CHAPTER-VII

Summary and Conclusions

CHAPTER - VII

SUMMARY AND CONCLUSIONS

The storage of solar energy during day time and its utilization latter, offers a challenge even today. The desired product is electricty. ECPV cell is one of the possible approaches for solar energy storage. Few reports are available on the storage cells. The use of the ECPV cell for storage of solar energy is one of the attractives because it offers an opportunity to store the solar energy in the form of a "fuel" which is easily transportable. Much attention is given to the formation and improvement of ECPV cells formed with new semiconductor materials. In the present investigation an attempt has been made to fabricate semiconductor-electrolyte junction cells based on chalcogenide films prepared by electro deposition technique.

The properties of ECPV cells have been studied with a special reference to the improvement of efficiency. The storage cells with different configurations have been studied for their use in chemical redox storage cells. The photoinduced charge transfer reaction is made to initiate a chemical reaction which is reversible during a discharge cycle. In order to improve the efficiency of ECPV cell and storage cell, the semiconductor photoelectrode should get large photovoltage which depends upon the band gap. Large band gap semiconductor can get higher photovoltage but much part of the solar spectrum left unused. Therefore, to fulfil the necessary requirements to use a large portion of solar spectrum

an appropriate band gap semiconductor photoanode is to be used in ECPV cells. Cadmium based alloyed chalcogenide films, Cd-Zn-S and Cd-Bi-S are prepared by electrodeposition technique under controlled conditions. The Cd-Zn-S film has the band gap between the band gaps of CdS and ZnS. The Cd-Bi-S film has the band gap, E_g = 1.9 eV which lies between the band gaps of Bi_2S_3 and CdS. Both alloyed semiconductor films were optimized with Zn and Bi compositions and preparative parameters were studied in detail. These films were employed in ECPV cell and storage cell.

The different phases of the work is described into six chapters. In the first chapter, subject of energy conversion, electrodeposition, ECPV cell, energy storage cell and purpose of dissertation is introduced in brief. The chapter second introduces the theoretical background of the subjects of electrochemistry, electrodeposition technique, the energy conversion by electrochemical photovoltaic cell and energy storage cell. The chapter third reports the electrodeposition of CdS, ZnS and Cd-Zn-S films. The cathodic polarization curves & the optimization of preparative parameters of these films have been studied in detail and reported. Electrodeposition method has been successfully employed for thin films of semiconductors like CdS, ZnS, Bi_2S_3, Cd-Zn-S and Cd-Bi-S. All films were electrodeposited under d.c. potentiostatic conditions. Three electrodes system was employed and the potentials were measured with respect to saturated calomel electrode (SCE). The substrates were stainless steel and Fluorine doped tin oxide (FTO) coated glass (sheet resistance 10-15 $\Omega/\square$). All solutions were unstirred and the layers were deposited at ambient temperature (25°C). In all cases H_2 evolution was not observed

until -1000 mV (SCE). The deposition potentials were found to be pH dependent. The deposition period was 30 min. for all films.

The CdS films were deposited from the solution containing 100 mM $CdSO_4$ and 100 mM $Na_2S_2O_3$ in the pH range between 2 and 5. The potentials were between -200 to -500 mV (SCE) and current densities were between 1 and 3mA/cm^2. The ZnS films were deposited from the solution containing 10 mM $ZnSO_4$ and 10 mM $Na_2S_2O_3$ in the pH range between 1 and 6. The potentials were between -200 to -600 mV (SCE) and current densities were between 0.5 and 5 mA/cm^2. The series of $Cd_{1-x}Zn_xS$ films (where x varies from 0 to 1) were electrodeposited from the bath containing the solutions of 100 mM $CdSO_4$, 100 mM $ZnSO_4$ and 100 mM $Na_2S_2O_3$. The solution composition was adjusted for getting the desired film deposition. The pH was between 2 and 5, the depositiion potentials were between -200 and -700 mV (SCE) and current densities between 0.5 and 5 mA/cm^2. The film thickness was between 2 to 3 μm.

The structural characterization of CdS, ZnS and $Cd_{1-x}Zn_xS$ films were studied. Microstructures of the films show that the films were uniform smooth and well covered substrates.

The XRD patterns for CdS, $Cd_{0.8}Zn_{0.2}S$ and $Cd_{0.4}Zn_{0.6}S$ indicate that films are polycrystalline in nature. The intensities and 2 θ values XRD lines for the films were measured. The 'd' values calculated for CdS films show that films consisted of a mixture of Hexagonal and cubic phases. The films of $Cd_{1-x}Zn_xS$ consisted of mixture of CdS and ZnS phases with free Cd,Zn and S. This might be due to the codeposition of Cd, Zn and S from acidic bath.

The optical characterization of CdS, ZnS and $Cd_{1-x}Zn_xS$ films was studied with variation of optical absorption coefficient (α) with wavelength (λ). The α is of the order of 10^4 cm^{-1} for all films and absorption edge shifted towards the shorter wave length side with increasing Zn content. The band gaps of the films were determined by using $(\alpha h\nu)^2$ versus ($h\nu$) plots. The band gaps of CdS and ZnS were 2.4 eV and 3.55 eV respectively and for $Cd_{1-x}Zn_xS$ films, band gaps shifted from 2.4 eV to the shorter wave length side as Zn content increased in the films. The dependence of band gap on Zn content was non linear.

The chapter four is devoted to the study of promising semiconductors CdS, Bi_2S_3 and Cd-Bi-S films prepared by electrodeposition technique under d.c. potentiostatic conditions. Polarizatiion curves were recorded to find deposition potentials. Bi_2S_3 films were electrodeposited from solution containing 100 m$\underline{M}$ $Bi(NO_3)_3$ and 100 m$\underline{M}$ $Na_2S_2O_3$ at the pH values between 2 and 3. The deposition potentials were between -70 mV and -100 mV (SCE). The current densities were between 0.5 and 2 mA/cm^2. The Cd-Bi-S films were deposited with bath containing the mixture of solutions of 100 m$\underline{M}$ $CdSO_4$, 100 m$\underline{M}$ $Bi(NO_3)_3$ and 100 m$\underline{M}$ $Na_2S_2O_3$. The deposition potentials were between -100 mV and -200 mV (SCE). Current densities were between 0.5 to 3 mA/cm^2. The variation of optical absorption coefficient (α) with wave length (λ) was studied. The absorption edge shifted towards the longer wave length side with increasing Bi content. It is observed that the band gaps of CdS and Bi_2S_3 were 2.4 eV and 1.8 eV respectively. The band gap of Cd-Bi-S film is shifted from 2.4 eV to lower side as Bi composition increases in the films. The dependence of band gap (E_g) on Bi content was

nonlinear. The structural studies showed that as-deposited Cd-Bi-S films were amorpous or consisted of fine grains.

The chapter fifth reports the variation of short circuit current (I_{sc}) and open circuit voltage (V_{oc}) of the ECPV cells formed with Cd-Zn-S and Cd-Bi-S films. The current of the ECPV cell as a function of applied voltage was recorded for all the cells formed with photoanodes CdS, ZnS, Bi_2S_3, Cd-Zn-S and Cd-Bi-S in dark and in light. The nature of I-V curves were rectifying for all cells. It is seen that I-V curves in light were shifted from I-V curves in dark which indicates that the ECPV cell is the generator of electricity. The efficiency and fill factor for the cell formed with $Cd_{0.8}Zn_{0.2}S$ films was found to be 0.24% and 30.1% respectively Similarly the efficiency and fill factor of the cell formed with Cd-Bi-S film were estimated 0.086% and 20.9% respectively. The spectral response of ECPV cells formed with Cd-Zn-S film and Cd-Bi-S film was studied. In photo response study, open circuit voltage (V_{oc}) varies exponentially whereas short circuit current varies linearly with light intensity.

The chapter sixth is concerned with the use of the ECPV cells in the storage of chemical energy. ECPV storage cell was formed with photoanodes Cd-Zn-S and Cd-Bi-S using two compartments system. These photoanodes and storage electrode Ag_2S were annealed in air at 200°C for 30 mins. The Ag_2S films were prepared at 25°C from unstirred solutions. The solutions were containing 100 mM $Ag(NO_3)_2$ and 100 mM $Na_2S_2O_3$ in acidic (pH = 2 to 3) medium. The deposition potentials were -300 mV to -600 mV (SCE). Photovoltaic activity of Ag_2S films were tested by forming ECPV cell. The storage cell configuration with photoanode/polysulfide/counter

electrode was in anodic compartment and storage electrode Ag_2S/1M NaOH was in cathodic compartment. Charging of storage cell was carried out with constant illumination (100 mW/cm^2) intensity for 1 to 2 hours. Two compartments were connected by a conducting salt bridge. Electrolyte 1 M ($NaOH-Na_2S-S$) was saturated by addition of 50:50% mixture of KCl and NaCl for stability of photoanode. It is found that, the energy can be stored electrochemically. Charging and discharging reactions were direct and reverse way

$$Ag_2S + 2\ e^- \longrightarrow 2\ Ag + S^{2-}$$

The electrons, thus liberated move through load to carbon electrode in the anodic compartment and interact with S_2^{2-} ions.

$$2\ e^- + S_2^{2-} \longrightarrow 2\ S^{2-}$$

Under steady state illumination the rate of electrons generated at the semiconductor-electrolyte interface is constant and gives a current equivalent to the saturation current. This mechanism yields the storage of photovoltaic energy into the chemical storage.

Therefore, in present investigations it is concluded that the preparation of thin film semiconductors with electrodeposition technique possesses many advantages over other methods of preparations. These are i)easy and economic process ii) no need of purified materials and iii) control over stoichiometry. Electrodeposition of binary and ternary compound semiconductors has become important in the fields of solar energy conversion. Band gap variation, control over stoichiometry&doping could be controlled with electrodeposition with a great accuracy. The new ternary

alloyed semiconductors like Cd-Zn-S and Cd-Bi-S are used for ECPV cell and storage cells. In the present investigation it has made possible to store the solar energy with ECPV cells. In brief the following are the conclusions drawn with respect to the storage of energy.

1) ECPV cells formed with Cd-Zn-S and Cd-Bi-S are successfully used in the storage of radiation energy.

2) ECPV cell formed with Cd-Bi-S photoanode is found more efficient in storage than that of storage system formed with Cd-Zn-S.

3) The rate of storage is found to depend on time of charging, photo-current and the quantity of material on storage electrode.

4) The radiation energy stored in the form of electrical energy.

5) The duration of discharge and the current drawn from storage cell depend on the magnitude of load resistance.