CHAPTER - IV

Effect of Al doping on Photoconductivity of CdS film

4.1 Introduction :

Cadmium Sulphide is a direct band gap Semiconductor. It has wide use for the intensive research because of its intermediate band gap, stability and low cost (1-3). The conduction of these films can be greatly increased by two main processes, incorporation of foreign atoms as donors and creation of excess cadmium by various heat treatements (3-5). The effect of doping and heat treatements as various properties have been observed by number of workers (2-4, 6-13).

The trivalent impurities acts as donor for CdS. Many workers (14, 15) have tried to increase the photoconductivity by doping trivalent impurities. Lokhande and Pawar (16) have reported that CdS films with 0.1 wt% Al doping gives good results for conductivity. The Chapter-IV deals with the deposition of Al doped CdS films by chemical bath deposition. The CdS films were prepared with Cd:S volume ratio as '5' and the effect of Al doping on the photoconducting properties of CdS thin film is reported.

4.2 Experimental procedure for deposition of Al doped CdS films :

a) Substrate Cleaning :

Cleaning of glass substrates was carried out as described in section - 3.3.1.

b) Preparation of Solutions :

Chemicals used for preparing CdS films were as follows: G.R. grade Cadmium Chloride, supplied by Glaxo Laboratories (India) Ltd., Bombay. G.R. grade Thiourea, supplied by Loba

Chemie and A.R. grade Aluminium Sulphate. All solutions were prepared in doubly distilled water.

c) Preparation of CdS films :

Freshly prepared doubly distilled water was used to prepare 0.1 M solutions of Cadmium Chloride and Thiourea and to clean the glass slides used as substrates. For deposition of the film, 125 cc of 0.1 M Cadmium Chloride solution was taken in 250 cc beaker and to it, ammonia solution was mixed to form the complex and the pH was raised to between 9-10. To this solution, 25 cc of 0.1 M Thiourea solution was added to maintain the Cd:S volume ratio as '5'. In this mixture, 0.1 wt% of Aluminium Salt [$Al_2(SO_4)_3$] solution was added for Al doping. Four glass substrates were kept rotating in the mixture at a constant speed of 75 rpm. This stirring action continuously exposes the substrates to a fresh body of reactants, which is an important for uniform deposition of the films. The reaction bath was heated in oil bath and the temperature of the mixture was kept at 65^{o}C for 90 minutes. The films formed were washed with doubly distilled water, dried and preserved.

Thickness measurements, film characterisation and photoconductivity study were carried out as described in Chapter III.

4.3 Results and discussion :

4.3.1 Characterisation of the CdS films :

a) Thickness measurement :

Thickness of the undoped and doped films were measured and it was found that doped films are slightly thicker than undoped films. The increase in thickness with Al doping can be understood as follows (17) : bath solution contain the ions of Cd^{+2}, Al^{+3} and S^{-2}. As Al has more sticking coefficient than Sulphur (14), it may be responsible for starting the nucleation, which helps to increase the film thickness.

b) Optical Transmission studies :

The band gaps 'E_g' of Al doped samples were estimated from the optical transmission spectra (18). The transmission spectra for the both undoped and doped films are shown in fig. 4.1. The band gaps of undoped and doped films are 2.47 eV and 2.42 eV respectively. This shows that there is no significant change in band gap for doped CdS films.

c) XRD stuides :

The XRD patterns of undoped and doped CdS films are shown in fig. 4.2 (a) and (b) respectively. The films were slow scanned between 20^{o} to 80^{o}. The grain sizes of the films were calculated by using equation 3.2. It was observed that the grain size is increased for Al doped sample ($68A^{o}$) compaired to undoped sample ($31A^{o}$). This can be attributed to the addition of impurity in the reaction bath as reported earlier for 0.075 wt% antimony doped CdS films (12).

d) SEM studies :

The Al doped samples were studied with SEM at 5000 x magnification. The SEM microstructure for both doped and undoped samples are shown in fig. 4.3 (a) and (b) respectively.

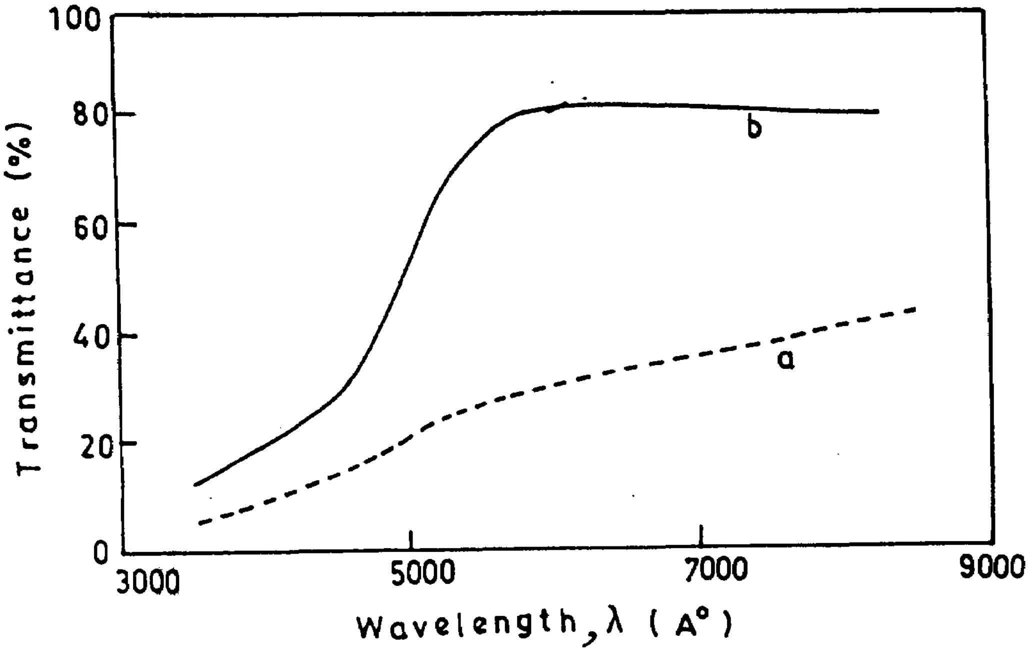


Fig.4.1

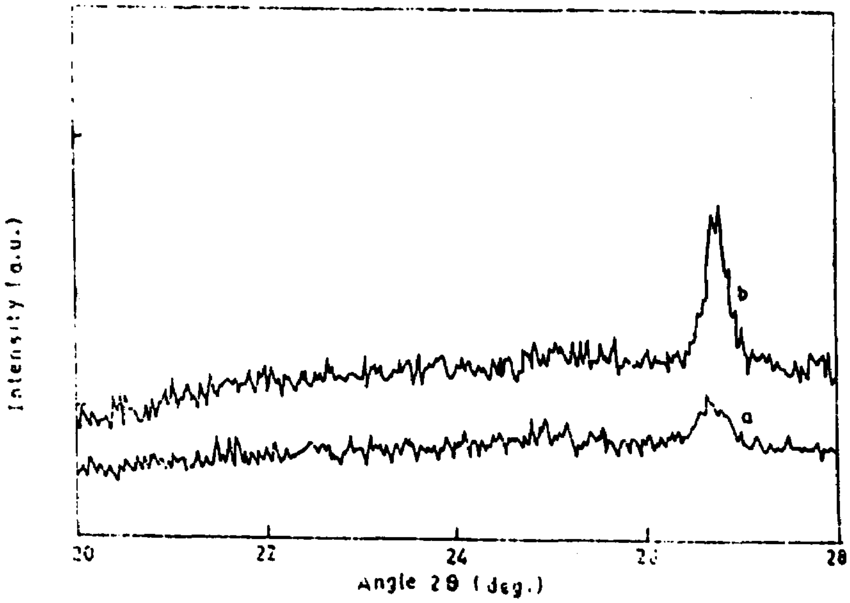
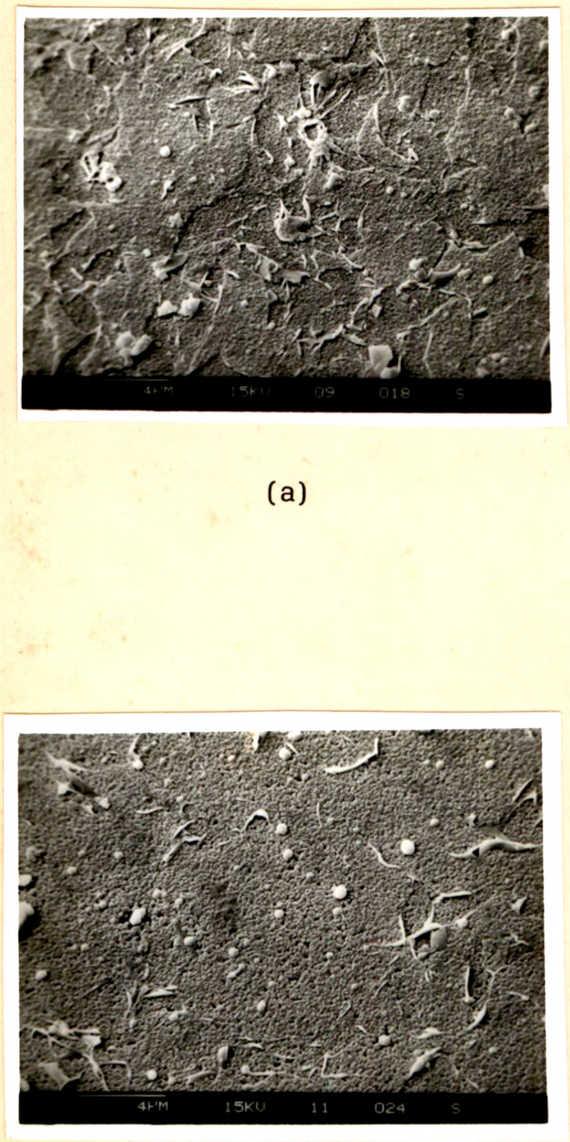


Fig.4.2

Fig.4.1 : Variation of optical transmittance (T %) with wavelength (λ) for (a) undoped and (b) 0.1 wt % Al doped CdS films.

Fig.4.2 : X-ray diffraction patterns for (a) Undoped and (b) 0.1 wt % Al doped CdS films.



(a)

(b)

Fig. 4.3 : SEM micrographs of (a) Undoped and (b) 0.1 wt % Al doped CdS films on glass substrates at 5000 X magnification.

It is seen clearly that the undoped film is polycrystalline in nature with defined grain boundaries. The grain size is small and the surface is nonuniform whereas, the SEM of 0.1 wt% Al doped film showed improved crystallinity over undoped one. Similar types of results are also reported by others(17, 19-21).

4.4 Photoconductivity Studies :

The I-V characteristics of contact between Al doped CdS and Ag was studied and is shown in fig. 4.4. The characteristics are found to be linear within the voltage range of study (± 30V), which show that silver paste produces ohmic contact with Al doped CdS.

a) Dark and photoconductivity measurements :

The dark and photoconductivities were studied at room temperature (300 K) in air as well as in vacuum (10^{-3} Torr), at light intensity of 10^3 lux. The results with undoped sample are comparied in Table 4.1.

It was observed that 0.1 wt % Al doped CdS has higher photoconductivty than undoped CdS. This increase in photoconductivity can be explained as follows : When Al is doped in CdS, it goes in trivalent state and replaces divalent Cadmium i.e. it goes in substitutional site of Cadmium. During substitution there is possibility of Cd^+ ions and/or Cd vacancies being formed to compansate the charge. The existance of such Cd^+ ions in the doped films has been corroborated by the presence of donor centers in such films where as Cd vacancies were indicated by the observation of acceptor centres. Since Al and Cd are deposited simultaneously there is less chance for formation of Cd vacancies. The observations showed increased photoconductivity for 0.1 wt% Al doped CdS films both in air as well as in vaccum which indicates the possibility of formation of Cd^+ ions.

b) Spectral response :

The spectral response curves studied in air at room temperature (300 K) are shown in fig. 4.5. The peak values of spectral response were observed at 425 nm and 450 nm for Al doped and undoped samples. These peak values shows that the peak for Al doped sample is shifted towards shorter wavelength side. This may be due to Al donors. The shift in spectral response peak towards shorter wavelength side was reported earlier by Lokhande and Pawar (20) for 0.1 wt% Al doped CdS film.

c) Photoconducting rise and decay curves :

The photoconducting rise and decay curves of the Al doped sample were studied for the three successive cycles with rise time of 15 minute and decay until the steady value is reached. The curves were studied in air as well as in vaccum (10^{-3} Toor) at room temperature (300 K). The rise and decay curves in air at light intensity 5×10^3 lux are shown in fig. 4.6 (a and b) and in vaccum at light intensity of 10^3 lux are shown in fig. 4.7 (a and b) for Al doped and undoped samples respectively. The curves show initially fast steep rise followed by slow increase in the photocurrent. The rise and decay curves for Al doped samples are more pronounced as compaired to undoped samples both in air

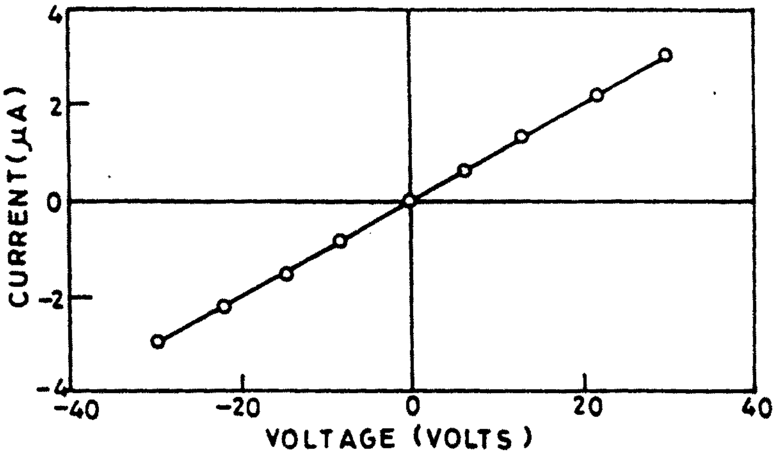


Fig.4.4 : I-V characteristics (forward and reverse) of contact between Al doped CdS and Ag film.

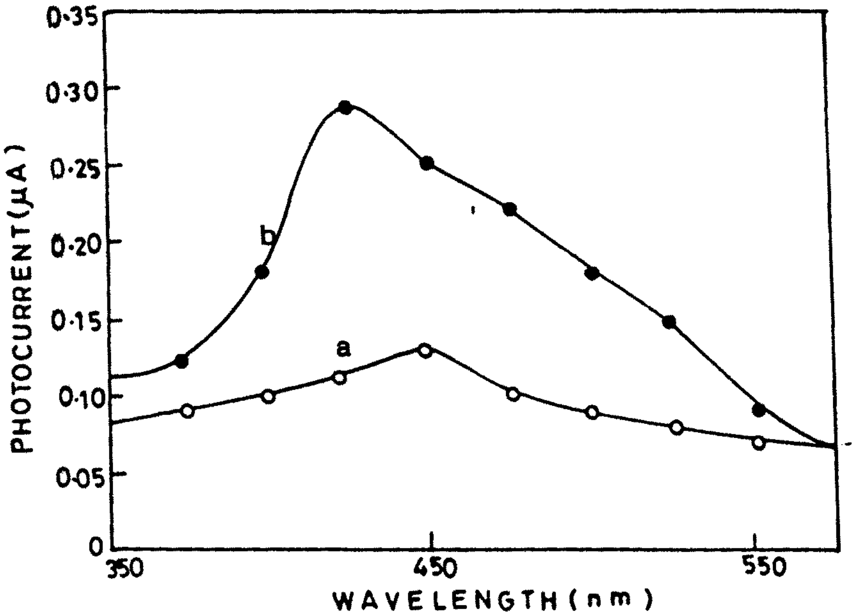
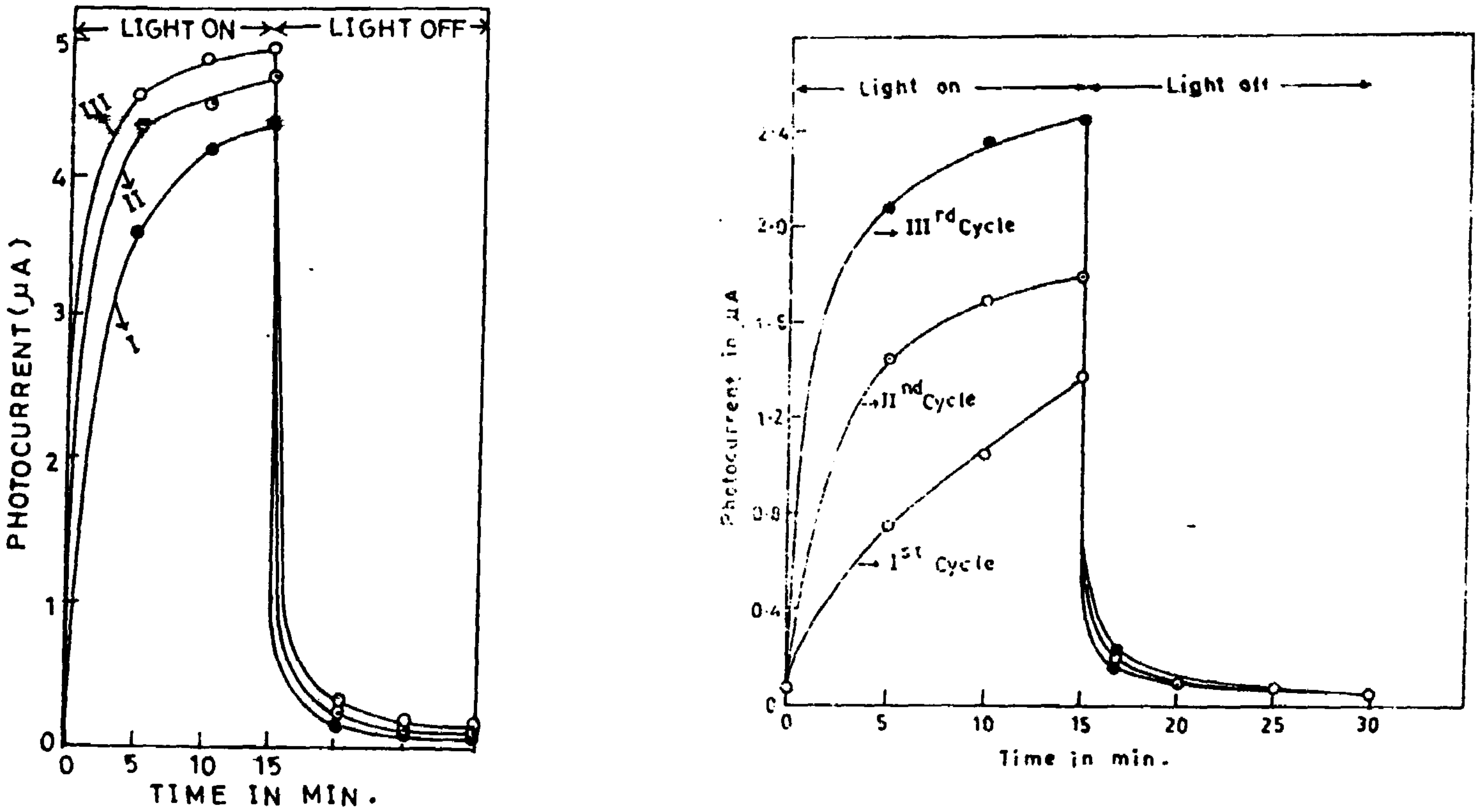
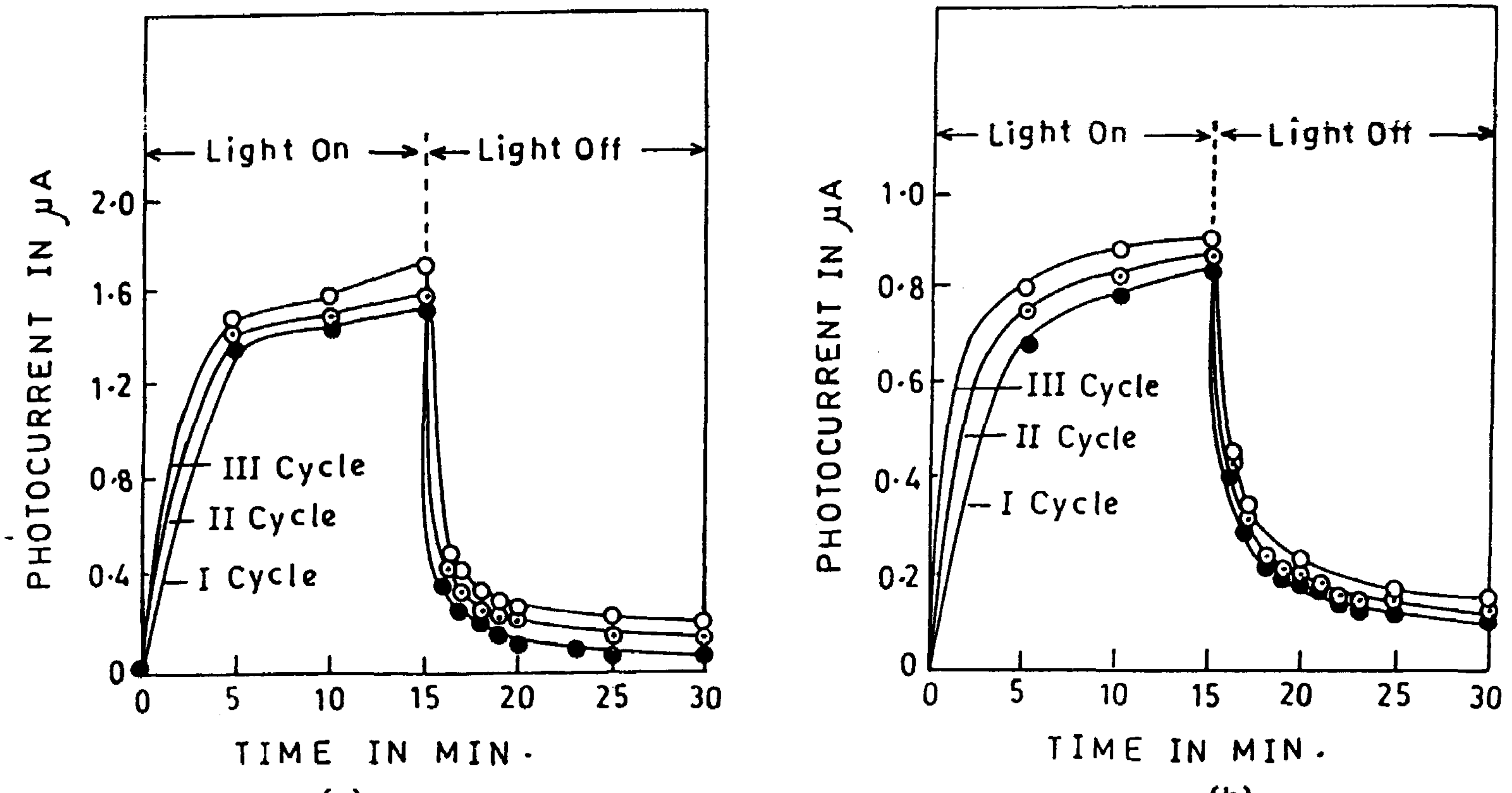


Fig.4.5 : The spectral dependence of the photoconductivity for, (a) Undoped and (b) Al doped CdS films, studied in air (at light intensity 5 X 10^3 lux), at room temperature (300 K).



(a) (b)

Fig.4.6 : Photoconducting rise and decay of (a) Al doped and (b) Undoped CdS films for first three successive cycles, each of 30 min. (15 min. rise and 15 min. decay) studied in air at excitation light intensity of 5 X 10^3 lux (at 300 K).



(a)

(b)

Fig.4.7 : Photoconducting rise and decay of (a) Al doped and (b) Undoped CdS films for first three successive cycles, each of 30 min. (15 min. rise and 15 min. decay) in vacuum (10^{-3} Torr) at exciation light intensity of 10^3 lux(300 K).

as well as in vacuum. As the rise and decay curves in air and in vacuum are at different light intensities, we are unable to compare them.

d) Rise and decay time constants :

The rise and decay time constants 't_r' and 't_d' were determined in vacuum (10^{-3} Torr) with the help of omniscribe recorder (X/t mode). The rise time 't_r' of Al doped sample was found to be smaller (0.08 sec) than the rise time of undoped (0.1 sec) sample while the reverse was happened in case of decay times 't_d' (0.5 sec and 0.3 sec) respectively.

. Fig. 4.8 shows the log of photocurrent versus log t drawn from photoconducting decay curves (fig.4.8 a and b) of Al doped and undoped samples in vaccum (10^{-3} Torr). The plots show that there are two linear regions i.e. region I and region II. The region I is associated with shallow traps while region II is associated with deep traps. The values of decay constants for region I and II are denoted by b_1 and b_2 respectively. The decay constants for Al doped and undoped samples estimated by relation (3.3) are given in table 4.2.

The decay constants for Al doped sample are smaller than undoped sample. The demarcation time for Al doped sample is larger as shown in table 4.2. Nature of the plots are similar to those reported by others (21) for Na doped CdS films at different temperatures.

Fig. 4.9 shows log of photocurrent versus time for Al doped and undoped samples. The decay for Al doped sample is

Table 4.1 : Dark and photoconductivities of undoped and Al doped samples in air as well as in vaccum (10^{-3} Torr) at light intensities of 10^{3} lux (Applied Voltage 30 V D.C.) at room temperature (300 K) ..

Sr. No.	Samples CdS	In air			In vaccum		
		Dark Conductivity Mho cm^{-1}	Photo-Conductivity Mho cm^{-1}	L/D Ratio	Dark Conductivity Mho cm^{-1}	Photo-Conductivity Mho cm^{-1}	L/D Ratio
1.	Undoped	2.2×10^{-4}	2.65×10^{-4}	1.204	3.9×10	4.4×10	11.28
2.	0.1 wt% Al doped	9×10^{-5}	3.7×10^{-4}	4.11	6.1×10^{-5}	1.1×10^{-3}	18.00

Table 4.2 : Decay constants for Al doped and undoped samples estimated from the decay curves in vaccum (10^{-3} Torr) at 300 K.

Sr. No.	Sample	Decay constants		Demarcation time in sec.
	CdS	$-b_1$	$-b_2$	
1.	Undoped	0.199	0.058	120
2.	0.1 wt% Al doped	0.128	0.024	300

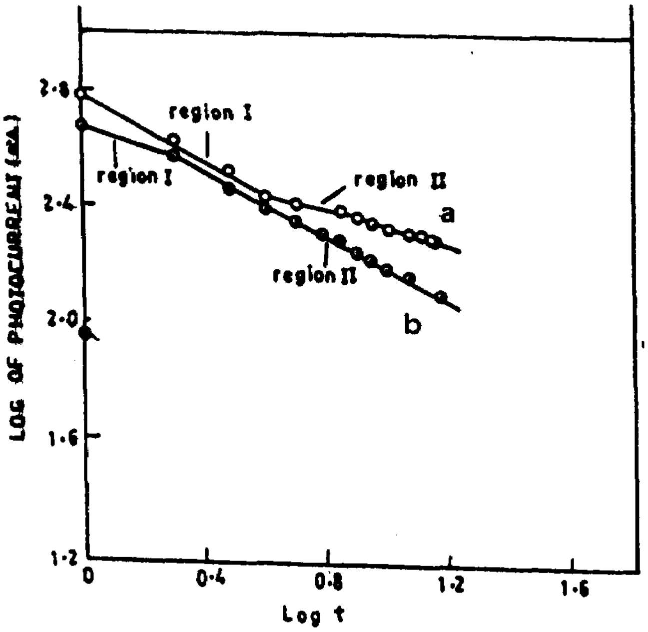


Fig.4.8 : log of photocurrent versus log t for (a) Al doped and (b) Undoped CdS films drawn from photoconducting dercay curves of Fig.4.7 (a and b).

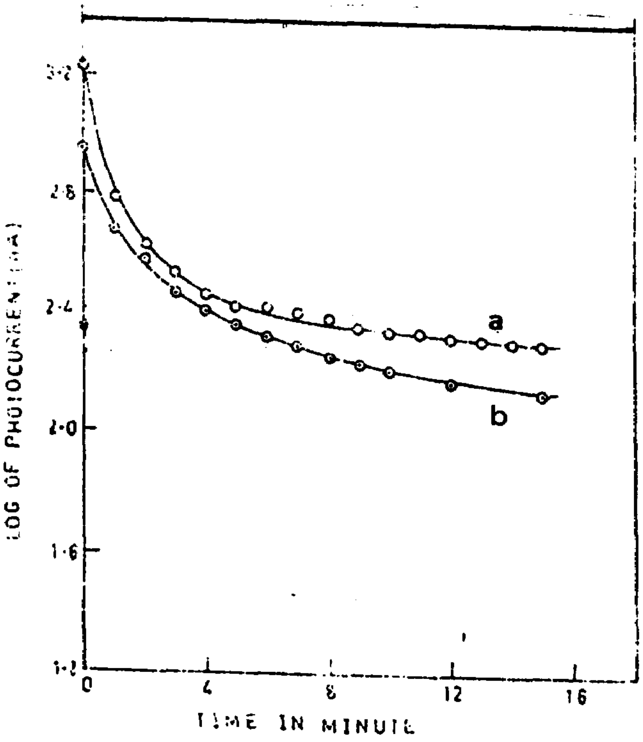


Fig.4.9 : Decay curves of (a) Al doped and (b) Undoped CdS films at room temperature (300 K).

slower as compaired to undoped sample. From the nature of the curve, it shows that there are two kinds of traps appear to be involved. Nature of the plots are similar to those reported for CdS:NaF, La doped CdS films (22).

e) Lux-ampere Characteristics :

The variation of photocurrent as a function of light intensity (log-log-scale) for Al doped and undoped films are shown in fig. 4.10. The samples exibited sublinear photoconductivity which has been reported earlier for PbS films (23). This means that the photo-excitation is changing the number of free carriers such that, for an increase in the intensity of excitation, there is a decrease in free carrier life time. The increase in photoconductivity is due to the number of photoelectrons created. The fig. 4.10 shows that at any intensity of light, the change in number of free carriers is more for Al doped CdS than for undoped CdS.

From all the results, it is concluded that the photoconductivity of CdS film with 0.1 wt% Al doping is increased.

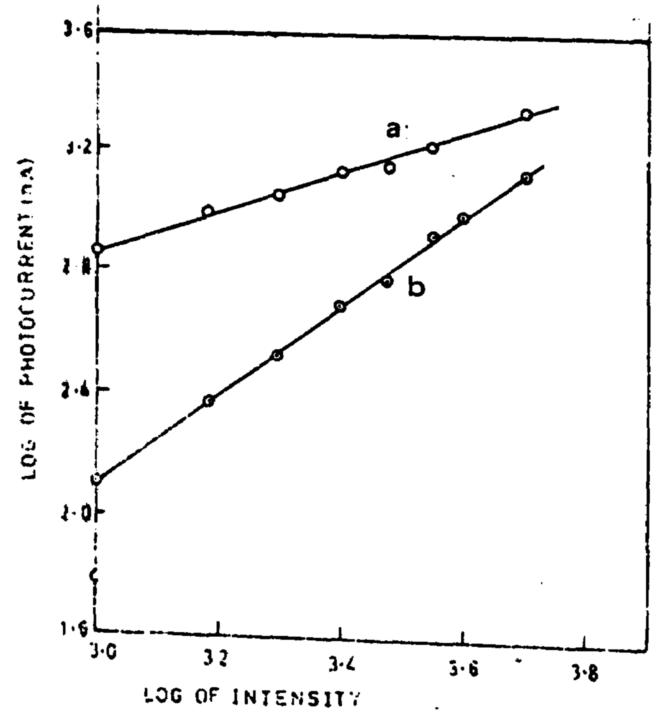


Fig.4.10 : Variation of photocurrent as a function of light intensity (log-log-scale) for (a) Al doped and (b) Undoped CdS films, studied in vacuum (10^{-5} Torr) at room temperature (300 K).

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