CHAPTER - I

INTRODUCTION

1.1 GENERAL

Thin film science is a relatively young and ever growing field in science and technology which is confluence of materials science, surface science and applied physics and has become an intentifiable unified discipline of scientific endeavour. The studies on thin films formation are being pursued with increasing interest on account of its proven and potential applications in variety of semiconductor devices such as solar energy converters [1-3], vidicon devices [4], etc. The development of thin film technology for the fabrication of large area photodiode arrays using physical and chemical deposition techniques has formed chemical kinetics into one of the most active field of the electrochemistry. The metal contacts and antireflection coatings of solar cells are usually prepared by thin film technology. A better understanding of either constituents of thin films can be obtained by studying their structural, optical and electrical properties.

There has been considerable interest in the development of the systems for deposition of thin films which are capable of converting and storing the solar energy. The necessity of finding alternative fuel sources has rekindled interest in solar energy and the interest in using semiconductor liquid (S-L) grew to form almost a separate discipline which was named photoelectro chemistry. The interest in energy resources through photoelectrochemical route has stimulated since 1973. 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 [5-6]. They

have non-solar applications also viz. etching [4], photoetcting [4,7], and photodepostion of metals on semiconductors [8,9].

When the semiconductor electrode has taken a separator of two aqueous compartments in photoelectrochemical (PEC) cells, it is called as semiconductor-septum (SC-SEP) cell. The idea of construction of PEC cell with semiconductor separator is basically taken from the modeling of natural synthetic systems with a pigmented bilayer lipid membrane. The single compartment construction limits the maximum photoelectric response to the degree of band bending and is controlled, therefore, by the Fermi level for a given semiconductor and redox couple. This major drawback has been overcome in the so-called SC-SEP cell. The SC-SEP cell can be used for electricity generation as well as for hydrogen production .

1.2 LITERATURE SURVEY ON Sb_2S_3 AND Sb_2Se_3

Sb_2S_3 and Sb_2Se_3 are layer structured semiconductors of orthorhombic crystal structure [10]. Sb_2S_3 is a weakly polar semiconducting ferroelectric which exhibits phase transition with small structural changes in the co-ordination sphere of Sb atoms [11].

The chalcogenides of bismuth, antimony and arsenic (Bi, Sb, As) are prepared by fusing the mixture of elements at 400-900^o C. Although the binary an ternary chalcogenide compounds have been prepared by the direct reaction with halogen sulphide, they have either complex ribbon or layer lattice structure and have been much studied because of their semiconducting properties. Both

n- and p-type materials can be obtained by appropriate doping. For compounds of the type Me_2X_3 , the intrinsic band gap decreases in the sequence As > Sb > Bi for a given chalcogen and in the sequence S > Se > Te for given group V-B element. The V-VI compounds are highly coloured; the colour of their chalcogenide compounds is often dependent on amorphous or crystalline form, purity, preparation conditions and deposition techniques [12].

1.2.1 Antimony trisulphide (Sb_2S_3)

Antimony trisulphide ($Sb_2 S_3$) has both amorphous and crystalline forms. Gray mineral sulphide is called as 'antimony glance' or 'stibnite'. Orange or red form is amorphous in nature. It is suggested that the red colour of Sb_2S_3 may be due to its closed ring structure. Artificial crystals appear as grayish black needles having an orthorhombic crystal structure and co-ordination of stibnite has been studied by Belov et al. [13].

The influence of departures from stoichiomentry of photoelectric properties was investigated by A.A. Mostovskii et al. [14] for evaporated amorphous films of Sb_2S_3. Badachhape and Goswami [15] had reported the fine grained amorphous structure of Sb_2S_3 evaporated at room temperature and orthorhombic structure at high temperatures ($T > 200\ ^oC$). The electrical and photoconductive properties of sintered layers of Sb_2S_3 have been investigated by Chockalingam et al. [16]. Optical properties and electrical contacts of thin Sb_2S_3 have been investigated by Ramanujam and Vetury [17] and Mitchall and Denure [18]. Ablowa et al. [19] reported on the switching effects in Sb_2S_3 single crystals.

The electrical dielectric, and photoelectric properties of vacuum evaporated antimony trisulphide films have been investigated by various authors to study the charge carrier transport mechanism, spectral distribution of photoconductivity [20-21]. The variation of the photosensitivity of evaporated Sb_2S_3 films with the condensation rate and the substrate temperature has been investigated by Bazakutsa et al. [22]. Mironyak et al. [23] reported the resistivity measurements of fused mixture of Sb_2S_3-SnS and Sb_2S_3 and As_2S_3. It was found that with an increase in SnS content of the melts, the charge transport mechanism changed from predominantly ionic, characteristics of an Sb_2S_3 melt, to predominantly semiconductive, typical of SnS. Botgros et al. [24] investigated the phase diagram of the system $(Tl_2S)_{3x}$ - $(Sb_2S_3)_{1-x}$ and confirmed the existence of the compounds $TlSbS_2$ and Tl_2SbS_3, which crystallizes in a monoclinic lattice with unit cell parameters a=11.28Å, b=9.65Å, c=7.45 Å and β=104^o.

Roy et al. [25] reported the magnetic and electrical properties of Sb_2S_3 crystal and mechanism of carrier tramsport in it. Ghosh and Verma [26-27] studied change in optical properties accompanying the amorphous to crystalline transition of vacuum deposited Sb_3S_3 thin films. George and Radhakrishnan [28] prepared stoichiometric films of Sb_2S_3 by three temperature method and found that stoichiometry is maintained in the temperature range of 323-373 K. Nayak et al. [29] has reported on Sb_2S_3 thin films preparation by ‘dip and dry’ technique and X-ray emission studies on Bi_2S_3, Sb_2S_3 and $Bi_{2-x}Sb_xSe$ [30] films confirming a definite chemical shift for Sb which is found to be highly

asymmetric. 'Solution gas interface' technique [31] has been employed by Pawar et al. for deposition of the films. The electrical resistivity of amorphous antimony trisulphide films was investigated in the temperature range 0 to 200 ^{o}C by Mady et al. [32]. By annealing, the conductivity reduces and the slope of the conduction is increased indicating that the mobility gap is appreciably enhanced by annealing. Fujita et al. [33-34] studied the photoluminescence, the fundamental absorption edge and electronic structure in single crystal of Sb_2S_3. The short range order for the Sb_2S_3 thin films was shown to be equal as for glassy bulk samples by Dalba et. al [35]. Droichi et al. [36] reported on study of localized states in amorphous chalcogenide Sb_2S_3 thin films with optical gap of 1.52 eV. Mandal and Mondal [37] reported the morphological, structural, optical and electrical properties of Sb_2S_3 thin films deposited by a chemical method using potassium antimonyl tartarate, triethanolamine (TEA), ammonia and thioacetamide. Some physical properties of evaporated thin films of Sb_2S_3 has been studied by Mandouch and Salama [38]. Lokhande [39] reported on solution growth of Sb_2S_3 and As_2S_3 thin films from acidic and alkaline baths and reported the optical gap of Sb_2S_3 to be 1.97 eV.

Savadago and Mandal [40-42] obtained n-type films using chemical bath deposition with thioacetamide as S^{2-} ion source and TEA as a complexing reagent and reported the solar conversion efficiency of 3.9% for the PEC cell formed with chemically deposited Sb_2S_3 thin films with silicotungstic acid [41]. Many workers [43-47] reported on PEC properties of Sb_2S_3 thin films. Bhosale et al. [48] prepared amorphous Sb_2S_3 films by spray pyrolysis method

with a band gap of 1.55 eV using oxalic acid as a complexing agent. Yesugade et al. [49] electrodeposited Sb_2S_3 polycrystalline films from aqueous medium with band gap energy of 1.74 eV. Desai and Lokhande [50-51] reported on solution growth of microcrystalline Sb_2S_3 films from thioacetamide bath at room temperature by the chemical method. The optical band gap is found to be 1.87 eV. Alkaline chemical bath deposition have also been studied [50]. Killedar et al. [52-53] deposited polycrystalline Sb_2S_3 films, by spray pyrolysis technique from non-aqueous medium with optical gap of 1.8 eV and solar conversion efficiency to be 0.058%. Arun et al. [54-55] reported on the laser induced crystallization in vacuum evaporated amorphous Sb_2S_3 films. The threshold laser power density required to induce crystallization was found to be 98 ± 5 W/cm^2. Analysis indicated Sb_2S_3 films as a potential material for WORM kind of storage applications. A chemical bath deposition method for thin films of Sb_2S_3 was investigated by Nair et al. [56]. Annealing in nitrogen at 250 ^oC improved the crystallinity of the films (Sb_2S_3, stibinite structure become evident). This was accopained by a decrease in the optical band gap from more than 2 eV to the bulk value, ~ 1.7 eV, and an increase in the photosensitivity. Recently Yu et al. [57] synthesized an ultrafine powders of Sb_2S_3 via a reaction between $SbCl_3$ and Na_2S_3 in benzene. The powder was single orthorhombic Sb_2S_3 phase and well crystallized with an average size of about 150 nm. It was found that the process in benzene prevents hydrolysis of $SbCl_3$ and avoides the presence of other impurites in the product.

1.2.2. Antimony triselenide (Sb_2Se_3)

Crystalline Sb_2Se_3 is an orthorhombic, which is isostructural to Sb_2S_3 and Bi_2Se_3, having a=11.62 Å, b=11.77 Å and c=3.69Å [58] of space group D_{2h}^{16}, type D_8^5 with 20 atoms, i.e. 4 molecules /unit cell. The atoms are arranged in a layer structure with layers ⊥ b and weak Sb-Se bonding [58] between layers and therefore, the crystals exhibit natural cleavage ⊥ b.

The optical properties of single crystal and amorphous Sb_2Se_3 in energy 0 to 24 eV were reported by Shaffer et al. [59]. The influence of the lack of long range order upon the electronic structure of the Sb_2Se_3 was confirmed to the conduction and valence bands of the material and loss of long range order altered the weakly bonding resonance electron states producing a substantial change in optical properties. Wood et al. studied the optical properties of evaporated amorphous films of Sb_2Se_3 [60] as a function of composition and compared the transport and optical properties of single crystal and amorphous films [61]. Optical gap of 1.36 eV due to nondirect transition in coevaporated films and 1.21 eV due to indirect transition in single crystals of Sb_2Se_3 were reported. The difference between the properties of amorphous and crystalline Sb_2Se_3 were attributed to the quite homogeneous environment of the Sb sites in amorphous Sb_2Se_3 than the crystal. The pattern of change of the electrical conductivity, photosensitivity and thermo-emf of evaporated Sb_2Se_3 films during ordering of their structure has been established by Bazakatsa et al. [62]. An empirical relation was proposed by K. Shimakawa [63] and Tichy et al. [64] to interpret the compositional dependence of the optical gap in amorphous semiconducting alloys. It was found that the variation of energy gap with

composition in amorphous semiconducting alloys Sb_xSe_{1-x}, Si_xGe_{1-x} and As_xTe_{1-x} can be described by the following simple relation $E_{AB}(Y) = YE_A + (1-Y)E_B$ where Y is the volume fraction of element A, and E_A and E_B are optical gaps for elements A and B respectively. Pramanik and Bhattacharya deposited the Sb_2Se_3 films by chemical bath deposition technique using potassium antimonyl tartarate as a Sb^{3+} ion source and sodium selenosulphate as a Se^{2-} ion source [65]. TEA was used as a complexing agent. The deposited films were amorphous with optical gap equal to 1.88 eV and having specific resistance of the order of 10^7 Ω.cm. The photoelectrochemical behaviour of chemically deposited Sb_2Se_3 films in polyiodide elelctrolyte was studied [66]. The short-circuit photocurrent was about 0.45 mA/cm^2 and open- circuit photovoltage was about 0.37 V. Youtsas et al. [67] determined the crystal structure of single crystal Sb_2Se_3 to be orthorhombic having cell constants a = 11.79Å, b = 3.98Å and c = 11.64 Å respectively. Investigation of electronic properties of Sb_2Se_3 in the crystal-melt phase transition (including the liquid phase) were made by Glazov et al. [68]. Nikam et al. have reported the composition dependence of electrical properties of simultaneously evaporated Sb-Se thin films [69] and the conduction mechanism [70] involved therein. The effect of a systematic variation of x in Sb_xSe_{1-x} thin films on its optical properties have been recently reported by Zayed et al. [71]. The two optical transition mechanisms, depending on the value of x, were reported. Indirect transition for Sb_xSe_{1-x} thin films (x=0.1, 0.4, 0.5, 0.7 and 0.9) and a forbidden direct transition for x=0.3. The optical energy gap Eg^{opt} was found to vary from 0.24 eV for (x=0.9) to

1.92 eV for (x=0). The frequency dependence of the optical constants n, k, ε′ and ε′′ has been computed by Zayed et al. [72]. Recently Kaito et al. [73] have shown that crystallization of small Sb crystals with (0001) orientation is necessary to form the spherical Sb_2Se_3 crystal. Using thermally evaporated Sb_2Se_3 films, optical disc recording of frequency modulated (FM) video signals by a diode laser has been demonstrated [74]. Recently, Arun and Vedeshwar [75] have studied the effect of instataneous heat treatment (of short duration ~ 60s) for thermally evaporated Sb_2Se_3 films using chemical compositional and optical analyses. The considerable optical constrast between amorphous and crystalline phases and their stability indicated a good potential for WORM kind of storage applications.

1.3 STATEMENT OF THE PROBLEM

There has been an increasing interest during past few decades in metal chalcogenide thin films because of their promising use in various fields of science and technology, a few to mention are in solar selective and conversion coating, thermoelectric coolers, optoelectronics, photoelectrochemical (PEC) and PEC based devices. Among various deposition techniques being used to deposit semiconducting thin films, spray pyrolysis has been attracting a great deal of attention because of its simplicity and low cost. Large area semiconducting, high Tc superconduting and magnetic films are being deposited by using this technique. Therefore in the present research work the attempts will be made to produce antimony chalcogenide compounds in the

form of thin films, both from aqueous and non-aqueous media by a spray pyrolysis technique.

The proposed work can broadly be divided into (a) preparation of thin films of antimony trisulphide (Sb_2S_3) and antimony triselenide (Sb_2Se_3), from aqueous and non-aqueous media (b) their physico-chemical and photoelectrochemical characterization and (c) finally their use in rechargeable semiconductor-septum storage cells. The thin films of Sb_2S_3 and Sb_2Se_3 will be prepared by spraying desired equimolar aqueous and non-aqueous solutions of antimony and sulphur or selenium salts in appropriate volumes onto preheated substrates. Both the amorphous glass and metallic substrates will be used for the deposition of the films. The non-aqueous solvents such as acetic acid (glacial), formaldehyde, dimethyl formamide, dimethyl sulphoxide etc. will be used to obtain the films of Sb_2S_3 and Sb_2Se_3. The different complexing agents such as EDTA, oxalic acid, tartaric acid, acetic acid etc. will be used to improve the quality and performance of deposites. Various preparative parameters such as substrate temperature, solution concentration, concentration of complexing agent etc. will be optimized. The prepared films will be annealed in a nitrogen atmosphere at optimized annealing temperature for optimized time-period.

The films will be characterized by using XRD and SEM techniques. The optical, electrical and PEC properties of the films will also be studied. PEC is one of the best known characterization techniques, by which many quantities like junction ideality factor (η), power conversion efficiency (n) and fill factor (ff) of a PEC cell, band gap of semiconductor and flat band potential etc. can

be determined. The PEC cell will be fabricated using Sb_2S_3 and Sb_2Se_3 thin films as a photoelectrode. The studies such as I-V characteristic, photovoltaic output characteristic, photoresponse, photovoltaic rise and decay, C-V characteristic and spectral response will be carried out.

The PEC cells have built-in-storage facility. The semiconductor septum rechargeable storage cell will be fabricated by employing Sb_2S_3 and Sb_2Se_3 thin films as one of the electrodes and its charging and discharging modes will be studied.

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