CHAPTER VII

SUMMARY AND CONCLUSIONS

Thin film science has large number of applications in diverse fields of technology. The rapid progress in thin film micro and nano materials has given birth to a new technology of junction devices and integrated circuits.

The search for new semiconducting materials in the form of thin films for solar energy applications is of particular importance. The properties of thin film material are ultimately connected with the method of their deposition. Hence the search for new materials also implies the exploration of deposition process. Cheapness is also one of the important criterion for solar cell fabrication. The development of thin film technology for the development and fabrication of large area photodiode arrays using physical and chemical deposition techniques has turned chemical kinetics in to one of the most active field of electrochemistry.

Cadmium sulfide is a material having proven and potential applications in solar energy conversion, and has been much investigated. But the large band gap of CdS limits its efficiency in the solar cell. There have been many attempts made to improve the PEC properties by doping another element into CdS. At the same time the search for ternary chalcogenide semiconductors is continuously being done to obtain new semiconducting material for solar energy conversion.

In the present work, an attempt has been made to improve the properties of CdS films by forming ternary compound Cd-Fe-S. By varying Fe proportion in Cd-Fe-S, the photoelectrodes have been formed and investigated for PEC properties.

In order to compare the performance of Cd-Fe-S, the components CdS and FeS have been deposited on conducting substrates separately and their (photo) electrochemical characterisation along with structural, optical and electrical properties have been investigated. For the deposition of CdS, Cd-Fe-S and FeS films, a more economical and convenient spray pyrolysis method has been used.

The first chapter is introductory. The various deposition techniques used for thin film deposition have been discussed in brief along with the classification of deposition techniques. A detailed survey of literature on CdS, Cd-Fe-S and FeS has been given.

The theoretical background for various characterisation techniques such as X-ray diffraction, optical absorption , electrical resistivity, thermoelectric power and photoelectrochemcial solar cells has been presented in brief in the second chapter.

Chapter III deals with the preparation and characterisation of CdS thin films using spray pyrolysis technique. The experimental set- up of pyrolysis system and various parameters of the system are discussed. The optimisaiton of preparative parameters for the deposition of CdS films has been given. Also the use of possible precursors combinations for obtaining a good quality CdS films have been tried. Suitable precursor combination as observed from PEC study is $CdCl_2 .H_2O$ and NH_2 - CS-NH_2 .

Following are the optimised preparative parameters for CdS film deposition

1. Solutions used: 0.05 M $CdCl_2 . H_2O$ (aq.) + 0.05 M NH_2 -CS-NH_2 (aq.)
2. Substrates: glass microslides and FTO coated glass substrates.
3. Substrate temperature: 300^0 C
4. Spray rate: 2 cc/min
5. Quantity of solution sprayed: 20 cc.
6. Film thickness 0.37 μm.

The structural optical and electrical characterisation of the optimised films has been carried out and the results have been discussed . The films are polyscrystalline with a direct band gap of 2.37 eV. They are found to be semiconducting with n-type conducting as revealed from resistivity and TEP measurements.

In chapter IV, the preparatioin and characterisation of FeS thin films has been discussed. The deposition of FeS thin films has been carried out by optimising the preparative conditions, and the optimised films are characterised by XRD, EDAX , optical absorption , electrical resistivity and TEP techniques. The optimised preparative parameters are as follows.

1. Solutions used: $FeCl_2$ (0.05 M)+ NH_2- CS-NH_2 (0.05 M)
2. Substrates: glass
3. Substrate temperature: 325^0C
4. Spry rate: 2 cc / min
5. Quantity of solution sprayed: 20 cc.
6. Thickness: 0.5 μm

The structural characterization studies by XRD reveal that the material formed is amorphous one since no intensity peaks are observed in the X - ray diffraction pattern. The identification of the material deposited is further taken up by EDAX technique. The EDAX data shows that the material is FeS with atomic weight percent of Fe to be 54.2 % and that of S to be 45.8 %. This also points out the fact that the material slightly differs from stoichiometry and is deficient in sulfur. This may be due to the excess evaporation of sulfur at the deposition temperature. The optical absorption studies show that the optical gap of FeS is 0.80 eV. The resistivity measurements reveal that the material is semiconducting with n - type conductivity which is confirmed by TEP measurements.

Chapter V contains detailed information on preparation and characterization of Cd-Fe-S thin films.

The deposition conditions are optimized and the Cd-Fe-S films are deposited at optimized conditions by varying Cd:Fe volumetric proportion onto glass and FTO coated glass substrates. The proportion of Cd:Fe is varied as 10:0 , 8:2, 6:4 , 4:6 , 2:8 , and 0:10.

The optimized preparative parameters are:

1. Solutions used: (0.05M) $CdCl_2.H_2O$ + (0.05 M) $FeCl_2$ +

   NH_2 - CS - NH_2 (0.05 M)

2. Substrates: glass and FTO coated glass substrates.

3. Substrate temperature: 325^0 C

4. Spray rate: 2 cc / min

5. Quantity of solution sparayed: 20 cc.

6. Thickness of film (typical): 0.47 μm

The structural characterization carried out by X - ray diffraction shows that the films containing small Fe proportion are polycrystalline but as the Fe content in Cd-Fe-S increases, the films change to amorphous ones. This may be due to the fact that the maximum amount of sulfur in the deposited film material is reacting with Fe to form amorphous FeS, thereby reducing the proportion of CdS which is polycrystalline in the deposited film material.

The optical absorption studies reveal that the optical gap varies with Fe content in Cd-Fe-S films and it lies in between the bandgap of CdS and FeS materials. This result is the desired change in the property of CdS, since by changing the Fe content; the band gap can be changed.

The resistivity and TEP measurements show that the films are highly resistive and semiconducting with n - type conductivity. The resistivity of the films is found to be increasing with increase in Fe content, which is contradictory as far as addition of a low band gap material into a higher band gap material is concerned. The increase in resistivity with increase in Fe proportion may be due to

1) The decrease in crystallinity of the material with increase in Fe content, and

2) Possible incorporation of oxygen during the film deposition process since carrier gas used is air ; is spray pyrolysis technique.

The (photo) electrochemical properties of Cd-Fe-S have been discussed in chapter VI. The Cd-Fe-S thin films have been deposited onto FTO coated glass substrates to form the photoelectrodes to be used in PEC cells. All the films with different proportions of Cd:Fe have been investigated for their photoactivity.

It is observed that the photoactivity of Cd-Fe-S films decreases with increase in Fe content in Cd-Fe-S films, and finally at cetrain Cd:Fe (4:6) proportion , photoactivity disappears. By considering values of short circuit current (Isc) and open circuit voltage (Voc) for different compositions, it is found that only 8:2 proportion gives relatively better values and hence only this composition is used for further characterization and has been compared with 10:0 (CdS) with respect to all the parameters that are estimated. From the I - V characteristics, junction ideality factor is calculated and is found to be 7.05 and 7.54 for the compositions 8:2 and 10:0 respectively.

From the photovoltaic output characteristics, the efficiency, fill factor and series and shunt resistance are estimated for the PEC cells formed. The efficiency for 10:0 compositions is found to be higher than that for 8:2. The actual values of these parameters are listed in Table 1 given below.

Composition Cd:Fe	Isc ($\mu A/cm^2$)	Voc (mV)	n (%)	f f (%)	Rs Ω	Rsh Ω	Vfb (v)
10:0	377	260	0.047	0.385	2330	125	- 0.5
8:2	305	115	0.019	0.414	835	75	-0.54

The spectral response characteristics indicate that peak values of current Isc is smaller in the case of 8:2 composition. This shows decrease in photoactivity due to Fe content in the films. The peak of the spectral response curve also shifts towards longer wavelength side because of the decrease in optical gap of the material with 8:2 proportion of Cd:Fe. The optical gap has been estimated from the same and it mateches to that obtained by optical absorption studies.

The photoresponse characteristics reveal that the current Isc increases linearly with intensity of incident light while Voc saturates at higher intensity. The values of junction ideally factor n_l are calculated and are found be 6.90 and 7.10 for 8:2 and 10:0 proportions respectively. The flat band potentials (Vfb) are estimated from the Mott - Schottky plots for 8:2 and 10:0 compositions. The values of V_fb are - 0.5 and - 0.54 for the compositions 10:0 and 8:2 of Cd:Fe in Cd-Fe-S films.

The compound Cd-Fe-S is a mixture of two compounds CdS and FeS. Normally, low band gap semiconductors have lower resistivity and their incorporation in the compounds of larger band gaps should decrease the resistivity of final mixed compound. But it has been observed that instead of decreasing, the resistivity observed to be increasing. Similar contradictory results have been observed for the photoactivity of the material. The incorporation of the low band gap material may produce the defects or deep level defects. There is great possibility of oxygen content in the film since during the pyrolysis of sprayed droplets, it is quite possible that these metallic ions may react with oxygen from the air and may from the metal oxide. The production of deep level defects and oxygen may have control over the conduction mechanism.