

Effect of wavelength and intensity of illumination on the photoelectronic properties of CdSe thin films

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Abstract Thermally evaporated CdSe thin films deposited under a vacuum environment of the order of 10' Torr, using high quality glass as substrate material, which are held at different elevated temperatures, are of polycrystalline nature having hexagonal structure whereas films grown at room temperature are amorphous. In gap type cell configuration of these films with thermally evaporated aluminium electrodes, the I-V characteristics are observed to be linear both under dark and under monochromatic illuminations of different intensities for low bias voltages, but such curves show Poole-Frenkel type of conductivity under the same illuminations for high bias voltages. In these cases the photocurrents, which are mainly controlled by different types of defects, vary widely with variation of intensities and wavelengths of light close to the threshold wavelength. The transport mechanism is generally not a single activated process and the traps have a very significant role in controlling the growth and decay of photocurrents.

Keywords CdSe thin films, Defects, Traps

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1. Introduction

CdSe is a binary semiconductor and among the II-VI group of semiconductor compounds, it is considered as an important material for the development of different opto- electronic devices [1,2,3] because of its high photosensitive nature and suitable intrinsic band gap (174eV) [4]. In recent years special attention has been given to the investigation of photoelectronic properties of CdSe thin films in order to improve the performances of devices and also for finding new applications [5,6]. Different growing methods for preparation of CdSe thin films have been reported [7,8]. Out of these physical vapour deposition method is often used because it offers many possibilities to modify the deposition parameters and to obtain films with determined structure and properties. Irrespective of preparation conditions such deposited films are associated with different type of defects which play dominant role in the photoconductivity processes. The nature and amount of inherent defects, which in turn effect the photoelectronic properties, depend on different deposition parameters such as vacuum inside the chamber, rate of deposition, substrate temperature *etc.* The grain sizes as well as intergrain boundary potential barriers along with these defects also have a prominent role to play. Study of photoelectronic properties of semiconducting films are essential requirements for proper application in different optoelectronic devices. Some optoelectronic properties of thermally deposited CdSe thir films, illuminated by monochromatic as well as white light of different intensities are reported in this paper.

2. Experimental

Thin films of CdSe of various thicknesses were deposited at different substrate temperatures. on chemically and ultrasonically cleaned glass substrates with the help of Hind Higt Vacuum Coating Unit at a vacuum of the order of 10^{-5} Torr. Pure (99.999%) bulk CdS₆ samples were used as the source material. Prior to deposition of the thin films, high purity aluminium electrodes were vacuum evaporated on glass substrates on which the films were then deposited to obtain a gap type cell configuration of 10mm x 7mm 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 thickness 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 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 pick-up noises. A set of C-Z metal interference filters of different wavelengths starting from 600 nm to 900 nm was used to obtain monochromatic radiations. Light intensities were measured by using a highly sensitive APLAB luxmeter.

X-ray diffractograms were obtained using a Phillips X-ray diffractometer (Xpertpro) for CuK α radiations. Surface morphology of the films were investigated by using scanning electron microscope (LEO 1430VP) with an accelerating potential of 18 kV.

3. Results and discussion

3.1. Structural property :

The X-ray diffraction profiles of the CdSe thin films reveal that films grown at room temperature were amorphous and those grown at elevated substrate temperatures (T_s) were (Figure 1) polycrystalline having hexagonal ZnS type structure. In these films reflections from the [002] planes were found to be very intense which indicated that the preferential growth of crystallites was in this particular direction. However depending upon the T_s of

deposition some percentage orientation of a few other planes were also observed. With the increase of T_s the grain sizes of the polycrystalline thin films were found to increase.



Figure 1. XRD patterns of CdSe thin films of the same thickness t = 2000Å and deposited at different T_S 573K, 473K and 303K respectively

The film morphology under SEM studies showed that the films deposited at higher T_s were fairly uniform, polycrystalline and free from macroscopic defects like cracks or peeling. So for the photoconductivity studies the qualities of the films grown at elevated T_s 's were quite suitable.



Figure 2. SEM of a CdSe thin film (t = 2000Å, T_s = 473K) Magnification 12 14 KX

3.2. I-V characteristics :

Variation of dark current, I_{D} , with applied bias voltage for the CdSe thin films are found to be linear (ohmic) within the applied bias range [(-108V)-0-(+108V)]. For the low bias voltages

of both polarities, current under illumination (I_L) varies linearly with bias and in high voltage range I_L increases nonlinearly with the applied bias. In these regions when In J_{ph} $(J_{pr})_{r}$ is the photocurrent density, photocurrent $I_{ph} = I_L - I_D$ is plotted against $F^{1/2}$ (F being the field corresponding to the applied bias) the plots (Figures 3 and 4) are found to be linear in high field regions and non-linear in low fields.



Figure 3. InJ_{ph} vs F^{1/2} pl at for a CdSe (t = 2000Å, T_s = 473K) thin film (a) under different monochromatic illuminations and white light (WL) of constant intensity and (b) under monochromatic illumination of 725m of different intensities



Figure 4. InJ_{ph} vs $F^{1/2}$ plot for a CdSe (t = 2000Å, $T_s = 573$ K) thin film (a) under different monochromatic illuminations and white light (WL) of constant intensity and (b) under monochromatic illumination of 725nm of different intensities

As is apparent from the ln J_{ph} vs $F^{1/2}$ characteristics depicted in Figures 3 and 4, the basic nature of the curves of white and monochromatic illuminations are similar apart from the numerical values, both in low and high field regions.

This clearly shows that in high field region the conduction mechanism is of Poole-Frenkel type. This type of conductivity mainly depends upon the grain boundary potentials. which may be modified by externally applied fields The current density due to such type of conduction mechanism is given by [9]

$$J = J_0 \exp\left(\beta_{PF} F^{1/2} / kT\right) \tag{1}$$

where $\sigma_0 F = J_0$ is the low field current density, β_{PF} is the Poole-Frenkel coefficient and other symbols have their usual significance. From the slopes of the $\ln J_{ph} vs F^{1/2}$ plots the Poole-Frenkel coefficients are calculated which are found to be in the range (4.4 - 4.9) x 10⁻⁴ eV V^{-1/2} m^{1/2}

As the average grain sizes in higher T_s grown films are higher (XRD patterns given in Figure 1), the corresponding average grain boundary potentials are lowered. The Poole-Frenkel effect of field lowering of built-in potentials in the body of the thin films decreases in the films deposited at higher T_s .

33 Intensity dependence of photocurrent

The nature of intensity (ϕ) dependence of photocurrent for the thin films is found to follow the relation

$$I_{ph} = C\Phi^{\gamma} \tag{2}$$

where C is a constant and γ is the power factor. The plots of $\ln I_{ph} vs \ln \phi$, are linear (Figure 5) under different monochromatic illuminations and also under white light (WL). From these curves γ is found to be close to 0.5. This sublinear dependence of I_{ph} on ϕ shows that photoconductivity in these thin films are of defect controlled type [10].



Figure 5. $\ln I_{ph}$ vs $\ln \phi$ plot for a CdSe thin film of t = 2000Å and deposited at $T_s = 473$ K

3.4 Temperature dependence of conductivity

The plots of $\ln \sigma vs$ 1000/T for the films, both under dark and under illuminations show two distinct conductivity regions (Figure 6), which means that in these films the conductivity σ cannot be represented by a single exponential form and the transport mechanism is

characterized by a double activated process of the form [11]

$$\sigma = (\sigma_0)_1 \exp(-E_1/(kT)) + (\sigma_0)_2 \exp(-E_2/(kT))$$
(3)

where E_1 and E_2 are the relevant activation energies and the other symbols have their usual significance.



Figure 6. In σ vs 1000/T plot for a CdSe thin film (t = 2000Å, T_s= 473K) (a) under dark and different monochromatic illuminations of constant intensity and (b) under monochromatic light of 725 nm at differen intensities

For the experimental film, activation energies (E_a) are calculated (Table 1) from the slopes of the ln σ vs 1000/T plots and the mobility activation energies (E_{ma}) are calculated (Table 1) by subtracting photo activation energies from the corresponding dark activation energies. For a film of t = 2000Å grown at T_s = 473K, the calculated values of E_a under dark have been found to be 1.17eV for high temperature region (R-I) and 0.572 eV for low temperature region (R-II), which are in agreement with the already reported results [4]

Wavelength	750 nm	700 nm	725 nm		
intensity (b) under	monochromatic illumination of	of 725 nm of different intensities	i.		
CdSe thin film (t	= 2000A and I_s =473K) (a)	under different monochromatic	c illuminations of constant		

ladie	1. U	aicui	ated	value	SOTA	cuvation	n Ener	gies ((E_a) ar	na me	ODIIITY	Activation	Energies	(E_{ma})	(ev	/) for '
CdSe	thin	film	(t =	2000	À and	$T_s = 47$	3K) (a) und	ler diff	erent	mon	ochromatic	: Illuminat	ions	of c	onstan*
Intensi	ty (b) une	der m	onoct	iromati	c illumi	nation	of 72	5 nm	of di	lferent	intensities	i .			

Region	R-I	R-11	R-1	R-11	R-I	R-11	
E,	0.98	0.48	0.94	0 43	0.92	0 37	
E _{ma}	0 19	0.09	0.23	0.14	0.25	0 20	
Intensity	30	lux	10	0 lux	15	50 lux	
Region	R-I	R-II	R-I	R-11	R-I	R-11	
Ę	0.94	0.43	0.89	0.38	0.86	0.32	
E _{ma}	0.23	0.14	0.28	0.19	0.31	0.25	

3 5 Growth and decay of photocurrent

The photocurrent at any instant of time during growth is given by the equation

$$I_{t} = I_{0} \{ 1 - \exp(-1/\tau_{r}) \}$$
(4)

where l_o is the maximum photocurrent and τ_r is the growth time of photocurrent. With passage of time the photocurrent reaches a steady state and when the light is turned off current decreases, because excess number of carrier decreases as a result off rapid recombination. The decay may be represented by the equation

$$I_t = I_0 \left\{ \exp\left(-t/\tau_d\right) \right\}$$
(5)

where τ_d is the photocurrent decay time. It is observed that the experimental CdSe thin films exhibit a rapid growth of photocurrent which is followed by an initial fast decay accompanied by a tail (Figure 7). The fast decay is associated with free electron-hole recombination and the subsequent region is due to release of electrons from traps



Figure 7. Growth and decay of photocurrent for a CdSe thin film (t = 2000 A T = 473K) (a) under different monochromatic illuminations of intensity 50 lux and (b) under monochromatic illumination of 725nm of different intensities

The trap depth E below the bottom of the conduction band or the top of the valenced band may be calculated using the simple decay law

$$I_t = I_0 \exp(-\rho t) \tag{6}$$

where p is the probability of escape of an electron from the trap per second and is given by [12]

$$\rho = S \exp(-E/kT) \tag{7}$$

Using these two relations, we get

$$E = kT \left[\ln S - \ln \left\{ \left(\ln I_0 / I_t \right) / t \right\} \right]$$
(8)

where *T* is the ambient temperature in *K*. I_o is the photocurrent at the instant of termination of illumination, I_t is the photocurrent at any instant of time *t* after the termination of illumination. *S* is the frequency factor defined as the number per second that the quanta from the lattice vibrations attempt to eject the electron from trap, multiplied by the probability of transition of the ejected electron to the conduction band [13] and is given by [14]

$$S = N_{eff} v_{th} S_t \tag{9}$$

where N_{eff} is the effective density of states in the conduction band, it is assumed that at comparatively low temperature the number of occupied energy in the conduction band *i.e. n* is identical with N_{eff} [15]. Now

$$n = \sigma/\dot{e}\mu \tag{10}$$

where σ is the conductivity corresponding to photocurrent l_{o} . μ is the mobility of electrons in CdSe sample which is taken to be 580 cm²V⁻¹ sec⁻¹[16].

 S_t is the capture cross section of electron at temperature T and is given by

$$S_t = \pi r^2 \tag{11}$$

where *r* radius of capture center. It is calculated by putting coulomb energy of interaction of an electron with the corresponding trap equal to the thermal energy of the electron at temperature T [17]. *i.e.*

$$e^2/r\varepsilon = kT \tag{12}$$

So

$$S_t = \pi e^{2/k^2 T^2 \varepsilon^2}$$
(13)

At 300K $S_r = 10^{-10} / \varepsilon^2 \text{ cm}^2$ [18] (14)

where ε is the dielectric constant of CdSe sample which is taken to be 5.76 [2].

The thermal velocity of an electron v_{th} is calculated by using the relation

$$v_{th} = (2kT \ m^*)^{1/2} \tag{15}$$

where m^* is the effective mass of an electron which is taken to be $0.13m_e$ [19].

For finding S, values of N_{eff} , v_{th} and S_t are separately calculated. Using the calculated values of S and p, evaluated from the slopes of $\ln(I_o/I_t)$ versus t plots (Figure 8), trap depths are calculated (Table 2)at different conditions of illuminations.

The vertical bars in different figures represent the experimental error calculated on the basic of standard deviation of the experimental data. Compared to the ranges of errors the resolutions of different results are acceptable.



Figure 8. $\ln(I_o/I_t)$ vs time t plot for a CdSe thin film (t = 2000Å, T_s = 473K) (a) under different monochromatic illuminations of constant intensity (b) under monochromatic light of 725nm of different intensities

Table 2. Calculated values of trap depths for a CdSe thin film sample (t = 2000Å, $T_{z} = 473$ K) (a) under different monochromatic illuminations of constant intensity (b) under monochromatic illumination of 725nm of different intensities.

llum	ination	$\sigma(\Omega)$	N _{off}	S	E (eV)		
Intensity (lux)	Wave ength (nm)	cm) ¹ (in 10 ⁵)	cm ³ (in 10 ¹⁰)	Sec ¹ (in 10 ⁶)	Ε,	Ε,	
50	700	0 41	4 50	2 69	0 39	0 42	
	750	0 35	3 77	2 25	0 39	0 42	
	725	0 43	4 63	2 76	0 40	0 43	
30		0 30	33	1 97	0 39	0 42	
40	725	0 39	4 28	2 55	0 40	0 43	
60		0 57	6 21	3 71	0 41	0 43	

4. Conclusions

Thermally evaporated polycrystalline CdSe thin films are found to be characterized by Poole-Frenkel type of conductivity and barrier modulated photoconductivity. Photoconductivity in 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. Rise and decay processes of photocurrent are effectively governed by different kind of traps.

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