

CHAPTER-V

**CHAPTER V****SUMMARY AND CONCLUSIONS**

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## CHAPTER V

### SUMMARY AND CONCLUSIONS

The range of thin film applications is so vast that it extends from micrometer dots in microelectronics to coatings of several square meters on window glasses. The thin film preparation methods and their industrial uses are so numerous and common that we are hardly aware of the extent to which they have become part of our way of life. Polycrystalline thin films of metals, metal oxides, and metal chalcogenides found wide spread utility in industrial applications such as electronics, optical devices, solar cells including photoelectrochemical cells etc. Compounds like  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{Se}_3$  are used in the vidicon type of television pick-up tube and  $\text{CdS}$  &  $\text{CdSe}$  films in photoconductors and solar cells. III-V compound films especially  $\text{InAs}$  and  $\text{InSb}$  are used in galvanomagnetic devices. Moreover, 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 monolithic and hybrid types. Dictated by the considerations of simplicity, economicability, and input energy, large area thin film materials necessarily have to be obtained by a solution growth processes. Of the various methods, chemical deposition process, that involves controlled but slow precipitation, is presently an attractive means (because of its simpleness, cheapness, and conveniency) for the preparation of large area II-VI and IV-VI compound thin films. A variety of substrates like metal, insulator, semiconductor etc can be used since the working temperature for this process is low. The

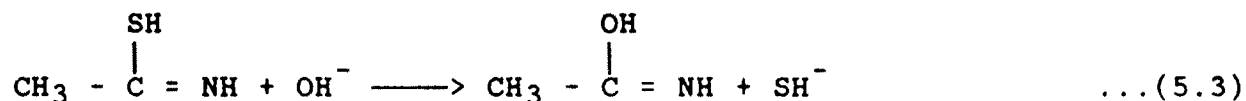
preparative parameters are easily controllable and better orientation of crystallites resulting into improved grain structure can be obtained [31,37,38,52,90-92]. The antimony trisulphide, a member of V-VI group compound, is technically important material in view of its high photosensitivity, photoconductivity, and thermoelectric properties. It has n-type electrical conduction, high optical absorbance, and direct mode of transition with an intermediate band gap of 1.87 eV. As the bandgap is fairly matching with solar spectrum and no literature data are available on its electrochemical behaviour, we thought it to be an interesting material for photoelectrochemical energy conversion. The plan of our research work was many fold and the actual work that has been carried out is divided into five chapters. Chapter I is a short survey of the thin film technology and photoelectrochemical cells. Essentially, it further describes the V-VI compounds and the minimum requirements of the photoelectrochemical (PEC) cells. Chapter II describes the designs, fabrications, and experimental techniques for carrying out the proposed plan. In chapter III various thin film preparation methods are described in short. The growth mechanism and detailed procedure for the deposition of  $Sb_2S_3$  thin films are also given. The structural, electrical and optical properties of the  $Sb_2S_3$  thin films are studied and discussed at length. The electrochemical cells were constructed with these films on pure stainless steel and the electrical and optical properties of the cell have been explained in terms of the I-V and C-V characteristics in dark, photovoltaic output

characteristic under  $100 \text{ mW/cm}^2$  illumination intensity, and photo, spectral, and speed responses. The various steps undertaken to carry out this work were as follows :

### 1] Preparation and Growth Mechanism of $\text{Sb}_2\text{S}_3$ Samples

The preparation procedure involved the reaction container consisting of 100 ml, 0.1M antimony potassium tartrate, 100 ml 0.1M thioacetamide, and solutions of triethanolamine and aqueous ammonia in appropriate amounts was raised to a deposition temperature of  $93 \pm 0.5^\circ\text{C}$ . The properly cleaned substrates (glass and stainless steel) were attached to a specially designed substrate holder and were kept rotating at a speed of  $80 \pm 2 \text{ rpm}$  in a reaction vessel for half an hour. These samples were used for further studies. All the chemicals used were AR grade.

The preparation of  $\text{Sb}_2\text{S}_3$  thin films is carried out in an alkaline medium in the presence of a complexing agent and therefore, the formation of  $\text{Sb}_2\text{S}_3$  films is made possible on the basis of the slow release of  $\text{Sb}^{3+}$  and  $\text{S}^{2-}$  ions and their subsequent condensation on the substrates [31,48]. The film formation takes place by the reduction of antimony using thioacetamide as the reducing agent. The series of reactions proposed are [31]:





It is seen from the above reactions that the growth rate is controlled by the concentrations of the potassium antimony tartrate, thioacetamide, and an aqueous ammonia. Ammonia slows down the rate of formation of  $\text{Sb}_2\text{S}_3$  and helps to adhere the films tightly to the substrates.

## 2] The $\text{Sb}_2\text{S}_3$ Samples

The growth of  $\text{Sb}_2\text{S}_3$  thin film takes place by slow release of  $\text{Sb}^{3+}$  and  $\text{S}^{2-}$  ions in a complex mixture that allows subsequent condensation and therefore, better orientation of the crystallites is possible. The good quality deposition of  $\text{Sb}_2\text{S}_3$  thin films with less consumption of active material and an electrical energy is possible. The as-deposited films are orange red in color and color changes red to dark-grey when heated to  $180^\circ\text{C}$ . Dark-grey samples are more coarse than an orange-red. The samples are smooth, uniform, diffusely reflecting, crackfree, and strongly adherent to the substrates.

## 3] Studies on Thin Film Properties

The structure and crystallinity of the  $\text{Sb}_2\text{S}_3$  samples (orange-red and dark-grey) were tested by XRD and SEM techniques. The as-deposited orange-red samples are amorphous (microcrystalline) and crystallinity improves after heat treatment. Dark-grey samples are more coarse and more crystalline. The observed 'd' values are in excellent agreement with the standard. The computation of lattice constants show orthorhombic type of lattice with  $a=11.220 \text{ \AA}$ ,  $b=11.283 \text{ \AA}$ , and  $c=3.837 \text{ \AA}$  [31,34]. The SEM micrographs show well defined grains and grain size



increases with baking temperature. The grain size is of the order of 0.2 to 0.5  $\mu\text{m}$  and is larger for dark-grey samples.

The dark resistance of the sample was measured in the 300k-575K temperature range. Thermal energy gap calculated from these observations is 1.60 eV. The room temperature conductivity is in the range  $10^{-8} - 10^{-9} \Omega^{-1} \text{cm}^{-1}$ . An activation energy of electrical conduction is calculated from the following standard relation [48,68]:

$$\sigma = \sigma_0 \exp [-E_a/KT] \quad \dots(5.5)$$

$E_a$  is found to be 0.80 eV and is comparatively smaller than those reported by others. Thermoelectric power was measured and the samples are of n-type conduction.

Optical scanning was done in the 3500  $\text{\AA}$  to 8400  $\text{\AA}$  wavelength range. The absorption coefficient is high ( $10^4 \text{cm}^{-1}$ ) and optical band gap (determined from  $(\alpha h\nu)^2$  vs  $h\nu$  variation) for an orange-red material is 1.83 eV. The dark-grey samples show maximum absorption in the range of energies from 1.62 eV to 3.1 eV. The absorption edge for these samples become still sharp and estimated bandgap is found to be 1.17 eV. The mode of transition in both the cases is of direct type [31,34].

#### 4] Studies on Photoelectrochemical (PEC) Properties

The PEC cell was constructed with n- $\text{Sb}_2\text{S}_3$  photoelectrode dipped in an electrolyte consisting of Ferrocene in DMSO as the redox couple. A graphite treated for 24 hours in a CoS solution was used as a counter electrode. Studies on I-V and C-V characteristics have been carried out to know about the charge transfer process across an electrode/electrolyte interface. The

junction is found of the rectifying type and the current through the junction relates to the applied voltage by a Butler-Volmer relation as [68]:

$$i = i_0 \left[ \exp(1-\beta) \frac{VF}{RT} - \exp \frac{-\beta VF}{RT} \right] \quad \dots(5.6)$$

where, symbols have their usual meaning.

The junction quality factor ( $n_d$ ) was calculated from the variation of  $\log I$  vs  $V$  and its typical value is 4.62.  $n_d$  deviates from its ideal value indicating the effects of series resistance of a cell and recombination mechanism at the interface. Capacitance voltage measurements were performed under reverse biased condition to determine the flat band potential from the Mott-Schottky variation.  $V_{fb}$  is - 0.36V. Barrier height ( $\Phi_B$ ) was obtained from the variation of reverse saturation current ( $I_0$ ) as a function of temperature. It is found to be 0.239 eV.

The properties of a cell under lighted condition was examined. At  $AM_1$  solar irradiance ( $100 \text{ mW/cm}^2$ ), the short circuit current ( $I_{sc}$ ) and open circuit voltage ( $V_{oc}$ ) are of the order of  $0.013 \text{ mA/cm}^2$  and  $0.29 \text{ V}$ , respectively. The solar to electrical energy conversion efficiency ( $\eta$ ) is typically, 0.0012%. The other cell parameters such as series resistance ( $R_s$ ), shunt resistance ( $R_{sh}$ ) and fill factor ( $ff$ ) have been calculated and are  $14.2 \text{ K}\Omega$ ,  $28.67 \text{ K}\Omega$ , and 31%, respectively.

### 5] Concluding Remarks

Although,  $Sb_2S_3$  samples deposited using a modified chemical deposition process are uniform, hardly adherent, smooth,



diffusely reflecting etc, their resistivity is quiet high and inturn it has reflected on its several electrochemical properties when it is utilised in a photoelectrochemical solar cell. The observed solar cell performance is below the expectation and this is because of i] high electrode resistivity, ii] thinness of the sample, iii] absence of the thorough pre and post preparative treatments, iv] absorption of the light in the electrolyte, and v] reflection losses from the glass and that from the photoelectrode surfaces. Detailed investigation on optimization of material parameters and therefore, the properties as well as of the electrolyte and cell design are essential.

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