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Thickness and Defect Dependent structural and Optical Properties of Cdse Nanocrystalline Thin Film

Physics

KEYWORDS : nano crystalline, grain size, band gap, refractive index, extinction coefficient, dielectric constants

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ABSTRACT

Nano crystalline CdSe thin films were prepared on glass substrates using by the thermal evaporation technique under vacuum (~10^{-5} torr) at substrate temperature 273 K. The structural and optical properties of CdSe thin films were characterized using by X-ray diffraction and ultraviolet visible spectrum. The optical band edge of the CdSe thin film having different grain distribution was estimated from absorption data of a UV-VIS spectrophotometer in the wavelength range from 300 to 1100 nm. The films have a direct allowed electronic transitions and the optical absorption are shifted to the low energies with the increase of thickness of the films. The optical band gap of CdSe thin films were estimated from experimental data and observed that the band gap energies decreased from 2.34 eV to 2.03 eV as the thickness of the films increased. The extinction coefficient, refractive index and the dielectric constants (real, imaginary) were investigated and found increased with the increases in thickness.

Introduction

The II-VI binary semiconducting compounds, belonging to the cadmium chalcogenide family (CdS, CdSe, and CdTe) are considered to be very important due to its great fundamental [1], experimental and applied interests. Cadmium selenide thin film has widely been studied because of its high absorption coefficient and nearly optimum band gap energy (1.73 eV), and it finds a wide range of applications in low cost devices such as PV cells [2], lasers [3], light-emitting diodes [4] and other nanoscale devices [5]. There are a number of reports on the different structural, optical and electrical properties of CdSe nanocrystalline thin films prepared by various techniques such as vacuum evaporation [6-8], quasi-closed volume technique[9], electrodeposition [10- 12], chemical bath deposition (CBD) [13-14], spray pyrolysis [15], sputtering [16] etc. In this work, CdSe thin films were deposited by thermal evaporation technique on glass substrates and their structural and optical properties are presented and discussed.

Experimental

In a vacuum of 10^{-5}torr (using a HINDHIVAC vacuum coating unit), the thin films of CdSe were deposited on to cleaned glass substrate. Glass slide substrates were first cleaned with detergent water, degreased with acetone and rinsed with deionized water in an ultrasonic cleaner for (30min), then immediately dried by blowing air and wiped with soft paper. CdSe powder with high purity (99.999%) was used in the films preparation (from Koch Light Lab. U.K.). Tantalum was selected as boat material as it has a low partial pressure up to the evaporation temperature of the material. The sublimation temperature of film material is achieved nicely by adjusting the heating current in the range 40-60 amp, at filament voltage 10 V. The source-to-substrate distance was measured as to be 10 cm. To study the heating effect, the prepared films were annealed at different temperatures in a vacuum of 10^{-3} torr. The thickness of the films was measured by using an interferometric method (Fizeau's method for equal thickness.

The absorption co-efficient had been calculated from the transmitted and reflected monochromatic radiation obtained from CZ matel interference filter (range 333 to 1050 nm). An Aplab luxmeter (model 5011S) was used to measure the transmitted as well as reflected monochromatic radiation from the thin films. The UV-VIS spectrophotometer (type SHIMADU 1800) was used to measure the absorptance and transmittance of the films in the wavelength range 300-1100 nm.

Result and discussion

The thickness dependence of XRD spectra of nanocrystalline CdSe thin films prepared at substrate temperature 373K has been shown in figure 1. The figures reveal that almost featureless spectra with weak peaks are observed for the films of lower thickness. Less number of XRD peaks appear for the films of lower thickness. But as the thickness of the films increase from 116.9 nm to 516.4 nm, 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 XRD spectra. As the thickness of the films are increased, the diffraction intensity increases due to the growth of the materials incorporated in the diffraction process. Moreover, a comparatively thick film bears increased grain size which on the other hand gives sharp intense XRD peaks [17].

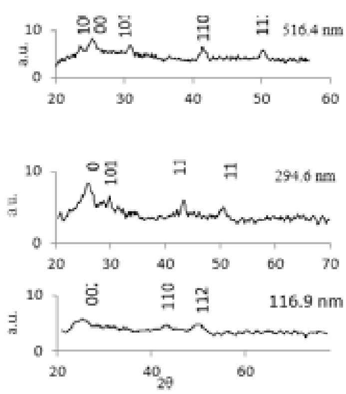

Fig. 4 : XRd spectra of CdSe thin films deposited at 330 K having thicknesses 116.9 nm, 294.6 nm and 516.4 nm.

From the Transmission spectra the optical absorbance (A) of the films is calculated using Swanepoel's method. The absorption co-efficient (α) is related with the absorbance through the following relation [18]

$$\alpha=2.303\,\frac{a}{t} \qquad (1)$$

Here t is the thickness of the thin films

The higher values of absorption coefficient, reflect the corresponding transitions among the extended states in both valence and conduction bands. The native defect states controll the absorption mechanism of CdSe thin films. The different trapping centres on grain boundary become the local photo absorbing centres for which the overall optical absorption capacity of the films reduce. Under the external illumination of radiation, the increases energetic photogenerated carriers reduce the number of defect centres. In such defect controlled condition photonic absorption is found more.

Fig. (2) Shows the optical absorption coefficient (ν) as a function of photon energy (hν) for the thin films with different thickness. In this figure, α increases with the increase of film's thickness for all the prepared films that have low absorbance in the visible/ near infrared region [19]. However, absorbance is high in the ultraviolet region.

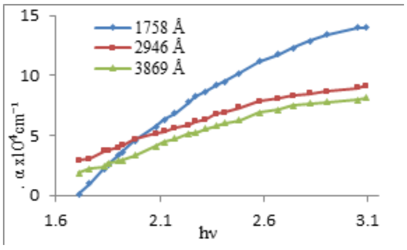

Fig.2: Plots of absorption co-efficient vs. photon energy of CdSe thin films of thickness 1758 Å, 2946 Å and 3869 Å deposited at elevated temperature.

The decrease in the optical absorption at the longer wave length resulted from the excitation of charge carriers across the optical band gap. The absorption co-efficient (α) can be written, in a general form, as a function of photon energy, hν [20] as

$$(\alpha h\nu)^r = B\,(h\nu - E_g) \qquad (2)$$

Where B is a characteristic parameter independent of photonic energy (hν), E_g is the optical band gap energy and r is a constant which depends on the nature of the transition between the top of the valence and bottom of the conduction band. The lowest optical band gap energy in semiconducting materials is referred to the fundamental absorption edge and the nature of integrand transition is characterized by r [21]. For allowed and direct transition r=2.

The observed trend at absorption edge towards lower photonic energies for the increasing film thickness could be attributed to the change in the grain size and the stoichiometry. The evaluated band gap energies are given in table 1 for the films of thickness 124.3 nm, 167.2 nm, 242.7 nm and 376.4 nm which indicate the dependence of band gap on thickness of the films. The estimated band gap values are in good agreement with those already published in the literature for CdSe. From fig.3, it is observed that the band gap energy decreases with increase of film thickness (2.3 ev for 386.9 nm, 2.2 ev for 294.6 nm and 2.1 ev for 175.9 nm) which matches with the earlier investigation on CdSe thin films [22, 23]. The observed band shift as a function of thickness may be described as a result of the presence of quantum size effect originated by microstructure nature. The decrease of the optical band gap may be attributed to the enhancement of grain size, improvement of film microstructure, decrease in strain and dislocation density and deduction of trapping centres.

Table1: Calculated vales of band gap energies of CdSe thin films of various thicknesses deposited at temperatures 300 K, 360 K, 400 K and 430 K.

T of the films (nm)	Deposition temp. (K)	E_g (ev)	Grain Size (nm)
124.3	300	2.34	72.8
167.2	360	2.17	76.0
242.7	400	2.13	81.4
376.4	430	2.03	84.7

The value of extinction co-efficient are calculated using the following relation [24]

$$K = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

Where λ is the wavelength of the radiation used.

Variation of the extinction co-efficient as a function of photon energy, hν, shows that the thickness of CdSe thin films has a direct impact on K. In fig 4, it is seen that K decreases with the increase of film thickness. The increasing nature of K, for all films up to 2.27 ev are linear, beyond which K becomes almost constant for comparatively thick thin films where as a sub linear increasing behavior of K is observed for the films of less thick thin films.

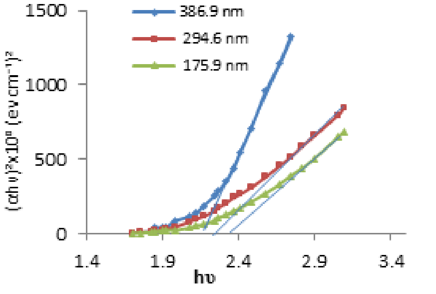

Fig.3 : Plots of $(\alpha h\nu)^2$ vs. energy (hν) of CdSe thin films of thickness 1759 Å, 2946 Å and 3869 Å deposited at room temperature.

The refractive index is an important parameter for optical materials and applications. Thus, it is necessary to determine optical constants of the films. The complex optical refractive indices of the films can be described by the following relation [25]

$$n_1 = n\,(\text{real}) + iK\,(\text{imaginary}) \qquad (4)$$

Where n is the real and K is the imaginary part i.e. extinction co-efficient of complex refractive index. In the spectral domain of the medium and strong transmission region, the refractive index n at different wavelengths is calculated using the envelope curves for interference of transmission maxima (T_{max}) and minima (T_{min}) [9] and is given by

$$n= \{N+ (N^2-n_s^2)^{1/2}\}^{1/2} \qquad (5)$$

Here

$$N=\{2n_s(T_{max}-T_{min})/T_{max}T_{min}\}+ \{(2n_s^2+1)/2\}$$

Where n_s is the refractive index of the substrate [in case of glass n_s = 1.5].

In the transparent spectral region, the transmittance extreme values occur at wavelengths λ_m which obeys the relation

$$2nt = m\lambda_m \qquad (6)$$

Where m is the interference order. For the maxima of the transmission spectra m is an integer whereas for minima of transmission spectra m is a half integer..

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Furthermore, the reflectivity (R) and the refractive index (n) at certain wavelength (λ) can be related through the following equations [26, 27].

$$n = \frac{1 + R^{1/2}}{1 + R^{1/2}} \qquad (7)$$

With the calculated values of the refractive index of nano crystalline CdSe thin films at different ambient conditions, the order (m) of the different extremes of the transmission curves are determined with the help of the equation (6). Here the values of m are approximated to m_o to the close integer for maxima and half integer for minima. The various values of m for different films at different conditions are listed in tables 2. The variation of refractive indices (n) and extinction co-efficient (K) as a function of wave length is presented in table 2, for the films of thickness 1758 Å, 2946 Å and 3869 Å respectively. It is observed that the refractive index of a comparatively thick thin film is found more as such film posses improved and increased crystallanity

In table 3, the experimentally collected data of absorption co-efficient (α), band gap energies (E_g), refractive indices (n) and extinction co-efficient (K) of nano crystalline CdSe thin films are listed. From the table, it is clearly seen that the refractive indices 'n' in the band edge region (λ=6520 Å) increases with the film thickness. The absorption co-efficient (α) shows remarkable decrease with the increase in film thickness at λ=6520 Å. The values of n vs. hυ were shown in fig. (5). This figures also verify that n increase with the increased of film thickness and applied photon energy. The peak values of the refractive index for the films with different thicknesses vary with the incident photon energy. Fig. (5) shows that for the films with thickness 1179 Å and 2946 Å, there are two well-defined maxima and two minima, and for the film with thickness 3869 Å, there are two well-defined maximum and one minimum. These behaviors are accounted to the particular structure of films and their thickness [28].

Table2: Experimentally evaluated values of n, m,m_0 and K at various wave lengths of different nanocrystalline CdSe thin film.

"t" of the films (nm)	W.L (λ) in Å	n of the films	Experlly evaluated m	Approximated m_o	Extin. co-eff. K
175.8	4250	1.92	1.58	1.5	0.43
	4780	1.51	1.11	1	0.42
	6800	1.21	0.54	0.5	0.20
294.6	4270	2.18	3.01	3	0.33
	4660	1.96	2.47	2.5	0.32
	5080	1.71	1.98	2	0.31
	5710	1.45	1.49	1.5	0.26
386.9	4320	2.52	4.51	4.5	0.29
	4640	2.39	3.99	4	0.28
	4990	2.25	3.49	3.5	0.27
	5290	2.11	3.08	3	0.25

The optical absorption in CdSe thin films is a phenomenon of fundamental as well as experimental interest because of its dynamical relation with electron and ions of the medium in presence of electromagnetic radiation. The optical absorbing medium is characterized by the complex di-electric constant which can be expressed as [29]

$$\varepsilon = \varepsilon_r - i\varepsilon_i \qquad (8)$$

Where ε_r and ε_i are the real and imaginary parts of dielectric constant of CdSe thin films respectively.

The di-electric constants ε_r and ε_i are theoretically related with absorption co-efficient and refractive index as [30, 31]

$$\varepsilon_r = n^2 - k^2 \qquad (9)$$

and $\varepsilon_i = 2nk$

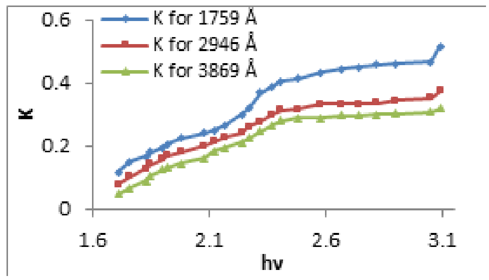

Fig.4: Change in extinction co-efficient with photon energy for CdSe thin films prepared with different thickness.

Fig.6 and fig.7 show the plots of real and imaginary part of di-electric constants of CdSe thin films with photon energy, hν as a function of the film thickness respectively.

Table 3: Optical parameters of some CdSe thin film samples.

't' of films (nm)	E_g (ev)	α (in cm^{-1}) x 10^5	n at λ= 6520 Å	Extin. Co-eff., k
124.3	2.16	0.54	1.29	0.29
167.2	2.04	0.45	1.34	0.24
242.7	1 .89	0.36	1.38	0.19
716.4	1.80	0.32	1.45	0.14

In fig.6, it is seen that the real part of dielectric constant (ε_r) increases slowly up to 2.12 eV then increases exponentially up to 2,58 eV. After that the real dielectric constant again increases slowly for further increase of photon energy. The thickness of CdSe thin films have direct impact on real dielectric constant such that with the increase of film's thickness ε_r decreases.

In fig. 7, the behavior of imaginary part of dielectric constant (ϵ_i) against hν as a function of film's thickness is shown. The imaginary part of dielectric constant (ϵ_i) represents the absorption of radiation by free carriers. The effect of the film thickness on optical absorption properties was investigated. The observed ϵ_i is inversely depends on film thickness.

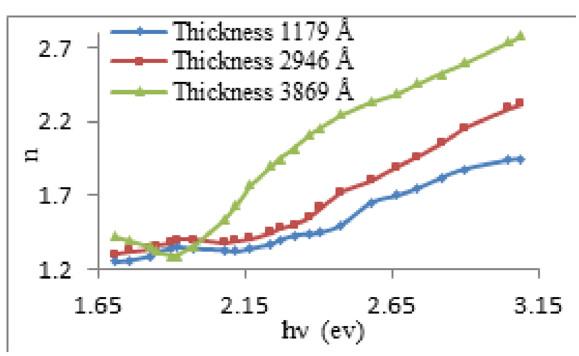

Fig. 5 : The refractive index(n) vs. photon energy(hν) for CdSe thin films prepared with different thickness.

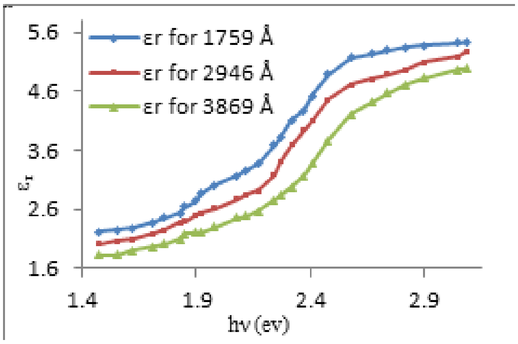

Fig. 6: plots of photon energy vs. real dielectric constant of CdSe thin films of thickness 1759 Å, 2946 Å and 3869 Å

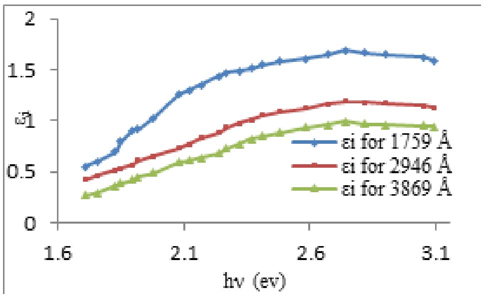

Fig. 7: plots of photon energy vs. imaginary dielectric constant of CdSe thin films of thickness 1759 Å, 2946 Å and 3869

Conclusion

The structural and optical property of CdSe nanocrystalline thin films deposited at 373K are taken for investigated.

XRD weak peaks are observed for the films of lower thickness.

Less number of XRD peaks appeare for the films of lower thickness.

Number of peaks and their intensities increase as the thickness of the films increase.

A comparatively thick film bears increased grain size which on the other hand gives sharp intense XRD peaks.

The thickness of the films has a great impact on the transmission co-efficient.

The native defect states of nanocrystalline CdSe thin films controll the absorption mechanism as the trapping centres become the local photo absorbing centres for which the overall optical absorption capacity of the films reduce.

Optical band gap decreases with the increase of films thickness.

The value of extinction co-efficient decreases with the increase of films thickness.

The refractive index of the CdSe thin film increases with the increase of film's thickness.

Real di-electric constant decreases with the increase of films thickness.

Imaginary di-electric constants inversly depens on films thickness.

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