CHAPTER-VII

SUMMARY AND CONCLUSIONS

Photoelectrochemical (PEC) cells for conversion of solar energy into either electrical or chemical energy is one of the attractive, efficient and reliable tools; which seems to be a promising answer to the problem of energy crisis to the decade. Much attention is given to formation and improvement of PEC cells and new materials for solar energy conversion are searched out. Considering the importance and scope of the subject in the present investigation, studies are made on some PEC cells formed with composite films deposited by successive ionic layer adsorption and reaction (SILAR) method.

Cadmium sulphide (2.4 eV) and bismuth sulphide (1.4 eV) are well-studied semiconducting materials and also useful for energy conversion. However, both of them do not satisfy all the necessary requirement of their bandgaps. For bismuth sulphide one can utilize maximum span of the solar spectrum but large photovoltage is not possible due to small bandgap. On other hand for cadmium sulphide, as it is large bandgap semiconductor one can get large photovoltage, but much part of the solar spectrum goes useless. Therefore, to correlate the properties of PEC cells formed with CdS and Bi_2S_3 both the films are prepared by SILAR method. In addition new semiconducting materials $(CdS)_x(Bi_2S_3)_{1-x}$ having bandgaps which lie between the individual bandgaps of CdS and Bi_2S_3 have been prepared successfully by SILAR method.

Successive ionic layer adsorption and reaction (SILAR) method is presently attracting considerable attention as this do not require sophisticated instrumentation like vacuum system and other expensive equipments. The starting chemicals are commonly available and

cheap. The preparative parameters are easily controllable and better orientation and grain structure can be obtained.

In the following a brief account of summary and conclusions drawn in the present work are given. The **Chapter-I** starts with introductory part regarding thin films and technological based information and contains update literature survey of CdS, Bi_2S_3 and $(CdS)_x (Bi_2S_3)_{1-x}$ thin films prepared by chemical and physical methods. The plan of work of present research is presented at the end of **Chapter-I**.

The relative theoretical background of successive ionic layer adsorption and reaction (SILAR) method, characterization techniques such as X-ray diffraction (XRD), optical absorption, electrical resistivity and thermoemf and photoelectrochemical cells is presented in short in **Chapter-II.**

Chapter-III deals with preparation of CdS thin films by successive ionic layer adsorption and reaction (SILAR) method. Since method involves low capital investment, particularly attracting for small scale industrial levels of production of the devices and coatings and useful for large area deposition. Thin films of CdS have been prepared onto glass substrates by optimizing preparative parameters such as concentration, immersion time, immersion cycles and rinsing time. The optimized preparative parameters are listed in Table 7.1. The deposition was carried out at room temperature (27°C) at 1h and 2h respectively. After annealing amorphous CdS films change into polycrystalline. There is improvement in grain size. Further characterizations are carried out only for annealed films (annealed at 200°C for 2h). The optical bandgap estimated to be 2.34 eV. The room temperature electrical resistivity is of the order of 10^4 Ω-cm with n-type electrical conductivity.

The details of preparation, including optimization and characterization of Bi_2S_3 thin films have been delt with the IVth Chapter. The preparative parameters used for deposition of Bi_2S_3 thin films by SILAR method are listed in Table 7.1. The Bi_2S_3 film deposition onto glass substrates was carried out at room temperature ($27^{\circ}C$). As deposited films were annealed at $200^{\circ}C$ for 1h to 2h respectively. After annealing amorphous Bi_2S_3 films changed into polycrystalline. There is an improvement in grain size. Further characterization was carried out for annealed films (annealed at $200^{\circ}C$ for 2h.) the optical bandgap was estimated to be 1.78 eV. The room temperature resistivity is of the order of 10^4 ohm cm with n-type electrical conductivity.

Chapter V^{th} deals with deposition of $(CdS)_x$ $(Bi_2S_3)_{1-x}$ composite thin films (x = 1, 0.8, 0.6, 0.4, 0.2 and 0) by SILAR method. All optimized parameters were same as for the deposition of CdS and Bi_2S_3 thin films except immersion cycles. The composition 'x' was optimized by adjusting CdS and Bi_2S_3 immersion cycles (SILAR) cycles. Table 7. 2 shows optimized growth cycle for different compositions. As deposited films were annealed at $200^{\circ}C$ for 2h and their structural, optical and electrical properties have been studied and are listed in Table 7.3.

The colour of $(CdS)_x$ $(Bi_2S_3)_{1-x}$ composite thin films changes from yellowish to yellowish orange to yellowish brown to greenish brown to dark greenish brown as composition 'x' changes from 1 to 0. The XRD showed that $(CdS)_{0.4}(Bi_2S_3)_{0.6}$ composite thin films have mixed structure (hexagonal CdS and orthorhombic Bi_2S_3). It is observed that bandgaps of $(CdS)_x$ $(Bi_2S_3)_{1-x}$ composite thin films are in between individual bandgaps of CdS and Bi_2S_3. The electrical resistivity decreases with the decrease in composition 'x'.

Thermoemf increases with decrease in composition 'x' . The composite films show n-type electrical conductivity for all values of 'x'.

Chapter VIth presents the phtoelectrochemical charactgerization of $(CdS)_x(Bi_2S_3)_{1-x}$ as photoelectrodes. The PEC cell was constructed by using $(CdS)_x(Bi_2S_3)_{1-x}$ thin films (x = 1, 0.8, 0.6, 0.4, 0.2 and 0) as photoelectrode, polysulphide as an electrolyte and graphite as the counter electrode. The PEC cell has the following configuration :

$$n- (CdS)_x (Bi_2S_3)_{1-x} / 1 \text{ M (NaOH} - Na_2 S - S) / C$$

It is found that in dark, PEC cell of various composition 'x' photoelectrodes give some dark voltage and dark current with negative polarity towards the photoelectrodes and graphite electrode as the positve. The origin of voltage and current is attributed to the difference between two half cell potentials of electrodes in PEC cells. In this system cathodic behaviour of the photovoltage of the semiconductor is observed which indicates that composite films are n-type semiconductors.

The parameters such as junction ideality factor (n_d) and (n_l) and fill factor (ff), conversion efficiency (η) and series and shunt resistances (R_s and R_{sh}) were calculated from current-voltage (I-V) and photovoltaic output characteristics, respectively. The bandgap energy (Eg), decay constant (b) and flat band potential (V_{fb}) were calculated from spectral response, transient response and capacitance-voltage (C-V) characteristics, respectively. All calculated parameters are listed in Table 7.4. The photovoltaic conversion efficiency 'η' of the cell increases as composition 'x' decreases. This may be due to decrease in bandgap and electrical resistivity of the films. Low values of conversion efficiencies are attributed to relatively high values of series and low values of shunt resistances. The bandgap energy values estimated from spectral response curves are agree well with the results from optical

absorption studies. The flat band potential (v_{fb}) values are found to be different for different composition 'x'. There is no systematic change observed in flat band potential with composition 'x'. This may be due to presence of different defects and surface states present in the films. The $(CdS)_x(Bi_2S_3)_{1-x}$ composite films show n-type electrical conductivity.

From above summary, it is concluded that successive ionic layer adsorption and reaction (SILAR) method may be considered as a versatile method for deposition of photoactive CdS, Bi_2S_3 and $(CdS)_x$ $(Bi_2S_3)_{1-x}$ composite thin films. Quality of films depend upon deposition conditions used for the deposition. From the photoelectrochemical study, it is concluded that the deposited films are photoactive. The conversion efficiency of the composite films increases as composition 'x' decreases in $(CdS)_x(Bi_2S_3)_{1-x}$.

Table 7.1 Optimized conditions for the deposition of CdS and Bi_2S_3 thin films by SILAR method

Parameters	Precursors			
	for CdS		for Bi_2S_3	
	Cationic	Anionic	Cationic	Anionic
	Cadmium acetate	Sodium sulphide	Bismuth nitrate	Thioacetamide
Concentration(M)	0.06	0.1	0.003	0.1
PH~	11	11	9	11
Immersion cycles	30	30	20	20
Immersion time (sec)	15	15	20	20
Rinsing time (sec)	40	40	40	40
Deposition temp.(°C)	27	27	27	27

Table 7.2 Optimized growth cycles for different composition (x) for the deposition of $(CdS)_x(Bi_2S_3)_{1-x}$

Sample	Growth cycles	CdS + Bi_2S_3 Cycles
CdS	30	1 + 0
$(CdS)_{0.8}(Bi_2S_3)_{0.2}$	30	9 + 1
$(CdS)_{0.6}(Bi_2S_3)_{0.4}$	30	7 + 3
$(CdS)_{0.4}(Bi_2S_3)_{0.6}$	30	5 + 5
$(CdS)_{0.2}(Bi_2S_3)_{0.8}$	30	2 + 8
Bi_2S_3	20	0 + 1

Table 7.3 Structural , optical and electrical properties of annealed ($200^{\circ}C, 2h$)(CdS)$_x$ (Bi$_2$S$_3$)$_{1-x}$ thin films

Sample	Crystal structure	Bandgap energy Eg eV	Resistivity at 450 k x 10^4 Ω cm	Activation energy E_a , eV	Thermoemf At $150^{\circ}C$ mV
CdS	CdS- Hex.	2.34	0.42	0.97	50
(CdS)$_{0.8}$(Bi$_2$S$_3$)$_{0.2}$	CdS-Hex.	2.22	0.29	0.75	68
(CdS)$_{0.6}$(Bi$_2$S$_3$)$_{0.4}$	CdS-Hex., Bi$_2$S$_3$ - Ortho.	2.12	0.28	0.74	80
(CdS)$_{0.4}$(Bi$_2$S$_3$)$_{0.6}$	CdS-Hex., Bi$_2$S$_3$ -Ortho.	2.00	0.21	0.73	110
(CdS)$_{0.2}$(Bi$_2$S$_3$)$_{0.8}$	CdS-Hex.	1.88	0.1	0.71	123
Bi$_2$S$_3$	Bi$_2$S$_3$-Ortho.	1.78	0.02	0.63	160

* Hex.- Hexagonal

Ortho. - Orthorhombic

Table 7.4 Performance of the photoelectrochemical (PEC) cells based on $(CdS)_x \ (Bi_2S_3)_{1-x}$ thin film electrodes with different 'x' composition.

Composition 'x'	Junction ideality factor		Shunt resistance R_{sh} (Ω)	Series resistance R_s (Ω)	Fill factor (ff)%	Conversion efficiency η %	Decay constant 'b'	'Eg' from Spectral response (eV)	Flat band potential (V_{fb}) Vs (SCE)
	n_d	n_l							
1	7.17	10.9	500	72	36	0.018	0.70	2.37	-0.49
0.8	9.37	11.65	475	80	34.6	0.023	0.53	2.27	-0.5
0.6	10.97	9.70	360	80	31.5	0.027	0.64	2.08	-0.48
0.4	13.88	10.49	257	78	33.4	0.036	0.51	1.99	-0.525
0.2	8.39	8.74	575	73	37	0.049	0.52	1.85	-0.51
0	12.43	9.54	625	53	39	0.056	1.33	1.78	-0.55