Chapter-I

CHAPTER - I

INTRODUCTION

1.1 GENERAL

Solar conversion is a young science with major growth began in the 1970s, spurred by the oil crisis that highlighted the pervasive importance of energy to our personal, social, economic, and political lives. The solar energy flux reaching the Earth's surface represents a few thousand times the current use of primary energy by humans. The potential of this resource is enormous and makes solar energy a crucial component of a renewable energy portfolio aimed at reducing the global emissions of greenhouse gasses into the atmosphere. Nevertheless, the current use of this energy resource represents less than 1% of the total electricity production from renewable sources. Even though the deployment of photovoltaic systems has been increasing steadily for the last 20 years, solar technologies still suffer from some drawbacks that make them poorly competitive on an energy market dominated by fossil fuels: high capital cost, modest conversion efficiency and intermittency. From a scientific and technical viewpoint, the development of new technologies with higher conversion efficiencies and low production costs is a key requirement for enabling the development of solar energy at a large scale. Although a majority of the scientific investigations were performed on single crystalline materials, it is generally recognized that any large scale application must rely on cheap polycrystalline materials, prepared by some thin films method that can be scaled up into an industrial process.

There has been considerable interest in deposition of binary, ternary and quaternary semiconductor thin films, which are capable of converting and storing the solar energy. In recent years, increasing attention has been devoted to the $A^{II}B^{III}{}_2X^{VI}{}_4$ ternary compounds, in particular for their electrical and photoelectronic properties. It can be deduced that one of the main characteristics of these semiconductors is the presence in their forbidden energy gap of different kinds of localized level. Some particular properties of the $A^{II}B^{III}{}_2X^{VI}{}_4$ systems, which are interesting for potential applications (high photoconductivity, negative resistance and charge storage effect), are clearly connected with the presence of these localized levels. Many $A^{II}B^{III}{}_2X^{VI}{}_4$ compounds possess a direct band gap which is of importance when developing optoelectronic devices and lasers [1]. To fabricate the solar cells, the prerequisite is the conductive material having band gap matching with solar spectrum and high mobility of charge carriers. Solar cell utilizing semiconductor-liquid junction (S-L) is the simplest way suggested for solar energy conversion. The most attracting feature of a S-L junction solar cell over a solid state junction solar cell is that it has in-built storage capacity. Therefore S-L junction solar cells are being extensively studied [2-5]. They have nonsolar applications also viz. etching [6], photoetcting [6-7], and photodepostion of metals on semiconductors [8-10].

1.2 LITERATURE SURVEY ON ZINC INDIUM SELENIDE ($ZnIn_2Se_4$)

In recent years there is much interest in the preparation and characterization of chalcogenides thin films because of their potential applications in the various fields [11-15]. Zinc Indium Selenide ($ZnIn_2Se_4$) thin films have wide applications in solar cells and optoelectronic devices [16]. $ZnIn_2Se_4$ is the ternary chalcogenide semiconductor of type $A^{II}B^{III}{}_2X^{VI}{}_4$, where A = Zn, Cd, or Hg, B= In or Ga, and X= Se, S or Te [17-19]. Hendia et al. [1] grown thin films of $ZnIn_2Se_4$ were at various deposition (60-150 Å s^{-1}) rates by evaporation under vacuum onto glass substrates, using Leybold Univex 300 coating unit. The evaporation rate was varied by changing the source temperature from 1073 to 1173 K. The substrate was cooled to room temp over period of 6 h. in order to fix the structure of the film. The thickness of the film was monitored using a quartz thickness monitor. The optical constants (the refractive index *n*, extinction coefficient *k* and dielectical constants ϵ' and ϵ'') are estimated for $ZnIn_2Se_4$ thin films. X-ray diffraction and electron microscopy were used to obtain an insight into the structural information. $ZnIn_2Se_4$ is a layer semiconductor of tetrahedral crystal. From the reflection and transmission data, the absorption coefficient was computed for amorphous and crystalline films. Analysis of absorption coefficient data reveled the existence of allowed direct and indirect transitions with optical energy gaps $E_d^{opt} = 3.38$ eV and $E_i^{opt} = 2.22$ eV at 300 K. Single crystal $ZnIn_2Se_4$ specimens were grown by gas transport reaction technique. Iodine crystals served as carriers. Grown crystals looked like planar plans having 8nm x 6nm x 1nm dimensions with natural mirror surfaces and typical metallic luster. The experiment was carried out with high voltage EMP 400 electrograph (V=350kV, $2L\lambda$ = 33.2 mmÅ). Electron diffraction patterns were studied for single crystal films obtained by adhesive tape spalling, and texture polycrystalline specimens. Texture diffraction patterns allowed lattice spacing a = 4.045 Å and c =59.29 Å to be determined. The presence of $-h+k+l \neq 3n$ types of reflections on the patterns indicated a rhombohedral structure [21]. The $ZnIn_2Se_4$ single crystals are also grown by chemical transport method and with the photoconductivity spectra photoconductivity behaviors have been studies at 4.2 K. [22]. Gariazzo et al. [23] have been studied the photoconductivity relaxation processes in 80-300K temperature range for vapour-phase chemically deposited $ZnIn_2Se_4$ monocrystals. Filipowier et al. [24] has reported the electro-optical memory effect and negative resistance effect of $ZnIn_2Se_4$ crystals. At low temperature $ZnIn_2Se_4$ material will present a high conductivity during and after illumination of light of energy greater than band gap. The high conductivity can be quenched by i) heating sample until it reaches room temperature, ii) illumination with monochromatic light of appropriate energy and iii) an electric field . Recently, Solimun et al. [25] have studied thermal properties of polycrystalline $ZnIn_2Se_4$. A plus method was used to measure the thermal conductivity, specific heat and thermal diffusivity of polycrystalline $ZnIn_2Se_4$ in temperature range 300 to 600K. The results showed that mechanism of heat transfer is due to mainly phonons, the contribution of electrons and dipoles being very small. Grilli et al. [26] has reported the recombination process of photoexcited carriers in $ZnIn_2Se_4$ by measuring luminescence, excitation, infrared stimulation spectra and luminescence decay curve.

1.4 STATEMENT OF THE PROBLEM

No attempts have been made to prepare these thin films by simple and low-cost chemical spray pyrolysis technique, where varying the precursor concentration can easily control the stoichiometry of the deposits.

The proposed work is broadly be divided into (a) preparation of Zinc Indium Selenide ($ZnIn_2Se_4$) thin films and optimization of preparative parameters (b) their physico-chemical characterization and (c) photoelectrochemical characterization. The $ZnIn_2Se_4$ thin films will be prepared by spraying desired equimolar aqueous solution of zinc, indium and selenium salts in appropriate volumes onto preheated substrates. Both the amorphous glass and fluorine doped tin oxide (FTO) coated glass substrates will be used for the deposition of the films.

The photoelectrochemical (PEC) cell will be fabricated using $ZnIn_2Se_4$ thin films as a photoelectrode. Various preparative parameters such as spray rate, substrate temperature, solution concentration, etc. will be optimized by novel, reliable PEC technique. The prepared films will be annealed and annealing temperature for time-period will be optimized.

The $ZnIn_2Se_4$ thin films will be characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis by X-rays (EDAX) techniques. The optical, electrical and PEC properties of the films will also be studied, structural analysis, chemical composition, band gap of semiconductor, thermo-electrical power and activation energy, etc. will be determined.

The $ZnIn_2Se_4$ thin films will also be characterized by using photoelectrochemical (PEC) characterization technique. The studies such as current-voltage (I-V) characteristic, photovoltaic output characteristic, capacitance-voltage (C-V) characteristic and spectral response will be carried out. The PEC is one of the best-known characterization techniques, by which many parameters like junction ideality factor (n), power conversion efficiency (η) , fill factor (ff) and flat band potential (V_{fb}) etc of a PEC cell will be determined.

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