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Photoelectronic properties of thermally evaporated CdSe thin films

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The samples for this study are CdSe thin films grown by thermal evaporation technique on the glass substrates held at different temperatures. The I-V curves of the films are linear up to some bias and nonlinear at high bias range. The present photoelectronic studies correspond to a bias in the linear region. The photocurrents are observed to be significantly defect controlled at all the wavelengths in the range 600 nm to 900 nm. The activation processes at dark and for different conditions of illuminations are found to contain two regions. The corresponding dark and photoactivation energies have been calculated. The spectral dependence of the absorption coefficient has been observed in the range 600-900 nm from the transmission spectra.

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Keywords: CdSe thin films, Photocurrent, Defect, Photoactivation energy, Absorption coefficient

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1. Introduction

CdSe is a compound semiconductor and is being regarded as a prominent member of II-VI group of semiconductors. It is widely preferred in the fabrication of different optoelectronic devices owing to its high photosensitive nature [1,2,3]. It has a direct intrinsic band gap of 1.74eV [4] and often possesses n-type conductivity in bulk as well as thin film form [5]. Semiconducting thin films grown at high temperatures are polycrystalline in nature and such films processes a large number of grain boundary potential barriers at the intergrain boundaries which play a significant role in effecting different optoelectronic properties. The dark and photoconductivity of these films are highly influenced by grain boundary potentials which may be modified by externally applied fields. The part of conductivity which depends upon the grain boundary potential is called the Pool-Frenkel conductivity. The photoconducting properties of these films are influenced by various kinds of native defects as well as foreign imperfections. These defects characterize the electronic properties of the material as they give rise to charge center acting as donors or acceptors [6]. In view of relative lack of information regarding the optoelectronic properties of thermally evaporated thin films such as Pool-Frenkel conduction mechanism, illumination frequency or temperature dependence of photoconductivity, an attempt has been made to make a quantitative and qualitative study of these properties under different ambient conditions.

2. Experimental

Thin films of CdSe of various thicknesses were deposited at different substrate temperatures, on properly cleaned glass substrates with the help of Hind High Vacuum Coating Unit at a vacuum of 10^{-6} torr. Pure (99.999%) bulk CdSe samples were used as the source material. High purity aluminium electrodes were vacuum evaporated on the deposited thin films to obtain a gap type cell configuration of 10 mm x 7 mm geometry. Thin tantalum boats of proper size and shape were used as the source heater. A suitably designed and assembled multiple beam interferometer was used to measure the thicknesses of the films with an accuracy of ±15Å. An ECIL electrometer amplifier (EA815) of input impedance of $10^{14}\Omega$ and higher was used to measure dark and photocurrents. To provide bias, a series of highly stable dry cells of emf 9 volt each were used. The sample, by placing in a suitable sample holder was kept suspended by thin enameled copper wires inside a continuously evacuated glass jacket. The entire experimental set up including the observer was housed in a suitably fabricated Faraday cage in order to avoid the pick-up noises. Filters of different wavelengths starting from 600 nm to 900 nm were used and these were calibrated by using highly sensitive APLAB luxmeter.

X-ray diffractogram (XRD) of different CdSe films were carried out by using Phillips X-ray diffractometer (Xpertpro) using CuKα radiation which was operated at 40 keV and 30 mA.

3. Results and discussion

3.1 Structural analysis

Fig. 1 shows the XRD pattern of three CdSe thin films of different thicknesses (t) but deposited at the same substrate temperature (T_s). The X-ray diffraction profiles of the films reveal that films grown at room temperature are amorphous (not shown in figure) and those grown at elevated substrate temperatures are polycrystalline having hexagonal ZnS type structure. In these thin films [002] plane is very clear and abundant which indicates preferential growth of crystallites in this particular direction. However small percentage of orientation of [110] and [112] planes are also observed depending upon the thickness of the deposited films. The preferential orientation is thus [002] plane of crystallites. Improvement of crystallinity of the films has been observed with the increase of thickness of the films. Of course at higher substrate temperatures in the formation of the film, atoms possess greater mobility along direction parallel to the substrate surface which may contribute to improvisation of the crystallization processes. The process of barrier modulation of the conductivity, as observed in the films, is mainly a consequence of intergrain potential barrier localized at the boundaries of these grains.

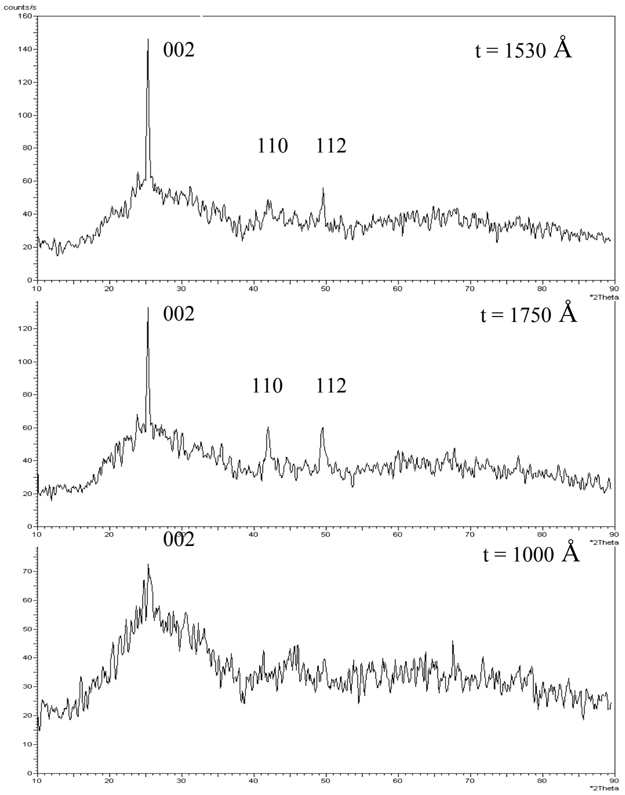

Fig. 1. XRD patterns of three CdSe thin films of different thickness but deposited at same $T_s = 473K$.

3.2 Optical properties

3.2.1 I-V characteristics

I-V characteristics under dark of the considered CdSe thin films deposited at different substrate temperatures are found to be linear (not shown in figure) within the range of applied bias voltage [(-108V)-0-(+108V)]. This confirms that under dark, electrode thin film contacts are ohmic within the experimental range of applied bias, i.e. there is no any rectifying potential barrier in the film-electrode contact. But I_{ph} (where photocurrent $I_{ph}=I_L-I_D$, I_L is the current under illumination and I_D is the current at dark) vs V_a (bias voltage) characteristics are linear and symmetrical about the origin only for low bias voltages of both polarities, i.e. in the low field region photo conduction mechanism is of ohmic nature.

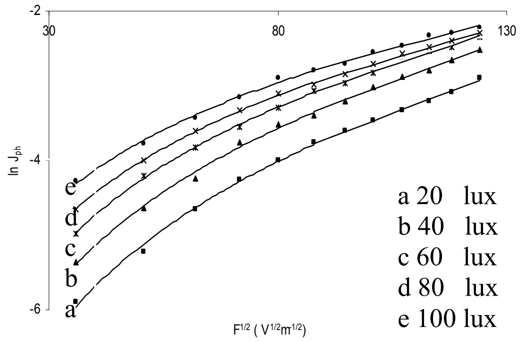

Fig. 2. lnJ_{ph} vs $F^{1/2}$ plot of a representative CdSe film of t=1750Å deposited at T_s=473K under different intensity of white light illuminations.

Beyond this low voltage range the photocurrent increases nonlinearly with the applied bias. Now when lnJ_{ph} (where photocurrent density $J_{ph}=J_L-J_D$, J_L is the current density under illumination and J_D is the current density under dark) is plotted against $F^{1/2}$ (F is the field corresponding to the applied bias), the plots are found to be linear only in the high field region. Fig 2 shows the lnJ_{ph} versus $F^{1/2}$ plot of a representative CdSe film under the illuminations of different intensity white light. Since the plots in the high field region fit well with the Poole-Frenkel function given by equation (1) so it is concluded that in the high field region the conduction mechanism is of Poole-Frenkel type.

The Poole-Frenkel effect is the lowering of Coulombic potential barrier while interacting with an electric field [7]. The current density due to Poole-Frenkel type of conduction mechanism may be expressed as

$$J_{ph} = J_o\exp(\beta_{PF}F^{1/2}/2kT) \quad (1)$$

where J_o is the low field current density, β_{PF} is the Poole-Frenkel coefficient and other symbols have their usual significances.

Due to illumination grain boundary potential barrier Φ_b is reduced which results in enhancing the effective mobility given by [8]

$$\mu^* = \mu_o\exp(-q\Phi_b/kT_o) \quad (2)$$

where T_o is the characteristics temperature of the film system, μ_o is the mobility of the carrier with no barrier effect.

As the intensity of illumination increases, increasing number of photogenerated carriers become available for reducing the grain boundary barrier height Φ_b, which is called barrier modulation. As a result the effective mobility increases exponentially with illuminations and this contributes another exponential factor to the Poole-Frenkel conductivity. So the effective Poole-Frenkel conductivity increases with illumination and the effective current density may be written as

$$J_{ph} = (J_o)_{ph}\exp\{(\beta_{PF}F^{1/2}/kT) - (q\Phi_b/kT_o)\} \tag{3}$$

The plot of $\ln J_{ph}$ vs $F^{1/2}$ gives a slop $m = \beta_{PF}/kT$ from where the Poole-Frenkel coefficient may be calculated. Table 1 gives the numerical values of Poole-Frenkel coefficients for a CdSe thin film of thickness 1750Å and grown at 473K, under the illumination of different intensity (Φ) white light.

Table 1. Poole Frenkel coefficients β_{PF} (in 10^{-4} eV $V^{1/2}$ $m^{1/2}$) for a CdSe thin film (t = 1750Å, T_s=473K) under different intensity Φ (in lux) of white light illuminations.

Φ	20	40	60	80	100
β_{PF}	6.08	5.84	5.38	4.81	4.22

3.3 Intensity dependence of photocurrent

In order to obtain information about recombination mechanism, the variations of photocurrent with intensity of white as well as monochromatic illuminations are studied in CdSe thin films. It is observed that the intensity dependence of photocurrent abide by the relation

$$I_{ph} = C\Phi^{\gamma} \tag{4}$$

where C is a constant of proportionality, γ is a power factor and Φ is the intensity of illuminations.

From the plots of $\ln I_{ph}$ vs $\ln\Phi$ under different ambient conditions, which are linear under the illuminations of white as well as monochromatic lights, it has been observed that the value of γ ranges between 0.4–0.6. One set of such plots for white light (WL) as well as different wavelengths of excitation, for a representative film, has been shown in the Fig. 3.

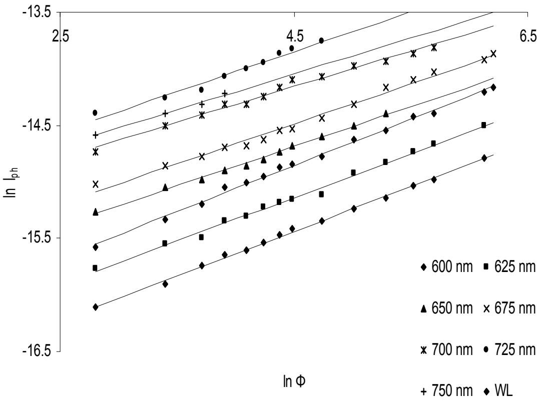

Fig. 3. $\ln I_{ph}$ vs $\ln\Phi$ plots under both white and monochromatic lights for a representative CdSe thin film of t = 1750Å and deposited at T_s= 473K.

The sub-linear nature of the plots shows that photoconductivity in these thin films are of defect control type. These defects are essentially localized in the grain boundaries and the surfaces, which are highly instrumental in effecting different optoelectronic properties of the films.

The nature of the photocurrent verses light intensity characteristics may be explained with the help of pertinent rate equation [9] given by

$$dn/dt = F - Bn\,(n+M) \tag{5}$$

where F is the light intensity in terms of photons per second incident on unit surface area of the film, n is density of conduction electrons, M is the density of recombination centers and B is the recombination probability. At the steady state condition

$$dn / dt = 0$$

So, for n<<M,

$$n = F/BM \tag{6}$$

for n>>M

$$n = (F/B)^{1/2} \tag{7}$$

Since light intensity Φ is directly proportional to F, the intensity of light in terms of photon per second incident on unit area, hence the photocurrent may vary linearly or sub-linearly with light intensity depending on the number of conduction electrons excited by incident radiation due to intrinsic absorption.

The inferences of equation (6) are valid only at lower level of excitation intensity, when density of photo-generated free carriers is less than the available recombination centers, whereas in the present experimental case, since higher excitation intensities are taken into consideration, equation (7) becomes valid indicating the predominance of bimolecular recombination process in spite of probability of presence of a substantial number of recombination centers in the films.

3.4 Temperature dependence of conductivity

From the plots of lnσ (σ is the conductivity) versus 1000/T (Fig 4) it is observed that for the experimental film, both at dark and under illuminations (white light), there are two distinct conductivity regions. Hence the conductivity σ cannot be represented by a single exponential form and the transport mechanism is assumed to be a double activated process.

For the polycrystalline films the phenomenological model of Snejdar and Jerhot [10] for the electrical conductivity in wide gap n-type films may be applied. The basic idea of the model is that, a certain interface state density exist at the grain inter grain domain interface. But in the limiting cases by assuming that (a) grain and intergrain domains are composed of same materials (b) no reflection occurs at the interface barrier (c) no interface states are present (d) no tunneling took place; etc., the same expression of Petriz [8] may be obtained where it is considered that transmission of electronic charge through these films mainly owed to thermoionic emission.

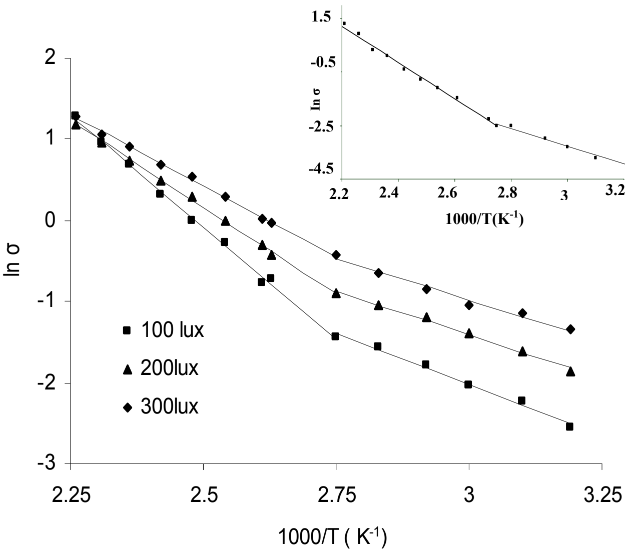

Fig. 4. lnσ vs 1000/T plot for a representative CdSe thin film of t = 1750Å and T_s= 473K under illuminations. Same plot at dark is shown in the inset.

These limiting cases are also applicable for polycrystalline CdSe thin films. The change in conductivity, Δσ, due to irradiation in the temperature range of the films, resulted from the change in carrier concentration and effective mobility, μ_{eff} , caused by the barrier modulation, is given by

$$\Delta\sigma = q\{(\mu_{eff})\Delta p + p(\Delta\mu_{eff})\} \quad (8)$$

where

$$\mu_{eff} = \mu_o \exp(-qV_B/kT)$$

so,

$$\Delta\mu_{eff} = -\{(q\mu_o/kT)\exp(-qV_B/kT)\}\Delta V_B$$

hence

$$\begin{aligned}\Delta\sigma &= \{q\mu_o\Delta p - q^2 p\mu_o\,(\Delta V_B/kT)\}\exp(-qV_B/kT)\\ &= \Delta\sigma_o\exp(-qV_B/kT) \quad (9)\end{aligned}$$

where ΔV_B is the change in barrier height produced by illumination.

It is observed that dark and photo activation energies decreases with the elevation of substrate temperature and the calculated values of photo activation energies are lower than the corresponding dark activation energies for the both temperature regions. Further the activation energy decreases with the increase in intensity of illumination. This is mainly due to the contribution from excess photo-generated carriers and the barrier modulation processes. The potential barriers localized at the grain boundary modulate the conductivity in the polycrystalline CdSe thin films. Because of the mobility activation under illuminations, for both activation regions $(\text{slop})_L<(\text{slop})_D$. These mobility activation energies go on increasing with the increase in the intensity of illuminations. Table 2 gives the calculated values of activation energies in dark (ΔE_D), under white light illumination (ΔE_L) and mobility activation energies (ΔE_μ), for a CdSe film in high temperature (R-I) and low temperature region (R-II) respectively. These calculated values are close to the already reported results [4].

Table 2. ΔE_D , ΔE_L and ΔE_μ values (in eV) for a representative CdSe thin film (t=1750Å, T_s=473K).

Φ	Dark		100 lux		200 lux		300 lux	
R	R - I	R-II	R-I	R-II	R-I	R-II	R-I	R-II
ΔE_D ΔE_L	1.17	0.57	0.95	0.44	0. 73	0.40	0.60	0.34
ΔE_μ			0.22	0.13	0. 44	0.17	0.57	0.23

3.5 Study of optical properties

Optical absorbance and transmittance of CdSe thin films of different thickness and deposited at different substrate temperatures are studied in order to ascertain the nature of optical transitions. To calculate the values of the absorption coefficients for different wavelengths of light near the absorption edge the following simple relation [11] has been employed

$$\alpha = \ln T/t \quad (10)$$

where T is the transmittance and t is the thickness of the film. Both direct and indirect transitions between the valanced band and the conduction band may be considered as allowed or forbidden depending upon the values of transition probability, p, in the following relation [12, 13]

$$\alpha = A(h\nu - E_g)^p \quad (11)$$

where p has discrete values like 1/2, 3/2, 2 or more depending upon whether the undergoing transition is direct, indirect, allowed or forbidden. This can be ascertained from the nature of the plots of α^2, $\alpha^{1/2}$ etc against photon energy, hν. E_g is the width of the forbidden gap.

Fig. 5 shows the plots of α^2 versus photon energy hν for three CdSe thin films of varying thickness, which are found to be linear towards the regions of higher photon energy. This means the optical transitions take place directly from band to band and the values of direct optical band gap have been determined by extrapolating the linear portion of the respective curves to $\alpha^2 = 0$. Obtained values of band gaps are presented in Table 3.

Table 3. Optical parameters of a few CdSe thin films of different thickness and grown at different T_s.

Films	a	b	c
T_s (K)	423	473	523
t (Å)	2000	1750	1640
E_g (eV)	1.69	1.70	1.70

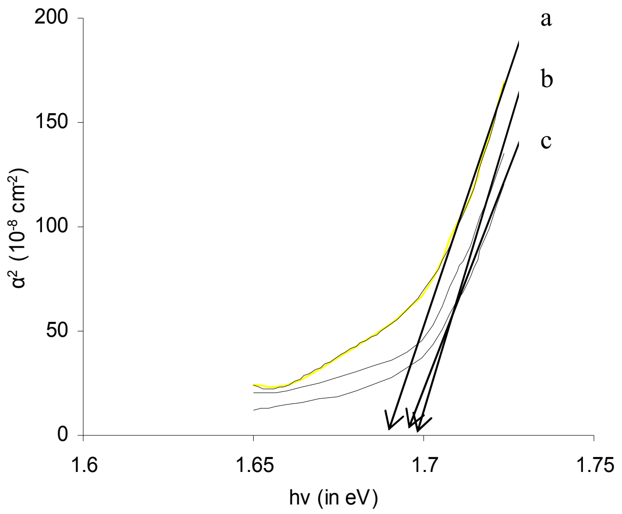

Fig. 5. Square of absorption coefficient versus photon energy plots for three CdSe thin films having different t and T_s.

The evaluated values of band gaps are found to be quite lower than that calculated by electrical method using the thermal excitation which is considered to be less reliable because of the fact that in polycrystalline thin films transport phenomenon are strongly influenced by crystalline size and the characteristics of grain boundaries [14]. Calculated results of direct optical band gap resembles well with the reported values [15-17]. Variations of optical band gap that has been observed for different CdSe thin films, are may be due to their different growing conditions.

4. Conclusions

Thermally evaporated CdSe thin films onto glass substrate at higher substrate temperature are of polycrystalline nature. Such films are highly resistive and resistively changes with substrate temperature of deposition. They are found to be characterized by Poole-Frenkel type of conductivity and barrier modulated photoconductivity. Photoconductivity of these polycrystalline films are basically controlled by the grain boundary defects. The photocurrent is dependent on the wavelength of excitation and increases towards the band edge of wavelength. The nature of the transmission spectra of the films is strongly influenced by the preparation conditions and films show direct nature in band to band transitions.

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