

**CHAPTER V**  
**SUMMARY & CONCLUSIONS**

## CHAPTER V

### SUMMARY AND CONCLUSIONS

5.1	General	80
5.2	Preparation and Growth Mechanism of $\text{As}_2\text{S}_3$ Thin Films	81
5.3	Physical Properties of $\text{As}_2\text{S}_3$ Samples	82
5.4	Electrical and Optical Properties of $\text{As}_2\text{S}_3$ Films	83
5.5	Structural and Microscopic Properties of $\text{As}_2\text{S}_3$ Samples	84
	References	85

## 5.1 General

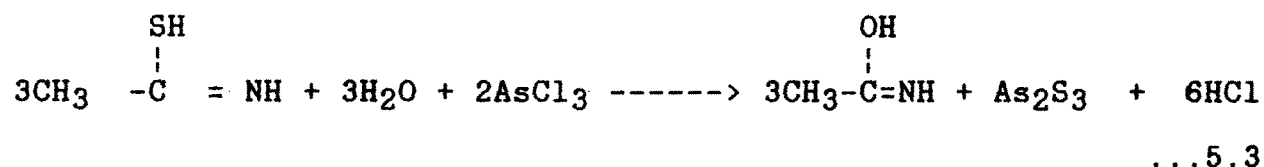
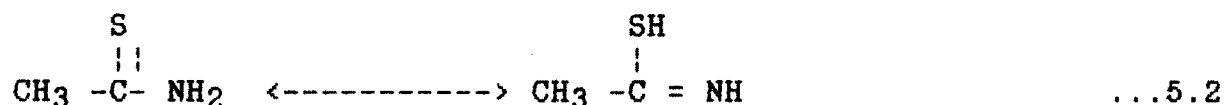
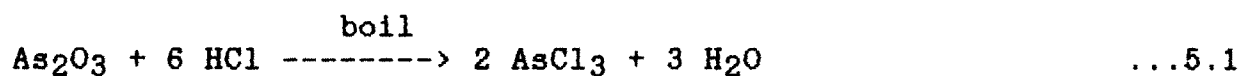
The range of thin film applications is so vast that it extends from micrometer dots in microelectronics to coatings of several square meter on window glasses. Their preparation methods and industrial utility are so enormous and common that we are hardly aware of the extent to which they have become part of our way of life. Polycrystalline thin films of metals, metal oxides and metal chalcogenides found wide spread utility in this respect (electronics, optical devices, solar cells etc.). Compounds like  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{Se}_3$  glasses have been widely used in IR optical devices because of their good transparency in the wavelength range from 0.7  $\mu\text{m}$  to 11.0  $\mu\text{m}$  and excellent resistance against devitrification, moisture and corrosive chemicals. III-V compound films, especially, InAs and InSb are used in galvanometric 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 bath deposition process is presently an attractive tool for the preparation of large area II-VI, IV-VI, III-V and V-VI compound thin films. A variety of substrates (metals, insulators, semiconductors etc.) can be used since the working temperature for this process is low. The preparative parameters are easily controllable and better orientation of the crystallites resulting into the improved grain structure can be obtained /1-5/. The arsenic trisulphide, a member of V-VI

group compounds, is a technically important class of materials. It has n-type electrical conduction, high optical absorbance and direct mode of transition with an energy gap of 2.4 eV. A relatively new method has been proposed and developed to prepare thin arsenic trisulphid films at relatively low temperature. 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. Essentially, it describes the V-VI compounds and a short survey of  $As_2S_3$  thin film material. Chapter II outlines the different thin film deposition methods. Further, it describes the chemical deposition method and detailed procedure for the preparation of  $As_2S_3$  thin film deposits, the mechanism and growth kinetics of film formation. In chapter III, the necessary designs, fabrications and experimental techniques for studying the electrical and optical properties of  $As_2S_3$  thin films are described. The structural and microscopic observations have been noted in chapter IV. The various steps under taken to carry out this work are as follows:

## **5.2 Preparation and Growth Mechanism of $As_2S_3$ Thin Films**

Thin film deposits of arsenic trisulphide were obtained onto the glass substrates using a solution growth mechanism in acidic bath/7,8/. The properly cleaned substrates (glass microslides) were attached to a specially designed substrate holder and were kept in the reaction mixture containing  $As^{+3}$ , and  $S^{2-}$  ions. The deposition was a slow process and carried out for a period of 96 hours to get thin uniform and adherent samples.

As the preparation is carried out in an acidic medium in the presence of a reducing agent, formation of As<sub>2</sub>S<sub>3</sub> films is made possible on the basis of slow release of As<sup>3+</sup> and S<sup>2-</sup> ions and their subsequent condensation on the substrates /1-8/. The film formation takes place by the reduction of arsenic ions using methanol as the reducing agent. The series of reactions proposed are/7,8/;



It is seen from the above reactions that the growth rate is controlled by the concentrations of As<sup>+3</sup> and S<sup>2-</sup> ions. The growth rate also depends on the bath temperature, pH of the reaction mixture, time for the deposition etc. The optimised conditions for the deposition As<sub>2</sub>S<sub>3</sub> thin films are :

- i) bath temperature = room temperature

ii) pH of the reaction mixture = 2.5

iii) time deposition = 96 hours

### 5.3 Physical Properties of As<sub>2</sub>S<sub>3</sub> Samples

The as - deposited As<sub>2</sub>S<sub>3</sub> films are pale yellow in colour and turns through dark yellow and finally faint - orange red above

200°C. The samples are extremely smooth, uniform, crackfree and adherent tightly to the substrates. The growth of As<sub>2</sub>S<sub>3</sub> thin film takes place by slow release of a As<sup>3+</sup> and S<sup>-2</sup> ions in a complex mixture that allows subsequent condensation and therefore better orientation of the crystallites is possible. Thus good quality deposition of As<sub>2</sub>S<sub>3</sub> thin films with less consumption of active materials and an electrical energy is made possible.

#### 5.4 Electrical and Optical Properties of As<sub>2</sub>S<sub>3</sub> Films

The electrical conductivity and thermoelectric power measurements were made on a good sample. The conductivity measurements showed semiconducting nature of the sample. The room temperature electrical conductivity is in the range of 10<sup>-8</sup> -10<sup>-9</sup> (ohm-cm)<sup>-1</sup>. The thermal energy gap (E<sub>gth</sub>) and conductivity activation energy (E<sub>aσ</sub>) have been determined following the standard relation as:

$$\sigma = \sigma_0 \exp (-E_{a\sigma}/kT) \quad \dots 5.4$$

The E<sub>gth</sub> and E<sub>aσ</sub> are, respectively, 1.66 eV and 0.83 eV. The sample showed n-type conduction as detected from the thermoelectric power measurements. Carrier concentration (n) and mobility (μ) have been calculated from these studies. The order of carrier concentration is 10<sup>17</sup> cm<sup>-3</sup>. The temperature dependence of n and μ showed grain boundary scattering mechanism associated with these films. Optical scanning was done in the 3000 Å to 8000 Å wavelength range. The absorption coefficient is high (10<sup>4</sup> cm<sup>-1</sup>) and optical band gap (determined from (αhν)<sup>2</sup> vs hν variation) for as-deposited sample is 2.35 eV. The samples baked at 200 and 250 °c show an increase in band gap (3.2 eV and

3.15 eV, respectively). Absorption edge for these samples becomes still sharp and the mode of transition in both the cases is of the direct type /6,8/.

### 5.5 Structural and Microscopic Properties of As<sub>2</sub>S<sub>3</sub> Samples

The structure and crystallinity of the As<sub>2</sub>S<sub>3</sub> sample (as - deposited and baked at different temperatures) were examined by XRD and SEM techniques. The X-ray diffraction studies showed the structure of the deposited films (both as - deposited + baked) consisting of monoclinic crystallites of AsS with a background of large number of microcrystallites of As<sub>2</sub>S<sub>3</sub>/7/. The structure remained more or less unaltered upto 200°C and become completely microcrystalline at higher temperatures. The grain size for AsS and As<sub>2</sub>S<sub>3</sub> phases have been determined using the Scherrer's relation;

$$\bar{D} = \frac{0.9 \lambda}{B \cos\theta} \quad \dots 5.5$$

where, symbols have their usual significance and typically they are 251.93 Å and 26 Å, respectively. The SEM observations as - deposited sample showed well defined grains of the spherical and pyramidal shapes with a very large number of small grained diffused crystallite background/7/. The grain sizes have also been computed and matched fairly with the XRD observations. The samples heat treated above 200°C, showed microcrystalline As<sub>2</sub>S<sub>3</sub>/7,8/.

## References

1. S.H.Pawar and L.P.Deshmukh, *Mat. Chem. Phys.* 10 (1984) 83.
2. L.P.Deshmukh, S.G. Holikatti, B.P. Rane, B.M.More, and P.P.Hankare, *J.Electrochem. Soc.*, Vol. 141. (1994) 1779.
3. L.P.Deshmukh, K.V.Zipre, B.P.Rane, A.B.Palwe, P.P.Hankare, and A.H.Manikshete, *Sol. Eng. Mat. & Sol. Cells.* 28 (1992) 249.
4. I.J. Kaur, D.K.Panday, and K.L.Chopra, *J. Electrochem. Soc.* 127 (1980) 943.
5. O.Savadogo and K.C.Mandal, *Sol. Eng. Mat. and Sol. Cells* 26 (1992) 117.
6. L.P.Deshmukh, S.G.Holikatti, B.P.Rane, and P.P.Hankare, *J. Bull. of Electrochem.* 9 (1993) 237.
7. L.P.Deshmukh, J.S.Dargad and C.B.Rotti, *Ind. J. Pure and Appl. Phys.* 33 (1995) 687.
8. L. P. Deshmukh, J. S. Dargad, C. B. Rotti, S. G. Holikatti, G. S. Shahane, K. M. Garadkar and P. P. Hankare, *Proc. Nat. Conf. on Thin Film Processing and Applications.* 23-24 Jan, 1995, S. V. University, Tirupati, AP (India) p.25.