EFFECT OF FILM THICKNESS ON PHOTOCONDUCTIVITY IN CDS THIN FILMS

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Abstract

Thermally deposited annealed CdS films at elevated substrate temperature exhibit good ohmic at electrode-film junctions at different film thickness. The photo-electrical property in fresh CdS films shows linear relationship with intensity of illumination, film thickness and applied bias. The photo-transport mechanism in photoconductivity process in the films revealed doubled activations due to direct and indirect transport of photo-activated carriers which co-relates with the spectral response properties of the films. The growth time (T_r) and the decay time (T_d) of photocurrents are strongly controlled by the extrinsic concentration of discrete trapped carriers being decreased with increasing film thickness. The estimated trap depths from exponential decay curves in the films are observed to decrease with increasing film thickness which transient direct relationship with the barrier modulation photo-electrical transport mechanism in the films.

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Keywords : A.Thin films, B.Thermal evaporation, D.Photoconductivity, E.Film thickness.

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1.Introduction

Photoelectrical properties of CdS thin films are strongly dependent on their film thickness, intensity of illumination, method of preparation etc. Among various methods, thermal evaporation has attracted the attention of solid state physicists, scientists and research workers for obtaining good quality adhisive films for fabrication of optical devices and applications. In recent times, CdS thin films have emerged as one of the promising materials for successful fabrication of solar cells [1,2] and other opto-electronic devices [3,4]. Potoconductivity process in poly CdS films is mainly governed by the inherent grain boundary states as well as native defects which may act, either trapping or recombination centres, greately influence in the photoconductivity process.

Trapping centres increase the photoconductivity while the recombination centres decrease photosensitivity [5].The mutual co-operation of traps and recombination centres, and their carrier life times depend on the intensity of illumination as well as on the ambient temperatures. The carrier recombinations at the grain boundaries thus play dominant roles in determining the carrier transport mechanism in the films. Thus, for fabrication of reproducible and reliable solar cells and other opto-electronic devices, it is important to control the electrical properties of CdS thin film layers.

Several workers have reported varied properties of CdS thin films by different deposition techniques like thermal evaporation, chemical vapour deposition, close space vapour transport technique (**CSVT**) and screen printing. However, an experimental study of thickness dependent photoconductivity in thermally grown CdS thin films of gap-type cell configuration is much less in comparison with other sandwich type relative to fabrication of efficient solar cells and many opto-electronic devices.

2. Experiment

Cadmium sulphide thin films with thickness (T_f) in the range (15 – 40) x *f*, where *f* = 100Å were thermally deposited onto previously ultra-cleaned amorphous glass substrates (15mm x 10mm x 1.35mm) at 200^0C in vacuum with the help of **Hind High Vacuum Unit** (**model 12A4**) at an appropriate source to substrate distance 5.0cm. High purity (99.99%) tantalum boat was used as source target heater. Un-doped CdS- specpure (99.99% purity) procured from Coach Light Laboratory, U.K. was used as source material. Prior to film deposition, the chamber was evacuated to pressure as low as ~ 1.33 x 10^{-5} Torr. The rate of deposition of the films was maintained at 2.14Å/S.The film thickness was determined using multiple beam interference

method. Copper-contatantant thermocouple was used to measure substrate temperature. CdS thin films of thickness 2500Å and 3500Å were annealed at 75^0C in vacuum for half an hour with a view to study the distinguishing photoelectrical properties of fresh and annealed films relative to different bias, film thickness and photon intensity. The samples were successively mounted on a suitably designed mica plate sample mount (82mmx20mmx2mm) facilitated with good metal-electrode contacts and suspended inside a continuously evacuated air tight standard corning glass jacket 750mm in length and 67mm in diameter with the help of thin enameled copper wires which served as current leads. A double stage rotary pump was used for evacuation of air from inside the glass jacket to a pressure as low as ~ 2.67Pa. A suitable optical arrangement was made to illuminate the gap films uniformly with white lights of intensities (11-960) x *f*, where *f* = 100*lx* and monochromatic lights of varied wavelengths (400-1000)nm for which a tungsten halogen lamp (250W-24V) attached with a parabolic focusing mirror was used as the white light source. A sensitive **APLAB-5011S luxmeter** was used to measure the intensity of light. High ambient temperatures for measurement of photocurrents and photoconductivity of the films in vacuum were achieved by means of a resistive heater coupled with a stabilized power supply and were measured with the help of the thermocouple connected with a digital microvoltmeter. A high input impedance (~$10^{14}\Omega$) **ECIL Electrometer Amplifier** was used to measure the dark currents [I_D] and the currents under illumination[I_L] under different d. c. bias for which a number of d. c. cells of e.m.f. 9 volts each connected in series were used. A suitably constructed and grounded Farady Cage was used in which the whole experimental set-up including the observer was housed for taking observations, preferably at night to minimize the external ground loop currents and high day time pick up noises.

3. Results and discussion

3.1. Structural properties:

The X-ray diffraction spectra of the grown CdS thin films were recorded with **Phillips X' pert Pro-Automated Powder X-ray diffractometer (model APD 1700**) using CuK_α –radiation (λ = 1.572Å). The diffraction patterns of all CdS thin films show single phase T_f dependent polycrystalline growth with h c p (wurtzite) structure which could be indexed along (002), (103) and (112) planes. The detail microstructural analysis of the films was published in our earlier paper [6].

3.2. Nature of film-electrode contacts

Fig.1 shows the T_f depended I-V characteristics of a few selected gap - type Ag/CdS/Ag films in dark and under illumination. The electrode-film contacts are found to be ohmic after annealing the films in vacuum in both polarities over wide range of applied bias without any rectifying barriers at the junctions. This may be explained that the contact resistance developed due to the formation of a Ag_2O insulating layer at the interface between the films and the electrodes has been eliminated considerably on annealing which improves the ohmic in the I-V characteristics [7].

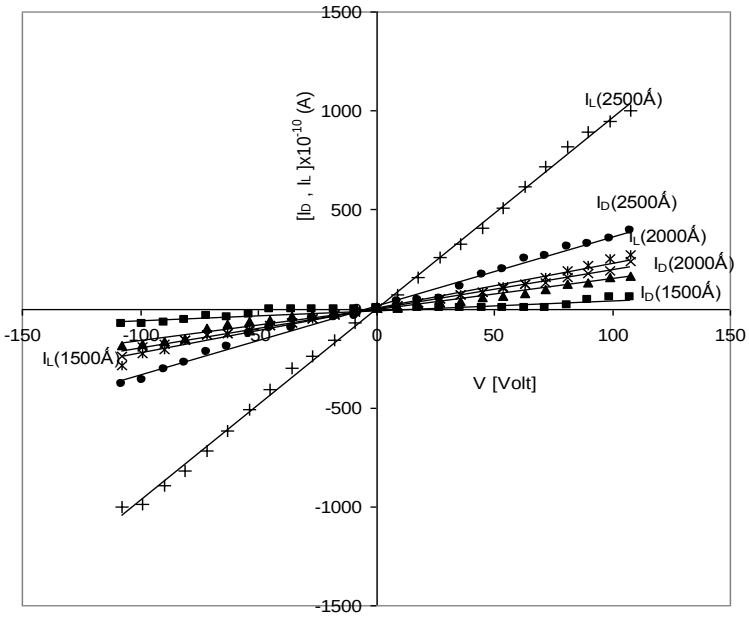

Fig.1. I-V characteristics (under dark and illumination) of CdS thin films grown at 473K(Ts).

3.3. Thickness dependent photocurrent

Fig. 2 represents InI_{ph} *vs.* $In\ \Phi$ plots of fresh (*f*) and annealed (*a*), at Ta = 348K of CdS films of different T_f under bias 36V, 63V and 90V andillumination with white photon intensities 1100 – 96,000 *lx* . Here, $I_{ph} = (I_L - I_D)$ is the photocurrent, the difference between current under illumination (I_L) and dark current (I_D). The photocurrent (I_{ph}) over the entire range of the illuminating intensity is related to the light intensity (Φ) through the power law relation, $I_{ph} \ \alpha \ \Phi^{\beta}$ where the exponent β is a number indexing the imperfection level in the films. In these films, the plots show linear relationship where I_{ph} increases with increasing Φ and T_f and reveals that the

photoconductivity in these films is mainly due to extrinsic type of carrier modulation. This may be explained that there is ambipolar excess impurity atoms in these non-stoichiometric films during vacuum evaporation. Beside the fundamental photoconductivity due to inter-band carrier

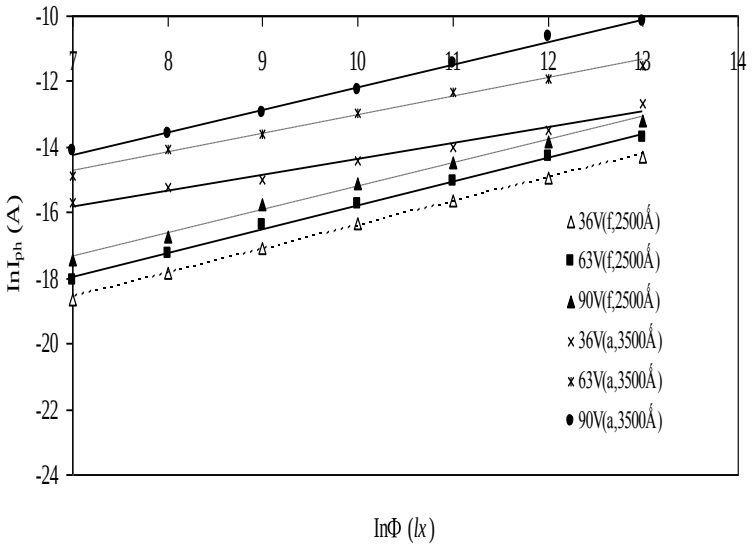

Fig. 2. InI$_{ph}$ vs. InF plots of fresh (f) and annealed (a) CdS thin films at 473K (Ts) under different bias.

transitions, these localized native defect centres effectively act as trapping centres which trap free carriers. The carrier density in the trapping centres increases with increasing film thickness, and after photo-excitation give rise to higher photoconductivity by increasing the carrier life times. It is observed that the average value of β evaluated from the slopes of the InI_{ph} *vs.* $In\ \Phi$ plots of all the films is not different from the mean value 0.65(Table-1).

Table-1. β-values under different bias in CdS films

fresh(f)			annealed(a)		
36V	63V	90V	36V	63V	90V
0.63	0.64	0.64	0.76	0.70	0.62
0.65	0.68	0.70	0.57	0.64	0.76

This suggests that bimolecular recombination between opposite charged types pre-dominate the photoconduction mechanism in these films [8,9]. The rate of carriers generation (g) can be determined from the relation [10]

$$g = c_n (\Delta n^2 + 2 n_o \Delta n) \quad (1)$$

where c_n is the capture coefficient at the hypothetical traps, Δn (excess carrier density) is above the density of thermally generated carriers (n_0). This implies that the transit time of photogenerated carriers do not have significient variations within the applied bias and film thickness. Such type of independence of β on applied bias and film thickness are in conformity with other workers [10,11].

3.4.Thickness dependence of photoconductivity

In general, the d c conductivity of a semiconductor can be expressed by the relation,

$$\sigma \alpha \exp. (-\Delta E/kT) \quad - (2)$$

where ΔE is the activation energy of the carriers, T the ambient temperature of the films and k the Boltzmann constant. Fig. 3 represents *Inσ vs.* $10^3/T$ plots of dark conductivity (σ_d) and photoconductivity (σ_l) of a few CdS films of different T_f , (15– 40) x 10^2 Å under constant illumination of white photons of intensity 4000 *Ix* under bias 27Volts across the films. It is observed that the dark and the photoconductivity in all vacuum evaporated CdS thin films increase exponentially with film thickness. The study of dark

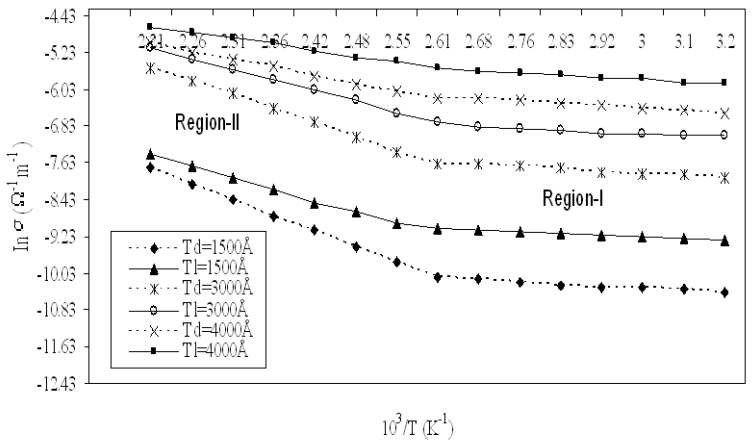

Fig. 3.Inσ vs. $10^3/T$ plots of CdS thin films at 473K (Ts) under illumination of 4000 *lx* (W.L) and bias 27 Volts.

conductivity and photoconductivity in these films shows distinct double photo-activations in the temperature range (313 – 453)K. The photo-transport mechanism in these films can, therefore, be represented by the relation,

$$\sigma = \sigma_1 \exp.(-\Delta E_1/kT) + \sigma_2 \exp.(-E_2/kT) \quad -(3)$$

where ΔE_1 and ΔE_2 are the corresponding carrier activation energies. The dark and photo activation energies in these films at low temperature (**Region–I**) and high temperature (**Region - II**) were evaluated from their corresponding slopes of the plots (Table-2). In LT- region (313 – 383)K for all the films, dark activation energy (ΔE_d) are observed increasing from (0.05 to 0.20)eV and photo-activation energy (ΔE_p) from (0.04 to 0.05)eV (**Region – I**), while the same decreasing from (0.51 to 0.34)eV and (0.34 to 0.32)eV respectively in the HT-Region - II with increasing film thickness. The dark activation energy may be attributed with the facts that after excitation of the films when the light is switched off, the charged carriers in the valence band as well as in various expected localized discrete trapping centres cannot be effectively reactivated for conduction, particularly in LT-region of the films. The conductivity under illumination, on the other

Table-2. Activation energies at different film thickness

Film thickness (Å)	Temperature (K)	Activation Energy (eV)	
		In dark (ΔE_d)	under light (ΔE_p)
1500	(313 – 383)	0.05	0.04
	(383 – 453)	0.51	0.34
2500	(313 – 383)	0.05	0.04
	(383 – 453)	0.48	0.36
3000	(313 – 383)	0.05	0.04
	(383 – 453)	0.44	0.35
3500	(313 – 383)	0.20	0.05
	(383 – 453)	0.34	0.32

hand, may be attributed by the band to band transition of photo-activated carriers as well as from the localized trapping centres produced by the grains in the grain boundaries whose sizes and carrier mobility increase with film thickness with comparatively less photoactivation energy.

The conduction mechanism in HT-Region -II may be explained on the basis of mobility activation process due to carrier modulation mechanism. In general, vacuum evaporated thin films consist of grain boundaries with grains whose sizes increase with film thickness and substrate temperature. So various kinds of lattice defects are present in the boundaries. This results in the formation of energy states e_1, e_2, e_3, ……..within the band gap which start effectively acting as trapping centres of carriers. When the films are illuminated, the energy states become electrically charged after the carriers being trapped. This results in the formation of built in potential barriers at the grain boundaries and play dominant role to modulate the conductivity in the films.

3.5. Effect of wavelength on photocurrent

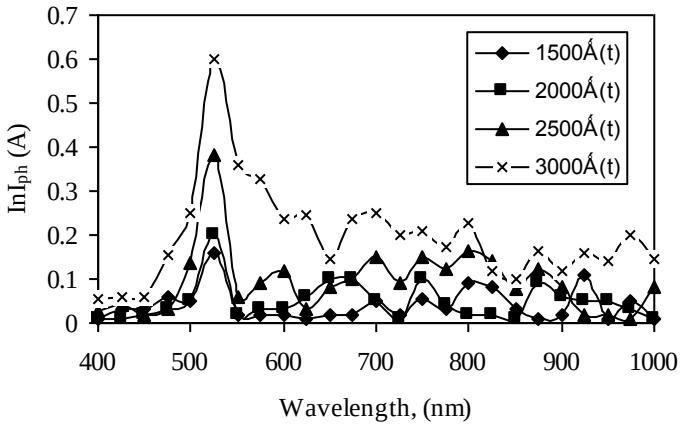

Fig. 4. Normalized spectral response curves of the CdS films at different film thickness.

The study of spectral response (I_{ph} vs. λ) plots of all CdS films under illumination of monochromatic normalized 100 *lx* intensity reveals that each film shows maximum peak at 525nm wavelength at which peak heights increase with increasing film thickness (Fig.4). It is observed that lights with wavelengths shorter than 525nm are strongly absorbed and produces excitation only near the surface. Similar results were also observed by other workers [12,13,14]. The low currents in all the films at shorter wavelengths may also be due to higher concentration of free carriers in the small surface area of the films where the recombination of carriers become high, thereby decreasing surface lifetime. Further, the increase of photocurrent with increasing film thickness is mainly due to increase of grain sizes, thereby decreasing the grain boundary barrier heights in the films. The optical band edges corresponding to maximum spectral

sensitivity in the films were determined at 525nm (threshold wavelength) and 800nm using the relation, E_g (eV) = 1.24/λ_g, where λ_g is in μm, and obtained closed to 2.36eV and 1.55eV respectively. The appearance of such double optical band edges attribute to direct and indirect carrier transition probabilities in thermally evaporated CdS thin films.

3.6. Growth and decay of photocurrent

The growth and decay of I_{ph} *vs. t(time of illumination and termination)* of all CdS thin films were studied successively with constant white photon intensities 4400 *lx* and *7300 lx* for 55 minutes under bias 36 Volts as shown in Fig.5 and Fig.6 respectively. The I_{ph} growths and decays of all the films were measured after an interval of 5 minutes and the corresponding times of rise (T_r) and decay (T_d) of I_{ph} were determined from the plots (Table-3).

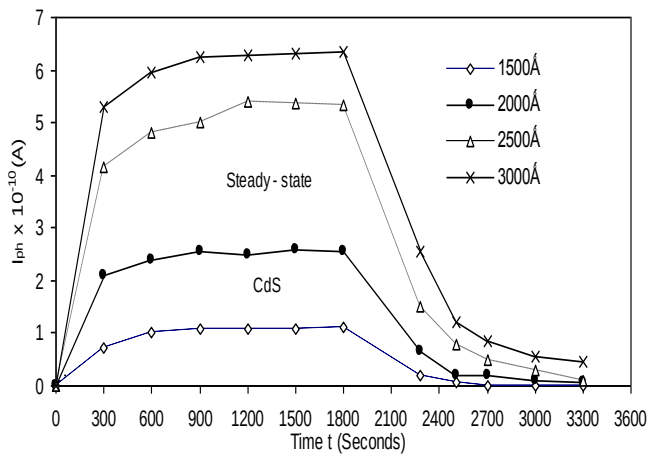

Fig. 5. Growth and decay of I_{ph} vs. time(t) curves for CdS thin films at 473K (Ts) illuminated with 4400 *lx* intensity (W. L.), Va = 36V.

Table-3. Growth and decay times of I_{ph} of CdS films at 473K (*Ts*) under 36V bias

W. L. (*Ix*)	Film thickness (Å)	Growth time T_r (min.)	Decay time T_d (min.)
	1500	7.5	9.0
4400	2000	8.0	11.0
	2500	5.5	12.5

	3000	6.0	15.0
	1500	14.0	9.0
7300	2000	6.0	12.0
	2500	7.1	12.0
	3000	5.5	14.0

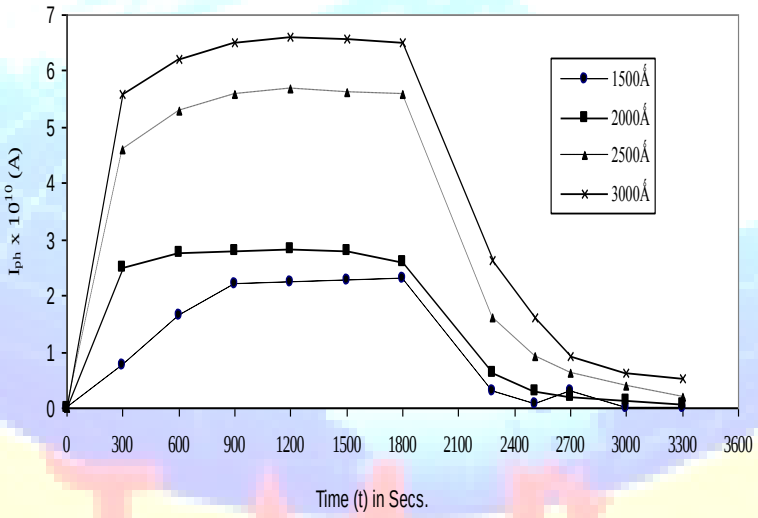

Fig. 6. Growth and decay curves of I_{ph} vs. time (t) of CdS thin films at 473K (Ts) illuminated with 7300 *lx* (W. L.).

Table -4. Trap depths estimated from I_{ph} –decay curves

Film thickness → Intensity (Ix)	1500Å (eV)	2000Å (eV)	2500 Å (eV)	3000Å (eV)
4400	0.75	0.77	0.76	0.78
7300	0.74	0.76	0.77	0.78
11000	0.72	0.75	0.76	0.77

It is observed that the values of T_r in CdS films for the same excitation intensities and bias decrease with increasing T_f on account of large ratio of concentrations of traps of free carriers being activated due to illuminations, thereby generating lower values of T_r in the equation of time rise and time decay of I_{ph} [14].The concentrations of such trapped carriers are observed decreasing with increasing time (t) in all the films. When the excitation of the films is removed, the traps already filled with trapped carriers are emptied and I_{ph} decay at a slower rate which takes longer times of decay depending on the capture cross-sections and the ionization energies. The experimental decays of I_{ph} reveal that re-trapping of carriers from traps are almost negligible. The photocurrent decay in the films can be expressed by the exponential relation,

$$I_t = I_o \exp. (-pt), \quad (4)$$

where I_t is the photocurrent at any time t after termination of illumination, I_o the maximum photocurrent at the moment of termination of illumination and p the probability of escape of a carrier from the trap per second given by

$$p = S \exp. (-E/kT), \quad (5)$$

where S is the frequency factor being 10^{10} C.P.S., E the trap depth below the bottom of the conduction band, k the Boltzmann constant and T the ambient temperature. Then, the trap depths E have been estimated from the relation [15,16]

$$E = kT [\ln S - \ln\{\ln(I_o/I_t)/t\}], \quad (6)$$

as shown in Table-4.The trap depths in all CdS films under increasing photon excitation intensity are observed to increase with increasing film thickness due to higher lattice defects present in the grain boundaries.

4. Conclusion

Thermally deposited basic poly CdS thin films on annealing show good ohmic contacts with silver deposited electrodes in wide range of applied fields. A linear relationship between photocurrent in the films with intensity of illumination and film thickness are observed. Bimolecular recombinations predominate the photoconduction mechanism in the films under varied experimental conditions. Dark and photoconductivity in all CdS films show double activation processes in the temperature range (313 – 453)K which increase with increasing film thickness. The dark activation energies in low temperature regions increase while the same decrease in high temperature regions with increasing film thickness within limits of grain

boundaries associated with trapping centres. The photo-activation energies at low temperature region is fairly unchanged at a relatively lower value independent of film thickness. The lowering of photo-activation energies in the films in high temperature region is observed with increasing film thickness due to mainly both by re-excitation of trapped and untrapped activated carriers to enhance higher photoconductivity. In the entire range of excitations with monochromatic light, CdS films show photosensitive threshold wavelength at 525nm. Two types of optical band edges 2.36eV (λ_1 = 525nm) and 1.55eV (λ_2 = 800nm) have been found in the spectral response which are expected to contribute direct and indirect transition probability in the films. The growth and decay of photocurrents in all CdS thin films are observed under exponential distribution of various discrete trap levels

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