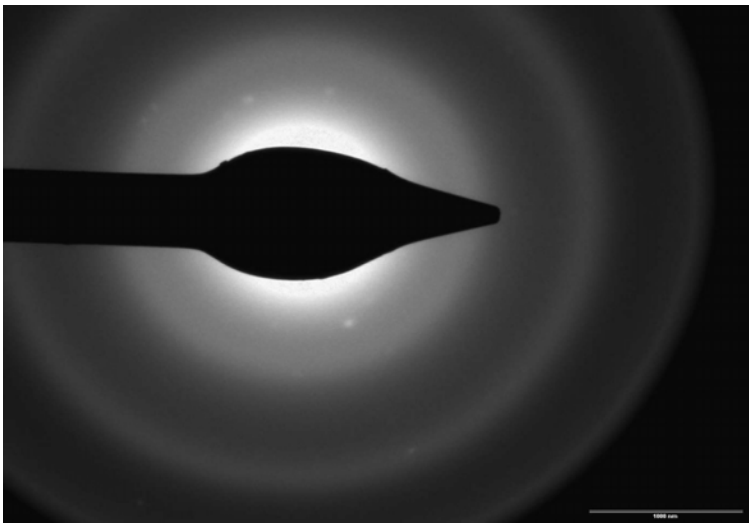


Fig.-2: Electron diffraction pattern of CdSe thin film of 2500 Å

Table 2 Results of TEM Analysis for CdSe Thin Films of 2500Å

Ring No.	Diameter of ring D cm	Interplaner spacing d = 2λL/D Å	Standard d-values Å	h k l
1	4.421	3.718	3.72	1 0 0
2	6.375	2.578	2.55	1 0 2
3	7.532	2.182	2.15	1 1 0

3.2 Optical Properties

The optical absorption spectrum of CdSe thin films have been recorded in the wavelength range 200nm to 3200nm. The results of these investigations have been used for the calculations of absorption coefficients and other parameters. The calculated absorption coefficient corresponding to each energy of incident radiation has been plotted with respect to the energy of photons. The fundamental absorption, which corresponding to the transition from the valance band to the conduction band, can be used to determine the band gap of the material. The relation between α and the incident photon energy (hν) can be written as [13],

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^r \tag{2}$$

where A is a constant, E_g is the band gap of the material and the exponent r depends on the type of transition. The parameter 'r' may have values 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. The value of E_g is evaluated by extrapolating the straight line portion of $(\alpha h\nu)^{1/r}$ vs hν plot by taking r =1/2. The plot of $(\alpha h\nu)^2$ vs hν has been shown in Fig.-3. The value of the direct band gap is 1.72 eV (as observed from Fig.-3) for the CdSe thin films in present investigations which is in agreement with the reported data [1].

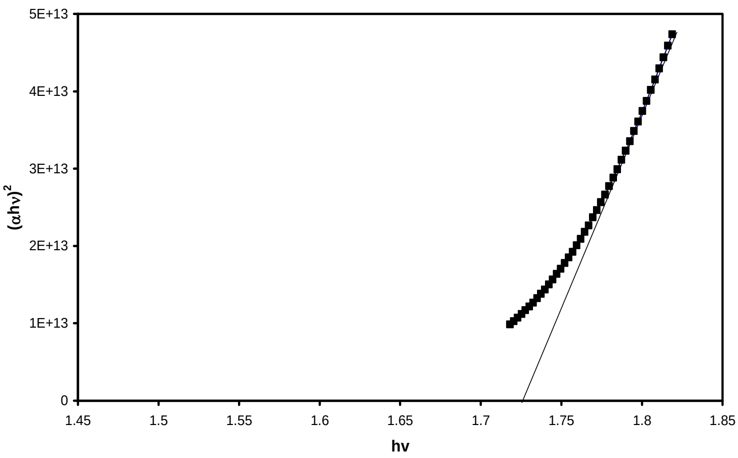


Fig.-3 Plot of $(\alpha h\nu)^2$ vs hv for CdSe Thin Film of 2500Å

Since all the curves indicate discontinuous straight line, it is quite possible that they represent indirect interband transitions involving the emission or absorption of phonons. In order to make an accurate determination of the points of discontinuities we have followed the method adopted by Elkorashy [14]. Accordingly, the graphical differentiation of the data represented in Fig. - 4(a) and 4(b) as a graph of $\delta\alpha/\delta E$ vs hν for CdSe powder and thin film respectively has been used. Similarly, the dependence of the derivatives $\delta(\alpha h\nu)^{1/2}/\delta E$ vs hν has been shown in Fig.- 5(a) and 5(b) for CdSe powder and thin film respectively.

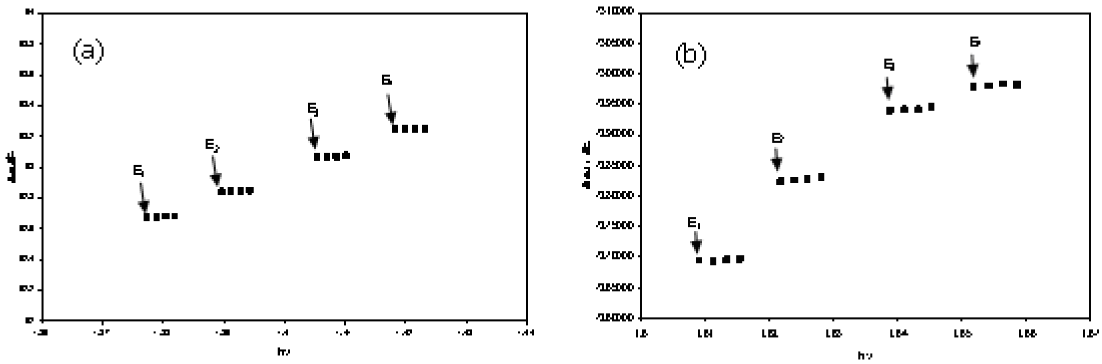
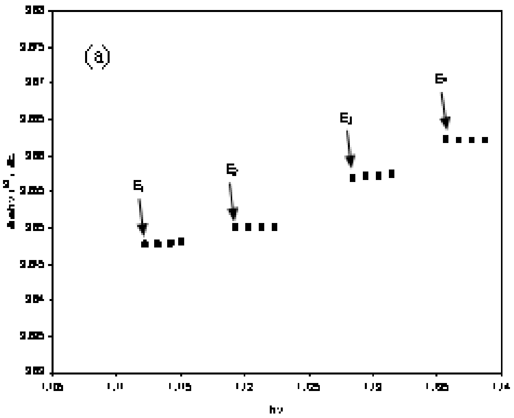


Fig.-4 Plot of $\delta\alpha/\delta E$ vs hv for (a) CdSe Powder and (b) CdSe thin film of 2500Å



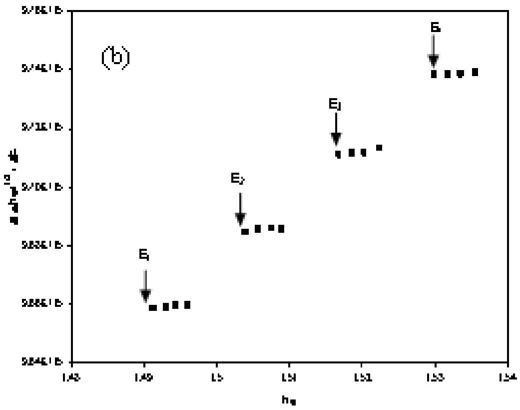


Fig.-5 Plot of $\delta(\alpha h\nu)^{1/2}$ / δE vs $h\nu$ for (a) CdSe Powder and (b) CdSe thin film of 2500Å.

The analysis of the absorption data presented above shows that direct and indirect allowed transitions give a good account of the absorption edge in CdSe powder and thin film. The values of phonon energies vary from 4 meV to 22 meV for CdSe compound. Various parameters and constants obtained through this analysis have been presented in table 3.

Table 3 Various Parameters and Constants Obtained From the Indirect Band Gap Measurements by Three and Two Dimension Model.

Constants	**3D**		**2D**	
	CdSe Powder	**CdSe Thin Film**	**CdSe Powder**	**CdSe Thin Film**
E_1 (eV)	1.11	1.49	1.38	1.61
E_2 (eV)	1.12	1.5	1.39	1.62
E_3 (eV)	1.13	1.52	1.41	1.64
E_4 (eV)	1.14	1.53	1.42	1.65
E'_g (eV)C	1.06	1.51	1.39	1.63
E'_g (eV)E	1.12	1.51	1.38	1.63
E_{p1} (meV)	11.7	19.25	20.45	21.4
E_{p2} (meV)	4.6	6.45	7.9	8.55

Using absorption spectra, transmission and reflection coefficients have been computed by equations,

$$T\ \% = (1/A) \times 100 \tag{3}$$

$$R = 1 - (T+A) \tag{4}$$

The variations of T, R and A with wavelength have been shown in graphical form in Fig.-6. It implies that the absorption and the reflection possess almost the same trend. But the value of absorption in percentile is more than that of reflection.

Furthermore, the reflectivity (R), the optical constants like the extinction coefficient (K) and the refractive index (n) at certain constant wavelength (λ) are related through the following equations (5) and (6) [15].

$$K = \frac{\alpha\lambda}{4\pi} \tag{5}$$

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \tag{6}$$

Using these relations, the values of K and n have been calculated at different input wavelengths from the measurements of T and R.

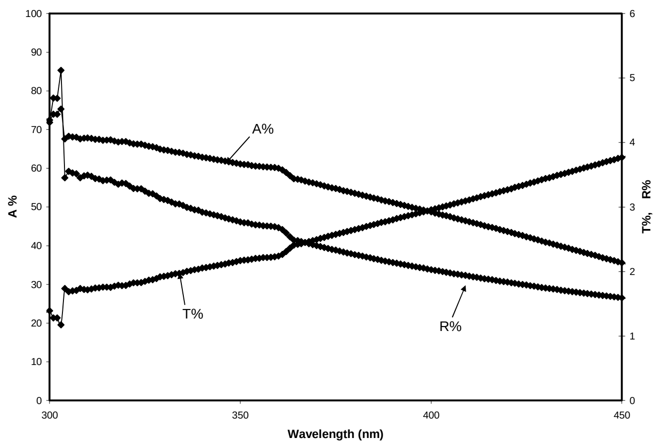


Fig.–6 The Absorption, Transmission and Reflection Spectra of CdSe Thin Film (thickness = 2500Å)

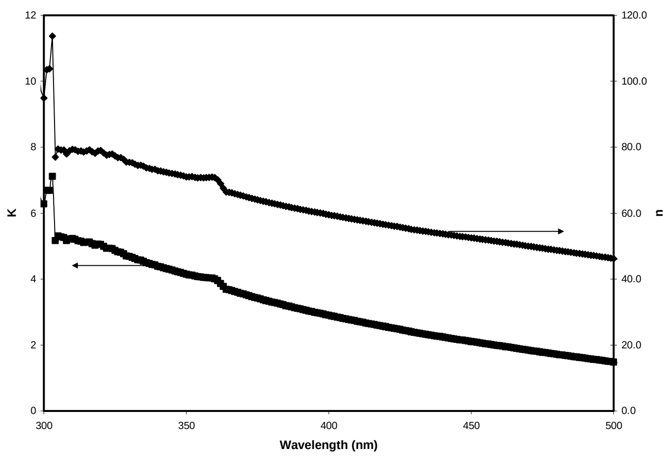


Fig.-7. Spectral Variation of the extinction coefficient (K) and the refractive index (n) of CdSe Thin Film (Thickness= 2500Å).

The relation of the extinction coefficient (K) and the refractive index (n) with wave length for CdSe thin films are shown in Fig.-7. The general trend of variation in these parameters is fairly the same for all the materials. For example, K and n values increase gradually up to about 303 nm and decrease suddenly up to 306 nm, then further decrease slowly up to 361 nm. Then the values of K and n again decrease sharply.

4. Conclusions

From above studies, it is concluded that the cadmium selenide films have been deposited on glass substrate by thermal evaporation method. CdSe charge used as a starting material for the thin film deposition possess the hexagonal structure. Also CdSe possess hexagonal structure in thin film form. It means that due to temperature rise during deposition process, the structure transition does not take place. The optical properties reveal that the direct band gap was confirmed and found to be around 1.72eV. The values of phonon energies vary from 4meV to 22meV for CdSe compound. The absorption and the reflection parameters possess almost the same trend but the value of absorption in percentile is more than that of reflection.

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