Chapter-VI

CHAPTER - VI

SUMMARY AND CONCULSIONS

Thin film science has widely spread applications in many fields of science and technology which consist of material science, surface science and applied physics. The range of thin film applications is so vast that it extends from micrometer dots in microelectronics to coating of several square meters of window glasses. The rapid progress in thin film micro and nano materials has given birth to a whole new technology of junction devices and integrated circuits of monoliths and hybrid types.

The search for new thin film materials appropriate to solar cell applications is of particular importance. Features such as the electronic structure, mobility and the characteristic optical absorption are frequently used determine the material stability. The properties of thin film materials are ultimately connected with method of their fabrication. Hence search for new material also implies the exploration of fabrication process. Cheapness is also one of the important criterions for solar cell fabrication. The development of thin film technology for the fabrication of large area photodiode arrays using physical and chemical deposition techniques has turned chemical kinetics into one of the most active field of the electrochemistry.

Electrochemical photovoltaic (ECPV) cells for the conversion of solar energy into either electrical or chemical energy is one of the attractive, efficient and reliable tool; which seems to be a promising answer to the problem of energy crises in the decade. Much attention is given to the formation and improvement of ECPV cell and new materials for solar energy conversion are searched out. In order to reduce the cost and have the quick access to physico-chemical properties of the materials, a relatively simple and quick deposition process is preferred.

Zinc indium selenide ($ZnIn_2Se_4$) is a layer structured photoactive semiconductor, which has received a little attention as a prospective material in ECPV cells. Considering the importance and scope of the subject in the present investigation, the studies are made on preparation and physico-chemical characterization of zinc indium selenide, thin films prepared from aqueous media by spray pyrolysis technique. Their photo-electrochemical characteristic has been investigated. The present work is divided into six parts.

Chapter-I opens with general preface of the subject matter. Extensive literature surveys on $ZnIn_2Se_4$ prepered by physical and chemical methods are given. The purpose of the present research work is stated at the end of the chapter.

The theoretical background of various characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), electron dispersive analysis by X-ray (EDAX), optical absorption, transport properties viz. electrical resistivity, thermo-electric power (TEP) is outlined in **Chapter-II**. Theory of semiconductor electrolyte interface, Helmotz's and Gouy-Champman layer, strain model along with conversion of light energy into electricity via photo-electrochemical route have been discussed.

Chapter-III opens with the introduction of one of the simplest deposition techniques; "Spray pyrolysis". It mainly deals with the spray deposition of $ZnIn_2Se_4$ thin film from aqueous medium and optimization of preparative parameters by photoelectrochemical technique. $ZnIn_2Se_4$ thin films have been deposited by spraying aqueous solutions of zinc sulphate ($ZnSO_4$), indium trichloride ($InCl_3$), and selenourea (CH_4N_2Se) onto preheated amorphous glass substrates. The films are prepared by taking equimolar solutions of $ZnSO_4$, $InCl_3$, and CH_4N_2Se in appropriate volumes so as to obtain the Zn: In: Se ratio as 1:2:4. The spray rate is kept constant at 5 cc min^{-1}. A 8cc solution of $ZnSO_4$, 16 cc solution of $InCl_3$, and 32 cc solution of

CH_4N_2Se have been mixed and immediately sprayed through glass nozzle onto the preheated amorphous and FTO coated glass substrates maintained at 325^0 C. When sprayed droplets of mixed solutions reach to hot substrate pyrolytic decomposition occurs and desired $ZnIn_2Se_4$ films forms on the substrate.

The effect of preparative parameters such as substrate temperature, concentration of spraying solution and annealing temperature on the film quality in terms of crystallinety, resistivity etc. has been studied. Following are the optimized preparative parameters for $ZnIn_2Se_4$ thin film.

1	Substrate Temperature	325 °C
2	Concentration of spraying solution	0.025 M
3	Annealing temperature	200 °C

In **Chapter–IV** the structural, optical and electrical characterization of the films deposited at optimized preparative parameters is carried out by means different characterization techniques.

Structural analysis of the $ZnIn_2Se_4$ films are carried out using XRD patterns, are recorded by varying diffraction angle (2θ) from 10 to 100°. Big hump in XRD pattern around 25–35° is due to amorphous nature of the glass substrate. It is found that the as-deposited films are microcrystalline in nature. Comparison of standard '*d*' values with ASTM data card as-deposited and annealed films confirms the formation of $ZnIn_2Se_4$ material with rhombohedral crystal structure. The films have been annealed at 100, 200 and 300°C in a vacuum for 1 hour.

The SEM studies reveal a compact morphology with large number of rhombohedral single crystals. This may be the unique feature of this material and those large numbers of small single crystals are formed when pyrolytic decomposition of material occurs at the upper surface of the substrate. The chemical compositional analysis of $ZnIn_2Se_4$ thin film deposited at optimized substrate temperature of 325°C is determined by EDAX technique. It is found that the films are nearly stoichiometric.

From the optical absorption studies, it has been found that that the optical absorption coefficient 'α' is a function of photon energy and is found to be of the order of 10^4 -10^5 cm^{-1} indicating the presence of direct optical transition. The band gap energy for $ZnIn_2Se_4$ films is estimated 2.82 eV. The two point d.c. dark resistivity measurement shows that the prepared $ZnIn_2Se_4$ film have dark resistivity in the order of (10^4-10^5 Ω cm). The variation of log (ρ) with reciprocal of temperature shows that resistivity decreases with increase in temperature and supports the semiconductor nature of the $ZnIn_2Se_4$ thin film. The activation energy is found to be 0.54 eV, which is very near to the value reported (1.18 eV) for single crystal. The result supports formation of perfect or nearly perfect stoichiometric compound ($ZnIn_2Se_4$).

In **Chapter-V** the construction of photoelectrochemical (PEC) cell along with experimental setup for electrical and optical characterization by PEC is discussed.

The requisites for photo-electrode, electrolyte and counter electrode are also discussed in this chapter. The performance parameters studies include open circuit voltage (V_{oc}), short circuit current (I_{sc}), junction ideality factor (n), fill factor (ff), efficiency (η), series(R_s) and shunt resistance(R_{sh}) etc. Variation of physical parameters of semiconductor and semiconductor-electrolyte junction band edge location has been reported.

Spray deposited $ZnIn_2Se_4$ thin film prepared on FTO coated glass for aqueous medium have been tested for their photoactivity by using them in photo-electrochemical (PEC) solar cell. All the films show good photoactivity only in polysuphide electrolyte. These films show n- type conductivity. Following results are obtained for V_{oc} and

I_{sc} for the as deposited and annealed films deposited on FTO coated glass substrates.

Films	I_{sc} (μA)	V_{oc} (mV)
As deposited	260	510
Annealed	300	570

It is found that annealed films deposited on the FTO glass shows the acceptable performance in PEC cell. Therefore annealed $ZnIn_2Se_4$ thin films have been further used in PEC characterization and calculations of physical parameters of the material.

PEC solar cell was fabricated using the electrode configuration comprising n- $ZnIn_2Se_4$ thin film as a photo-anode, graphite as a counter electrode and saturated calomel electrode (SCE) as a reference. The PEC cell has the configuration

F: SnO_2 – n- $ZnIn_2Se_4$ / polysulphide/C

It is observed that even in dark PEC cell gives some dark voltage with –ve polarity towards $ZnIn_2Se_4$ thin film electrode. The origin of this voltage is attributed to the difference between two half-cell potential of the electrode in PEC cell. After illumination of the junction, catholic behavior of photovoltage of semiconductor is observed which indicates that the $ZnIn_2Se_4$ thin films are n-type.

Current-voltage characteristics of PEC cell in dark and under illumination are studied at room temperature. The nature of I-V curves indicates the formation of rectifying junction and the cell is a generator of electricity. The junction ideality factor is 5.6. The plot of log I_L against V_L under illumination also shows linear behavior with junction ideality factor 'n_L' determined to be 1.9.

Various parameters obtained from power output plots using annealed n- $ZnIn_2Se_4$ films are tabulated below

Condition of film	I_{sc} ($\mu A/cm^2$)	V_{oc} (mV)	η (%)	ff (%)	R_s (Ω)	R_{sh} ($K\Omega$)
Annealed FTO Glass	300	570	1.47	43.5	165	18.5

The spectral response of the PEC cell with film on FTO glass is studied in the wavelength range of 300 to 800 nm. It is seen that the I_{sc} attains maximum value at λ=525 nm and decreases with further increases in λ. Maximum value of I_{sc} has been observed at wavelength around 525 nm, which corresponds to photon energy ~ 2.37 eV. The lower photocurrent on the shorter wavelength side is due to the strong absorption of light in the electrolyte and the larger amount of surface recombination of the photo generated minority charge carriers on longer wavelengths.

The plot of C^{-2} versus voltage is used to determine the flat bond potential (V_{fb}) for $ZnIn_2Se_4$ based PEC cell. Positive slopes of the plots again confirm the n-type conductivity of $ZnIn_2Se_4$ thin films. The value of flat band potential $V_{fb,}$ is obtained at $1/C_s^2 = 0$ on the potential axis according to well-known Mott-Schotty relation and is found to be -0.8775 V versus SCE for $ZnIn_2Se_4$ thin films.

The **Chapter-VI** deals with summery and conclusions drawn from present research work.