CHAPTER 4

PREPARATION AND CHARACTERISATION OF CdSSe THIN FILMS

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PREPARATION AND CHARACTERISATION OF CADMIUM SELENOSULPHIDE THIN FILMS.[CdS/CdSe hetero junction]

4.1 General Aspects

Ternary I-III-VIand II-IV-V semiconducting compounds, are found have energy gaps in the range of interest for solar photovoltaic conversion. CdSiP2 , $CdGeP_2$, $CdSnP_2$ and $CdGeAs_2$ are some of the cadmium based ternary compounds of this category. Cadmium seleno sulphide belongs to this group of semiconductors.

Cadmium seleno sulphide, CdS_xSe_{1-x}, is a ternary chalcogenide semiconductor whose band gap varies between 1.7 and 2.5eV. It is widely used as a semiconducting material, mainly as a photoconductor. Of late an increasing interest of use of this material is in photovoltaic and photo electrochemical devices. CdSSe is a photo conducting material sensitive to the visible wavelength of light.The addition of selenium , a chacogenide element to binary chacogenide compound like CdS is found to reduce the band gap and provide improved solar energy conversion efficiency. By varying the amounts of sulphur and selenium, variation in the band gap of the compound is reported. [75,76]. With the variation in the value of x from 0 to 1, a steady variation in the band gap in the range 1.7 to 2.4eV is observed.

CdSSe has been prepared earlier by several methods such as chemical deposition **[70]**, Thermal evaporation **[24]**, and Chemical vapor deposition and electrochemical deposition from aqueous and non-aqueous solutions such as ethylene Glycol [77]. In the present study an attempt is made to prepare CdSSe by the electrochemical deposition at simple laboratory conditions. The stoichiometric compositions were not varied, as the deposition of thin films of this material is the primary objective of the work. Further, the study on variation of compositions of CdS_xSe_{1-x}, has been reported. **[78]**

ITO glass was used as the substrate material as the depositions can be clearly observed as the compound is coloured. The electrolyte was a simple aqueous solution of cadmium chloride, sodium thio sulphate and selenium oxide. The electrodeposition was carried out under the following conditions.

4.2 Preparation of thin films of CdSSe

Aqueous solutions of sodium thio sulphate, cadmium chloride and selenium oxide were prepared . Initially carefully measured volumes of 30 ml of cadmium chloride, 15 ml each of sodium thio sulphate and selenium oxide were mixed together and used as the electrolyte solution. The solution was slightly acidified to provide better electrical conduction. As this was found to affect the pH of the system as in the case of CdS in the earlier case, the volume was controlled by adding it drop wise [approximately 3ml].

The substrate ITO was cut to the required size, cleaned and air dried. The electrolytic cell was formed with this as the cathode and platinum electrode as the anode. The same parameters as considered in the case of the CdS films were taken into account to maintain uniformity viz., deposition potential, pH, time of deposition, annealing , composition and electrode separation distance.

1.Deposition Potential: The codeposition range of the electrolyte mixture was considered and depositions were carried out in the range of 0.4 to 0.8. Good films were obtained in the potential range of 0.5 and 0.7. No significant change was observed in the XRD data. Visual changes were rather apparent. Bright yellow coloured films were formed at about 0.65 V - 0.7V. Films formed at potentials 0.7 and above appeared metallic and with a gray tinge obviously due to the cadmium rich deposits. Optimized voltage was chosen to be 0.6V as in the earlier case.

2.pH: Good films were formed at higher pH range i.e., 3.0. Smooth and uniform coatings were formed with less acidic bath

3.Time: As was observed in the case of cadmium sulphide films depositions were obtained after10 minutes. However, time of depositions was varied between 10 and 30 minutes. Beyond this period the nature of films did not indicate any further improvement. Further, the XRD data indicated a decrease in the peak intensity, which is due to reduced crystallinity as discussed in the previous chapter.

4. Annealing: Films were annealed at a temperature of 200 degrees in an oven. The duration was reduced to 15 minutes as the longer duration of annealing is reported to lead to loss of selenium.[70].

5.Composition: Depositions were carried out in the electrolyte ratio as mentioned earlier to maintain stoichiometry as was intended.

6. Electrode separation distance: As in the earlier case of CdS deposition, the electrode separation was maintained at 1cm.

4.3 X Ray diffraction results

X-ray diffraction was carried out to identify the material and its crystallinity. The effects of annealing and time of deposition was studied from the data obtained.

At the optimal conditions as was set the XRD showed 2θ =30.805.corresponding to the 200 reflection of the cubic phase of CdS and 2θ = 63.765 corresponding to the 400 reflection of the hexagonal phase of CdSe. **[Fig 4.1]**. Such mixed structures are reported for the codeposition of CdS and CdSe by other preparation methods. [79]

Variation of potential and composition did not show any notable change in the XRD data.

Table 4.1 gives the comparison between the observed **d** values of the XRD data and the standard values.

Table 4.1 Comparison between observed and standard 'd' values of CdSSe [70]

Sl No.	Standard d	Observed d	Plane/Crystal struc
1	2.9	3.0145	200 / cubic
2	2.9	2.9806	200 / cubic
3	1.45	1.4745	400 / hexagonal
4	2.9	2.8779	200 / cubic
5	2.9	2.6902	200 / cubic
6	2.9	2.9002	200 / cubic
7	1.45	1.4584	400 / hexagonal

Deposition carried out at low ionic concentration which was obtained at half of the originally set value of concentration, showed no specific peaks, which was related to its amorphous nature. Amorphous films are reported in earlier works **[70]**

Coatings were obtained on silicon substrate as in the case of CdS. These coatings though visible did not show any specific XRD peaks. **[Fig. 4.2]**

The duration of deposition was found to have a notable change in the peak intensity, which decreased with increase in time .The decrease in the intensity, was related to the crystallinity. **[Fig 4.3]**. The diffraction angles showed slight variations.

The following **table 4.2** gives the variations observed at different duration of deposition.

Table 4.2

Time [minutes]	d [Ang]	2θ [deg]	peak intensity [cts]
10	2.9002	30.805	2905
20	2.9806	29.955	1592
30	3.0145	29.610	1282

The effect of annealing was similar as discussed under cadmium sulphide. The crystallinity was more pronounced for the annealed samples indicated by the peak intensity. **[Fig 4.4]**

From the above data the following conclusions were drawn which are in agreement with the earlier obtained data of cadmium sulphide i.e.,

* Annealing yields better crystallinity of the material

* Lower time intervals formed better depositions in terms of crystal nature.

* Peaks corresponding to cubic CdS and hexagonal CdSe were observed consistently. However at certain times no significant peak was observed with reference to CdSe.

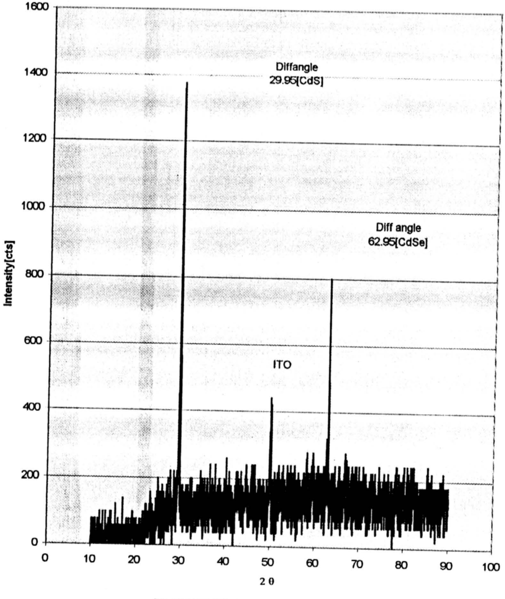

Fig. 4.1 XRD of CdSSe thin film

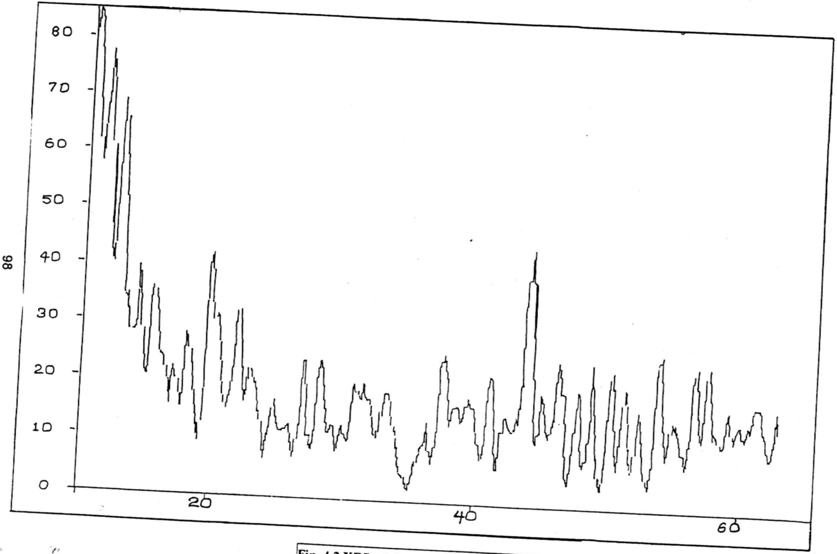

Fig. 4.2 XRD of CdSSe on silicon substrate

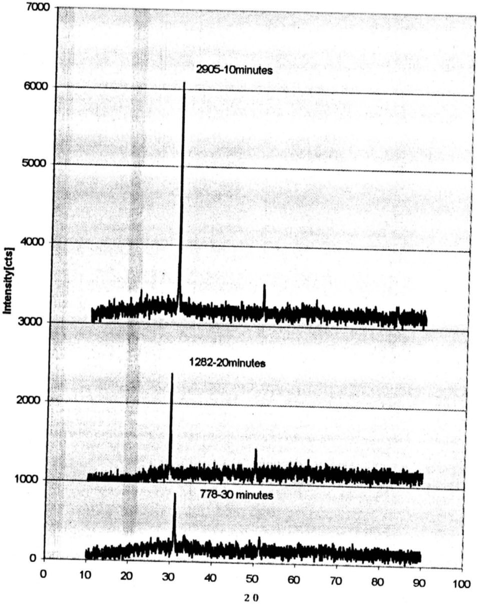

Fig. 4.3 Comparison of XRD of CdSSe at different times of deposition

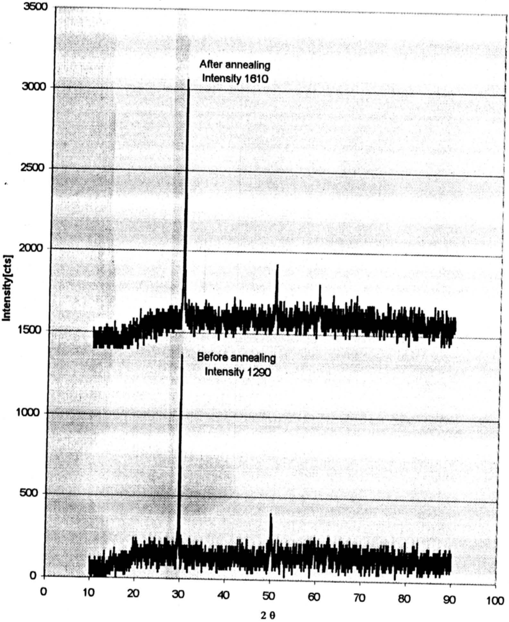

Fig. 4.4 Effect of Annealing on CdSSe films

4.4 Scanning Electron Microscopy results of CdSSe

Scanning electron microscopy of the CdSSe thin films were obtained as in the case of cadmium sulphide . It was noticed that the films were uniform with well-defined crystal formation. The finer crystal growth was attributed to the addition of selenium. **[Fig 4.5,4.6,4.7,4.8]**

The following conclusions were arrived at:

- It is confirmed that it is possible to obtain a noticeably uniform coating from electrodeposition

- The crystal sizes varied from 100 nm to 200 nm with distinct boundaries

- The crystal formations in the CdSSe films were different from those observed in the case of CdS.

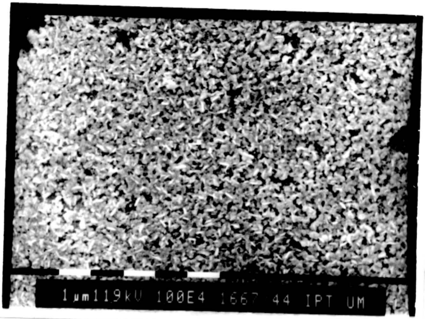

Fig 4.5 SEM photograph of CdSSe thin film [10']

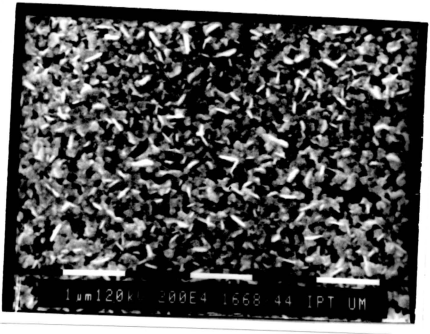

Fig. 4.6 SEM photograph of CdSSe thin film [10'] on higher magnification

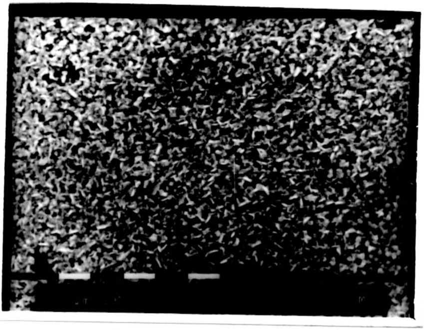

Fig 4.7 SEM of CdSSe [20']

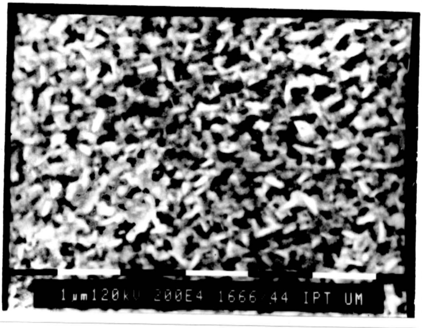

Fig. 4.8 SEM of CdSSe [30']

4.5 EDAX results of CdSSe thin films

EDAX results of the thin films of CdSSe were found to contain presence of elemental Cadmium, Sulphur and Selenium. **[Fig 4.9,4.10]**

The presence of sulphur was less than expected in the stoichiometry. This was related to the annealing of the films, which normally is found to lead to loss of selenium and Sulphur. **[5]**.

The presence of Si, In, Sn etc. were found to be due to the background material

The presence of Cadmium and Indium [of the ITO substrate] almost in the same stoichiometric ratio was observed. The low concentrations of the elements were related to the thin coatings, which are only a few nm in thickness and very thin compared to the ITO coating. This again depended on the short duration of the coating, which was deliberately maintained to obtain uniform smooth films with fewer impurities.

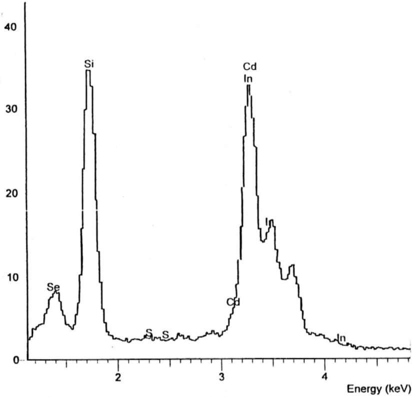

Fig. 4.9 EDAX of CdSSe sample 1

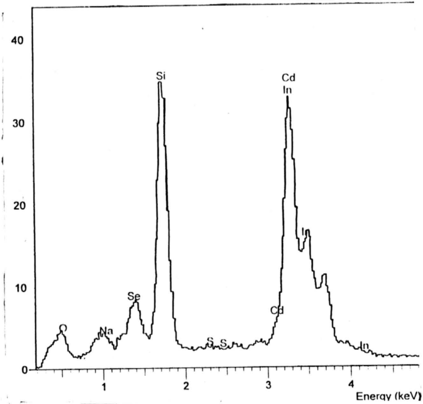

Fig. 4.10 EDAX of CdSSE [sample 2]

4.6 Optical characterization of CdSSE thin films

Optical characterization was carried out to obtain optical constants of the CdSSe. thin films i.e., refractive index [n], extinction coefficient [k] and absorption coefficient [α]. The transmission spectrum of the film was obtained in the wavelength range of 200nm and 800nm. **[Fig 4.11]**

The enveloping of the maxima and minima points was fitted manually **[Fig.4.12].** The mathematical relations for obtaining these values are given in chapter 3.

The values obtained are indicated in **Table 4.3**

Table 4.3 Comparison of n and λ of CdSSe thin film from transmission spectrum

SL NO	λ	T_{max}	T_{min}	n
1	410	73.5	65	2.4201
2	425	75	67.5	2.41960
3	440	71.5	71.5	2.4192
4	480	80	73.5	2.4192
5	505	81.3	73.5	2.4191
6	540	82	75.5	2.41908

The plot of n vs. λ is given in [Fig **4.13**]

The thickness of the film was calculated as under CdS and the results are tabulated in **Table 4.4.**

Table 4.4 Data to calculate thickness of CdSSe film

SL NO	λ_1	λ_2	n_1	n_2	d nm
1	410	440	2.4201	2.4192	686
2	440	505	2.4192	2.4191	353
3	410	5 05	2.4201	2.4191	449

Average 496 nm

The average thickness of film was found to be **496** nm.

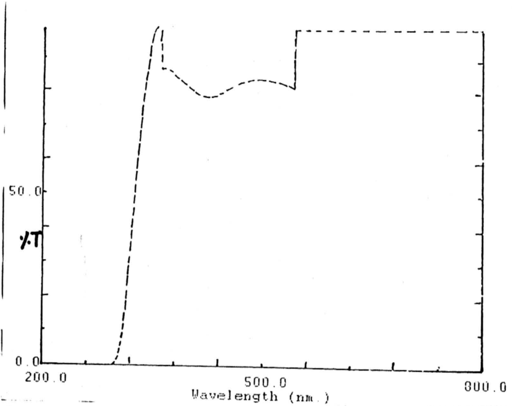

Fig. 4.11 Transmission spectrum of CdSSe thin film

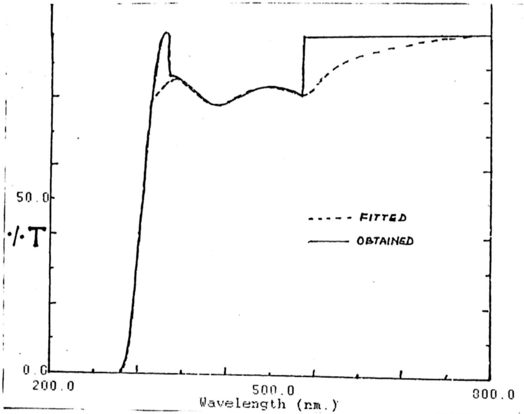

Fig. 4.12 Fitted curve for the calculation of optical data of CdSSe

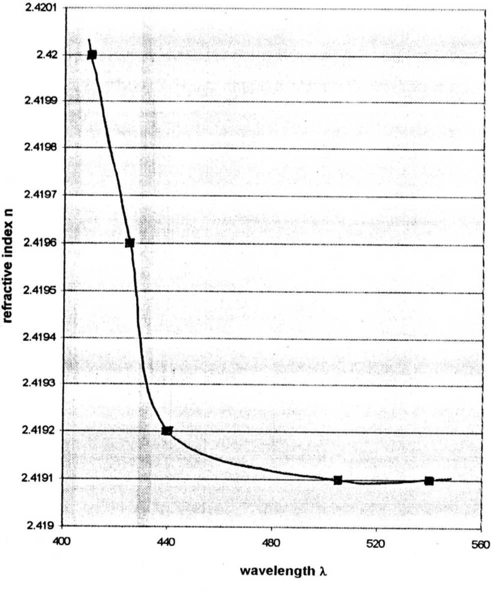

Fig 4.13 Plot of n vs. λ for CdSSe

4.7Resistivity/Conductivity Measurements - Four Probe method [CdSSe]

The Resistivity/conductivity measurements were carried out for the electrical characterization of the CdSSe films by this method. The variation in voltage was measured against raise in temperature at constant current conditions.

The results are tabulated in **Table 4.5.** for constant current condition of I=5mA
The plot of **log** ρ vs. **1/T** is shown in **Fig 4.14**

It was observed that the resistivity curve with an initial raise of resistivity with temperature showed a decrease with increase in temperature. This is in agreement with the behavior of semiconducting materials. The energy gap Eg was calculated from the slope of the curve.

$$Eg = 2 \times 2.303 \times k \times slope$$

$$Eg = 1.73 \text{ eV.}$$

Table 4.5: Conductivity measurements of CdSSe Thin Films

[t=496 nm, I = 5 mA]

SL NO.	V	T	1/Tx 10^{-3}	ρ x 10^{6}	σ x 10^{-7}	log ρ
1	13.4	50	3.10	6.7898	1.4727	6.8318
2	13.4	55	3.05	6.7898	1.4727	6.8318
3	13.5	60	3.03	6.8405	1.4618	6.8350
4	13.5	65	2.96	6.8405	1.4618	6.8350
5	13.6	70	2.92	6.8912	1.4511	6.8382
6	13.6	75	2.82	6.8912	1.4511	6.8382
7	13.7	80	2.83	6.9419	1.4405	6.8414
8	13.7	85	2.79	6.9419	1.4405	6.8414
9	13.8	90	2.75	6.9925	1.4301	6.8446
10	13.8	95	2.72	6.9925	1.4301	6.8446
11	13.9	100	2.68	7.043	1.4197	6.8477
12	13.7	105	2.65	6.9419	1.4405	6.8414
13	13.7	110	2.61	6.9419	1.4405	6.8414
14	13.6	115	2.57	6.8912	1.4511	6.8382
15	13.5	120	2.54	6.8405	1.4618	6.8350
16	13.4	125	2.514	6.7898	1.4727	6.8318
17	13.4	130	2.481	6.7898	1.4727	6.8318
18	13.3	135	2.451	6.7392	1.4838	6.8286

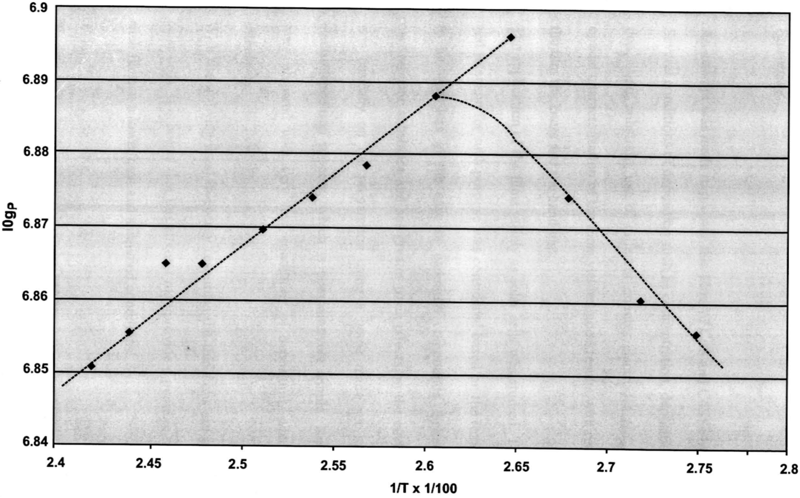

Fig4.14 Resistivity curve of CdSSe