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Effect of phase transition on the structure and optical properties of chalcogenide nanostructured thin films

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The optical and structural properties of Nanocrystalline thin films of Cd_xSe_{100-x} (x=54, 34) and CdSe powder are studied. The films are deposited by the vacuum evaporation technique on ultra cleaned glass substratesat room temperature. Thin film was characterized through the XRD, and it is found to be polycrystalline in nature, having preferred orientation along (002) plane. The grain sizes of the films are calculated from XRD data. Absorption spectra of the thin films are recorded using a UV-VIS-IR spectrophotometer, and determined the band gap; it is found that the band gap of Cd_xSe_{100-x} films varies between 1.69 to 2.2 eV.

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Keywords: Cadmium Selenide, Thermal evaporation, Optical properties, Structure properties

1. Introduction

II-VI compounds are widely used in solid state devices such as infra-red detector, photo-voltaic cells, nuclear radiation detectors and windows for IR laser etc. These are the important semiconductors for opto-electronic devices. This group is much more important for photo-conductive and photo-electric devices [1]. The alloys Cd(Se,Te) are usable in laser windows and photo-electric cells [2]. The compound CdSe is one of the elements of the group II-VI having wide range of applications. It is of n-type electron conductivity [3] [4]. The way of preparation and the heat treatment limit the crystal structure to be cubic or hexagonal. Order of vacuum, thickness of the film, substrate temperature etc. are the factors affecting the optical properties. This present study aims determination of the optical constants of $Cd_x Se_{100-x}$ and their variation with composition.

2. Experimental

Cd_xSe_{100-x} has been prepared by direct reaction of high purity Cd (99.9%) and Se (99.999%). Of various compositions (X=53, 34) were in a quartz tube (length ~10 cm, internal diameter ~0.8 cm), and ampoules sealed at 10^{-5} torr. The quartz ampoule is heated to 900 ^{0}C for 15 hours frequent rocking to ensure the homogenization of the melt. The molten sample was then rapidly quenched in ice cooled water. Thin films of Cd_xSe_{100-x} and CdSe powder (high purity 99.995% from Alfa Aesar company) were deposited on a glass substrate using the vacuum evaporation technique at room temperature in a vacuum of ~10^{-5} torr, achieved through a molybdenum boat [5] [6]. The films were kept inside the deposition chamber for 24 h to achieve the metastable Equilibrium. The thickness of the films was measured using Ellipsometry technique and it was found as ~ 200 nm.

3. Results and discussion

3.1. EDS Measurements

The results of EDS (Energy Dispersive Spectroscopy) measurement is shown if Fig. 1 for the case of $Cd_{34}Se_{66}$. These data have been used to calculate the weight percentages of Cd and Se. The obtained values are presented in Table 1.

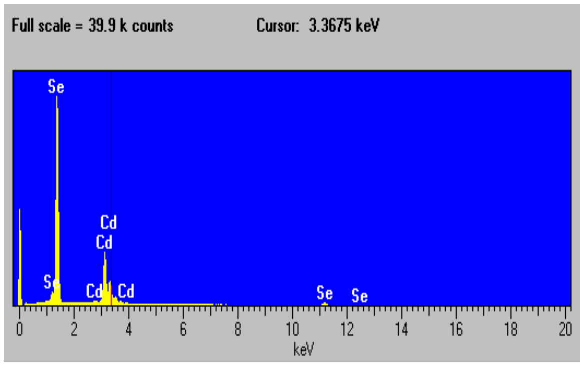

Fig. 1. EDS of $Cd_{34}Se_{66}$ powder.

Table 1. Atomic percentage for Cd-Se.

Element Name	Atomic Percentage	
	Sample 1	Sample 2
Selenium (Se)	46	66
Cadmium (Cd)	54	34

3.2. X-ray diffraction studies

Fig. 2 shows the X-ray diffraction (XRD) of CdSe thin film the intensity of the peak corresponding to (002) orientation is observed in all cases. The peak corresponding to the (002) plane at 2θ =25.445º and substantially broad at the base and another small intensity peak at 2θ = 27.005º at plane (101) and the type of structure of hexagonal wurtzite (W) are found to be in agreement with the standard value JCPDS. Fig. 3 shows the X-ray diffraction (XRD) of $Cd_{54}Se_{46}$ powder which was used for deposition. All the peaks of CdSe corresponding to (100), (002), (101), (110), (103) and (200) reflections are observed. These reflections indicate the formation of single phase material. The peaks corresponding to hexagonal CdSe are observed. Elemental Se or Cd peak was not observed [7]. Fig. 4 shows the XRD of thin film $Cd_{54}Se_{46}$ the intensity of the peak corresponding to (002) orientation is observed. The peak corresponding to the (002) plane at 2θ =25.405º and substantially broad at the base and another small intensity peak at 2θ =45.785º at plane (103) and the type of Structure of hexagonal wurtzite (W) [7], are found to be in agreement with the standard value JCPDS. Fig. 5 shows the XRD of thin film $Cd_{34}Se_{66}$ the intensity of the peak corresponding to (002) orientation is observed in all cases. The peak corresponding to the (002) plane at 2θ=25.410º and the type of structure of hexagonal wurtzite (W) are found to be in agreement with the standard value JCPDS. The observation of X-ray peaks in all the three CdSe films shows that the thermally evaporated films are polycrystalline in nature.

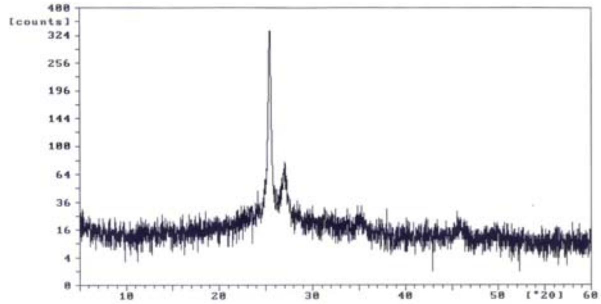

Fig. 2. XRD of CdSe thin film.

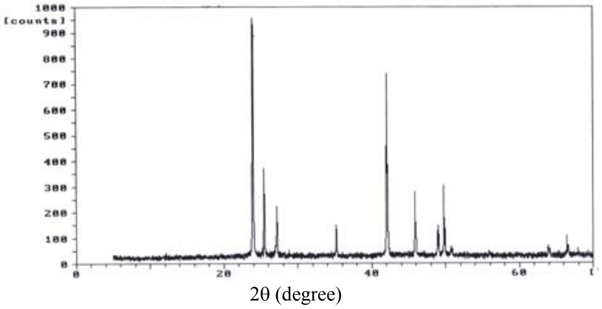

Fig. 3. XRD of $Cd_{54}Se_{46}$ powder.

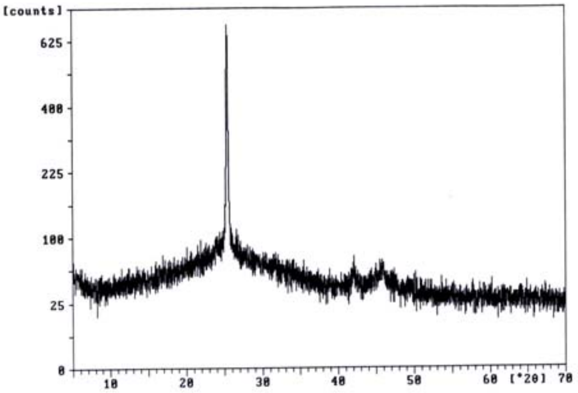

Fig. 4. XRD of $Cd_{54}Se_{46}$ thin film.

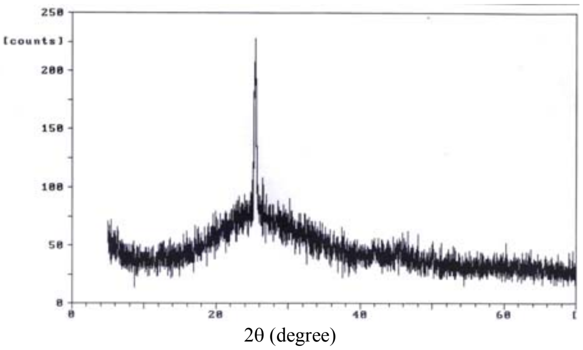

Fig. 5. XRD of $Cd_{34}Se_{66}$ thin film.

The crystalline size (grain diameter (D)) of the crystallites can be determined using the Scherrer's formula from the full width at half maximum (FWHM) β [7], [8].

$$D = 0.94\lambda/\beta\cos\theta \qquad (1)$$

where λ is the wavelength of the X-ray used, β is the FWHM and θ is the angle between the incident and scattered X-ray. The strain values ε can be evaluated using the following relation,

$$\varepsilon = \beta\cos\theta/4 \qquad (2)$$

The lattice spacing d is calculated from the Bragg's formula,

$$d = \lambda/2\sin\theta \qquad (3)$$

The lattice parameters "c" and "a" is determined for hexagonal structure by the following expression.

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

where h, k and l represent the lattice planes. The crystallite size of the thermally evaporated CdSe thin films is calculated and the results are given in Table 2. The intense and sharp peaks in the X-ray diffraction pattern reveal the good crystallinity of the films and also confirm the stoichiometric nature of CdSe films. We find the intensity of the peak decreased with increasing Se for thin films $Cd_{54}Se_{46,}$ CdSe and $Cd_{34}Se_{66,}$ respectively which means that the crystalline nature of the film is decreased. The most dominant plane (002) was observed in all the films and the films nanocrystalline in nature and had Hexagonal crystal structural. Schottmiller et al [9] studied the effect of various elements (S,Te,Bi,As,Ge) on the structure of glassy Se by infrared and Raman spectroscopy. They reported that in glassy Se about 40% of the atoms have a ring structure and 60% of the atoms are bonded as polymeric chains. The presence of additive might increase the concentration of change carriers and there may be a shift of the Fermi level.

Table 2. Structural parameters 2θ, hkl, grain size and strain of Cd_xSe_{100-x} system films.

Samples	Grain size, D(nm)	Strain(ε)* 10^{-4}	2θ	hkl
CdSe thin film	82.98	4.361	25.445	002
$Cd_{54}Se_{46}$ Powder	59.27	6.105		
$Cd_{54}Se_{46}$ thin film	41.47	8.724	25.405°	002
$Cd_{34}Se_{66}$ thin film	29.609	12.23	25.410°	002

3.3. Optical properties

The absorption coefficient spectra of CdSe, $Cd_{54}Se_{46}$ and $Cd_{34}Se_{66}$ thin films deposited onto a glass substrate are studied at room temperature in the range of wavelengths 300–800 nm. Fig. 7 shows the variation of absorption coefficient (α) with wavelength (λ). We find the absorption coefficient spectra for Cd-Se system is blue shifted that is due to increase in optical band gap for these materials. The value of optical band gap 'Eg' is calculated using the following relation [6] - [11].

$$\alpha = A\,(h\nu - Eg)\,n/h\nu \qquad (5)$$

Where A is a constant and n is equal to 1/2 for direct band gap semiconductors. The plots of $(\alpha h\nu)$ 2 versus hν are shown in Fig. 7 for CdSe and Cd_xSe_{100-x} system films. It is observed that the optical band gap increase with Se content. The increase in the optical band gap on the addition of Se in the Cd_xSe_{100-x} system films may be explained on the basis of the model of density of states in amorphous semiconductor proposed by Mott and Davis [12]. According to this model, the width of localized increase in the optical band gap on the addition of Se in the Cd_xSe100_{-x} system films may be explained on the basis of the model of density of states in amorphous semiconductor proposed by Mott and Davis [12]. According to this model, the width of localized states near the mobility edges depends on the degree of disorder and defects presented in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds are produced as a result of insufficient number of atoms deposited in the amorphous films [13]. The localized state decreased with decreasing Cd and the grain size decrease which is responsible for the increase optical band gap [14], [15]. Where A is a constant and n is equal to 1/2 for direct band gap semiconductors. The plots of $(\alpha h\nu)$ 2 versus hν are shown in Fig. 7 for CdSe and Cd_xSe_{100-x} system films. It is observed that the optical band gap increase with Se content. The extinction coefficient k has been calculated using the well known relation [7], [12].

$$\alpha = 4\pi\kappa / \lambda \qquad (6)$$

where λ is the wavelength of incident beam. The absorption coefficients of these films are high (≈ 104 cm^{-1}) and the optical band gaps were given in Table 4.

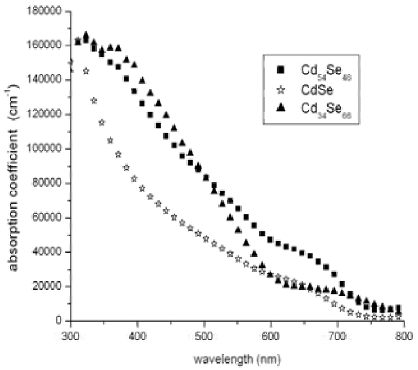

Fig. 6. Absorption coefficients (α) with wavelength (λ). For Cd-Se system.

Fig. 7. Plots of $(\alpha h\nu)^2$ versus hν for CdSe, $Cd_{54}Se_{46}$ and $Cd_{34}Se_{66}$ thin films.

Table 3. Structure parameteres d (Å), c (Å) and a (Å) of Cd_xSe_{100-x} system films.

Samples	Lattice spacing parameter		
	d(Å)	c(Å)	a (Å)
CdSe thin film	3.4976	6.9953	4.318
$Cd_{54}Se_{46}$ thin film	3.5030	7.004	4.315
$Cd_{34}Se_{66}$ thin film	3.5024	7.002	4.309

Table 4. Optical parameteres of Cd_xSe_{100-x} system films at 600 nm.

Samples	$\alpha * 10^4\ cm^{-1}$	k	Eg (eV)
$Cd_{54}Se_{46}$ thin film	4.7	0.225	1.69
CdSe thin film	2.7	0.129	1.77
$Cd_{34}Se_{66}$ thin film	2.6	0.124	2.2

4. Conclusion

We have instigated the optical and structure properties of the CdSe. In spit of the insignificant change in the structure with the variation of (Se) content the intensity of the peak of XRD decreased for thin films variation of Se increase, it is found that the optical band gap increase with increasing (Se) content, a result has been attributed to the decrease in the localized tail states.

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