Study of Stuctural, Optical and Morphologycal Properties of Post Annealed Nanocrystalline CdSe Thin Films

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Abstract

CdSe nano crystalline thin films are deposited on cleaned glass substrates using the thermal evaporation technique under vacuum (~10-5 torr). The prepared films are post annealed at 330K, 333K, 360K,373K,410K, 473K and 450K. The structural and optical properties of CdSe as-grown and annealed nano crystalline thin films are studied. The CdSe nano crystalline thin films are characterized by X-ray diffraction, ultraviolet visible spectroscopy and scanning electron microscopy techniques. A set of 30 nos CZ metal interference filters (ranging from 333 to 1050 nm) are used for monochromatic radiation. Annealing improves the crystalline of CdSe thin films and the FWHM of XRD peaks decreases. It is found that annealing increases the transmittances. The optical band edge of the CdSe thin films having different grain distribution is estimated from the absorptance data of UV-VIS spectrophotometer. The calculation of optical band gap by UV-VIS spectrum reveals strong red-shift with increase in crystallite size indicating the charge confinement in CdSe nanocrystallite. The optical band gap at different annealing temperatures is estimated from experimental data. The influence of the annealing at different temperatures are studied both on real and imaginary di-electrict constants of CdSe nano crystalline thin films.

Keywords: Nano crystalline, polycrystalline, grain size, band gap, di-electric constant.

1. Introduction

Thin films of several semiconducting material have been deposited for optoelectronic device applications. The II-VI binary semiconducting compounds, belonging to the cadmium chalcogenide family (CdS, CdSe, and CdTe) are considered to be very important due to their potential use in photoconductive devices and solar cells [1]. The structure of CdSe thin films depends on the rate of deposition, substrate temperature, vacuum conditions, film thickness, etc. 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 light emitting diodes, solar cells, photo detectors, electro photography and laser [2]. The methods commonly used for depositing CdSe thin films are chemical bath deposition (CBD) [3], vacuum evaporation [4], electro-deposition [5], spray pyrolysis [6], thermal evaporation [7]. In this work, the effect of annealing temperature on the structural, optical and morphological properties of thermally evaporated CdSe thin films on glass substrates are studied.

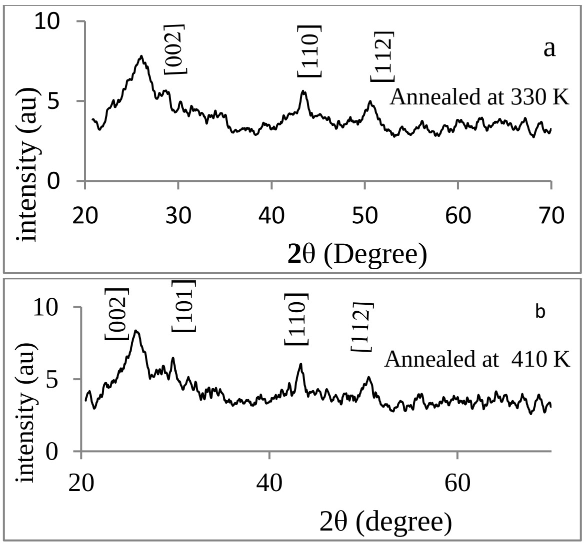
2. Experimental

In a vacuum of 10^{-5} torr (using a HINDHIVAC vacuum coating unit), the thin films of CdSe are deposited on to cleaned glass substrate. Glass slide substrates are 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%) is used in the films preparation (from Koch Light Lab. U.K.). Tantalum is selected as boat material as it has a low partial pressure upto 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 is measured as to be 10 cm. To study the heating effect, the prepared films are annealed at different temperatures in a vacuum of 10^{-3} torr. The thickness of the films is measured using an interferometric method (Fizeau‟s method for equal thickness [10]. The absorption co-efficient has been calculated from the transmitted and reflected monochromatic radiations are obtained from CZ metal interference filter. An Aplab luxmeter (model 5011S) is used to measure the transmitted as well as reflected monochromatic radiation from the thin films. The UV-VIS spectrophotometer (type SHIMADU 1800) is used to measure the absorptance and transmittance of the films in the wavelength range 300-1100nm. Surface morphology of the films is studied with the help of a scanning electron microscopy (Carl Zeiss, Sigma VP). To study the heating effect, the prepared films are annealed at different temperatures at a vacuum of 10^{-3} Torr

Result and Discussion

(a) X- Study

The X–ray diffraction Pattern of CdSe thin film of thickness 1179 Å and annealed at 330 K, 410 K and 450 K are shown in Figures 1. It is important to note that annealing at higher temperature improves the crystalline of thin films. All the films have a hexagonal structure [11]. From the XRD patterns of annealed CdSe thin films, it is clear that the sharp diffraction peak is observed at angular position 25.73^0 corresponding to the prominent plane of reflection at (002). The FWHM of XRD peaks of thermally annealed CdSe thin films decreases though more number of X-ray peaks appears showing formation of the polycrystalline films. Annealing at high temperature can change the position of XRD peaks.



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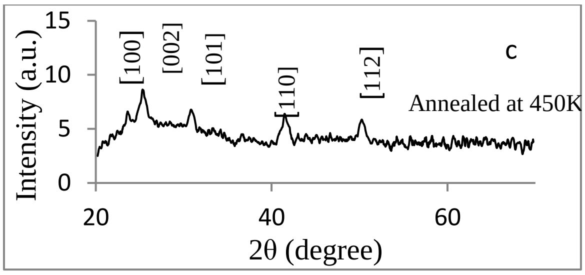


Figure 1 : XRD spectra of three typical CdSe thin films annealed at (a) 330K, (b) 410K and (c) 450K (T_s=117.9nm) .

The particle size (D) and lattice parameter depend on the annealing temperature and an increase in annealing temperature leads to expansion of the lattice [12, 13] by increasing the particle size and lattice parameter, mentioned in Table 1. From the observation of full-width-at-half-maximum of the peaks at the highest angles gives a clear indication of the nanometer domain size [14]. The size of CdSe nano-particles are found to be 76.2 nm, 81.32 nm and 82.67 nm when the samples are annealed at 330 K, 410K and 450K for two hours.

Table 1: Effect of annealing on micro-structural parameters of nano-crystallite thin films.

Annealing temperature (K)	2θ	hkl	a_{hex} Å	c_{hex} Å	D_{hkl} Å
330	25.77 43.53 49.97	002 101 110	5.487	8.893	762
410	25.77 29.49 43.53 49.97	002 101 110 112	5.498	8.901	813
450	23.41 25.77 29.49 43.53 49.97	100 002 101 110 112	5.503	8.903	826

(b) Optical Study

(i) Transmitance

The transmission co-efficient of annealed CdSe thin films are found to be greater [15] than the fresh one. This fact is due to the increase in the crystallite size observed for annealed sample. The inter-grain boundaries of a fresh CdSe thin film contains structural defects, impurities, trapping centres etc and these factors might influence the photo absorption process. But annealing improves the crystallites of CdSe thin films that reduce the trapping centres. In Figure 2, the differences of optical transmittance of annealed and fresh CdSe thin films, deposited at elevated temperature are shown distinctly.

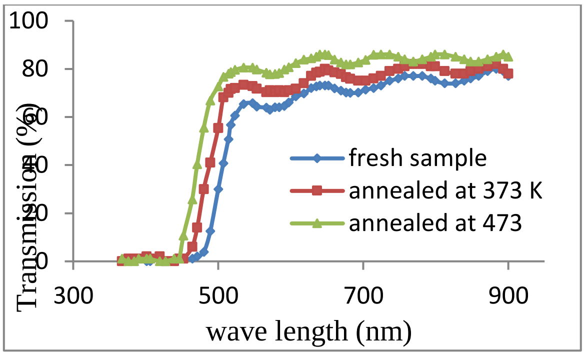


Figure 2: Transmission spectra of CdSe nanocrystalline thin films of fresh sample (Deposited at300K) and annealed samples at 410K and 450K., (thickness 175.9 nm.)

(ii) Absorption

From Figure 3, it can be established that the optical band gap energy of as deposited amorphous CdSe thin films is found to be 2.16 eV which gradually decrease to 1.83 eV through 1.91 eV when the films are annealed [16] at temperatures 410K and 360K respectively. Figure 4 reveals that as the annealing temperature is increased, the crystallite size of CdSe thin films increases resulting decrease in band gap energy. Therefore, annealing the films at high temperature, exhibits strong red shift [17] in their optical spectra due to localization of charges in individual nano-particles [18, 19]**.** This is the common behavior of nano-particles that as and when annealing temperature is increased, the optical band gap energy decreases. Such behavior usually is attributed to the size-increase of the nano-particles with increasing in annealing temperature [20, 21].

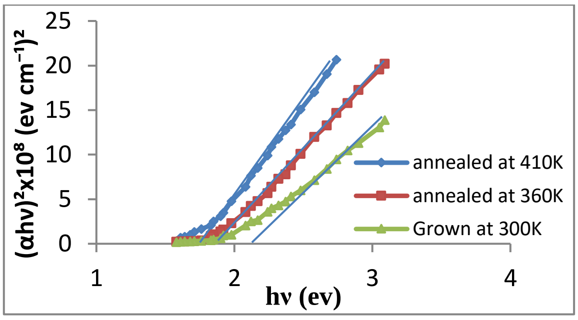


Figure 3: Band gap plots of typical CdSe thin films of thickness 1179 Å deposited at (a) 300K and annealed (b) 360K and 410K temperatures respectively.

The observed trend of shift of absorption edge towards the lower photonic energies for the increasing thickness of annealed films can be expressed on the basis of the change in the grain size and the stoichiometry. The evaluated band gap energies 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 thin films.

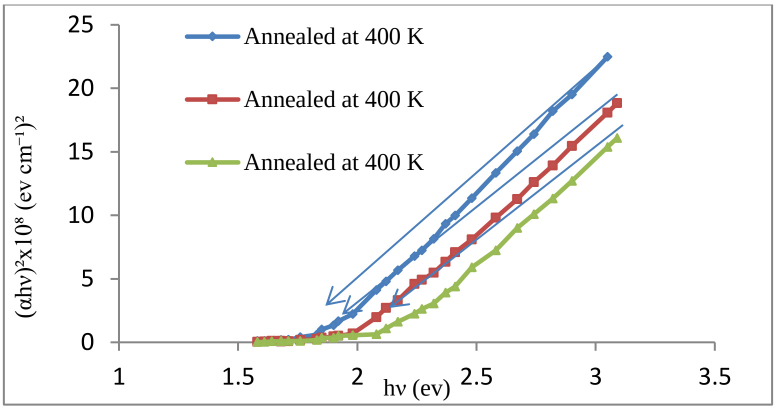


Figure 4 : Plots of $(\alpha h\nu)^2$ vs. photon energy (hν) of CdSe thin films of thickness 1759 Å, 2946 Å and 3869 Å deposited at room temperature and annealed at 400 K.

(iii) Di-electric Constant

The effects of annealing temperatures on real and imaginary dielectric constants (ε_r) are illustrated in Figure 5. and Figure 6. The Figure 5., when observed, it is seen that the increasing nature of real dielectric constant are linear and smooth up to 2.48 ev. After that the increasing mode of the plots are very slow. Annealing has a good influence in case of imaginary di-electric constant (ε_i) of CdSe thin film at temperatures 333K, 373K and 410K. The increasing behavior of ε_i up to 2.48 eV is quite linear and then decreases with further increase of photon energy. But ε_i for the film annealed at low temperature i.e. at 333K shows linear throughout the experimental energy range. For both the cases, it is suggested that these may be due to the reduction of local trapping centres and improvement of crystalline lattice structure of the films.

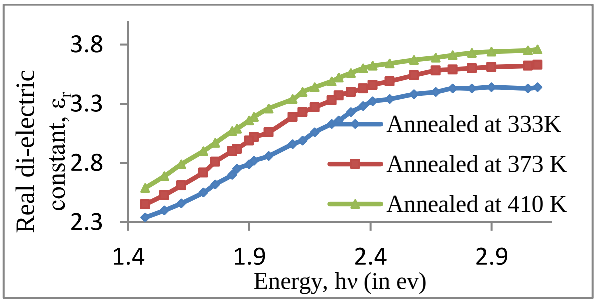


Figure 5: Real dielectric constant vs. photon energy characteristics of CdSe thin films annealed at temperatures 333 K, 373K and 410K.

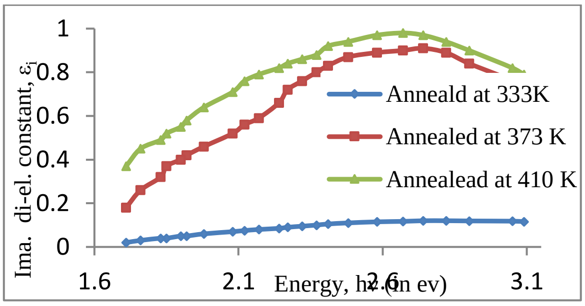
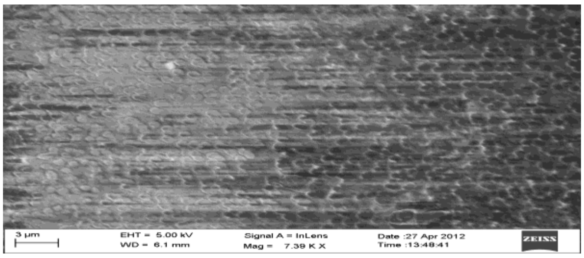


Figure. 6: Imaginary dielectric constant vs. photon energy characteristics of CdSe thin films annealed at temperatures 333 K, 373K and 410K.

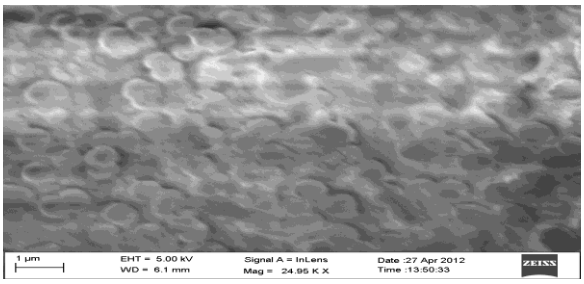
© Surface Morphology

The pictures of scanning electron microscopy (SEM) of CdSe thin films deposited at 300K and annealed at temperatures 360K and 450K, are shown in Figure 7(a), Figure 7(b) and Figure 7(c).

The SEM of the annealed CdSe thin films at 360 K and 450 K clearly indicates that annealing improve the crystalline size of CdSe films by changing it to polycrystalline one. The increase of grain size at high annealing temperatures, confirms transformation of cubic phase to hexagonal phase structure [22]. The crystalline sizes seen from SEM micrograph are found to be from 73.63-89.72 nm which are little higher than the average crystallite size values obtained from the XRD patterned.



(a)



(b)

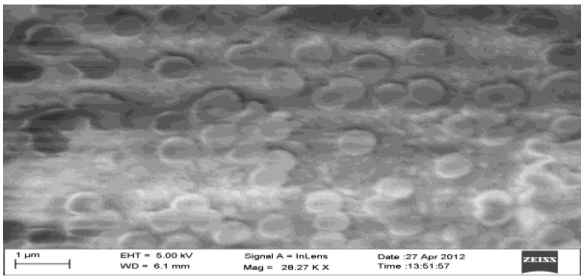


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Figure 7. SEM micrograph of CdSe thin films deposited at (a) 300K and annealed at (b) 360K and (c) 450K.

(c) Conclusion

Annealing (at high temperatures) improves the thermally evaporated CdSe nano crystalline thin films. The FWHM of XRD peaks decreases and number of peaks increases. The nano crystalline particle size of CdSe thin films are studied and found to be 76.2 nm, 81.32 nm and 82.67 nm at annealing temperatures 330 K, 410K and 450K. The lattice defects of CdSe thin films are reduced due to annealing and as a result optical transmittance increases. Gradual increase of annealing temperatures correspondingly reduced the optical band gaps of CdSe nano crystalline thin films. A strong red shift is observed for the films those annealed at high temperatures. Real di-electric constant of annealed CdSe nano crystalline thin films linearly increases upto the applied external radiation of energy 2.48 ev and then the increasing mode become slow. Similarly imaginary di-electric constant smoothly increases upto

2.48 eV and then decreases. The SEM micrographs reveal that annealing changes the films to polycrystalline structure.

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