CHAPTER V

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SUMMARY AND CONCLUSIONS

5.1 General

There has been an increasing and continued interest in semiconducting thin films due to their enormous applications. Their preparation methods and industrial utility are so vast and common that we are hardly aware of the extent to which they have become a part of our way of life. The polycrystalline thin films of metals, metal oxides and metal chalcogenides found wide spread utility in this respect. The properties of the films (structural, optical, microscopic, transport, optoelectric, electronic etc) have direct bearing on the method of formation and therefore it is obvious that no one technique can built the films of desired properties. Among the various deposition techniques , chemical deposition process which involves controlled but slow precipitation is presently an attractive means for the fabrication of large area II–VI, IV–VI , III-VI, I-III-VI etc compound thin films. The preparative parameters and deposition conditions are easily controllable and better orientation of the crystallites can be obtained resulting into the improved grain structure. Tin sulphide is a member of IV-VI group compounds and is technically important class of materials. Its layer-structure is important for holographic recording and switching applications. The material has high prospectus as opto-electronic material and has p-type electrical conduction, high optical absorbance and direct mode of optical transitions with an energy gap of 1.32 eV. It has proved its worthiness in sensor and switching applications and has gained much popularity in holographic recording systems. It exhibits two types of conductivities and that the conductivity modulation could easily be achieved by simply doping it with a suitable dopant material, thus broadening its scope of applications. As SnS satisfies most of the

requirements of a photovoltaic material, we have planned, within our laboratory limits, for a multi-step programme for its fabrication and utilization. The first step of the programme was the survey of the literature and the basic understanding of the research problem. In the second phase of the programme materials synthesis was undertaken and the various deposition conditions and preparative parameters were studied and finalized. The third phase was devoted to the materials characterization through the various materials properties whereas in forth step the electrochemical conversion device was fabricated and studied through its various electrochemical properties to understand its usefulness in energy conversion process. The last stage is the survey of the studies that we have made and the conclusions drawn out of the studies. The stepwise development of the programme is as under.

5.2 The SnS Thin Films: Synthesis and Growth Mechanism

Thin film deposits of tin sulphide were obtained onto the glass substrates using a solution growth process in an alkaline medium . The properly cleaned substrates (glass microslides) were attached to a specially designed substrate holder and were kept rotating at a constant speed (72 ± 2 rpm) in the reaction mixture containing Sn^{2+} and S^{2-} ions. The deposition was an ion-by-ion condensation process and carried out for a period of 110 minutes to get thin, uniform and adherent samples.

For the preparation of the films, stannous chloride was first dissolved in acetone to form a paste-slurry and then complexed with triethanolamine to form a Sn^{2+} - TEA complex. The thioacetamide in an alcoholic medium supplies S^{2-} ions. The complex releases Sn^{2+} ions slowly to combine with S^{2-} ions and their subsequent condensation on the substrate forms a thin and adherent deposits.

A series of the reactions proposed are :

$$SnCl_2 . 2H_2O + (O=C\begin{matrix}CH_3\\CH_3\end{matrix}) \xrightarrow[(pH = 10.5)]{70^{\circ}C}$$

$$Sn^{2+} + O^{-}=C\begin{matrix}CH_3\\CH_3\end{matrix} + 2Cl^{-} \qquad (5.1)$$

$$2N(CH_2CH_2OH)_3 + Sn^{2+} \rightarrow [Sn\{N(CH_2CH_2OH)_3\}_2] \downarrow Sn^{2+} + TEA \qquad ...(5.2)$$

$$H_3C-\overset{\overset{S}{\|}}{C}-NH_2 \xrightarrow[2\,OH^-]{pH} CH_3-COONH_4 + S^{2-} \qquad ...(5.3)$$

$$Sn^{2+} + S^{2-} \rightarrow SnS \qquad ...(5.4)$$

It is seen from the above reactions that the growth rate is controlled by the concentrations of Sn^{2+} and S^{2-} ions. The as-grown samples were thin, uniform, smooth, diffusely reflecting and adhered tightly to the substrate support. The various preparation parameters and deposition conditions which were optimized so as to obtain good quality films are:

1. Deposition temperature : $70 \pm 2\ ^{\circ}C$
2. Speed of the mechanical churning : 72 ± 2 rpm
3. pH of the reaction mixture : 10.5 ± 0.1
4. Deposition time : 110 min.

5.3 Thin Film Properties

The thin film properties studied are: the structural, microscopic, optical and electrical transport. These are studied in view to obtain various thin film characteristics and to understand the valuable

informations on the structure, surface features, optical sensitivity, lattice dynamics, current transport mechanism etc.

a) The structural and microscopic properties

The structure and crystallinity of the as-deposited and baked (100°C) SnS samples were examined by an XRD and SEM techniques. The X-ray diffraction studies showed that SnS is microcrystalline in nature and the crystalline nature becomes more coarser after baking at 100 ^{0}C. The grain size for SnS phase was determined by using the Scherrer's relation

$$D = 0.9 \lambda / B \cos \theta \qquad (5.5)$$

where, symbols have their usual meaning. The average grain size is of the order of 267 A°.

The SEM observations on as-deposited sample showed loose packing and random distribution of the tinny spherical crystallites. After heat treatment (100^{0}C) crystalline nature becomes more and more clear with intercrystelline spacings reduced and grain structure improved significantly.

b) The optical properties

The optical sensitivity of the SnS (baked) thin film was tested in the wavelength range from 350 nm to 1000 nm and the absorption spectrum was analysed to determine the absorption coefficient (α), optical energy gap (E_g) and the nature of the optical transitions. The absorption coefficient is high (10^4 to 10^5 cm^{-1}) and optical gap for as-deposited sample is 1.32 eV. Absorption edge is sharp and the mode of transitions is of the direct type.

c) The electrical transport properties

The electrical conductivity and thermoelectric power measurements were made on the good quality samples. The conductivity measurements showed semiconducting nature of the sample. The room temperature electrical conductivity is of the order of 10^{-6} $(ohm.cm)^{-1}$. The conductivity activation energies ($E_{a\sigma}$) have been then determined using the following standard relation as

$$\sigma = \sigma_o \exp (-E_{a\sigma} / kT) . \quad \ldots (5.6)$$

The values of $E_{a\sigma}$ are 0.12eV and 0.71eV for low and high temperature regions. The sample showed p-type conduction as detected from the thermoelectric power measurements. The carrier concentration (p) and mobility (μ) were then calculated from theses studies. The order of carrier concentration is 10^{19} cm^{-3}. The temperature dependence of carrier concentration and mobility showed grain boundary limited scattering conduction mechanism associated with these films.

5.4 SnS Thin Film Electrode: A Photoelectrochemical (PEC) Cell Approach

A photoelectrochemical (PEC) cell was constructed with SnS as a photoelectrode and the various cell performance parameters were determined.

a) The electrical properties

The performance parameters viz. n_d, ϕ_B, V_{fb}, V_{oc}, I_{sc}, n_L, η %, ff %, R_s, R_{sh} etc were determined for the cell. The results show that the energy conversion efficiency depends mainly on I_{sc} and V_{oc}. Low value of I_{sc} is due to the high photoelectrode resistance. Similarly V_{oc} is also low and can be correlated to the small flat band potential, V_{fb} and built-in-potential, (ϕ_B).

b) The optical properties

The measurements on the photo response showed that the short circuit current varies slowly but almost linearly with the incident light intensity whereas open circuit voltage deviates from the linearity at high level of input illumination. The lighted ideality factor (n_L) was then calculated for the cell configuration.

The spectral response peaks around 900 nm and shows decay on both sides.

The speed response showed presence of defect states in the material.

5.5 Remarks

The present status of the tin sulphide as a photovoltaic material is not encouraging. It appears that the major reason is its material resistivity. The other reasons viz

1. thinness of the SnS layer.
2. absence of thorough pre and post deposition treatments.
3. electrolyte absorption and
4. reflection losses from the glass and film surfaces,

are also probable.