CHAPTER 3

PREPARATION AND CHARACTERISATION OF CdS THIN FILMS

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3.1 General Aspects

Of the many available materials for use as photovoltaic materials, which find several applications such as in solar cells, the cadmium compounds are quite important. This is because these materials have a convenient band gap of 1.7 to 2.5 eV, which is suitable for use as solar cells. Single junction solar cells such as silicon cells, gallium arsenide cells and indium phosphide cells have well established preparation methods and applications.[22,68] The quest for simpler available materials and methods of obtaining them has led to the search of new materials for applications in photocell materials. Cadmium Sulphide is well established for applications in solar cells as a window material.[52,53]. Several notable methods also are identified to obtain it[54-56]. The Electrodeposition is one such method and attracts attention basically due its simplicity as established in earlier discussions [57,60]. Notable work has been done by several researches to deposit it from aqueous and non-aqueous solutions [61,62]. The present study is an attempt to obtain such films under the restricted laboratory conditions and to characterize them from the available data. Emphasis is to simplify the electrodepositon conditions and compare the efficiency of films thus obtained with the standard data.

CdS cells have a history of development dating back to 1954. The striking feature of these cells is the ease with which they are fabricated. The heterojunction involving p-Cu_2S/n-CdS is found to have efficiency upto 9%. A large number of binary and ternary compounds have been obtained by cathodic electrodeposition [63-64].

Thin film heterojunction solar cell using transparent conducting glass has of late attracting attention due to its transparent nature. Conducting glasses include oxide semiconductors such as indium oxide [Eg= 3.5eV], tin oxide [Eg=3.5eV]& indium tin oxide [ITO, Eg = 3.7 eV]. These oxide semiconductors in thin film forms have unique properties of good electrical conductivity & high optical transparency. They serve not only as part of the heterojunction but also as an anti reflection coating. ITO is a degenerate n-type semiconducting material that has wide applications in optics and optoelectronics. [22,59]

This aspect was considered in selecting ITO conducting glass as a substrate. Initial depositions were carried out with the ITO substrate as the nature of deposit could be easily identified due to its bright colour.

3.2 Thin Film Preparation

The aqueous solutions of Sodium thio sulphate and cadmium chloride were prepared. To start with, equal volumes of these solutions were transferred so as to maintain equimolar ionic concentrations of cadmium and sulphur. The reaction involved is given below:[67]

$$Cd^{2+} + S_2O_3^{2-} + 2e^- = CdS + SO_3^{2-}$$

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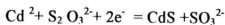
The solution was acidified using hydrochloric acid added drop wise. The ITO glass substrate cut to the required size as mentioned earlier was cleaned and air-dried. This was included in the electrodeposition unit as the cathode. A platinum electrode was used as an anode counter electrode. Alternately, copper electrodes were also employed. The Si substrate was employed under similar conditions.

Some of the ideal parameters identified in the earlier works were considered and followed to a certain extent to obtain good films.

The following parameters were taken into account:

1. Deposition potential

2. pH

3. Time

4. Annealing

5. Composition

6. Electrode separation distance

1. Deposition Potential: The codeposition range of cadmium and sodium thio sulphate and the mixture thereof were obtained from standard voltammograms. The codeposition range was found to be between 0.4 to 0.8V. At 0.4V no deposit was found even after 60 minutes. Between 0.5 & 0.7V bright orange yellow deposits

were obtained indicative of cadmium sulphide. At 0.8V, films with greenish yellow colour with metallic luster were obtained possibly indicating more cadmium in the deposit. Depositions beyond 0.8V were not carried out to avoid hydrogen overpotential [67].

2.pH: Different amounts of hydrochloric acid in the range of 2ml to 6ml, to a total volume of 60ml of the electrolyte were added. At very low concentration of the acid, i.e., pH>5,the deposition was very slow. At about 5ml addition of the acid corresponding to a pH range of 1.5, measured using a pH meter, good deposit with visible uniformity were obtained. Higher acid concentrations were avoided to prevent hydrogen evolution.

3. Time: Deposition time was maintained between 10 to 60 minutes. Deposits carried out for duration less than 10 minutes were found to have poor adhesion.
The colour of the deposits varied from orange yellow to greenish yellow, with respect to time, possibly indicating varying thickness and cadmium rich deposits. These depositions were carried out at static potential of 0.6V.

4.Annealing: Annealing of the films was done at a temperature of 200 degree centigrade to allow recrystallisation and better conducting nature. **[68]** This is shown in the XRD data.

5. Composition: Initially equimolar concentrations [1:1] of the two solutions were maintained. The further compositions were in ratio by volume, 1:2, 2:1, and intermediate compositions. No significant change in the nature of deposits was found with change in composition.

6. Electrode separation distance: The electrode separation distance was varied between 1cm and 4cm. At higher separation distances the rate of deposition was extremely slow or no deposition took place. At a distance of approximately 1cm the deposition was apparent which led to the conclusion that shorter distances between the electrodes was required to obtain good depositions as the ion concentration would be maximum. A electrode separation of 1 cm was maintained throughout the experiment.

The following conclusions were arrived at:

- Potential of 0.6V was found to be optimum for a good adhesive deposit as reported in earlier works

- A pH range of 1 to 1.5 was found to be favorable

- Visibly smooth and uniform films were obtained at time intervals of 10 – 30 minutes

- Annealing was found to improve the quality of the deposits

- Rate of deposition was swifter when the electrodes were maintained at a distance of 1 cm apart.

3.3 X Ray diffraction results

X-Ray diffraction was carried out basically to identify the crystalline nature of the material and also in its identification. The cadmium compounds are often found to be polycrystalline in nature [69]. The study was also used to find the effect of annealing and time of deposition on the material. The material coated on ITO was used for the x-ray analysis and the values of defraction angles were compared with the reported data.

On comparison it was observed that at the fixed voltage of 0.6 V the defraction angle was normally found to be at 30.455 degrees, [I/ Imax = 100, d=2.9328Ang] which coincides with the 200 reflection of the **wurtzite**[cubic] structure of cadmium sulphide[70] [**Fig. 3.1**]. The sharpness of the peak is in concordance of crystallinity [81], which is supported by the SEM data. **Table 3.1** provides a comparison between observed d values and standard d values of CdS films.

Table 3.1 Comparison of observed values and standard 'd' values of CdS [70]

Sl No	Standard d [Ang]	Observed d [Ang]	Plane/crystal struc
1	2.90	3.0056	200/ cubic
2	1.453	1.4803	400/ cubic
3	2.90	3.0336	200/ cubic
4	2.058	2.2148	220/ cubic
5	2.9	2.9328	200/ cubic
6	2.9	2.98	200/ cubic

The disadvantage of ITO substrate was felt at this point. Crystalline ITO gives $2\theta = 28.87^0$ at maximum significance, which is very close to the observed value of diffraction angle of CdS. However the intensity of the peaks obtained for the coated films are notable which have a very significant raise over the uncoated film.

With varying deposition conditions a slight shift of θ values were observed. This was related to the enlarging of the crystal lattice.

The annealed films were found to have an increase in the peak intensity. This indicates improved crystallinity, which is the result of annealing. [**Fig.3.2**]

The films were also deposited at different time intervals. It was observed that there was no significant change in 2θ values, but a notable change in the corresponding peak intensities at point of maximum significance. At shorter intervals of time [10 min], the peak intensity was maximum while at longer intervals [30 minutes] the intensity was found to be less. [**Fig.3.3**]

From these observations it is possible to arrive at the conclusion that, though the films are deposited over a period of time, longer intervals of deposition time only reduces the fine crystalline nature of the deposits. In other words longer deposition times only led to amorphous film formation.

The bath composition and other parameters were uniformly maintained for all the depositions. The data is given in **Table.3.2**

Table. 3.2 Comparison of 2θ of the CdS filmsand peak intensity

Time [minutes]	D [Ang]	2θ	Peak intensity [cts]
10	2.9855	29.9	1537
20	3.005	29.7	1282
30	3.0336	29.42	1197

The following conclusions were drawn from the above data:

* Annealing of the films provided better crystallinity.

* Lower time intervals provided better crystal nature.

The XRD patterns obtained for the silicon substrate were not in concordance with the ones obtained using ITO, though they were deposited under similar conditions. The films appeared to have a amorphous form with no specified peaks. Some films deposited at lower time intervals did not show any XRD data. [**Fig 3.4 a & b**]. This was due to the formation of very thin films on silicon. However, a visible coating was clearly observed on the films which appeared yellowish in colour as was in the case of ITO coated films.
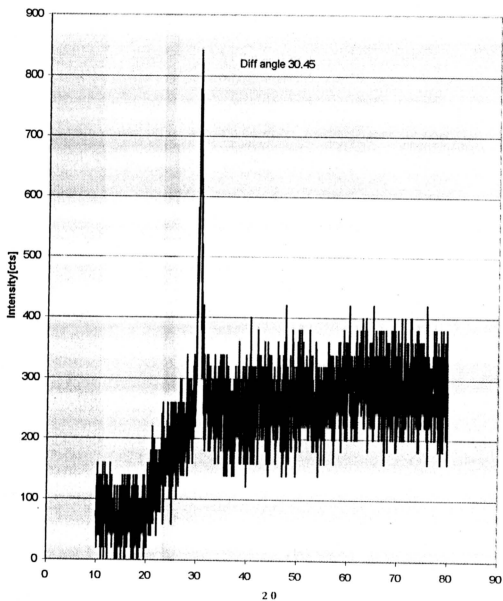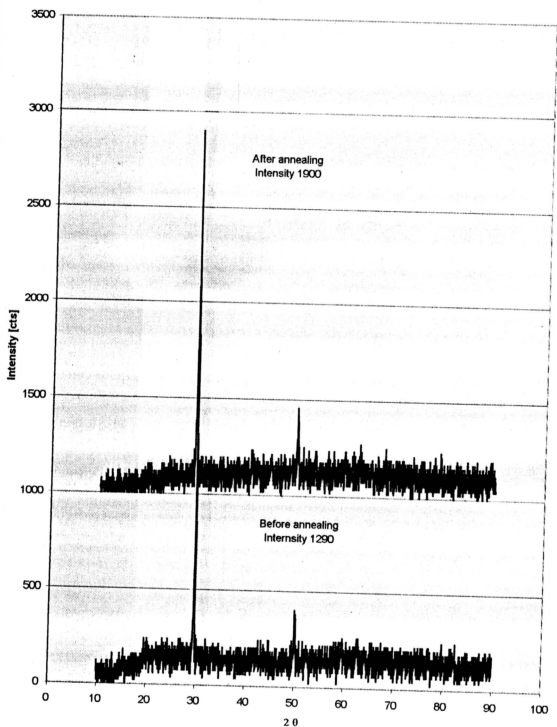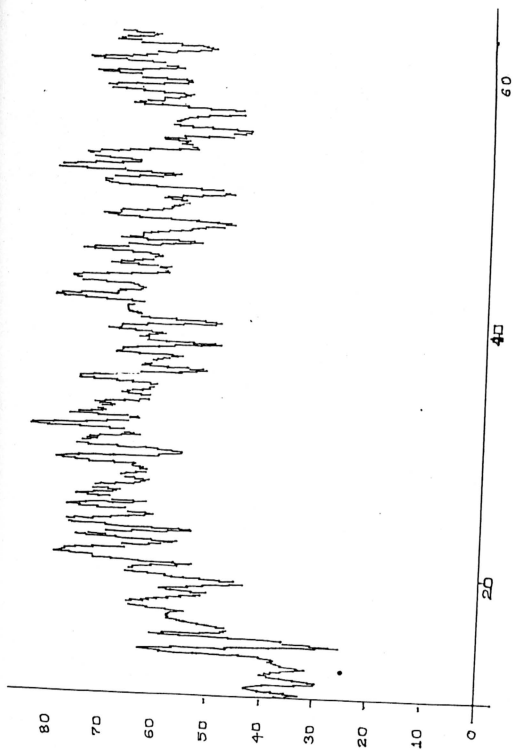
Fig. 3.1 XRD of CdS thin film

After annealing
Intensity 1900

Before annealing
Intensity 1290

Fig. 3.2 Comparison of XRD of CdS before and after annealing

Fig. 3.4 XRD CdS on silicon substrate

## 3.4 Result and analysis of Scanning Electron Microscopy data for CdS films

SEM analysis was carried out with the optimized conditions as obtained from the electrodepositions. The films were coated with gold before carrying out the analysis. The SEM pictures indicated uniform growth of the films with a few clusters. The crystals appeared distinctly noticeable with well-defined boundary.

[Figs 3.5,3.6,3.7&3.8]

Based on the data the following conclusions were arrived at.

* Uniform crystal growth was possible from the electrodeposiotion process
* The crystal sizes obtained were in the range of 50 - 100 nm with distinct boundaries.
* The clusters were attributed to stacking faults most often reported for cadmium sulphide films [71] which may be due to deposition conditions.

It was concluded that better stirring conditions so as to maintain uniform concentrations around the electrodes, proper control of potential and low currents, use of non interactive counter electrode may further improve the quality of the films.
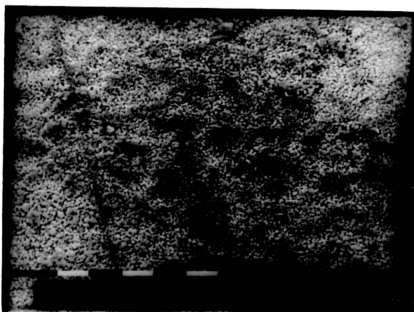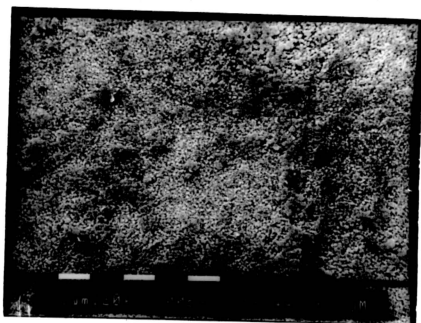
Fig 3.5 SEM Photograph of CdS Thin film1 coated for 10' duration

Magnification 1.00E4
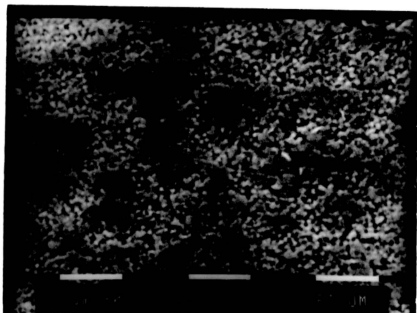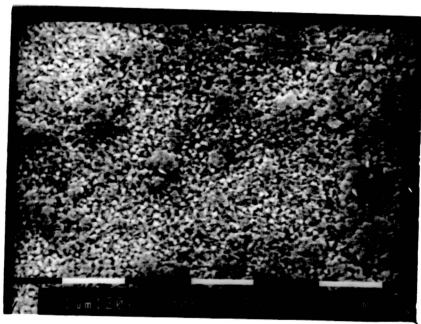

Fig. 3.6 SEM photograph on higher magnification for the CdS Thin film1

Magnification 2.00E4

Fig 3.7 SEM photograph of CdS Thin Film2 coated for duration of 30'

Magnification 1.00E4

Fig 3.8 SEM photograph on higher magnification for CdS Thin film 2

Magnification 2.00E4

3.5 EDAX results for the CdS Thin Films

EDAX data indicated the presence of elemental cadmium and sulphur . It was evident that very short duration of deposition led to the low concentrations of cadmium and sulphur in the case of ITO substrate.

Further, the deposition of copper from the copper counter electrode especially in the case of silicon substrate was observed which was expected[74]. The copper acts as a trap for the photoelectrons and prevents the material from acting as a solar cell. Hence, shorter intervals of deposition were found to be favorable and the same carried out. This would lead to the prevention of any such impurity deposition, which may hamper the photocell activity. But, the small quantities of deposition, which is a result short duration, may escape detection by EDAX and XRD, as observed in the case of silicon substrate. However these thin coatings were found to give notable photovoltaic activity. The relatively lower quantities of sulphur were identified with annealing which may lead to the removal of sulphur from the films to some extent.

The presence of the other elements such as Si, In, Sn etc. was found to be due to the background material.
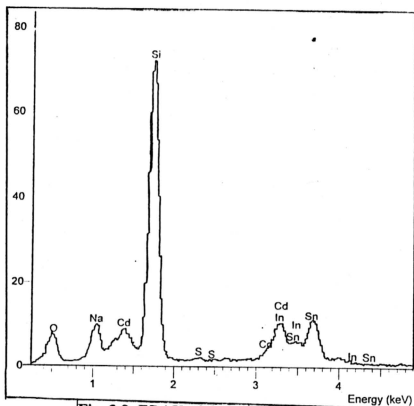
Fig. 3.9 EDAX of CdS thin film on ITO
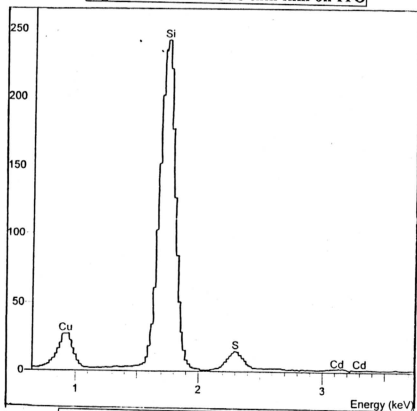
Fig 3.10 EDAX of CdS on Silicon substrate

3.6 Optical Characterization Of Cadmium Sulphide thin film.

Optical characterization was carried out to obtain optical constants of the cadmium Sulphide thin films i.e., refractive index [n] and the thickness of the films obtained. The knowledge of optical characteristics is important in order that the material be used in photoelectronic devices. It further helps in the identification of the material itself, on being compared with the standard data. The optical constants are sensitive to the microstructure of the material, which are related to the crystal structure and thickness of the film.[72,73]

The UV-VIS spectro photometry is an important technique for the determination of optical constants and thickness. This technique was applied in the present study to obtain data on the refractive index n, thickness of the film d, and the interrelation between n & λ using the transmission spectrum of the deposited film.

The transmission spectrum of the CdS film was obtained in the wavelength range 200 nm to 800 nm. The enveloping of the maxima and minima points on the plot was fitted manually. [Fig.3.11, 3.12]

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The refractive indices at the various maxima and minima points corresponding to specific wave length regions was obtained using the following mathematical relations:[74]

$$n = [N + (N^2 - n_s^2)]^{1/2} ,$$

where, n is refractive index,

$$N = \{ n_o [1+ n_s^2] + 2 n_s [T_{max} - T_{min}] / (T_{max} . T_{min}) \},$$

n_s = Refractive index of the substrate,

n_o = Refractive index of vacuum,

T_{max} & T_{min} refer to the crest and trough points on the curve of the transmission spectrum. The values obtained are indicated in **Table 3.3** .

Table 3.3 Comparison of λ vs. n of CdS thin film from transmission spectrum

Sl No	λ [nm]	T_{max}	T_{min}	n
1	370	84	72	2.430
2	400	85	73	2.426
3	429	87	78	2.420
4	500	88	80	2.419
5	579	89	82	2.418

The plot of **n** vs. λ is given in Fig **3.13**

The   average thickness of the film 't' was calculated by considering the **n** and λ values corresponding to two consecutive maxima or minima at a time. The table below gives the details of the selected combinations and the corresponding **t** values. The average thickness of the film is calculated using these.

Thickness **t** is calculated using the relationship, $t = M \lambda_1 \lambda_2 / [\lambda_2 n_1 - \lambda_1 n_2]$, where M is a constant, $\lambda_1 n_1$, $\lambda_2 n_2$,are the wavelength and refractive index at the selected maxima or minima points[**Table 3.4**]
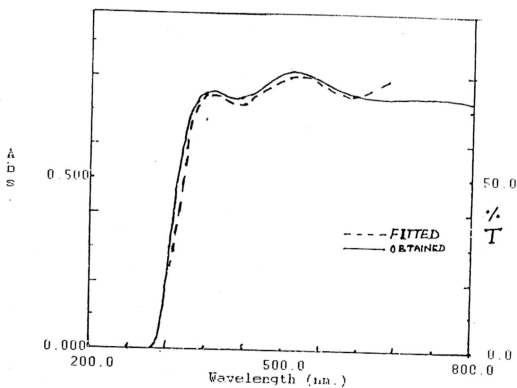
TABLE 3.4 Data to calculate thickness t of CdS Film

Sl No.	λ_1	λ_2	n_1	n_2	t [nm]
1	370	500	2.43	2.419	289
2	429	579	2.42	2.418	341
3	370	429	2.43	2.420	270
4	579	500	2.419	2.418	377

The average thickness of the film was found to be **319 nm**. The refractive index **n =2.42**, is in agreement with the reported data.2.46 [67]
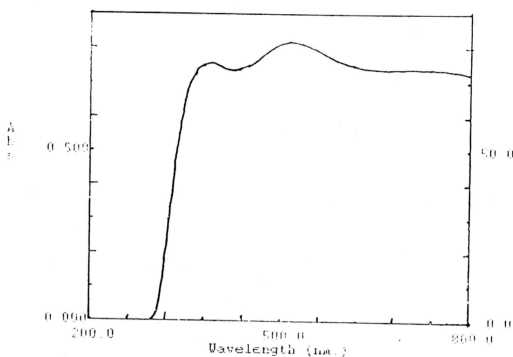
3.11 transmission spectrum of CdS thin film

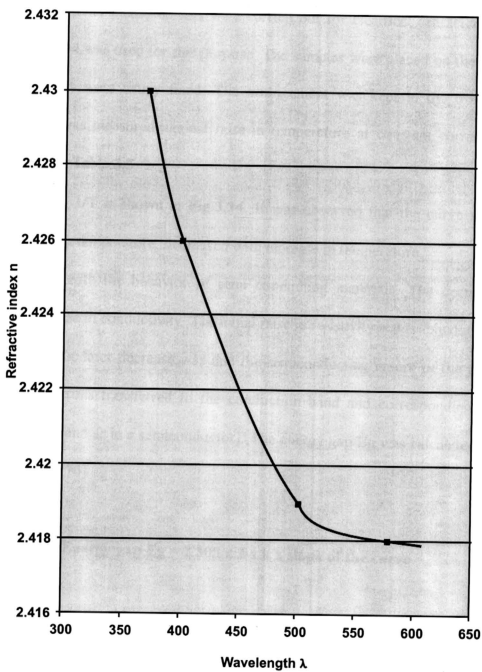**3.12 Fitted curve for the transmission spectra of CdS**

Fig. 3.13 Plot of n vs. λ For CdS

3.7 Resistivity/Conductivity Measurements - Four Probe Method:

The resistivity/conductivity measurements were carried out for electrical characterization. The four-probe method was used for this purpose. The samples were placed on the sample holder and the probes were firmly fixed. The arrangement was kept in the oven. The variation in voltage was measured against raise in temperature at constant current. The results are tabulated in Table.3.5

The plot of log ρ vs. 1/T is shown in **Fig.3.14.** It was observed that the curve with an initial raise with raise in temperature, decreased with increase in temperature.

This is in agreement with the behavior of semi conducting materials. The decrease in resistivity means increase in conductivity. The initial raise in resistivity is possibly due to the impurity carriers and the later decrease was due the semiconducting nature of the deposit [i. e., due to the electrons transferred to the conduction band and corresponding holes created in the valence band as in a semiconductor]. The energy gap Eg was calculated from the slope of the curve. [70]

Energy gap Eg = 2.303 x 2 x k x slope of the curve

Eg = 2.38 eV.

Table 3.5 RESISITIVITY/CONDUCTIVITY MEASUREMENTS OF CdS

[t= 319 nm , I= 5 mA]

| SL NO.	V	T	$1/T. 10^{-3}$	$\rho \times 10^6$	$\sigma \times 10^{-6}$	Log ρ
1	8.8	75	2.87	6.9331	1.4423	6.8409
2	8.9	80	2.83	7.0119	1.4261	6.8458
3	9.0	85	2.79	7.0907	1.4103	6.8506
4	9.1	90	2.75	7.1695	1.3947	6.8554
5	9.2	95	2.72	7.2483	1.3796	6.8602
6	9.5	100	2.68	7.4846	1.3360	6.8741
7	9.6	105	2.65	7.8786	1.2692	6.8964
8	9.8	110	2.61	7.7210	1.2952	6.8876
9	9.6	115	2.57	7.5634	1.3221	6.8787
10	9.5	120	2.54	7.4846	1.3360	6.8741
11	9.4	125	2.513	7.4058	1.3503	6.8696
12	9.3	130	2.48	7.3271	1.3648	6.8649
13	9.3	135	2.46	7.3271	1.3648	6.8649
14	9.1	140	2.44	7.1695	1.3947	6.8554
15	9.0	145	2.42	7.0907	1.4103	6.8505
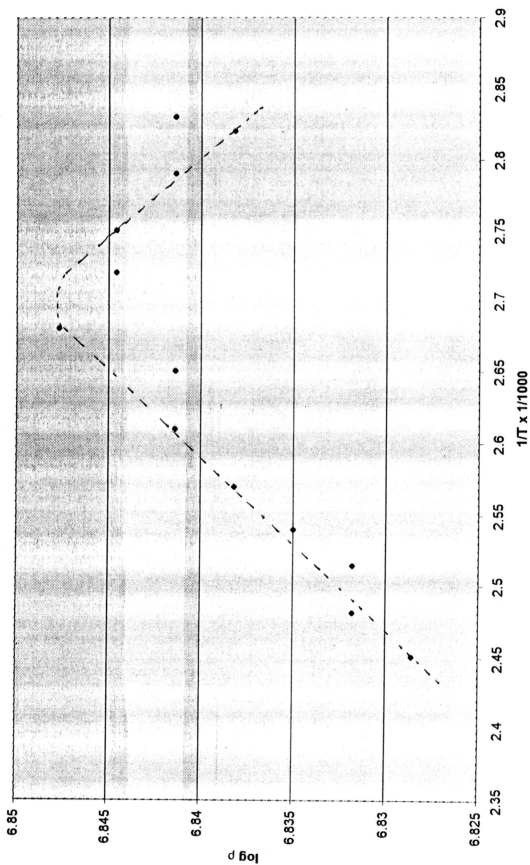
Fig. 3.14 Resistivity curve of CdS

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3.8 I-V Characteristic of CdS thin films

The I-V characteristics of CdS thin film were measured in order to identify the use of these films as solar cells. The study was carried out by measuring the current density as a function of voltage. The current was measured at various voltages using a rheostat to control the voltage applied in the circuit. The cell was kept under illumination during the measurement. [Fig 3.15]

In case of solar cells, the current drawn decreases as the voltage is increased till it can no more deliver any measurable current. A similar observation was made with the CdS films, which showed a steady decrease till an open circuit voltage of 90 mV, beyond which it failed to give any measure current. [57]

Fig. 3.16 shows the plot of voltage vs. current density. The maximum power rectangle is also shown in the figure.
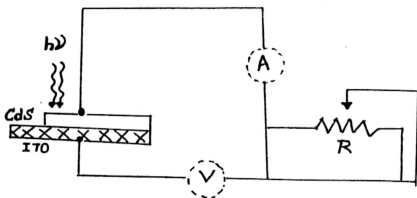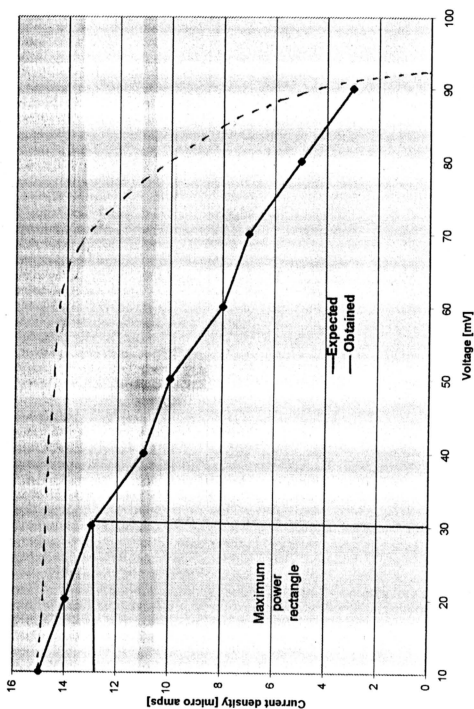

Fig. 3.15 circuit used for the measurement of I-V characteristics

Fig. 3.16 I-V characteristics of CdS