CHAPTER-V

.

Effect of Cu doping on photoconductivity of CdS thin film

5.1 Introduction

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5.1 Introduction :

Monovalent impurities acts as an acceptor in CdS material (1). Various monovalent impurities such as Cu, Li, Na etc. (2-7) have been doped in CdS films using various methods. It is found that such impurities acts as electron acceptors and affects the crystalline nature and other properties of the films.

In the present Chapter-V, the CdS film with Cd:S volume ratio as '5' is doped with Cu. The effect of 0.1 wt% Cu doping on photoconducting properties of CdS films are reported.

5.2 Exparimental procedure for deposition of Cu doped CdS films :
a) Substrate Cleaning :

Cleaning of glass substrates was carried out as described in section \$.3.1.

b) Preparation of solutions :

Chemicals used for preparing CdS films were as follows: G.R. grade Cadmium Chloride, supplied by Glaxo Laboratory (India) Ltd., Bombay. G.R. grade Thiourea, supplied by Loba Chemie and L.R. Grade Copper Chloride. All solutions were prepared in doubly distilled water.

c) Preparation of the 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 qC 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'. For Cu doping, 0.1 wt% CuCl solution was added in the mixture. Four glass substrates were kept rotating in the reaction mixture at a constant speed of 75 rpm. The reaction vessel was heated in oil bath and the temperature of the mixture was kept at 65° C for 90 minutes. The films formed were washed with distilled water, dried and preserved.

5.3 Experimental Procedure :

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

5.4 Results and Discussion :

5.4.1 Characterization of CdS films :

a) Thickness Measurements :

Thickness of the Cu doped film was found to be slightly less (1056 A^{O}) than undoped (1078 A^{O}) sample. No considerable change in thickness has been observed.

b) Optical Transmission studies :

The band gap ${}^{'E}g'$ of Cu doped samples were estimated from optical transmission spectra (8). The transmission spectra for both Cu doped and undoped films are shown in <u>fig. 5.1</u>. The band gaps of Cu doped and undoped films were found to be 2.49 eV and 2.47 eV respectively, which showed that there is no significant change in band gap for doped CdS films.

c) XRD studies :

The XRD patterns of Cu doped and undoped CdS films are shown in fig. 5.2 (a, b) respectively. The films were slow



Fig.5.1 : Variation of optical transmittance (T %) with wavelength (λ) for (a) Cu doped (0.1 wt %)and (b) Undoped CdS films.



Fig.5.2 : X-ray diffraction patterns for, (a) Cu doped (0.1 wt %) and undeoped CdS films.

scanned between 20° to 80° . The grain size of the film was calculated by using equation 3.2. It was observed that the grain size is increased for Cu doped sample (70 A°) as compaired to undoped one (31 A°).

d) SEM Studies :

The Cu doped sample was studied with SEM at 5000 x magnification. The SEM microstructure for Cu doped and undoped samples are shown in <u>fig. 5.3</u> a and b respectively. The SEM microstructure of undoped sample shows that the grain size is small and the surface is non-uniform whereas the SEM of 0.1 wt Cu doped sample showed improved crystallinity over undoped one.

5.4.2 Photoconductivity Studies :

The I-V characteristics of contact between Cu doped CdS and Ag were studied and are shown in <u>fig. 5.4</u>. The characteristics are found to be linear within the voltage range of study (± 30 V), which showed that the silver paste produces ohmic contact with Cu doped CdS film.

a) Dark and photoconductivity measurements :

The dark and photoconductivities were studied at room temperature (300 K) in air as well as in vacuum (about 10^{-3} Torr), at light intensity of 10^3 lux. The results with undoped samples are compaired in <u>Table 5.1</u>.

The table shows that the 0.1 wt% Cu doped CdS film has lower photoconductivity than that of pure CdS. This can be explained as follows : Since Cu^{+2} goes in monovalent state it replaces divalent Cadmium, Cd^{+2} . When Cd^{+2} is removed it leaves two



(a)



(b) Fig. 5.3 : SEM micrographs of (a) Undoped and (b) Cu doped CdS films on glass substrates at 5000 X magnification.

Table 5.1 : Dark and photoconductivities of Cu doped and undoped samples in air as well as in vacuum $(10^{-3}$ Torr) at light intensity of 10^3 lux (Applied voltage +30 V D.C.) at room temperature

(300 K).

	L/D ratio	11.28	ດ
In vacuum	Photocondu- ctivity mho cm ⁻¹	4.4 x 10 ⁻⁴	1 × 10 ⁴
	Dark con- ductivity mho cm ⁻¹	3.9 x 10 ⁻⁴	1.8 x 10 ⁻⁵
	L/D ratio	1.204	1.05
In air	Photocondu- ctivity mbo cm ⁻¹	2.65 x 10 ⁻⁴	6.3 x 10 ⁻⁵
	Dark con- ductiwity mho cm ⁻¹	2 x 10 ⁻⁴	6×10^{-5}
Samples CdS		Undoped	0.1 wt% Cu doped
Sr.	Sr. No.		5

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positive charges in its place. The Cu⁺ in its place has one positive charge. There is one excess positive charge. To compensate the charge, one electron is accepted from neighbouring sulphur atom causing decrease in number of electrons in the conduction band. The observations showed decrease in photocurrent, indicating the possibility of forming Cd vacancies.

b) Spectral response :

The spectral response curves studied in air at room temperature (300 K) are shown in <u>fig. 5.5</u>, for both the samples. The peak values of spectral response were observed at 475 nm and 450 nm for Cu doped and undoped samples. The peak shifts towards larger wavelength side due to formation of acceptor states due to Cd^{+2} vacancies.

c) Photoconductivity rise and decay curves :

The photoconducting rise and decay curves of Cu doped samples were studied in air as well as in vacuum at light intensities of 5 x 10^3 lux and 10^3 lux respectively. The curves were studied for three successive cycles of excitation with rise time of 15 minute and decay until the steady value was reached. The curves for both Cu doped and undoped samples in air as well as in vacuum are shown in <u>fig. 5.6</u> (a and b) and <u>fig. 5.7</u> (a and b) respectively. The curves showed that curves of Cu doped samples have less photocurrent response as compaired to undoped sample. d) Photoconducting rise and decay time constants :

The photoconducting rise and decay curves in vacuum were recorded by omniscribe recorder (X/t mode) for Cu doped



Fig.5.4 : I-V characteristics (forward and reverse) for contact between Cu doped CdS and Ag (at 0 to 30 V dc).



Fig.5.5 : Spectral dependence of the photoconductivity for, (a) Cu doped and (b) Undoped CdS films, studied in air at room temperature (300 K).

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Fig.5.6 : Photoconducting rise and decay of (a) Cu 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.



(b) Fig.5.7 : Photoconducting rise and decay of ,(a) Cu doped and (b) Undoped CdS films for first three successive cycles, each of 30_min. (15 in. rise and 15 min. decay) studied in vacuum (10 Torr) at excitation light intensity of 10 lux (at 300 K).

sample. The rise and decay time constants were determined. The rise time 't_r' for Cu doped sample was found to be larger (0.2 sec.) as compaired to rise time of undoped(0.1 sec.). Sample while the reverse was happened in case of decay times 't_d' (0.06 sec. and 0.3 sec.) respectively.

<u>Fig. 5.8</u> shows the log of photocurrent versus log t drawn from the photoconducting decay curves of Cu doped and undoped (fig. 5.7 a and b) samples in vacuum (10^{-3} Torr). The plots show that there are two linear regions. The region-I is associated with shallow traps and region-II with deep traps. The values of decay constants for region-I and II are denoted by 'b₁' and 'b₂' respectively. The decay constants for Cu doped and undoped samples were calculated by using the relation 3.3 (Chapter-III) and are given in <u>table-5.2</u>.

Table 5.2 ; Decay constants for Cu doped and undoped samples estimated from the decay curves in vacuum (10^{-3} Torr) at room temperature (300 K).

Sr. No.	Samples	Decay constants		Demarcation
	CdS	-b	'-b ₂	- time in sec.
1.	Undoped	0.199	0.058	120
2.	0.1 wt% Cu doped	0.163	0.029	180

The decay constants for Cu doped samples are smaller as compaired to undoped sample while demarcation time for Cu doped sample is larger than undoped sample.

Fig. 5.9 shows log of photocurrent versus time for Cu doped and undoped samples. The decay for Cu doped sample is faster as compaired to undoped sample. From the nature of the curve it shows that two kinds of traps appear to be involved. Nature of the plots are similar to those reported for CdS:NaF, and La doped CdB films (8).

e) Lux-ampere characteristics :

The variation of photocurrent as a function of light intensity (log-log scale) for Cu doped and undoped samples are shown in The samples exibited sublinear fig.5.10 (a,b). photoconductivity (9). The curves showed that for an increase in the intensity of excitation, there is decrease in free carrier life The increase in photocurrent due to number time. is of The curves show that for any intensity photoelectrons created. of light, the change in number of free carriers is less for Cu doped sample than for undoped sample.

From all the above results, it is concluded that the photoconductivity of CdS film with 0.1 wt% Cu doping is decreased than undoped samples.



Fig.5.8 : log of photocurrent versus log t for, (a) Cu doped and (b) Undoped CdS films drawn from photoconducting decay curves of fig.5.7.



Fig.5.9 : Decay curves of (a) Cu doped and (b) Undoped CdS films at room temperature (300 K).

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Fig.5.10 : Variation of photocurrent as a function of light intensity (log-log-scale) for (a) Cu doped and (b) Undoped CdS films studied in vacuum (10 Torr), at room temperature (300 K).

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