CHAPTER - III

Effect of Cd:S volume ratio on photoconducting properties of CdS films.

3.1 Introduction :

Metal Chalcogenides (Sulphides, Selenides and Tellurides) have been studied intensively over the past 25 years in view of their actual and potential applications as photoconductive cells and other optical devices. The widely used photoconducing films are CdSe, CdTe, CdS, GaAs, Ge, Si, PbS and some organic materials. Cadmium Sulphide is one of the members of the family of group II-VI Compounds and it is one of the best photoconducting material. Cadmium Sulphide is primarily photoconductive only in the short wavelength visible region; but specimens prepared by various ways have been shown to be sensitive to ultra-violet, infra-red, X-radiation and to gamma rays and alpha rays (1).

Many investigations of the films of CdS have been carried out concerning its photoconducting properties. Many attempts have been made to increase the photoconductive properties of CdS films by adding the impurities (2-6); however, little study has been reported with the variation of Cd:S ratio.

Nair and Nair (7) have reported highly photosenstive CdS thin films by solar assisted chemical deposition. Bath constitution were changed by varying the molar ratio of Cadmium to Thiourea in the bath viz. 1:1, 1:0.5 and 1:0.25. All depositions were carried out directly under sunlight; outside the laboratory during 11.00 to 14.00 hours (local time) of a day. The solar assisted deposition were reported for the films deposited from 1:0.5 bath for 1 hour 30 minutes; under the solar radiation intensity of

600 W/m^2. It was seen that the photocurrent was highest for the film deposition from the 1:0.5 bath for the deposition time 1 hour 30 minutes. The photocurrent obtained at end of 400 S exposure was 1.5 mA/cm^2 for 300 W/m^2 simulated solar radiation. This gives the photoconductivity of 0.12 $ohm^{-1} - cm^{-1}$. Nair et al (8) have studied the photocurrent response for the Cadmium to Thiourea molar ratio as 1:1 and 1:0.5 with deposition time 14 and 17 hours for 1:1 molar ratio and 18 hours for 1:0.5 molar ratio and reported photocurrent to dark current ratio (I_{ph}/Id) of 10^6.

In view of the improvement in photoconductivity of CdS, in the present investigation the Cd:S volume ratio is changed and its effect on the photoconducting properties of CdS films is studied.

3.2 Chemical bath deposition technique :

3.2.1 Experimental Set-Up :

The outline of the experimental set-up needed to carry out the chemical bath deposition of CdS films with various Cd:S volume ratio is shown in fig. 3.1. It consists of following parts

a) Constant temperature oil bath :

It is a cubic metal pot of 30 cm each side. Glass wool is used in order to avoid the heat loss. Parafin oil is used as a liquid bath, in which a 1000 watts heater is placed to heat the oil bath. Thermostastic arrangement is used to control the temperature of the oil bath. The oil is well stirred with electrically driven stirrer to keep the temperature constant throughout the oil bath. The oil bath can be kept at any desired temperature between 30° to 200° C.

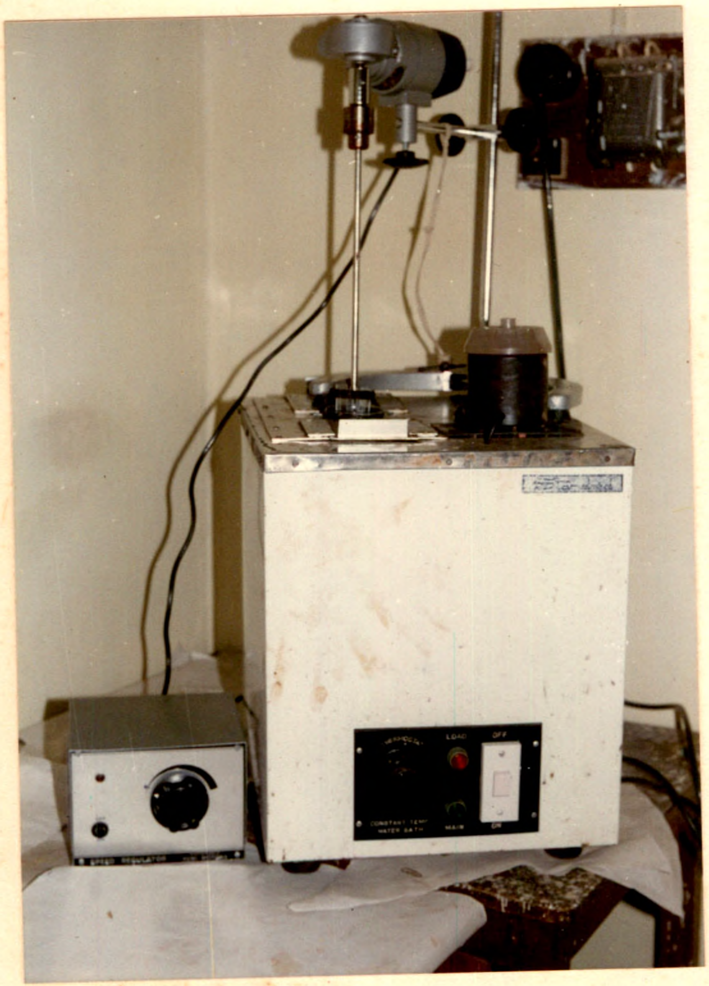


Fig. 3.1 : Photograph of experimental set up for chemical bath deposition.

b) Chemical bath :

A 250 cc glass beaker with the mixture of chemical reactants, which serves as the chemical bath, was immersed in the constant temperature oil bath. The chemical mixture was stirred with the substrates rotating in it. The temperature of chemical bath was found to be less by about 10 °c than the temperature of the oil bath.

c) Substrate holder and substrates :

Microslides (Blue star) of dimensions 75 x 10 x 1 mm were used as substrates for the deposition of the films. To mount these substrates, a holder was designed as shown in Fig.3.2(a). It consists of circular bakelite disc of diameter 5.5 cms and thickness 1.2 cm with four grooves in it to fit the glass substrates. This disc is held with a metal rod as shown in Fig. 3.2(b), which is then fitted to a synchronous motor.

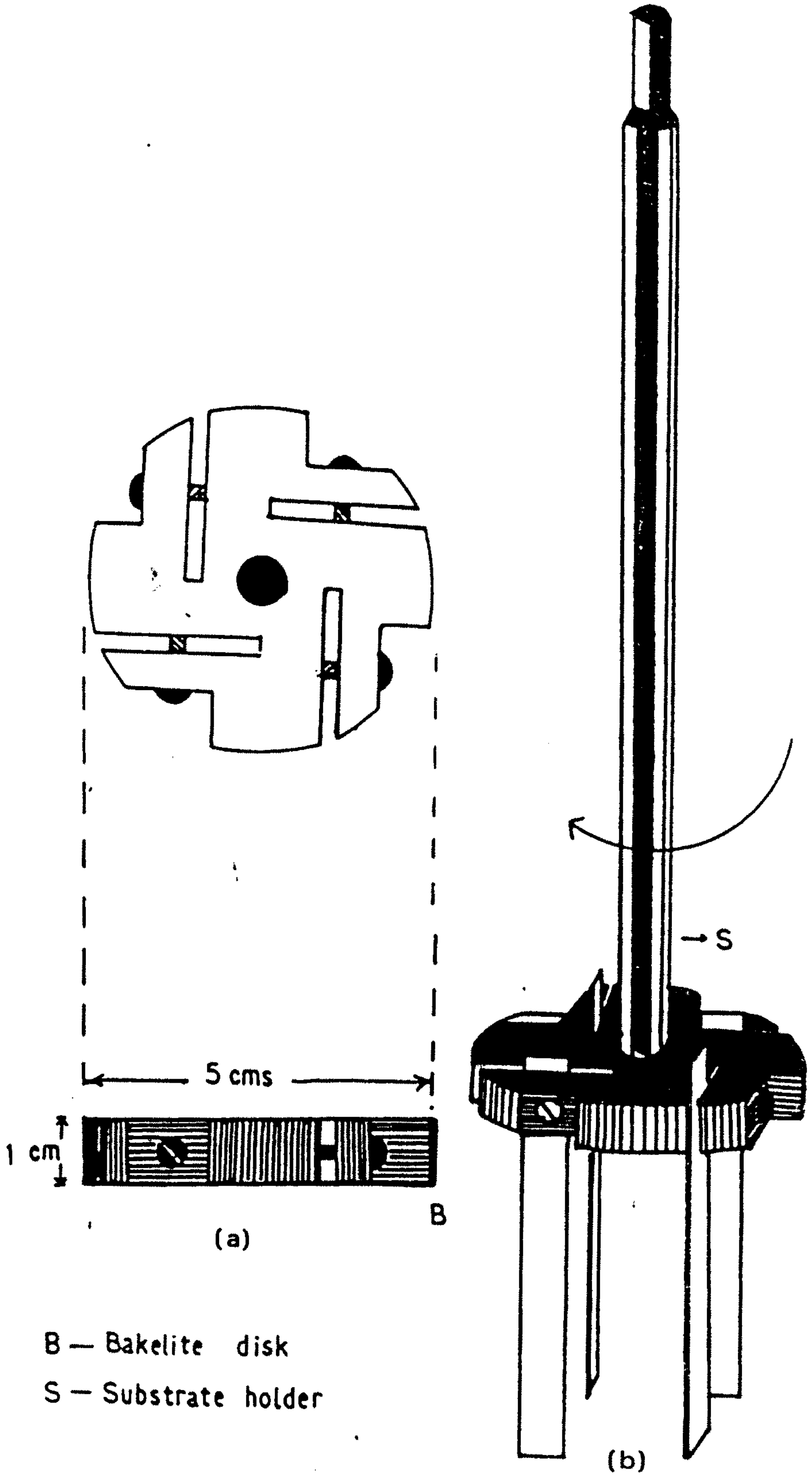
3.3 Experimental procedure for deposition of the films :

3.3.1 Substrate cleaning :

Substrate cleaning is one of the most important factor for obtaining the reproducible properties of the films. It also affects stoichiometry, adhension, smoothness, brightness and uniformity of the film. The following procedure was adopted for cleaning the glass substrates :

a) Substrates were boiled in chromic acid for five minutes and were washed with doubly distilled water.

b) Substrates were dipped in 'labolean' detergent solution and again washed with distilled water.



B — Bakelite disk

S — Substrate holder

Fig.3.2 (a) Substrate holder (b) Metal rod with substrate holder and glass substrates.

c) Substrates were cleaned with ultrasonic cleaner for five minutes and were exposed to alcohol vapors for some time.

d) Substrates were kept immersed in doubly distilled water.

3.3.2 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. All solutions were prepared in doubly distilled water.

3.3.3 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, 50 cc of 0.1 M Cadmium Chloride solution was taken in a 250 cc beaker and to it, ammonia solution was added slowly to form the complex and the pH was raised to between 9-10. To this solution, 50 cc of 0.1 M Thiourea solution was added. Four glass substrates were kept rotating in the reaction mixture at a speed of 75 rpm. This stirring action continuously exposes the substrates to a fresh body of reactants which is also important for uniform deposition of the films. The reaction vess was heated in oil bath and the temperature of the mixture was kept at 65^{0}C for 90 minutes. The films formed were washed with distilled water, dried and preserved. By varying the volume of Thiourea solution in the bath CdS films with various Cd:S volume ratios as, 1, 1.25, 1.66, 2.5 and 5 were prepared. Photoconducting films prepared by chemical bath deposition techniques were uniform, adherent to substrate and yellowish in colour.

3.4 Thickness measurement :

Amongst the different methods for measuring the thickness, the fizzau fringes method was used. The relation used was,

$$t = \frac{\lambda}{2} \times \frac{d}{D} \qquad \text{......... 3.1}$$

Where 't' is the thickness, λ - is the wavelength of the monochromatic light; d - is the displacement of the fringes and D - is the fringe spacing.

3.5 Characterisation of the films :

The CdS films were characterised using following techniques :

a) Optical absorption and Transmission :

The optical absorption and Transmission of films was carried out in the wavelength range 3500-8500 A^{o} , with the spectrophotometer, Hitachi-330. For this, the films were cut in to the size of 1 cm x 2.5 cms.

b) XRD study :

Philips PW-1710, X-ray diffractometer using CuK_{α} radiation with wavelength 1.542 A^{o} , was used to study the nature of the film. The X-ray was operated on 25 KV, 20 MA. The line profiles were measured by means of point by point cutting, using a fix time period 10 sec. and 2θ increment of 0.02^{o}.

c) SEM study :

The SEM of the films were taken with the help of cambridge sterioscan 250-MK_3 assembly (≈ 10KV). The films were coated with gold palladium (Au-Pd) of thickness 100 A^0 using polaron SEM sputter coating unit, E-5200 before taking SEM.

3.6 Photoconductivity studies :

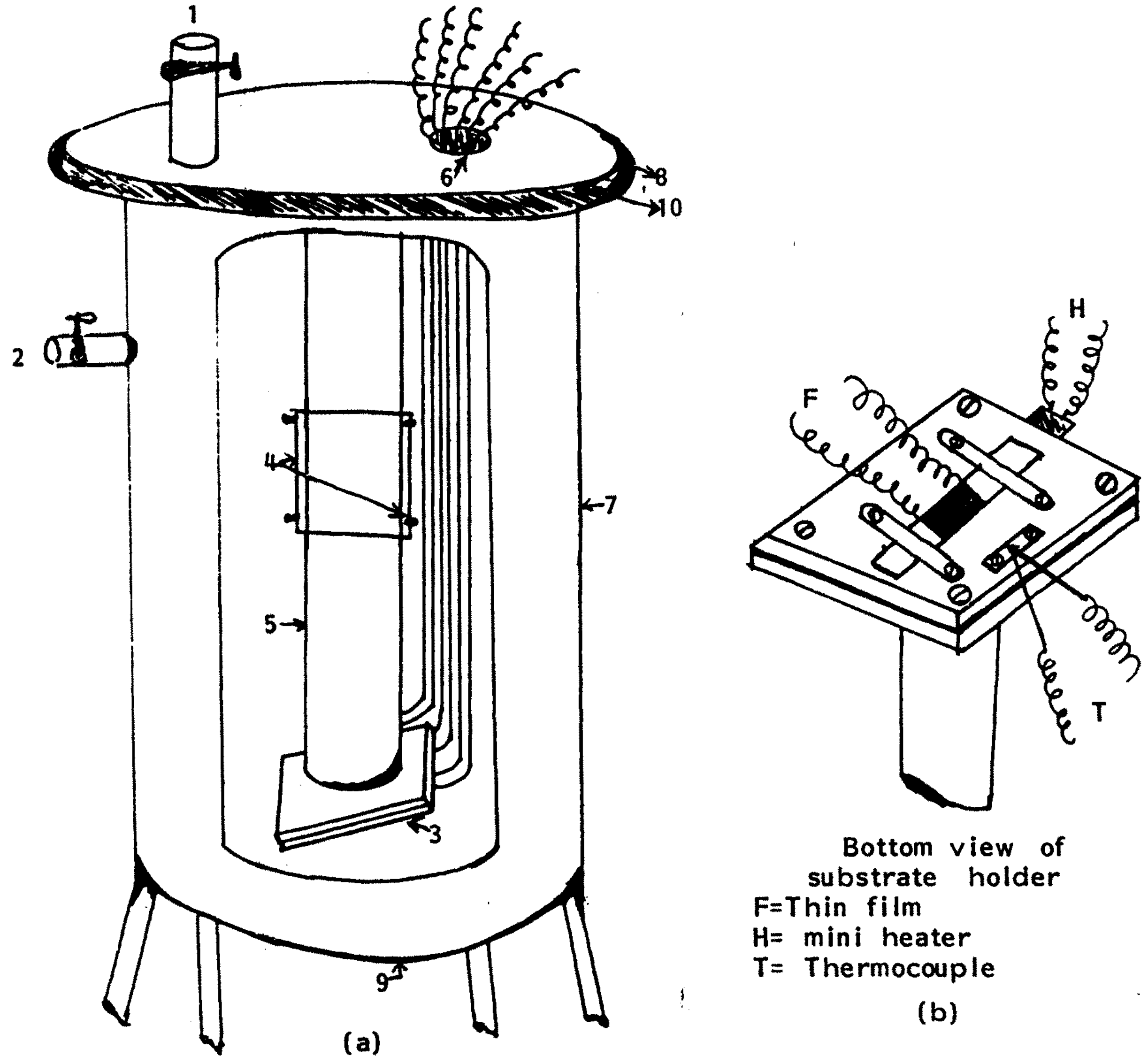
The photoconducting properties such as, light and dark conductivity, spectral response, rise and decay curves and intensity response were studied.

3.6.1 Experimental Set up for Photoconductivity :

To study the photoconductivity properties of the films at different temperatures, the photoconductivity unit is designed and fabricated in our departmental workshop. The photograph of the instrument is shown in fig.3.3, and it's sketch is shown in fig. 3.4 It consists of an iron pipe of 4 cm in diameter and 10 cm in length. A small pipe is fitted on the side for air outlet to be connected to vacuum pump. The glass window is provided at the bottom of this cylinder to illuminate the sample. The upper end is closed with circular metal flange by bolting. A copper pipe of 1 cm in diameter is welded at the centre of the flange and to the other end of the copper pipe, a substrate holder assembly is fixed. The flange has two holes, to be used as air inlet and to take out wires for the electrical connections. All the holes are made air tight by M-seal.

To excite the film, the tungsten filament lamp of 500 watt (being filament temperature 2850 K) was used. The light intensity was varied by changing the distance between the lamp and the film. To avoid the heating of the fil due to light

Fig. 3.3 : Photograph of photoconductivity unit.



(a)

Bottom view of substrate holder
F=Thin film
H= mini heater
T= Thermocouple

(b)

1.	Air Inlet	2.	To vacuum pump
3	Substrate holder	4	Aluminium strips
5	Copper pipe	6	Wires for external connections
7	MS pipe	8	MS Flange
9	glass window	10	O' ring

Fig.3.4:a) Schematic diagram of internal arrangement of photoconductivity unit and (b) Bottom view of substrate holder.

excitation a water filter (0.7 cm thick) was interposed in between the lamp and the film. The intensity of light was measured with Lux meter. Focussing arrangement was used to focus the beam.

3.7 Experimental procedure for photoconductivity studies :

3.7.1 Electrical contacts and I-V characteristics of CdS films :

In order to measure the electrical and photoconducting properties of CdS film, it is necessary to make an electrical contact with CdS by means of metal electrodes. The metal electrodes would be considered ideal if they satisfy the following conditions :

i) introduce no resistance to the flow of current in either direction,

ii) do not get affected by variation in temperature, illumination, electrical field or any other ambient, and

iii) does not react with chemically with CdS.

While making the electrical contacts, the existance of barriers are usually observed between metal and semiconductor. Such barriers usually demonstrate their presence by giving rise to rectification characteristics, instability, photocurrent noise etc. A contact between metal and semiconductor are called as 'ohmic' when no such barriers exist and current passing through contact obeys 'Ohms law' over a wide range of applied voltage. As many workers have reported (2,9) that silver paste gives good ohmic contact with CdS, the electrical contacts were made by silver paste. The nature of contact was checked by current voltage characteristics.

Current Voltage characteristics :

The current voltage characterstic was studied by D.C.

method. A sample is shown in fig. 3.5(a) with silver paste electrodes, leaving a CdS strip 1 cm in length and 0.5 cm in its width on a glass substrate of 2.5 x 1 cm^2 was mounted on substrate holder. D.C. regulated variable voltage power supply with high current rating was used as a voltage source and current was measured by microammeter. The circuit diagram is as shown in fig. 3.5(b). The I-V curves were plotted both in forward and reverse directions.

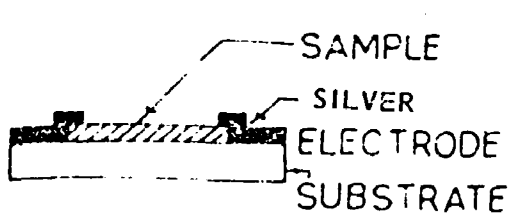
3.7.2 Photoconductivity Measurements :

a) Preparation of sample :

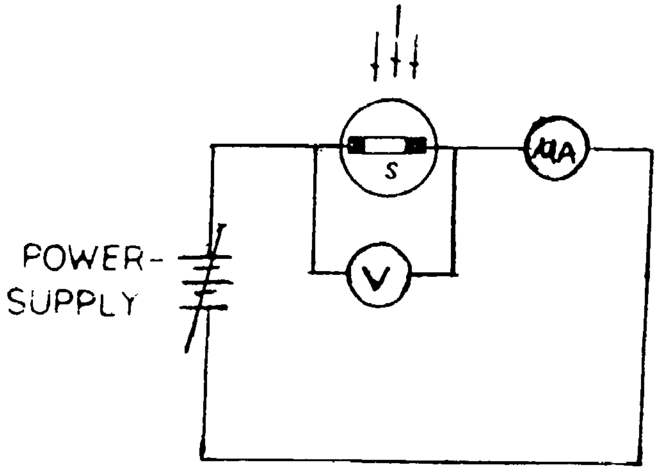
The films of 1 cm in length and 0.5 cm in width were used for all experiments. The ohmic contacts were made by silver paste.

b) Dark and light conductivity measurements :

Dark and light conductivities of all the samples were measured in air at room temperature(300 K). The electrical contacts were made by silver paste. The sample was fixed on a sample holder in a photoconductivity unit. A d.c. field applied was 30 volts and 500 W projection lamp was used as a light source. D.C. voltage was changed from 0 to 30 volts and the corresponding current change was measured by microammeter. The measurements were carried out at fixed intensity of light (about 5 x 10^3 lux). Water filter (about 0.7 cm thick) was interposed between the source and the sample to avoid heating of the sample. For Dark and light conductivity measurement in vacuum; the sample was mounted on a substrate holder in the photoconductivity unit and vacuum of



(a)



(b)

Fig.3.5(a) : Sectional diagram (side view) of the film used in photoconducting measurements.

Fig.3.5(b) : Circuit diagram used for I-V curves (d.c. method), at ± 30 V dc.

the order of 10^{-3} Torr was obtained using oil pump. The circuit arrangement for both the measurements is shown in fig. 3.6.

c) Spectral response :

Spectral response of the film was studied in air at room temperature (300 K) by measuring a photocurrent change corresponding to different wavelengths. A d.c. applied bias was 30 V. A calibrated higher monochromator with 500 W projection lamp was used as a light source in the wavelength range of 3500-7000 A^{0}. The circuit arrangement for spectral response is shown in fig. 3.7.

d) Photoconducting Rise and Decay curves :

The rise and decay curves of all the samples were carried out in air. The samples were mounted on sample holder in photoconductivity unit. A 500 W tungsten filament lamp was used for excitation. To avoid the heating, water filter was interposed between source and sample. The photoconducting rise and decay curves were recorded with omniscribe recorder (X/t mode).

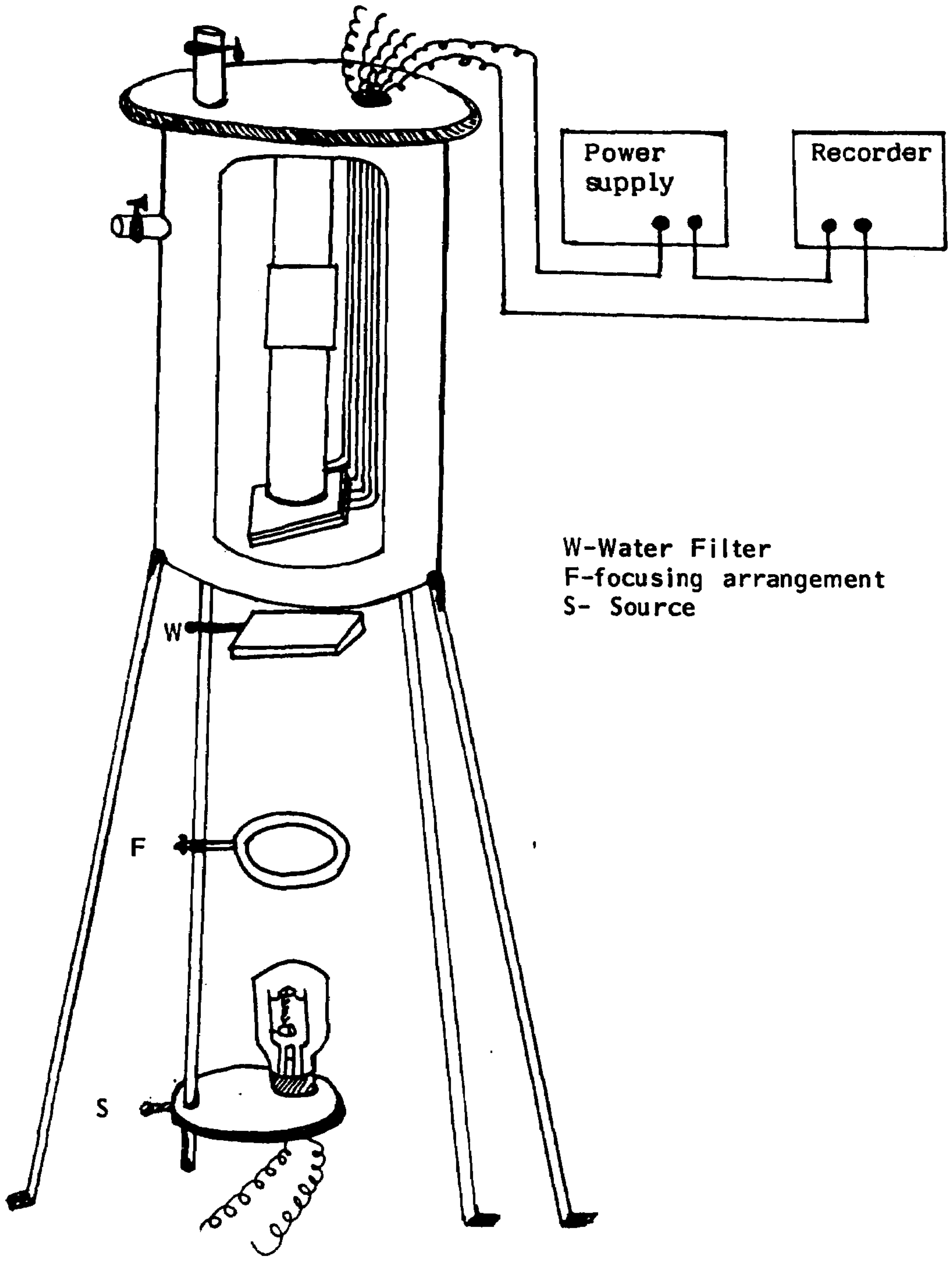
3.8 Results and discussion :

The thicknesses of the films were found in the range of 1078-1278 A^{0}. The wavelength of the light used was 5500 A^{0}.

3.8.1 Characterisation of CdS films :

a) Optical absorption and Transmission :

The band gaps 'E_g' can be estimated by two ways (i) from the plots of $(\alpha h \nu)^2$ Vs $h\nu$ and (ii) the method explained by Gorer and Hodes (10) from optical transmission spectra of the



W-Water Filter
F-focusing arrangement
S- Source

Fig.3.6 : Schematic diagram of experimental set up for photoconductivity studies in air and in vacuum.

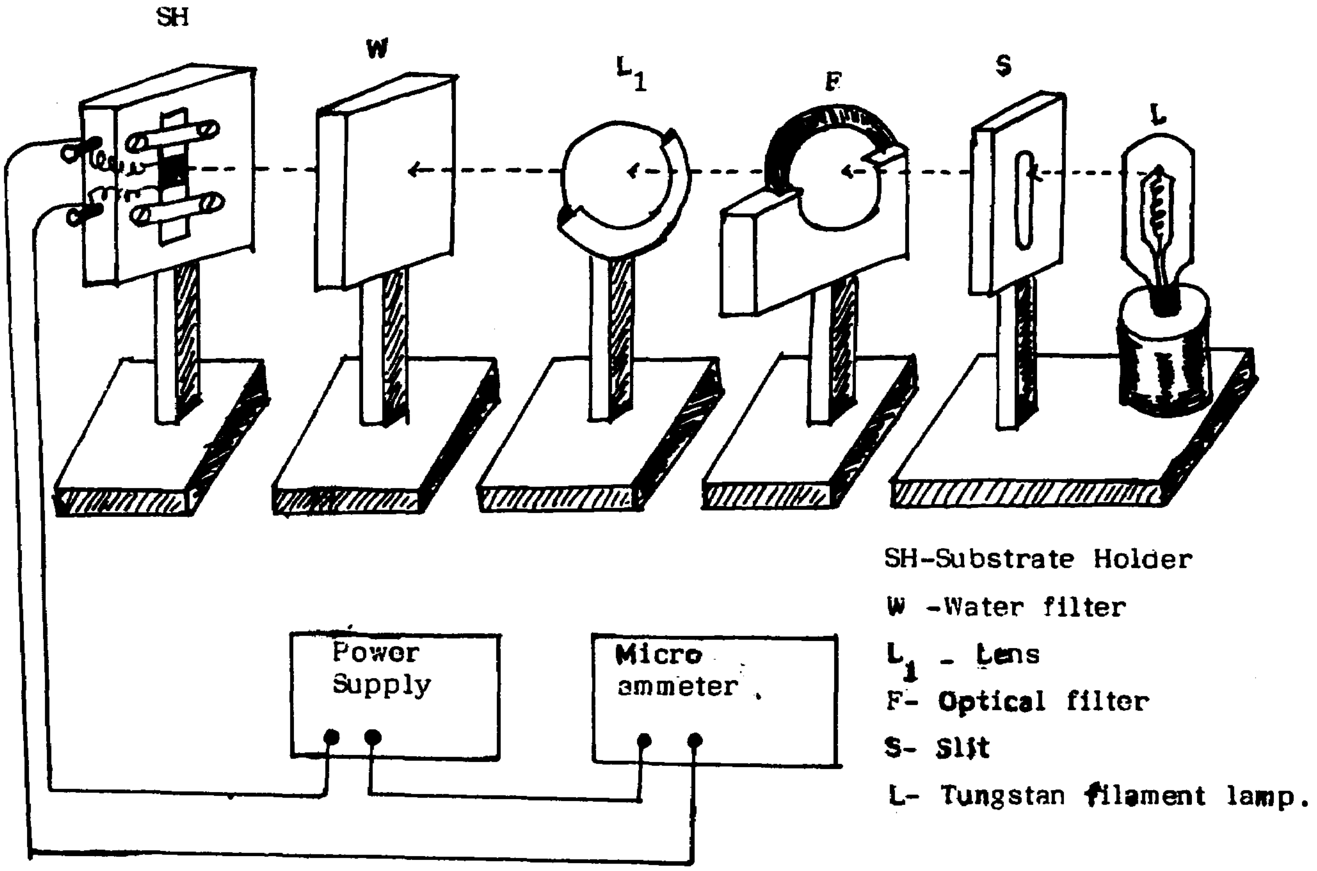


Fig.3.7 : Circuit arrangement for spectral response study in air.

films. We have estimated the band gap (E_g) by the second method. The transmission spectra of the films with different Cd:S volume ratio are shown in fig. 3.8 (a). Films were annealed in nitrogen atmosphere at 673 K for 30 minutes. The optical transmission spectra for the annealed films are shown in fig. 3.8 (b). The 'E_g' of the unannealed and annealed films are listed in table 3.1.

From the optical transmission study of annealed and unannealed films, it was observed that 'E_g' decreases with increase in Cd:S volume ratio. The 'E_g' of Cd:S volume ratio '5' was found to be minimum. These observations can be explained as follows :

Undoped CdS films are cadmium rich and sulphur deficient. As the Cd:S volume ratio increrases, the cadmium concentration increases still further. Excess cadmium gives rise to donor levels in the band gap of CdS. A large concentration of cadmium in the lattice makes these donor levels degenerated and merge in to the conduction band of CdS (11).

The same films were annealed in nitrogen atmosphere at 673 K. The 'E_g' of the annealed films were found to be decreased. This decrease in 'E_g' may be due to the increased deficiency of sulphur in the films.

b) X-ray studies :

In order to study crystalline nature of the films with different Cd:S volume ratios, the XRD patterns were studied. The films were slow scanned between 20 to 28°. Fig. 3.9 shows such

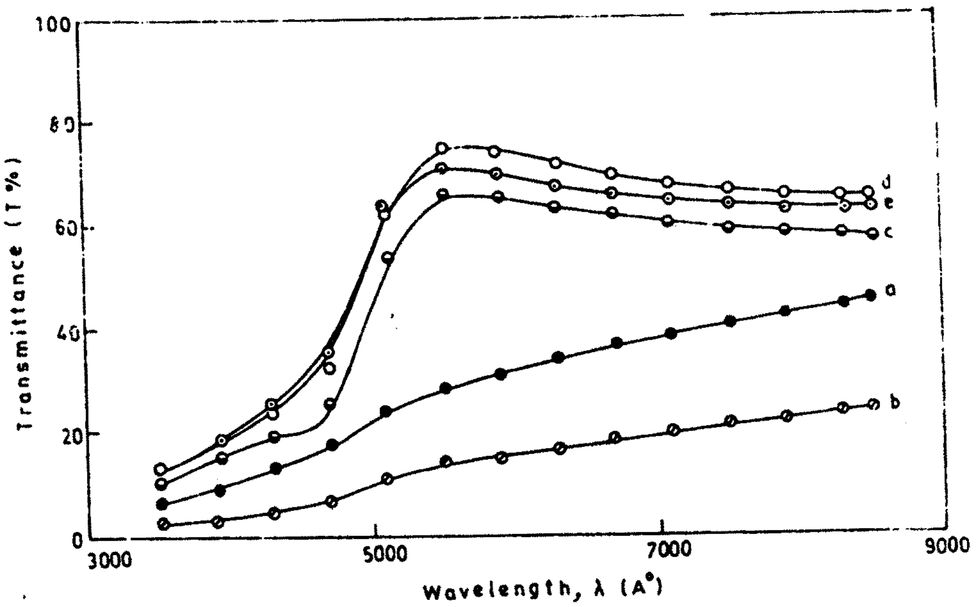


Fig.3.8(a) : Variation of Optical Transmittance (T %) with wavelength (λ) for different Cd : S Volume Ratio as (a) 5.0 (b) 2.5 (c) 1.66 (d) 1.25 (e) 1.0 CdS Films (Unannealed)

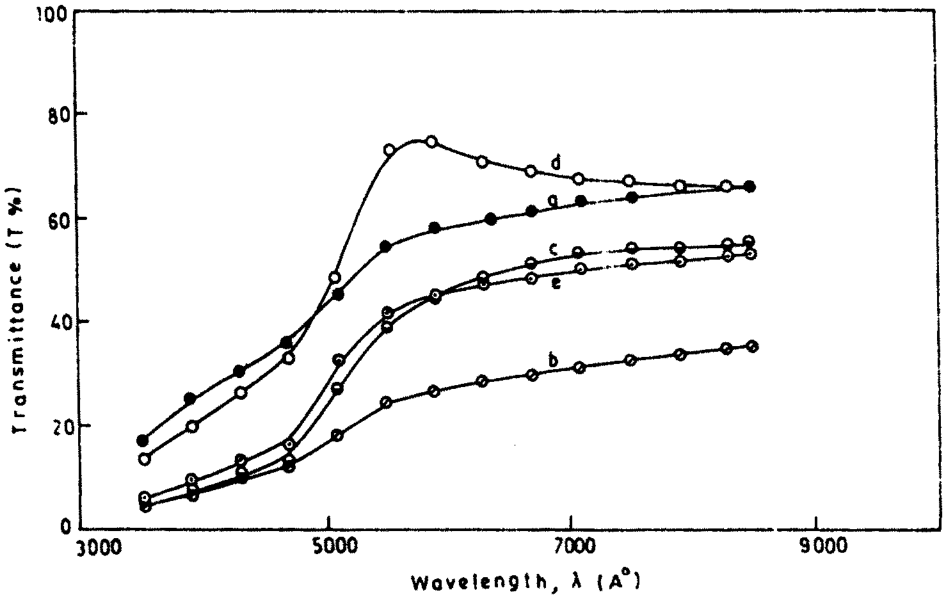


Fig.3.8(b) : Variation of Optical Transmittance (T %) with wavelength (λ) for different Cd : S Vlume Ratio as (a) 5.0 (b) 2.5 (c) 1.66 (d) 1.25 (e) 1.0 CdS Films (Annealed)

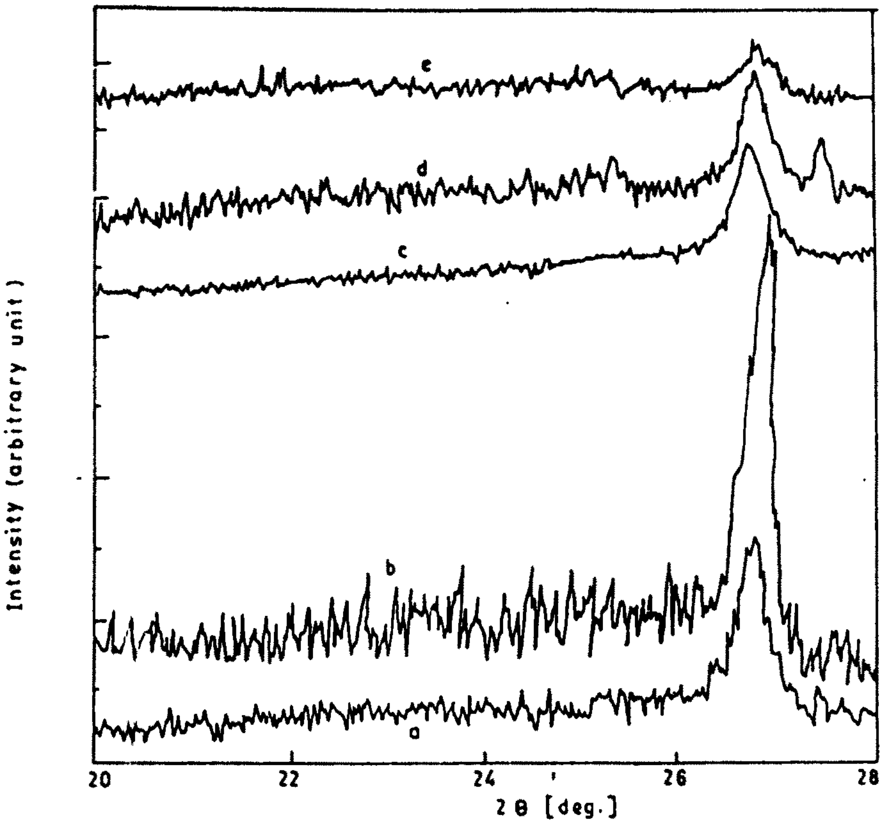


Fig.3.9 : X-ray Diffraction Patterns for Different Cd :S Volume Ratio as (a) 5.0 (b) 2.5 (c) 1.66 (d) 1.25 (e) 1.0 CdS Films.

scans for the films with different Cd:S volume ratios. It is seen clearly that the films are polycrystalline in nature. The grain sizes for different Cd:S ratio films were calculated by Scherer's formula (12).

$$d = \frac{\lambda}{D \cos \theta} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \; 3.2$$

Where, d = crystal size, λ = X-ray wavelength used, θ = Angular line width of half maximum intensity, θ - Bragg's angle. The calculated grain sizes for different Cd:S volume ratio films are given in table 3.2.

From the table 3.2, it is observed that as the Cd:S volume ratio increases, the grain size decreases.

c) SEM Studies :

The sample with Cd:S volume ratio as 5 was studied with SEM. The SEM study was carried out for both unannealed and annealed films. The film was annealed in N_2 atmosphere at 673 K for 30 minutes. The SEM micrographs of unannealed and annealed films at 5000 x magnifications are shown in fig. 3.10(a) and 3.10(b) respectively. The microstructure shows that grain size of unannealed film is small and the surface is rough. While the microstructure of annealed film shows uniform surface with increased grain size. This supports to the transmission study. Due to annealing grain size increases slightly. Similar effect of annealing on grain size has been observed by call et al (13).

3.8.2. Photoconductivity Studies :

a) Dark and photoconductivity studies :

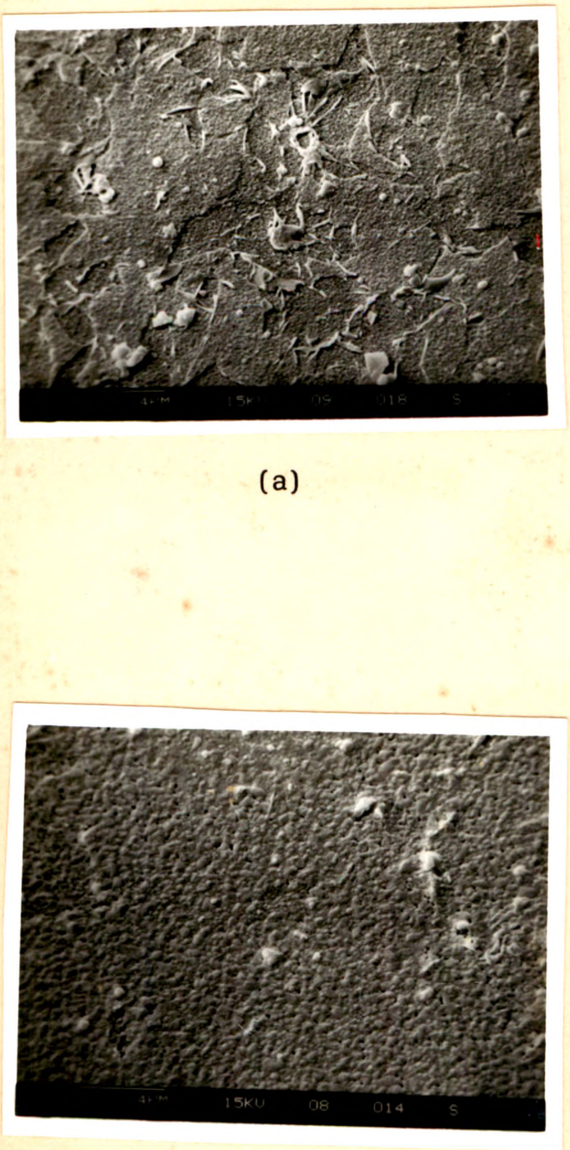
The I-V charracteristics of CdS/Ag contact were studied

Table 3.1 : Estimated band gaps 'E_g'' for different Cd:S volume ratio CdS films (Transmission Method).

Sr. No.	Cd:S ratio	Without annealed films 'E_g' eV	annealed films 'E_g' eV
1	5 .0	2.47	2.42
2	2.5	2.51	2.44
3	1.66	2.53	2.51
4	1.25	2.54	2.52
5	1 .0	2.55	2.54

Table 3.2 : Estimated grain sizes for different Cd:S volume ratio CdS films from XRD patterns.

Sr.No.	Cd:S volume ratio	Grain size A^o
1	5.0	31
2	2.5	44
3	1.66	49.4
4	1.25	54.6
5	1.0	54.6



(a)

(b)

Fig. 3.10 : SEM micrograph of (a) Unannealed and (b) Annealed CdS films with Cd:S volume ratio as '5' at 5000 X magnification.

for all the CdS films. The I-V characteristics of Cd:S volume ratio as '5' is shown in fig. 3.11 as as representative example. The characteristic was found to be linear within the voltage range of study (±30 V), which shows that silver paste electrodes produce ohmic contact with CdS. The linearity of the plot is the characteristic of good ohmic contact.

The dark and photoconductivities of different Cd:S volume ratio films were measured at room temperature (300 K) under identical conditions in air. The I-V curves of dark and photoconductivity for Cd:S volume ratio '5' and '1' are shown in figs. 3.12 and 3.13 respectively as representative examples. The dark and photoconductivity results for the films with different Cd:S volume ratios are given in table 3.3.

It was observed that as the Cd:S volume ratio increases the photoconductivity also increases. This can be explained as follows : Undoped CdS films are cadmium rich and sulphur deficient. As Cd:S volume ratio changes from '1' to '5', the concentration of cadmium increases. The excess cadmium acts as donor of electron. When such films are excited in light, large number of electrons are found to be available in conduction band for he same intensity of light. The sample having Cd:S volume ratio as '5' was found to be more photoconductive.

Further the dark and photoconductivity of the sample with Cd:S volume ratio '5' were studied in air as well as in vacuum (about 10^{-3} Torr), at light intensity of 10^3 lux and are listed in table 3.4.

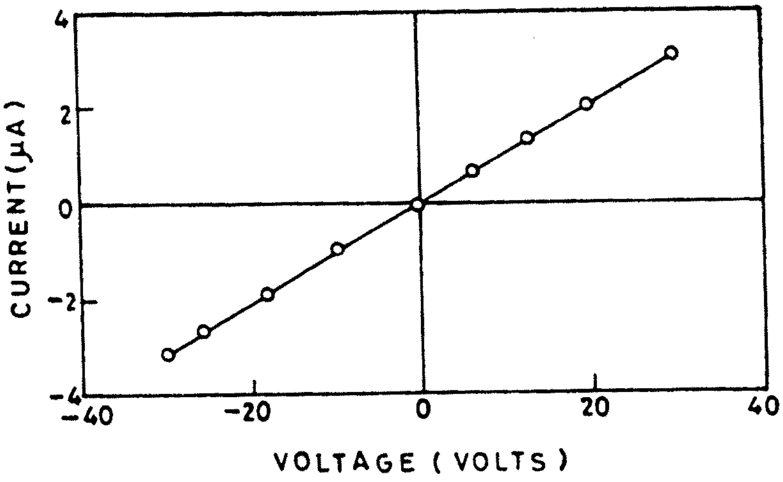


Fig.3.11 : I-V Characteristics (Forward and Reverse) of Contact between CdS and Ag for CdS Film with Cd:S Volume Ratio as '5'

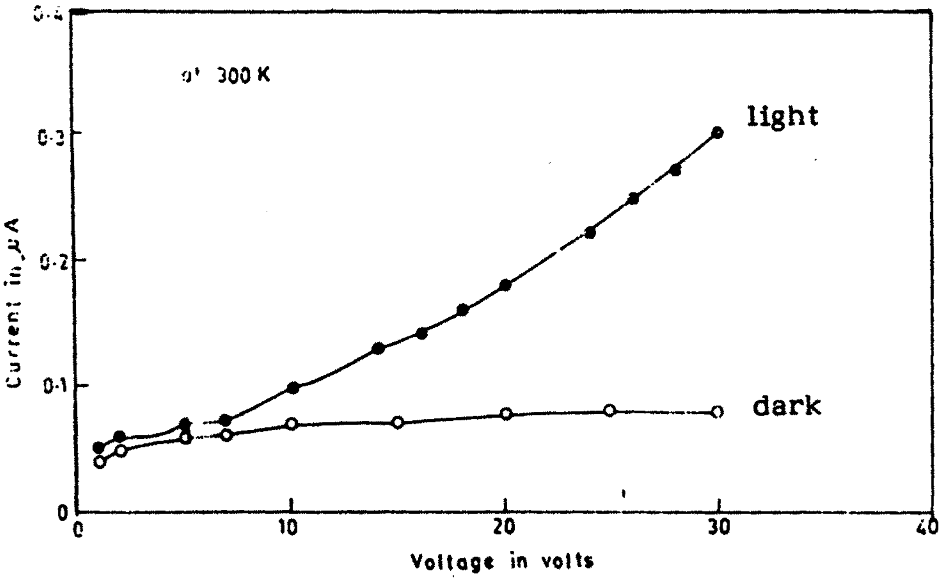


Fig.3.12 : I-V Characteristics for Dark and Photoconductivity for Cd:S Volume Ratio as '5'.

Table 3.3 : Dark and photoconductivity for different Cd:S volume ratio measured in air at light intensity 5×10^3 lux (at 30 V d.c.)

Sr. No.	Parameters	Cd:S volume ratio as				
		5	2.5	1.66	1.25	1
1	Dark resistance Rd ohm	3.75×10^8	5×10^8	5×10^8	5×10^8	5×10^8
2	Dark conductivity σd ohm cm^{-1}	2.2×10^{-4}	2.1×10^{-4}	1.6×10^{-4}	2.1×10^{-4}	1.9×10^{-4}
3	Photoresistance R_L ohm	1×10^8	1.3×10^8	1.66×10^8	1.89×10^8	1.96×10^8
4	Photoconductivity σL mho-cm^{-1}	8.5×10^{-4}	6.5×10^{-4}	4.98×10^{-4}	4.9×10^{-4}	4.5×10^{-4}

Table 3.4 : Dark and photoconductivity of Cd:S volume ratio as 5, measured in air as well as in vacuum (10^{-3} Torr) at light intensity 10^{3} lux (at 30V D.C.)

Cd:S volume ratio	measurements in air			measurements in vacuum		
	Dark conductivity mho-cm^{-1}	Photoconductivity mho-cm^{-1}	L/D conductivity ratio	Dark conductivity mho-cmm^{-1}	Photoconductivity mho-cm^{-1}	L/D conductivity ratio
5	2.2×10^{-4}	2.65×10^{-4}	1.204	3.9×10^{-5}	4.4×10^{-4}	11.28

It has been observed that the photoconductivity increased in vacuum.

b) Spectral response studies :

Spectral dependance of photocurrent for different Cd:S volume ratio films studied in air at 300 K are shown in fig. 3.14 and the peak values of photocurrent and corresponding energy values are listed in table 3.5.

The values given in table 3.5 shows that as Cd:S volume ratio increases, the peak values of spectral response shifts towards the higher energy side. These value shows that the films have greater blue response than the corresponding CdS crystal. This shift may be due to sulphur deficiency (11).

c) Photoconducting rise and decay curves :

The rise and decay of the photoconductivity in freshly prepared different Cd:S volume ratio films, was studied in air for the light intensity 5 x 10^3 lux with an applied voltage of 30 V D.C. The rise and decay curves for three successive cycles with rise time of 15 minutes and decay until the steady value is reached are shown in fig. 3.15(a) and 3.15(b) for the Cd:S ratio '5' and 2.5, fig. 3.16(a) and 3.16(b) for the Cd:S volume ratio 1.66 and 1.25 and fig. 17 for Cd:S volume ratio 1. The photoconducting rise and decay curves show initially fast steep rise followed by slow increase in the photocurrent. This is the typical of the presence of shallow and deep traps (14). Similar nature of the curves has been observed by (4). The curves show that the rise and decay curves of photoconductivity are more pronounced for Cd:S volume ratio as '5'.

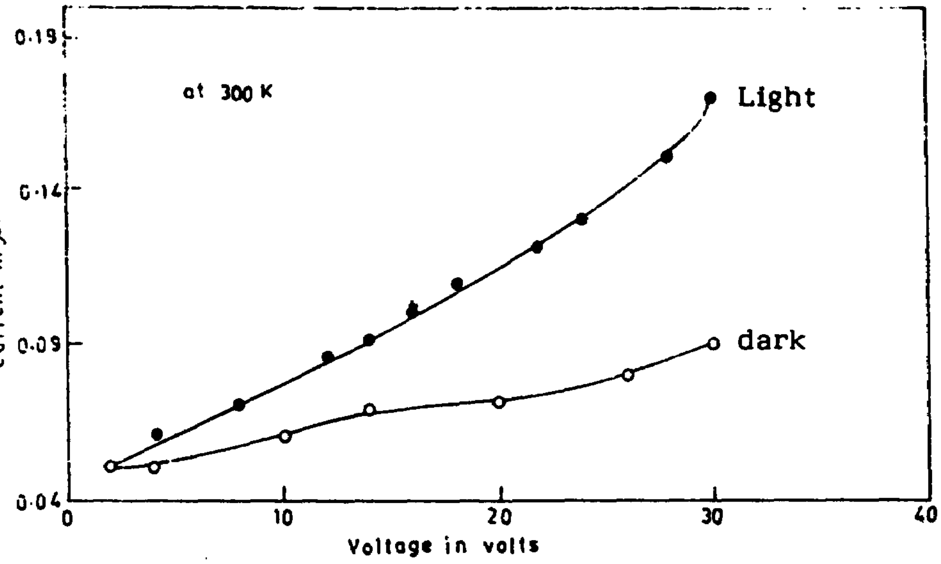


Fig.3.13 : I-V Characteristics for Dark and Photoconductivity for Cd:S Volume Ratio as '1'

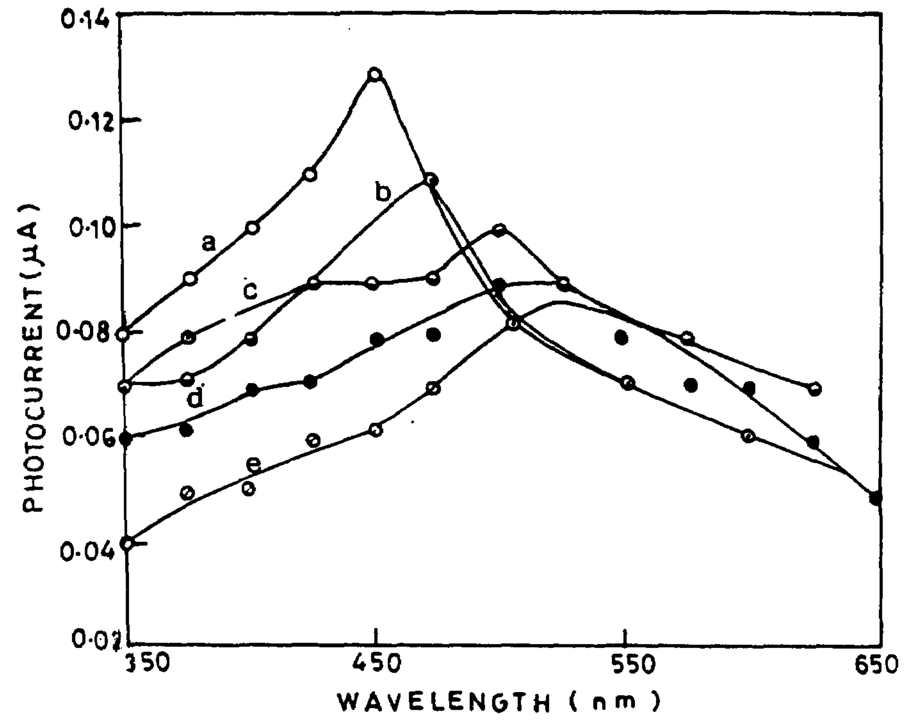


Fig.3.14 : The Spectral Dependence of the Photoconductivity for (a) 5.0 (b) 2.5 (c) 1.66 (d) 1.25 (e) 1.0 CdS Films, Studied in Air at Light Intensity of 5 X 10^3 lux , at room temperature (300 K). at 30 V d.c.

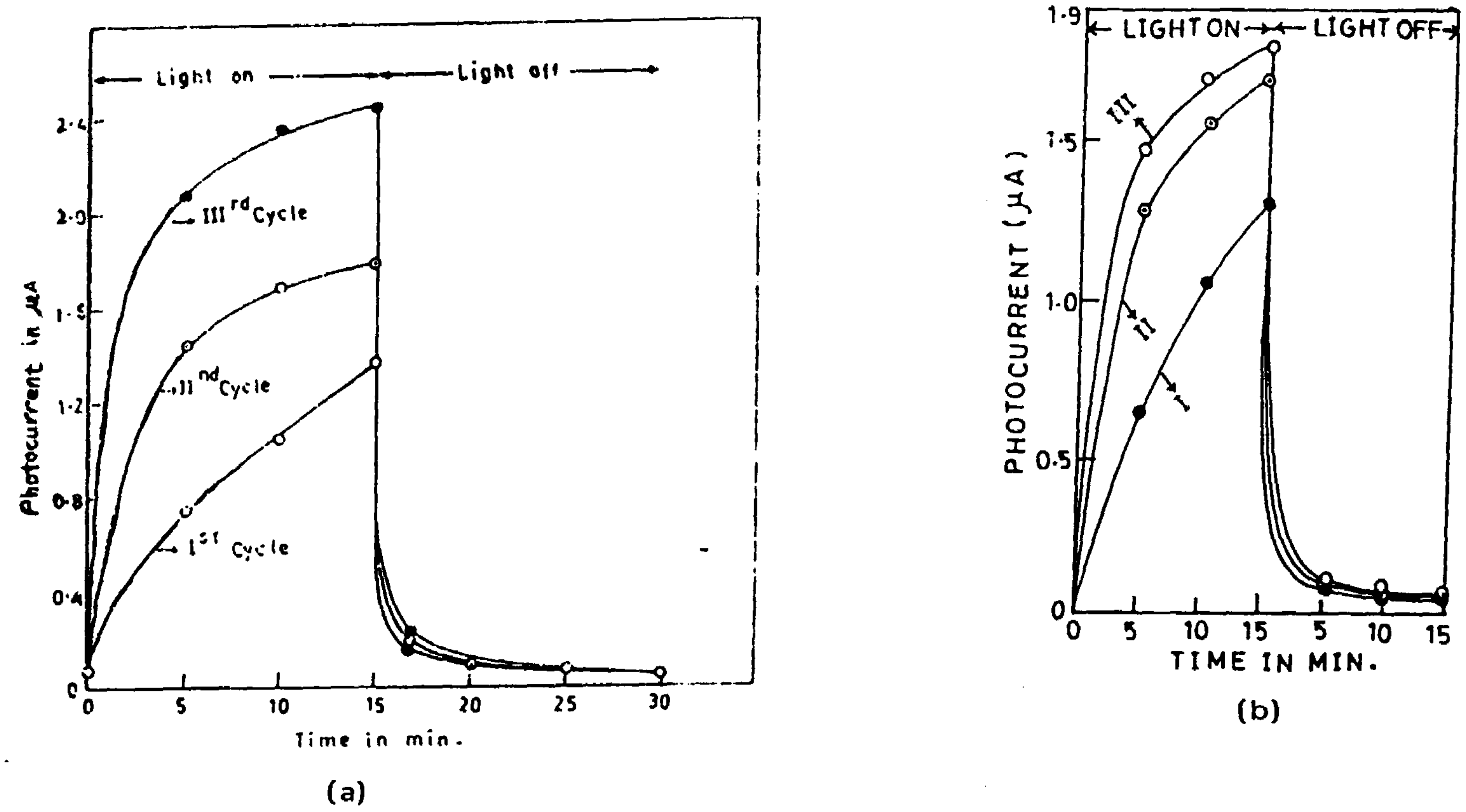


Fig.3.15 : Photoconducting rise and decay curves of Cd:S volume ratio as (a) 5.0 and (b) 2.5 CdS Films for first three successive Cycles, each of 30 min. (15 min. rise and 15 min. decay) Studied in Air at excitation light intensity of 5 X 10^3 lux (at 300 K).

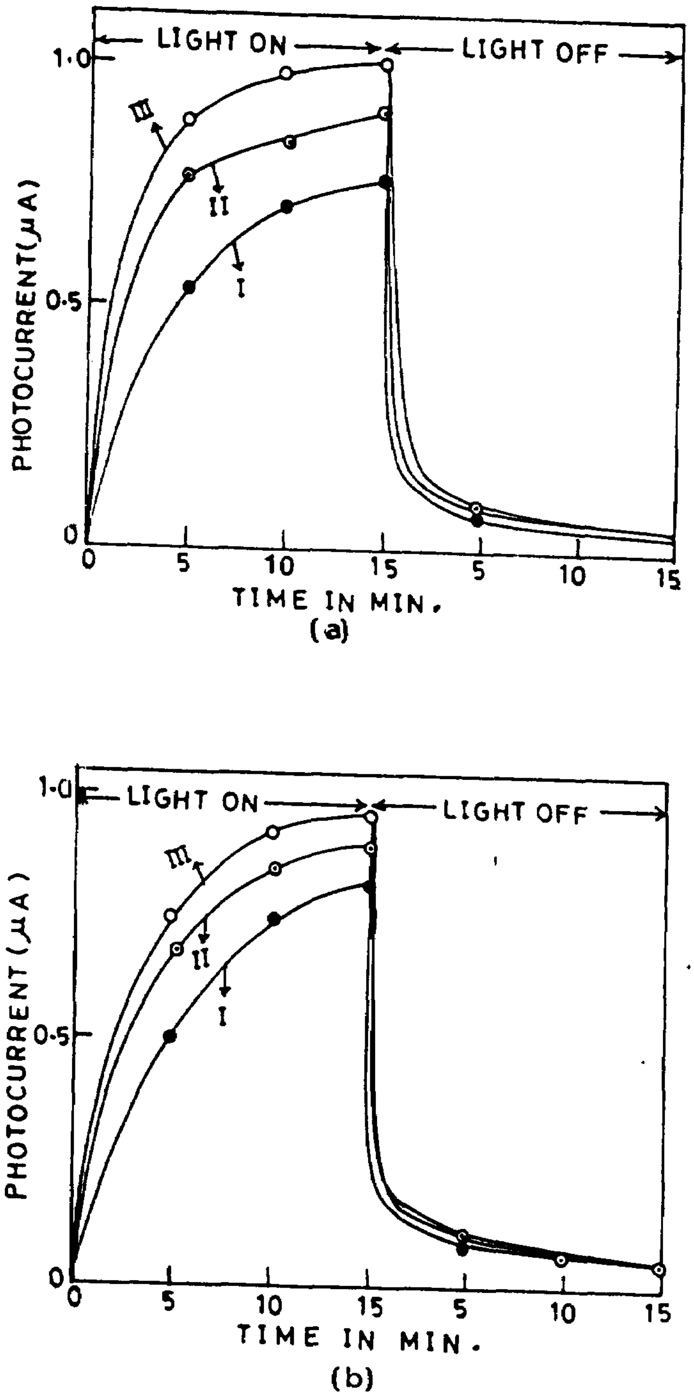


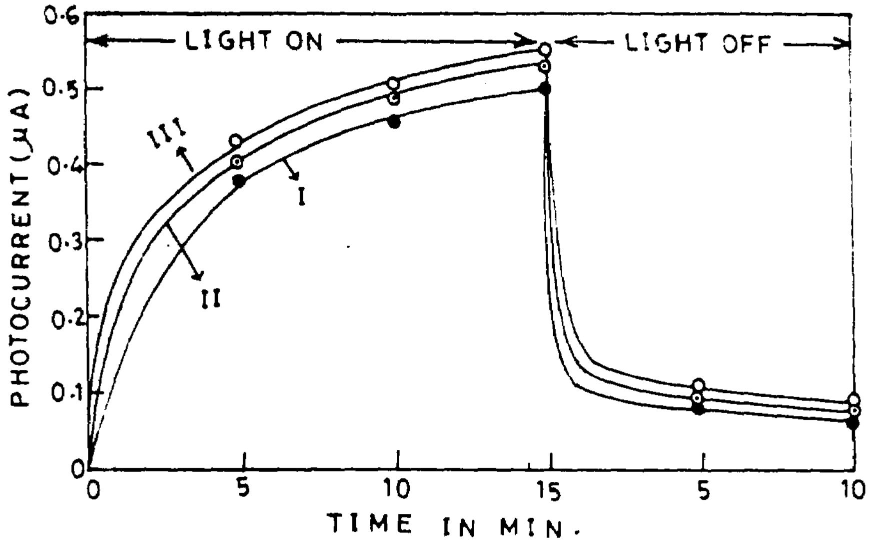
Fig.3.16 : Photoconducting rise and decay curves of Cd:S volume ratio as (a) 2.5 and (b) 1.66 CdS films for first three successive cycles, each of 30 min. (15 min. rise and 15 min. decay) studied in air at exciatation light intensity of 5 X 10^3 lux (at 300 K).

Further the sample with Cd:S ratio as '5' was used to study the rise and decay of photoconductivity in vacuum (10^{-3} Torr) at light intensity of 10^3 lux. The rise and decay for three successive cycles with rise time of 15 min and decay until the steady value is reached is shown in fig. 3.18.

d) Effect of oxygen adsorption on rise and decay :

As shown in fig. 3.18, in the first cycle of excitation, the photocurrent increases slowly but not linearly with time. The linear nature of photocurrent with time for first cycle of excitation was observed in amourphous films as reported by Bargale and Pawar (3). No steady state photocurrent was obtained even after 15 minutes but the curve bends just towards saturation. However, in the second and third cycles the rise is much steeper and the curve bends towards steady state value. It was observed that both photocurrent and dark current have been increased, but the increase in photocurrent is very large. The similar observations have been reported earlier (15).

As the films were prepared by the chemical bath deposition technique, oxygen molecules are assumed to be physically adsorbed on to the surface of CdS films. The oxygen molecules adsorbed on the surface act as electron traps (16-19). The oxygen molecules physically adsorbed on to the surface CdS films, becomes chemisorbed having captured a conduction electron, which binds them to the surface. The energy levels of such bound electrons are sufficiently below to the conduction band that in the dark, the rate of escape of electrons from the surface to the conduction band



(a)

Fig.3.17 : Photoconducting rise and decay curves of Cd:S volume rato as (a)1.0 CdS film for first three successive cycels, 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).

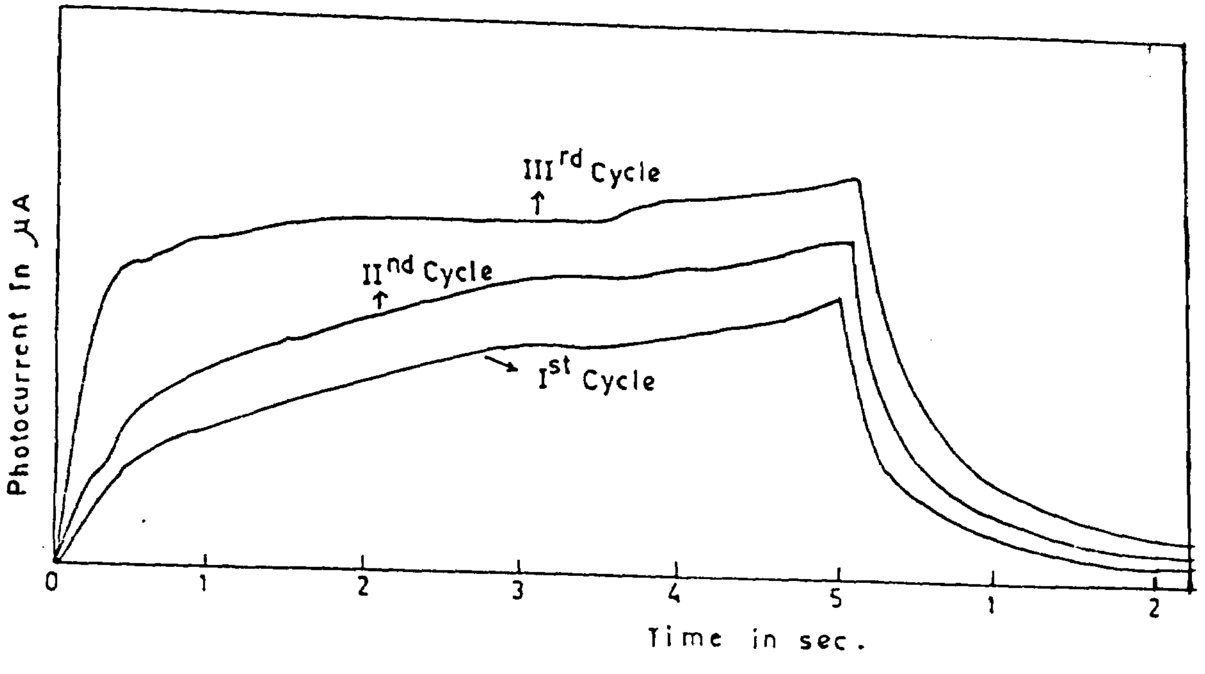


Fig.3.18 : Rise and decay curves for Cd:S ratio as '5' recorded with omniscribe recorder.(X/t mode) to find rise and decay times.

is negligible. When the film is exposed first time to light under vacuum, holes moves to the surface under illumination and are captured by negatively charged oxygen molecules, giving neutral molecules which are weakly bound and can be escape from the surface. This process is called as photodesorption. This process is responsible for the low values of both the dark current and photocurrent in the first cycle of excitation. In the second and successive cycles, the larger number of oxygen molecules are desorbed, resulting in the faster rise time and higher photocurrent. The effect of chemisorbed oxygen on dark and photoconductivity of CdS film is also reported earlier (20).

e) Rise and decay time constants :

The rise and decay time constants, 't_r' and 't_d' defined as the time required for the photocurrent to rise 63% of the stationary value or to decay to the same percentage of the priliminary value. To find the rise and decay time constant, the rise and decay of the curves was studied with the omniscribe recorder (λ/t mode). The rise and decay curves for three successive cycles, for the sample with Cd:S volume ratio as '5' are shown in fig. 3.18. The 't_r' and 't_d' are found to be 0.1 sec and 0.3 sec. respectively. The former was found to be smaller. Fig. 3.19 shows log of photocurrent Vs log t for photoconducting decay of Cd:S volume ratio as '5' at room temperature (300 K), for three successive cycles of excitation, drawn from decay curves of fig. 3.18. The plots shows that there are two linear regions, I and II obeying the relation,

$$I_t = I_o t^{-b} \qquad \text{.................. 3.3}$$

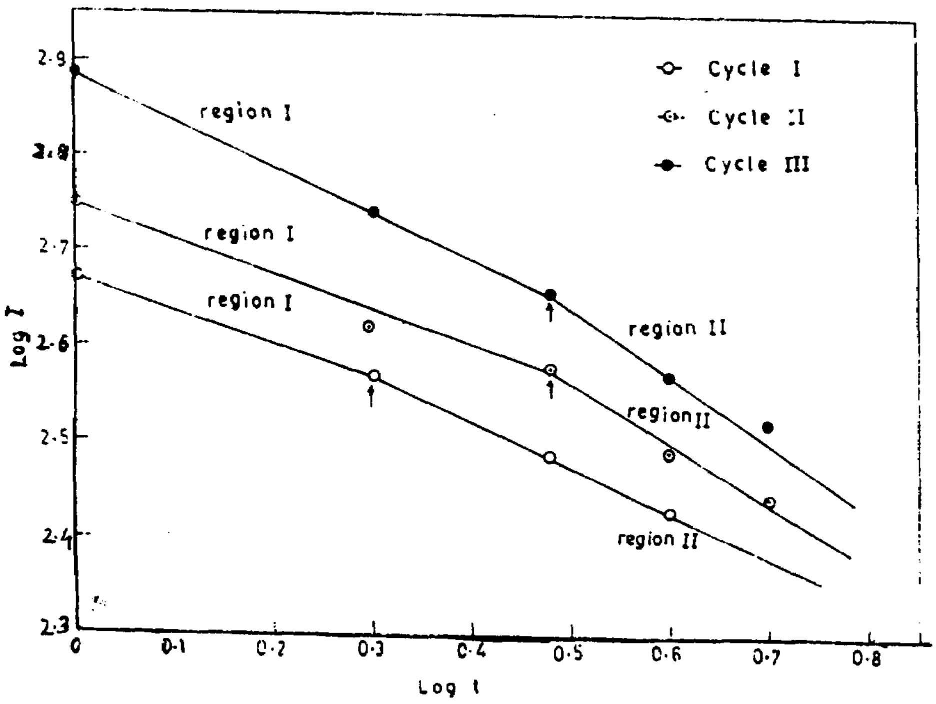


Fig.3.19 : log of photocurrent versus log t for Cd:S volume ratio as '5', for first three successive cycles, drawn from decay curves of figure 3.18.

Where I_t is the photocurrent at time 't' after switching of the excitation, I_o - the initial photocurrent at t=0, and b-the decay constant. The values of decay constants in region - I and region - II are denoted by b_1 and b_2 respectively and are listed in Table 3.6.

The region-I is associated with shallow traps, while region-II is due to deep traps. The demarcation time between region-I and region-II is shifting towards the longer value for the increase in number of excitation cycles.

Table 3.5 : Spectral response peak values and corresponding energy values for different Cd:S volume ratios at light intensity 5×10^3 lux.

Discription	Cd:S volume ratio as				
	5	2.5	1.66	1.25	1
Peak 'nm' values	450	475	500	515	525
Energy 'eV'	2.77	2.62	2.49	2.42	2.37

Table 3.6 : Decay constants for three successive cycles of excitation for the Cd:S volume ratio '5' studied in vacuum about 10^{-3}Torr (at 300 K) at light intensity 10^3 lux.

Cycle of excitation	$-b_1$	$-b_2$	Demarcation time sec.
Ist	0.44	0.24	2
IInd	0.33	0.19	3
IIIrd	0.30	0.16	3.5

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