
EFFECT OF DEPOSITION TEMPERATURE ON STRUCTURAL AND CARRIER MOBILITY OF THERMALLY EVAPORATED NANOCRYSTALLINE CDSE THIN FILMS

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Abstract : XRD studies on nanocrystalline CdSe thin films deposited on suitably cleaned glass substrate at temperatures 303K, 373K and 473K, using thermal evaporation method is performed. The effect of substrate temperature on structural and electrical properties of CdSe thin films has been studied. X-ray diffraction (XRD), Scanning Electron Microscopy(SEM), ECIL electrometer, CZ motel interference filters (ranging from 333 to 1050 nm) and a highly sensitive APLAB luxmeter are used to characterize the CdSe nanocrystalline thin films. Film deposited at 303K is amorphous but films deposited at higher temperatures are polycrystalline in nature. The average grain size is found to increase with the increase of deposited temperatures. Effect of illumination on mobility of nanocrystalline CdSe thin films, deposited at different temperature has been studied from the photoconductivity decay characteristics. The photocurrent decay times as observed are found to decrease at the end of removal of each increased illuminating intensity inferring the improvement of lattice imperfection due to application of external applied radiating photo energy. Also it is found that the energy of incident illumination activates the mobility of the carriers of different trap levels, resulting existence of two distinct trap levels. Observation made clear that trap depth are not single valued but varies over a range beneath the conduction band with temperature. Further it is also found that substrate temperature has a great influence on photoconduction process.

Keywords : nanocrystalline, substrate temperature, grain size, photoconductivity, decay time, trap centre.

Introduction : Presently much importance has been given on the study of II-VI class of compound semiconductor because of their photo electronic properties and application [1]. Recently attention has been paid about photo electronic properties of CdSe thin films, especially to improve the performances of devices and findings new applications [2, 3]. CdSe thin films are prepared by using a number of methods and techniques among which physical vapour deposition is one out of them. It is important to note that irrespective of the methods and conditions of films preparation, the prepared films associate different types of native as well as foreign imperfections which have a great influence on optoelectronic properties of films. The properties of CdSe thin

films are critically dependent on the substrate temperature. The native defects measured by energy traps can cause considerable change in electrical and optical properties of semiconductor giving interesting importance in fabricating different optoelectronic and other devices related to the materials [4]. Illuminating the concerned nanocrystalline CdSe thin films, deposited at different temperature by using different light intensities, an interesting result on trapping spectrum are observed. The influence of illumination on the CdSe films can cause a vast change in mobility activation and trap depth at various ambient conditions. However, little attention has been paid to the various properties of physically vapour deposited CdSe thin films where structural and electrical

properties of the CdSe nano particles are paid attention for study

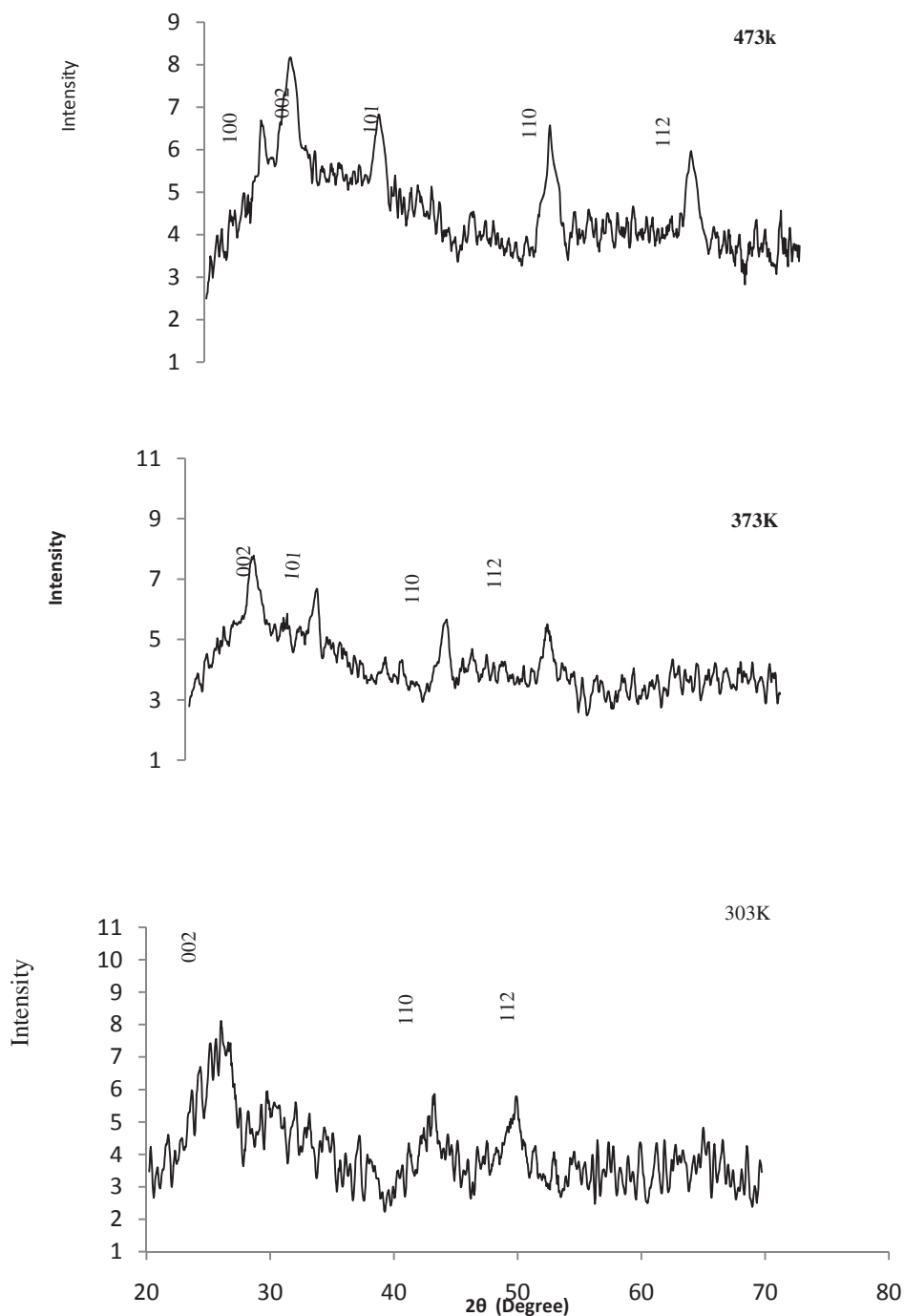


Fig. 1 XRD pattern of nanocrystalline CdSe thin film deposited at temperatures 303K, 373K and 473K respectively.

Experimental

CdSe thin films were deposited on chemically and ultrasonically cleaned glass substrates at

elevated temperatures using by evaporation technique at pressure better than 10^{-5} torr. Highly pure (99.999%) bulk CdSe polycrystalline

powder was used as a source material for the preparation of the thin films. Thin tantalum boat of proper shape and size was used to evaporate CdSe powder. The thickness of the films was measured by a suitably designed and assembled multiple beam interferometers with accuracy of $\pm 15 \text{ \AA}$. The crystallographic study on the films were carried out using by Philips X-ray diffractometer (Philip-X' port pro) with $\text{CuK}\alpha$ radiation of wave length 1.54 \AA . Microstructure of the films was studied by using a scanning electron microscope (Car Zeiss, Sigma VP). An ECIL electrometer amplifier of input impedance of $10^{14} \Omega$ (and higher) was used to measure photocurrent. To apply dc bias, a series of highly stable dry cells of emf 9V each was used. Inside a continuously evacuated glass jacket, sample was kept suspended by thin enameled copper wire. A tungsten halogen projector lamp of 250 watt, operating at maximum voltage 24V was used for white light illumination. A highly sensitive APLAB luxmeter was used to measure intensities.

1. XRD Study

X-ray diffractograms of CdSe thin films deposited at different substrate temperatures ranging from 303K, 373K and 473K are shown in fig. 1. From the XRD patterns it is found that the CdSe thin films prepared at highest temperatures 473K and 373K are polycrystalline, whereas the films deposited at room temperature are amorphous in nature. The main features of the diffraction patterns are same but only the peak intensity is found to vary. More number of X-ray peaks appear as the substrate temperatures increases, showing formation of polycrystalline films. All the films have a hexagonal structure. It has been observed that FWHM of XRD peaks decrease with the increase of temperatures. It is well known that the lattice parameters are temperature dependent and an increase in temperature leads to expansion of the lattice[5,6]. The peaks become sharper at elevated substrate temperature indicating larger

crystallite size D shown in table 1. It is found that the size of CdSe nanoparticles are around 72.4 nm at 303K, which increase to 74.97 nm and 97.37 nm when the samples are deposited at 373K and 473K for the orientation of (002).

The grain size of crystallites was calculated using a well-known Scherer's formula

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where k is a constant taken to be 0.94, λ the wavelength of X-rays used ($\lambda=1.54 \text{ \AA}$), β is the broadening of diffraction line measured at half its maximum intensity in radians and θ is the angle of diffraction.

Lattice constant 'a' and 'c' of the unit cell of the hexagonal CdSe thin films have been evaluated using the following relation

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

and

$$\sin^2\theta = \frac{\lambda^2}{3a^2} (h^2 + hk + k^2) + \frac{\lambda^2}{4c^2} l^2 \quad (3)$$

Where d is the inter planer spacing. According to Ostwald ripening, the increase in the particle size is due to the merging of the smaller particles into larger ones as a result of potential energy difference between small and large

Table 1. Lattice parameters of nanocrystalline CdSe thin films deposited at various substrate temperature

Deposited Temp (K)	a in \AA	c in \AA
303	5.45	8.89
373	5.48	8.91
473	5.53	8.95

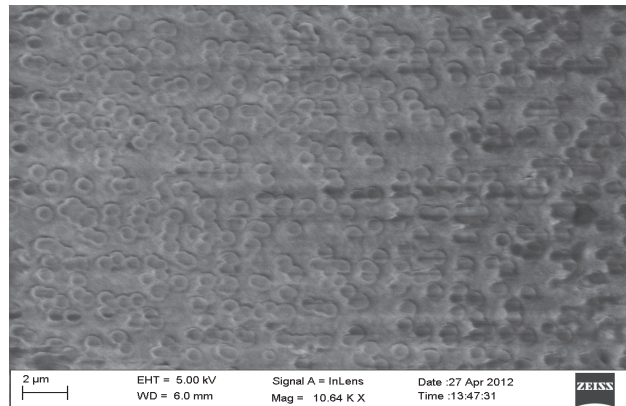
particles that occur through solid-state diffusion [7, 8]

2. Surface morphology:

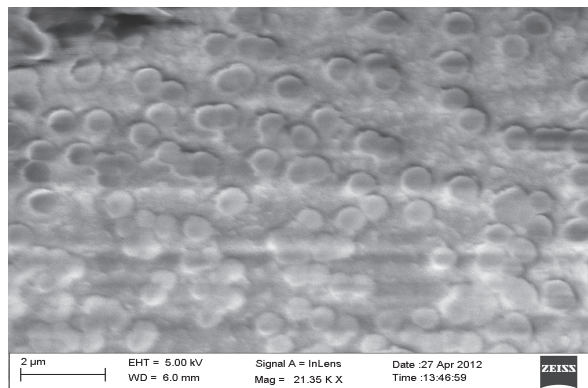
SEM is a convenient technique to study micro structure of thin films. fig 2(a), fig 2(b) and fig 2(c) show the scanning electron micrographs of typical CdSe thin films deposited at surface

temperatures 303K, 373K and 473K. The grains of the films deposited at higher temperatures are densely packed, well defined and having increased grain size. The film morphology under SEM studies shows that the annealed films are more fairly uniform, polycrystalline and free from macroscopic defect like cracks, or peeling. Therefore, for the photoelectrical observation the qualities of such films are quite suitable.

The SEM micrographs of all three thin films clearly shows the improvement in crystallite size of CdSe thin films with increase in substrate temperature. The increase of grain sizes for films deposited at higher substrate temperature, may be attributed to the coalesce of the smaller grain in to effectively larger grains[9]. The crystallite sizes revealed from the



(a)



(b)

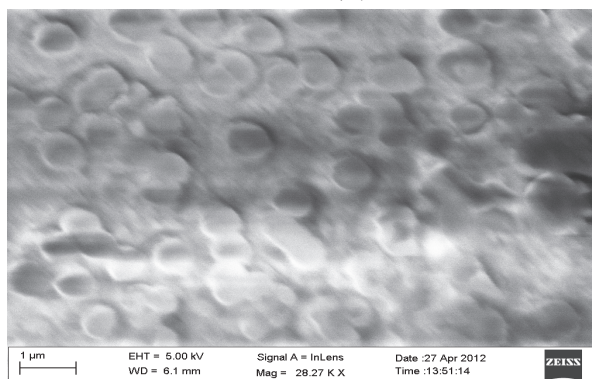


Fig.2. (a) SEM Photograph of nanocrystalline CdSe thin film deposited at substrate temperatures (a)303K, (b) 373K and (c) 473K.

SEM pictures are 76.77nm, 79.56nm and 100.52 nm for the films deposited at temperatures 303K, 373K and 473K which are a little higher compared to the sizes obtained from XRD pattern. Such difference is due to presence of some amorphous phase in the films along with their predominant crystalline phase.

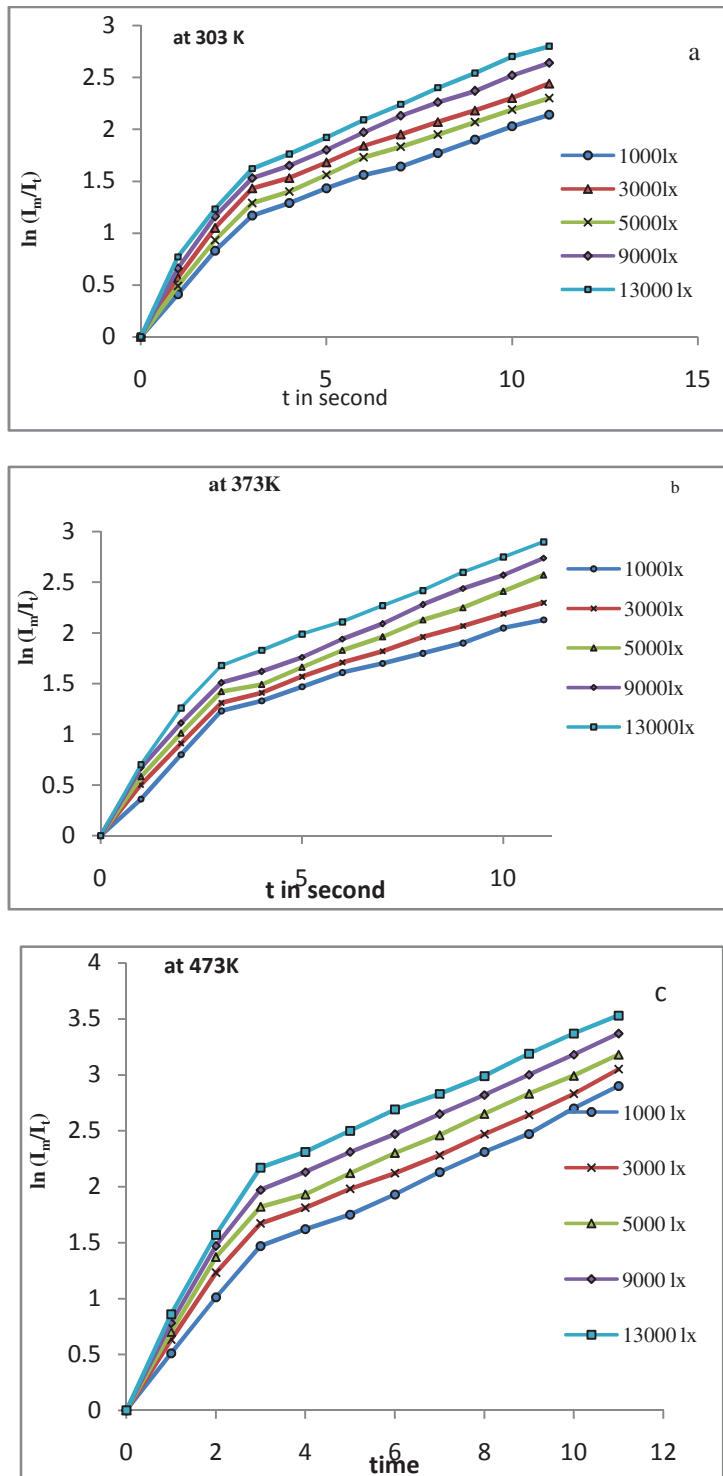


Fig.3 (a) plot of Ttime vs. $\ln(I_m/I_t)$ ystalline CdSe thin films, deposited at substrate temperature(a) 303K, (b) 373K and (c) 473K under the illumination of white lightof intensities 1000lx, 3000lx, 5000lx, 9000lx and 13000lx.

3. Carrier mobility:

The photo current decay time, when illumination is removed from a photosensitive CdSe thin film, can be calculated from

$$I_t = I_m \exp (-t/\tau) \quad (4)$$

Where I_m is maximum photocurrent, I_t is photocurrent at any time t and τ is photo current decay time constant.

There are different traps with different energetic depths in the band gap of thermally deposited photosensitive CdSe thin films and the trap depth E can be calculated by using decay law multiplied by the probability of transition of the ejected electron to the conduction band. [11,12].

From relation (5) and (6) the expression to calculate trap depths can be formulated as [13]

$$E = KT [\ln S - \ln\{(I_m/I_t)t\}] \quad (7)$$

Table 2. Calculated value of trap depth of nanocrystalline CdSe thin film, deposited at different substrate temperature.

Substrate Temp (K)	Trap depth in ev ($\times 10^{-1}$)	
	E_1	E_2
303	2.77	2.78
375	3.35	3.37
473	4.10	4.34

The probabilities (p) of escape an electron from trap per second are taken from the slope of time vs. $\ln(I_m/I_t)$ deposited at substrate temperatures 303K, 373K and 473K shown in fig. 3(a), fig.3(b) and fig.3(c). Observation of the above figures reveal that there are two distinct slopes for CdSe films deposited at any temperatures indicating two energy trap levels [14], namely E_1 and E_2 . From the above observation, it may be concluded that photocurrent measured in CdSe the table 2, it is cleared that trap depths E_1 and E_2 are not single valued but varies over a range with temperature.

The photocurrent decay time (τ) is given by $P = 1/\tau$. τ for the trap depths E_1 and E_2 are calculated for illuminating intensities 1000lx, 3000lx,

$$I_t = I_m \exp (-Pt) \quad (5)$$

Where P is the probability of escape of a carrier from the traps per second which is given by [10]

$$P = S \exp (-E/KT) \quad (6)$$

Here E is the trap depth bellow the conduction band or top of the valence band, K is the Boltzmann constant, T is ambient temperatures in Kelvin and S is the frequency factor which is defined in terms of number per second that the quanta from the lattice vibrations attempt to eject the electron from the trap

thin films shows a sub-linear relationship with the photo current decay time. Using the value of p and S , the trap depths E_1 and E_2 of CdSe thin films are calculated and listed in table 2. The depth E , which a trap require to posses in order that an electron may be trapped in it, varies with depth of trap. Hence the number of traps in which an electron spends a mean time will vary with substrate temperature and therefore, I_t varies with substrate temperature. In table 2 the variation of trap depths E_1 and E_2 are shown. From

Table 3. Calculated valu of photocurrent decay time of nanocrystalline CdSe thin films.

Intensity of illumination in lx	Photocurrent decay time (second)	
	$\tau_1 (10^{-2})$	$\tau_2 (10^{-2})$
1000	3.04	4.02
3000	2.82	3.69
5000	2.64	3.32
9000	2.59	3.26
13000	2.53	2.81

5000lx, 9000lx and 13000lx which are listed in table 3. From the table 3, it is seen that τ_1 and τ_2 corresponding to E_1 and E_2 decrease at the end of each increased external intensity of illumination. The dependence of photoconductivity on external intensity of illuminations for CdSe thin

films deposited at different temperature are shown in fig 4. From the plots it is seen that photogenerated carriers are found more for the nanocrystallite CdSe thin films deposited at

higher substrate temperature. This is because of the increase of grain size and reduction of grain boundary defect states

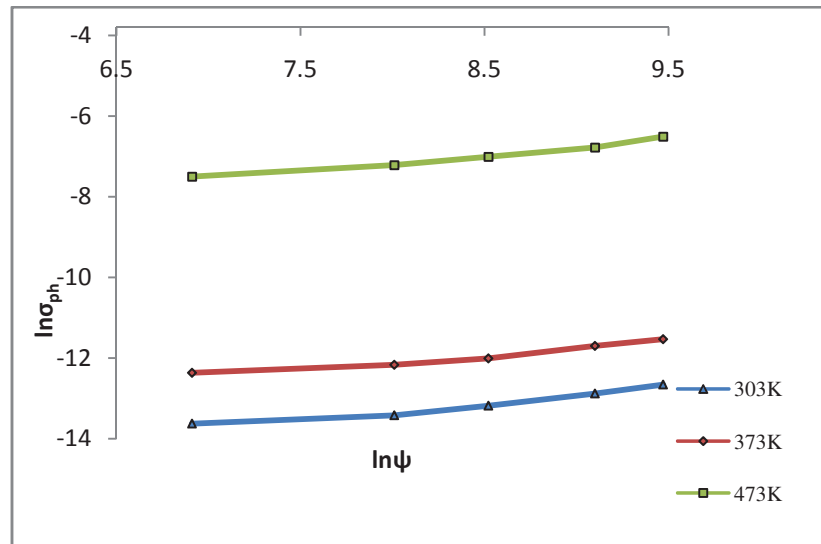


Fig.4: Plots $\ln\psi$ vs. $\ln\sigma_{ph}$ at ambient substrate temperatures 303K, 373K and 473K.

for the CdSe thin films deposited at higher temperature.

Conclusion

In present work, the structural and electrical properties of CdSe thin films have been studied. By using thermal evaporation technique, amorphous and polycrystalline CdSe thin films have been prepared. XRD and SEM measurement showed that the structure of CdSe thin films greatly depend on substrate temperature. Thin films deposited at room temperature are amorphous and those which are deposited at 373K and 473K are nanocrystalline with hexagonal ZnS type structure. SEM micrograph of polycrystalline thin films shows that the crystallites with average grain size

around 76.77nm to 100.52 nm are uniformly distributed over the glass substrate. Also the photoconductivity of these polycrystalline films shows a sub-linear behavior. The sub-linear photoconductivity is basically controlled by the grain boundary defects. The photocurrent decay time decreases at the end of removal of each increased illuminating intensity inferring the improvement of lattice imperfection due to application of external applied radiating photon energy. In these films trapping centres are responsible for controlling the photocurrent. Both shallow and deep traps are found to be available in these films. The observed traps depths are not single valued and there is a quasi-continuous distribution of various traps.

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