



CHAPTER

II

## **CHAPTER II**

### **THE SYNTHESIS, GROWTH KINETICS AND PHYSICAL STUDIES ON SnS THIN FILMS**

2.1	Introduction	22
2.2	Experimental Details	23
2.2.1	The deposition system	23
	a) A dust proof chamber	23
	b) An oil bath and the temperature controller	23
	c) A reaction vessel	25
	d) A substrate holder	25
2.2.2	The substrates	25
	a) Preparation of the glass substrates	25
	b) Preparation of the stainless steel substrates	27
	c) Substrate cleaning	27
2.2.3	Synthesis of the SnS thin films	27
	a) Preparation of the solutions	27
	b) Preparation of the SnS thin films	28
2.3	Results and Discussion	29
2.3.1	The mechanism of the film formation and growth kinetics	29
	a) The mechanism of the film formation	29
	b) The growth kinetics	30
	i) The effect of deposition time	32
	ii) The effect of pH	32
	iii) The effect of deposition temperature	34
	iv) The effect of concentration	34
2.3.2	Physical observations on SnS thin films	35
	References	36

## 2.1 Introduction

The science and technology requires various types of thin films for a variety of applications / 1-5 /. The thin films can be single or multi component, alloy / compound or multilayered coatings on substrates of different shapes and sizes / 1-5 /. The required thin film properties can be depending on the applications such as high optical reflection / transmission, hardness, wear resistances, single crystal nature etc. Such a versatility in thin films can be brought about by the techniques of thin film deposition / 4,5 /.

Although thin films are of technologically great importance, their structure is complex in view of their applications, which demands tailor-made properties. Due to this, sophisticated techniques are required to characterise the films and to know about the multifarious properties. No one technique is sufficient to characterize a thin film completely in any one domain such as crystal structure, chemical and physical nature etc. Further the film properties are sensitively dependent on the deposition method and it is quite obvious that no one technique can deposit the film covering all the beneficial aspects (such as temperature, cost of the equipments, deposition conditions, preparative parameters and other selective properties of the thin films).

Thus taking the practical importance of the tin sulphide material into account and with the available laboratory facilities we have synthesized the SnS thin films by a solution growth process developed in our laboratory and set for its various physical conditions /6-8 /.Section 2.2 gives a brief idea of the deposition system and procedural part for the materials synthesis. The mechanism of film formation, growth kinetics

and few of the physical observations on the SnS thin films are outlined in section 2.3.

## **2.2 Experimental Details**

### **2.2.1 The deposition system**

Among the most widely used methods for deposition of II-VI, IV-VI, III-V and I-III,V materials, the solution growth process is relatively less expensive, simple and convenient technique by which a variety of substrates can be coated [6-13]. Here an usual chemical bath deposition method reported elsewhere is modified and attempted to make it more convenient, optimistic and an easily operatable deposition system. A photograph displaying the system is shown in fig. 2.1. The experimental set-up consists of a dust proof chamber, an oil bath with a temperature controller, a reaction vessel and a substrate holder.

#### **a) A dust proof chamber**

A metallic dust proof chamber of the dimension 180 cm x 80 cm x 100 cm was fabricated and used to avoid contamination of the samples from the dust particles. It provides a clean and contaminant free ambient necessary for the thin film deposition. An exhaust fan is fitted at the top of the chamber to remove the gases evolved during the film deposition.

#### **b) An oil bath and the temperature controller**

An oil bath with a constant temperature assembly supplied by the Modern Industrial Corporation, Bombay was used to achieve the desired deposition temperature. A 2 KW electric heater was used to heat the paraffin oil with an accuracy of  $\pm 0.5$  °C. A synchronous universal motor was used for continuous stirring of the oil to maintain the uniform temperature throughout the oil bath.

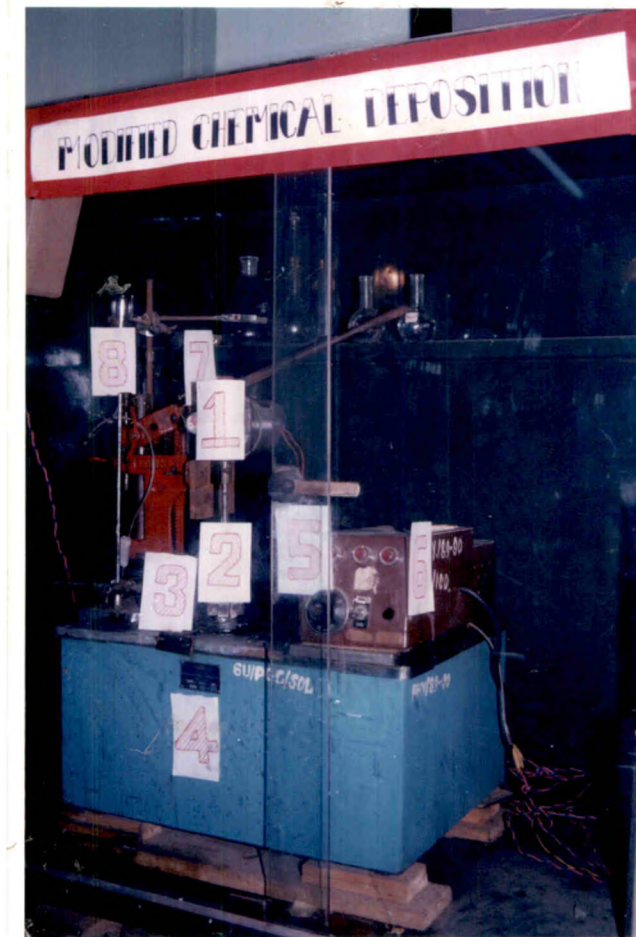


Fig.2.1 Photograph showing the essentials of a chemical deposition system.

1. Constant speed AC gear motor,
2. Substrate holder,
3. Reaction container,
4. Paraffin oil trough,
5. Temperature controlling assembly with sensor indicator,
6. Oil stirring motor
7. Drilling machine stand

**c) A reaction vessel**

It was a 250 ml glass beaker in which appropriate amounts of the solution were mixed together. The reaction vessel was adjusted in the oil bath by means of a suitable O-ring fabricated by us. The reaction mixture was then heated to a suitable deposition temperature.

**d) A substrate holder**

A substrate holder as shown in fig. 2.2 was used for positioning the substrates vertically into the reaction mixture. It was a circular bakelite disc slotted to fix the substrates in such a fashion that each of the substrates falls exactly perpendicular to the next. The continuous and proper bulk churning of the solution in the reaction vessel was made automatically that helps in depositing uniform films with better orientation of the crystallites / 6-8,13 /. This slotted circular bakelite disc was fitted to an universal constant speed gear motor. The motor was mounted on a drilling machine stand and the stand was modified in such a way that height of the motor can be properly adjusted. For our experimental purpose, we adjusted the position of the motor so as to dip more than 80% portion of the substrates into the reaction vessel.

**2.2.2 The Substrates**

The substrates used in various stages of this work were amorphous glasses (microslides) and stainless steel strips. The stainless steel substrates were used especially for photoelectrochemical application. The film properties were studied on the films deposited on the glass substrates.

**a) Preparation of the glass substrates**

The amorphous glass substrates of the dimension 72 mm x 25 mm x 2 mm (Blue Star, Mumbai) were finely cut into the desired substrate

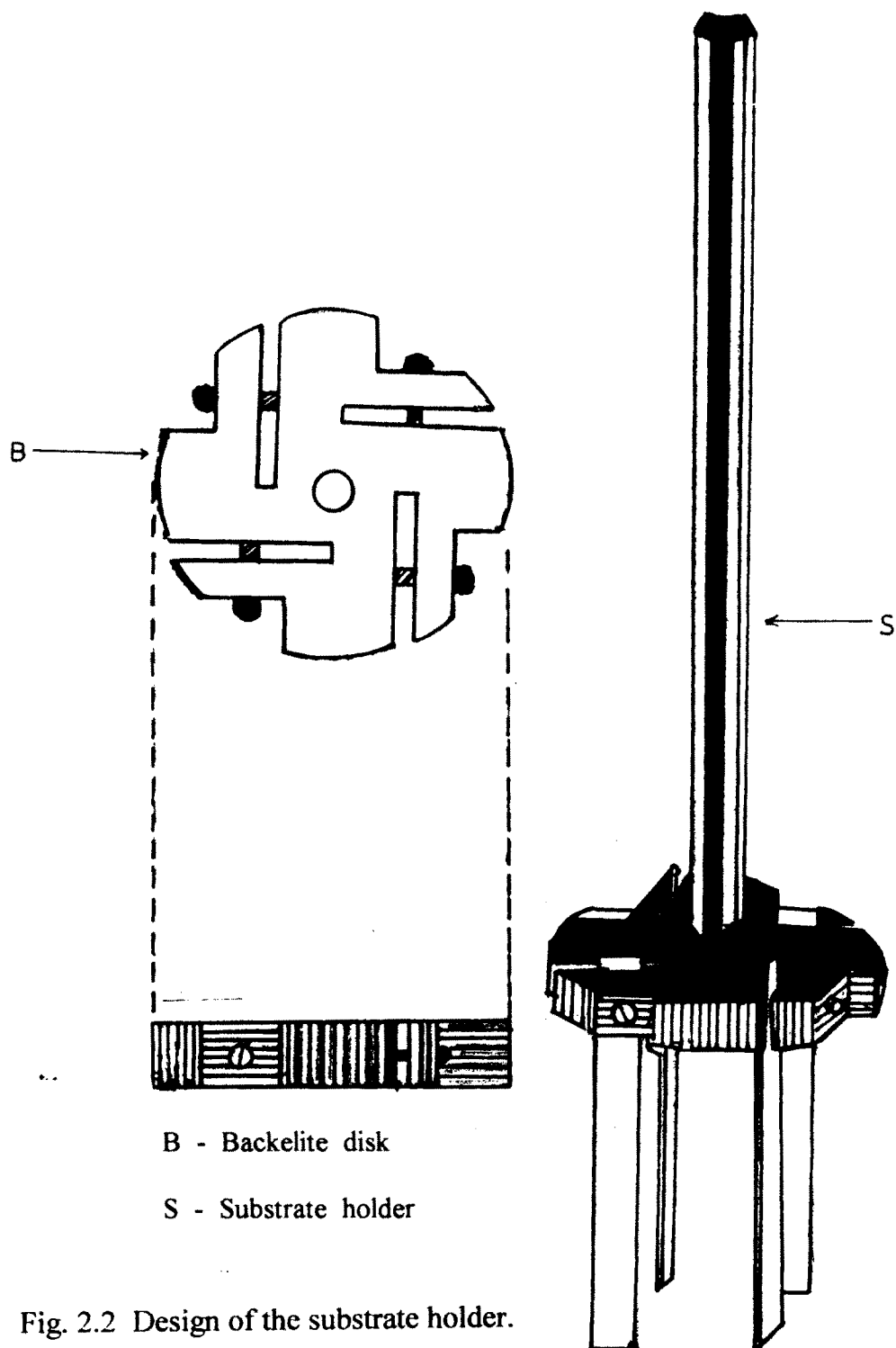


Fig. 2.2 Design of the substrate holder.

dimension (72 mm x 9 mm x 2 mm). These glass strips were utilized for deposition and further studies.

#### **b) Preparation of the stainless steel substrates**

A stainless steel sheet of the suitable gauge (24) was cut into strips of the size 75 mm x 9 mm x 24 gauge and were polished by using an emery cloth and a polishing paper (O-paper). These stainless steel substrates were then employed for the film deposition.

#### **c) Substrate cleaning**

The key precaution taken before deposition of the thin films is the careful cleaning of the substrates. As the film adherence depends on cleanliness of the substrate, following procedure was adopted for cleaning the substrates. The glass substrates were degreased in a chromic acid for about 24 hours and then boiled and washed several times with a double distilled water. They were further dipped into a medium concentrated detergent solution and washed with a double distilled water and then with an ultrasonic cleaner. All the substrates were kept under double distilled water before use. The stainless steel substrates were first degreased with a detergent solution and then polished (mirror smooth) on a sylvate emery cloth.

### **2.2.3 Synthesis of the SnS thin films**

#### **a) The preparation of the solutions**

The basic starting materials used for deposition of the SnS samples were essentially the AR grade and solutions were prepared in a double distilled water. The different chemicals used were:

1. AR grade stannous chloride, supplied by s.d. fine-chem Ltd., Boisar, Mumbai.



2. Acetone (A.R. grade ), supplied by s.d.fine-chem. Ltd; Boisar, Mumbai.
3. Triethanolamine ( A.R. grade), supplied by BDH, E-Merck, India Ltd.
4. AR grade thioacetamide, supplied by Central Drug House (P) Ltd., Mumbai.
5. AR grade ammonia, supplied by s.d. fine chem. Ltd., Boisar, Mumbai.

#### **b) Preparation of the SnS thin films**

The substrates used for deposition of the SnS samples were nonconducting glass microslides and stainless steel strips of the dimensions mentioned earlier. The procedure in detail for deposition of the samples is as under /6-8/:

To deposit the SnS samples, the host materials used were stannous chloride and thioacetamide. The supplementary materials were acetone, triethanolamine and ammonia. In actual, 2gm stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) was dissolved in a 10 ml acetone, which was then complexed with a 15 ml triethanolamine (TEA). The solution was then stirred rigorously. To this, 8ml 1M thioacetamide (TA) and 20ml, 14N ammonia were added so as to adjust the pH of the reaction mixture equal to  $10.5 \pm 0.1$ . The total volume of the reaction mixture was then made 200 ml by adding double distilled water and the beaker was then transferred to an oil bath whose temperature was controlled to  $70^\circ \text{C}$ . Thoroughly cleaned substrates were positioned vertically on a specially designed substrate holder as mentioned earlier and rotated in the reaction mixture with a  $72 \pm 2$  rpm speed. The deposition was allowed for 110 minutes and then the samples were detached from the substrate

holder and washed several times with a double distilled water. The samples were then preserved in a dark desiccator.

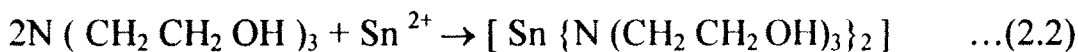
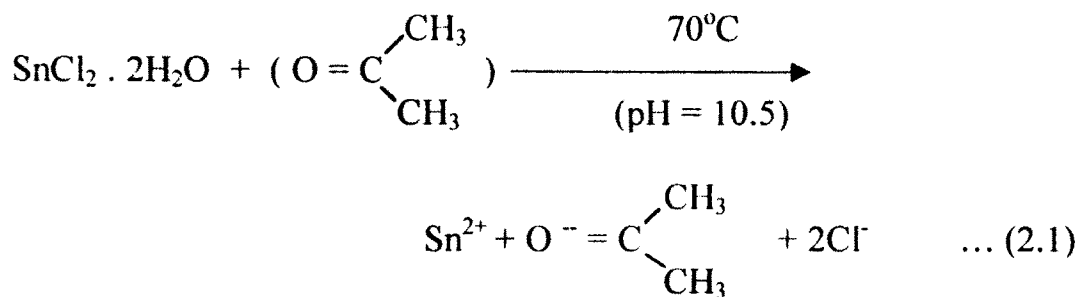
## **2.3 Results and Discussion**

### **2.3.1 The mechanism of the film formation and growth kinetics**

#### **a) The mechanism of the film formation**

In chemical bath deposition of the SnS thin films, the films are allowed to deposit on the glass substrates kept in an aqueous solution of the reactants. The preparation of the SnS thin films was therefore carried out in a basic medium under the presence of a complexing agent that allows the  $\text{Sn}^{2+}$  and  $\text{S}^{2-}$  ions to condense slowly on the substrate surface. Depending on the deposition conditions (viz temperature, pH of the solution, solution concentrations and their purity and quality of the substrates), the film growth can take place either by an ion-by-ion condensation of the materials particles on the substrates or by adsorption of the colloidal particles from the solution on the substrates /16-17/ The process of precipitation of the SnS from the solution onto the substrate depends on the formation of nucleus and the subsequent growth of the thin film. The concept of nucleation in solution is that the clusters of the molecules formed undergo rapid decomposition and the decomposed particles combine to grow up to a certain layer thickness of the film beyond which no further building up of thickness occurs /13-17/. The nucleation starts at some local inhomogeneity when ionic product exceeds the solubility product of a system. Growth of these nuclei by addition of the more and more ions from the solution results in formation of the stable nucleoid of the size greater than the critical size and further growth results in formation of the colloidal dispersion. Actually the film deposition was carried out at the optimized

conditions. Bath composition was 2 gram  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in 10 ml acetone + 15ml TEA + 8ml (1M) TA + 20ml ammonia. The reaction temperature was  $70^\circ\text{C}$  at a pH value of around 10.5. The time of deposition was 110 minutes. The  $\text{Sn}^{2+}$  and  $\text{S}^{2-}$  ions condense on the glass substrates to produce SnS. A series of the chemical reactions proposed for the film formation are / 6-8 /:



### b) The growth kinetics

The growth kinetics of SnS thin film could be understood in two steps : i) First, it initiates by an ion-by-ion condensation at the nucleation sites on the immersed surfaces. The ion-by-ion growth has been reported for PbSe, CdS, CdSe, PbS and HgS etc thin films / 6-12 /. ii) Secondly, nucleation takes place by adsorption of the colloidal particles and growth results by the surface coagulation of these

particles giving thin, uniform and adherent films. This is known as cluster-by-cluster growth of the films. The growth kinetics is a dependent function of various deposition conditions and parameters. In the case of alkaline baths, the growth kinetics is reported to be both by an ion-by-ion and cluster-by-cluster deposition of molecules under different deposition conditions / 6-12 /. An ion-by-ion growth results in thin, uniform, hard, adherent and specularly reflecting films whereas cluster-by-cluster growth gives less adherent, thick, powdery, flaky and diffusely reflecting films /6-12/. Once the nucleation occurs, the deposition rate rises rapidly and becomes almost zero resulting in a terminal thickness of a layer which is the maximum attainable thickness under given experimental conditions. For nucleation to start at a certain local inhomogeneity, certain time is required referred to as "incubation period". It was observed that when substrates are suspended in a container before forming the complex in the solution, film thickness increases in a manner similar to that of the pre-sensitized surface thereby showing that the nuclei for the formation of the film are provided by the solution itself / 9-12 /. The rate of deposition and terminal layer thickness both depend on the number of nucleating centers, supersaturation of the solution and stirring rate. The growth kinetics depends on the concentrations of the ions, their velocities and nucleation and various growth processes upon immersed substrates. The effect of various deposition conditions on these parameters is discussed below.

The deposition rate and thickness of the film depend on the pH of the reaction mixture, temperature of the reaction bath and the concentration of the chemicals used. The optimum conditions for getting thin

adherent, uniform and reproducible SnS thin films have been obtained by varying the concentrations of the starting materials, temperature of the deposition bath, time of the deposition etc. In our case, SnS film formation was carried out under the optimum conditions discussed in article 2.2.3.

#### **i) The effect of deposition time**

The time dependent growth rate was studied for the SnS films at 70<sup>0</sup> C. Fig 2.3 (a) shows its variation with the time. It has been seen that the variation of growth rate with time is initially almost linear and then it becomes quasilinear / 6-8 /. The growth rate (Measured in terms of layer thickness) is almost linear for shorter durations whereas a saturation in growth rate (thickness) has been observed at higher deposition times. This time dependent behaviour could be justified from the following facts. Initially at smaller deposition time the number of Sn<sup>2+</sup> and S<sup>2-</sup> ions, to be deposited on the substrate surface, is large and these ions have free access to condense on the substrate surface. As the time passes, the solution bulk becomes depleted of the Sn<sup>2+</sup> and S<sup>2-</sup> ions decreasing the further growth rate / 6-8 /. For further deposition time, the solution bulk still becomes depleted of the ions reducing growth rate to a practically zero value that causes thickness of the film to saturate / 6-8 /.

#### **ii) The effect of pH**

The addition of OH<sup>-</sup> i.e. increase in pH, makes the complex more stable provided the OH<sup>-</sup> ions take part in the complex formation. The metal ion concentration is reduced leading to a decrease in the deposition and increase in the terminal thickness with increasing pH

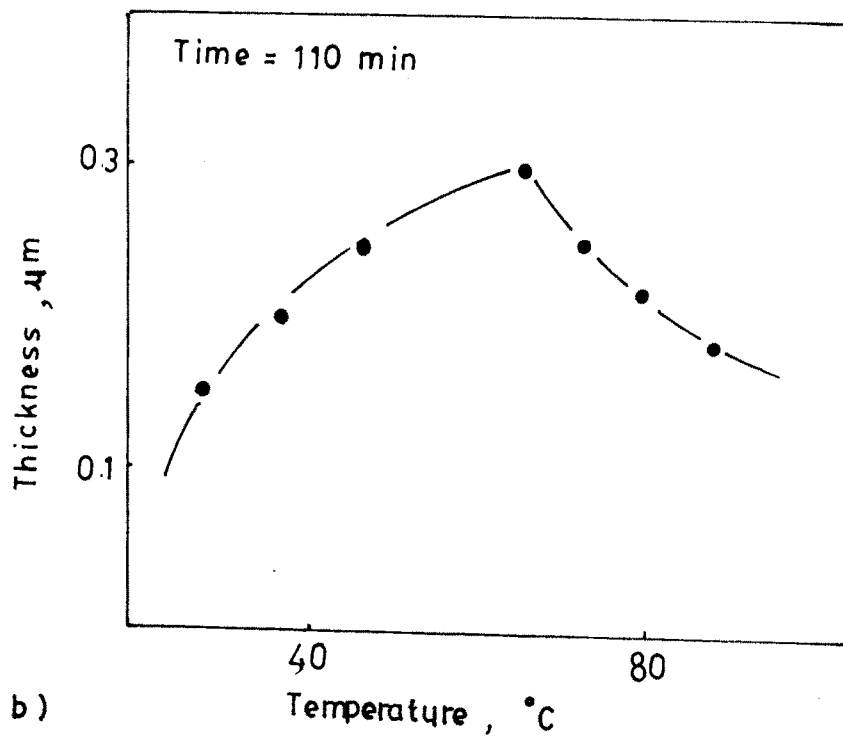
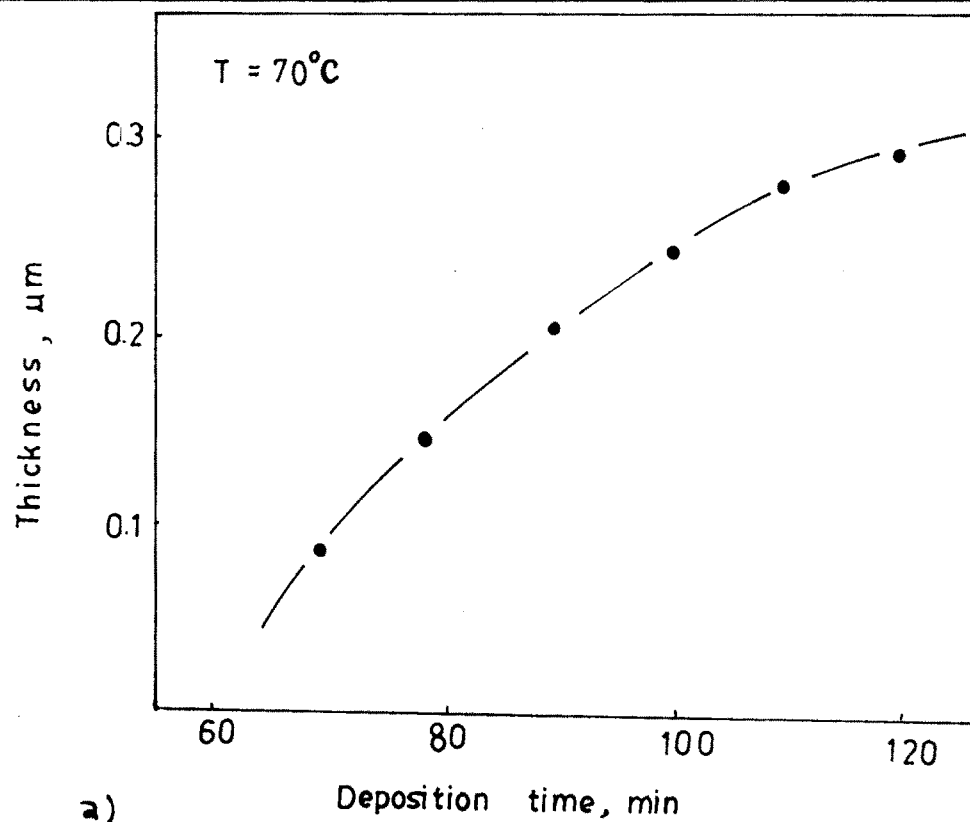


Fig. 2.3 Kinetics of the film growth:  
(a) film thickness vs time of deposition for SnS film,  
(b) terminal film thickness vs deposition temperature for SnS film.

value. In our case we increased the pH value from 8 to 11.5 and found that relatively better deposits are obtained around a pH value equal to 10.5 / 6-8, 11, 12, 16 /.

### **iii) The effect of deposition temperature**

The rate of deposition is found to depend on the bath temperature. The increase in temperature enhances the film formation process resulting into the grained structure / 14,15,17,18 /. The bath temperature was therefore varied from 40 °C to 90 °C. The variation in the film thickness with temperature is shown in fig. 2.3 (b).

The film thickness increased initially with rise in temperature and attains a maximum value at 70 °C and decreased thereafter at a faster rate. This temperature dependence of growth rate could be understood as: Initially an increase in temperature causes an increase in the rate of release of ions making them available for reaction to take place. At still higher temperature, more and more ions will be released causing a shift in the rate of reaction towards precipitation rather than the film formation. This causes layer thickness to decrease /18 /. In our case we have obtained practically smooth and uniform SnS films at 70 °C deposition temperature / 6-8 /.

### **iv) The effect of concentration**

The growth kinetics depends on the nature of the compounds used for the metal and chalcogenide ion sources. In general, growth rate and the terminal thickness are higher for the sulphides than for the corresponding selenides under similar conditions of the deposition. The deposition rate and the terminal layer thickness increase with increase in metal and chalcogen ions concentrations. In our case the quantity of  $\text{Sn}^{2+}$  and  $\text{S}^{2-}$  ions was increased from 0.25M to 2M. It was observed that

for 1M concentration of the reactants the films are uniform and adherent. At higher concentrations of both  $\text{SnCl}_2$  and TA, precipitation is more significant giving rise to a decrease in film thickness.

### **2.3.2 Physical observations on SnS thin films**

It is observed from the reaction mechanism and growth kinetics that the rate of film formation would increase with increasing the concentrations of chemical constituents. The as-deposited layers are thin ( $t \cong 0.3\mu\text{m}$ ), uniform, highly adherent and moderate reflecting with a pleasant brown chocolate colour / 6-8 /. The increase in deposition temperature changes the colour blackish and the deposits become less adherent and uniform / 6-8 /.



## References

1. K.L. Chopra and I. J. Kaur, in "Thin Film Device Applications", Plenum Press, N.Y., 1983.
2. K.. L. Chopra, in "Thin Film Phenomena", Mc. Graw Hill, N. Y. , 1969.
3. R.F. Bunshaw, in "Deposition Technologies For Thin Films and Coatings",(ed) R. F. Bunshaw, Noys Publications, N.J.,(1982).
4. V. D. Vankar in "Thin Film Technology and Applications", (eds) K.L. Chopra and L.K. Malhotra, T.M.H. Publishing Co. Ltd, India,(1984), p-14.
5. S. Mohan, in Proc. "Advanced Course on Thin Film Processing", Instrumentation and Services Unit, I.I. Sc. Banglore, India , (1994).
6. B. T. Raut, D. S. Sutrave, V.B. Patil, G. S. Shahane and L. P. Deshmukh, National Seminar on Recent Trends in Materials Science, Sri Venkateshwara University, Tirupati, India, 25-28 Nov,1999.
7. B. T. Raut, V.B. Patil, E. U. Masumdar, G. S. Shahane, and L. P. Deshmukh, "A Symposium on Fundamentals of Crystal Growth", Crystal Growth Center, Anna University, Chennai, India, 6-7 Nov. , 2000.
8. B. T. Raut, V.B. Patil , P. D.More, V. S. Karande and L. P. Deshmukh, Ind. J. Pure & Appl. Phys.(Commun).
9. C. V. Suryanarayana, A. S. Laxmanan, V. Subramanian and R. K. Kumar, Bull. Electrochem. 2 (1986) 57.
10. L. P. Deshmukh, A. B. Palve and V. S. Sawant, Solar Cells 28

- (1990) 1.
11. R.C. Kainthla, D. K. Pandya and K. L. Chopra, J. Electrochem. Soc. 127 (1980) 277.
  12. I. Kaur, D. K. Pandya and K. L. Chopra, J. Electrochem Soc. 127 (1980) 943.
  13. L. P. Deshmukh, K. V. Zipre, A. B. Palwe, B. P. Rane and A. H. Manikshete, Sol. Ener.Mat and Sol.cells 28 (1992) 249.
  14. L. P. Deshmukh and S. G. Holikatti, J. Phys. D: Appl. Phys. 27 (1994) 1786.
  15. R. N. Bhattacharya and P. Pramanik, J. Electrochem Soc. 129 (1982) 332.
  16. A. B. Lundin and G. A. Kitaev, Soviet J. Inorg. Chem.15 (1970).
  17. L. P. Deshmukh, S. G. Holikatti, and B. M. More, J. Electro. Soc. 141 (1994) 1779.
  18. A. R. Patil, V. N. Patil, P. N. Bhosale and L. P. Deshmukh, Mat. Chem. and Phys. 65 (2000) 266.