Bull. Mater. Sci., Vol. 3, Number 4, December 1981, pp. 403–408. © Printed in India.

New chemical methods for the deposition of $Cu_{1.8}S$ and TlSe thin film

R N BHATTACHARYA and P PRAMANIK
Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India

MS received 29 January 1981; revised 30 March 1981

Abstract. New chemical methods for the deposition of thin film of $Cu_{1.8}S$ and TlSe have been developed. The deposition of $Cu_{1.8}S$ thin film has been performed by thiourea, ammonia and Cu^{2+} ions at room temperature, while TlSe thin films are obtained from triethanolamine as complexing agent, ammonia, sodium selenosulphate solution and Tl^{1+} ions at room temperature. The electrical resistance, mobility, carrier concentration and optical band gap have been measured.

Keywords. Copper sulfide; thallium selenide; thin film; chemical deposition.

1. Introduction

Recently thin films have been the object of many scientific investigations because of their interesting properties and potentials for direct application. For example, metal chalcogenides are used for photoconducting cells, photovoltaic cells, and other electrical devices. The present paper has been confined to the preparation of thin films of $Cu_{1.8}S$ and TlSe by chemical methods. The superiority of chemical deposition technique over conventional methods lies in the advantage of having variety of substrates (insulators, semiconductors, and metals) for deposition, larger surface area, lower cost and ease of doping. Thiourea and selenourea are the commonly used compounds which furnish sulfide and selenide ions by hydrolysis in alkaline solution. In the present method, sodium selenosulphate and thiourea have been used for the purpose of generation of selenide ions and slow release of sulfide ions respectively.

The chemical methods of thin film formation of chalcogenides of Pb^{2+} (Bloem 1956; Acharya *et al* 1971), Bi^{3+} (Pramanik *et al* 1980), Tl^{2+} (Mary Juliana *et al* 1969), etc have already been published. But similar methods of deposition of thin films of copper chalcogenides have not yet been reported.

In the earlier work, Mary Juliana *et al* (1969) reported deposition of thin film of TlSe with sodium selenosulphate solution in the presence of sodium hydroxide and hydrazine. This paper presents a new chemical method for the deposition of TlSe thin film in presence of triethanolamine and ammonia.

2. Experimental details

2.1 *Preparation of $Cu_{1.8}S$ thin film*

2·4 g $CuSO_4$ is dissolved in 100 ml water to obtain $CuSO_4$ solution, and 7·6 gm thiourea to the same amount of water to obtain thiourea solution. 20 ml Cu^{2+}, 30 ml

ammonia and 20 ml water are taken in a beaker and stirred. 10 ml thiourea solution is added to it. Two cleaned glass slides are clamped vertically into the glass beaker containing the solution. When it is kept at room temperature (30°C) for about 2 hr, uniform films of $Cu_{1.8}S$ are obtained on the glass substrate. They are taken out, washed with water and dried in open air. The $Cu_{1.8}S$ films are found to be 0·05—0·1 microns thick. Film thickness has been measured by Fizeau method of interference fringes using sodium vapour lamp and from the difference in weight assuming that the density of the film is same as that of the bulk.

2.2 *Preparation of TlSe thin film*

A sodium selenosulphate solution is prepared by refluxing 5 g selenium powder with 12 g of sodium sulphite (anhydrous) in 200 ml water for about 10 hr. It is subsequently cooled for 10-12 hr, when a little selenium separates out from the solution. It is then filtered to obtain a clear solution. 3·2 g thallium sulphate is dissolved in 100 ml water to obtain a solution of thallium sulphate.

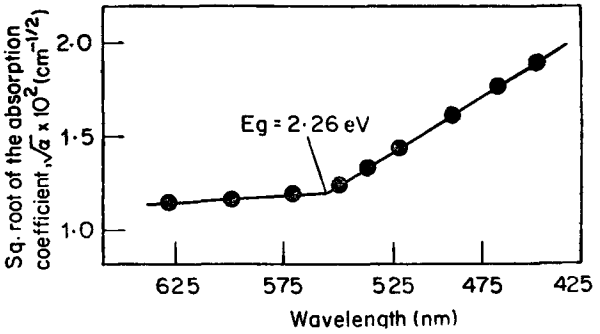


Figure 1. Square root of the absorption coefficient as a function of wavelength ($Cu_{1.8}S$).

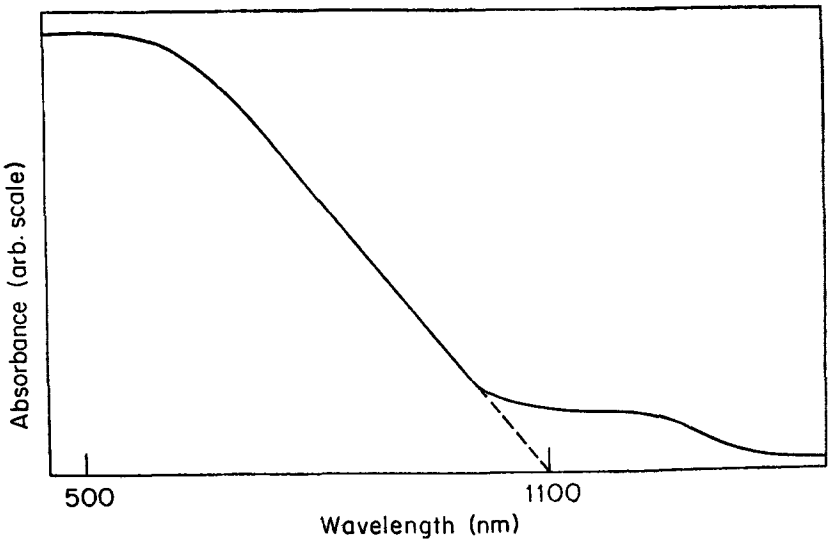
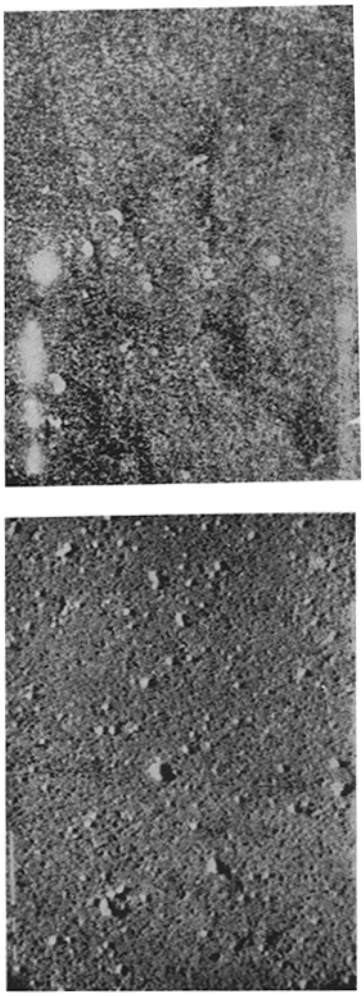


Figure 2. Electronic spectra of TlSe.



(a) (b)

Figure 3. Scanning electron micrograph of (a) $Cu_{1.8}S$ and (b) TlSe.

7 ml thallium solution is taken in a glass beaker, 9 ml triethanolamine and 50 ml 17 (N) NH_4OH are added to it and stirred. To this solution 7 ml sodium selenosulphate is added. Two cleaned glass slides are clamped vertically into the glass beaker containing the solution. When it is kept at room temperature (30°C) for about 15 min, uniform films of TlSe are obtained on the glass substrate. As in the previous experiment they are taken out, washed with water and dried in open air. The TlSe films are found to be 0·1-0·3 microns thick. Film thickness has been measured as in the previous experiment.

Thallium selenide films have been prepared using the following over-all reaction

$$Tl(A)^{1+} + SeSO_3^{2-} + 2OH^- + O_2 \rightarrow TlSe + nA + SO_4^{2-} + H_2O$$

where A is a complexing agent $N(CH_2CH_2OH)_3$.

3. Results

X-ray diffraction data for TlSe films show distinct *d*-lines. TlSe films are polycrystalline in nature, having tetragonal lattice with parameters *a*8·02 Å and *b*7·00 Å. Debye Scherrer photographic method is applied for the determination of d-spacings of copper sulfide thin films. Powder sample of copper sulphide is collected from a large number of thin films, more than a fifty, prepared by the chemical deposition method.

The conductivity, mobility and carrier concentration of the copper sulpfide and thallium selenide have been determined from the resistivity measurement and Hall effect, and are listed in table 1. Both the films are *p*-type conductors. In all electrical properties measurement silver is used as ohmic contact. The resistivity is measured by four-probe method and by electrometer amplifier (EA 815) (Serial 088, Electronics Corporation of India Limited). In Hall effect measurement Philips DC-Microvolt-meter (PP 9001) is used for voltage measurement. The current is passed through the sample by polytronic regulated power supply (Type PHY-22).

Assuming an indirect transition, the absorption coefficient can be expressed by the following equation (Mack Farlane and Roberts 1955)

$$\alpha = A\left[\frac{(h\nu - E_g + K\theta)^2}{(\exp \theta/T - 1)} + \frac{(h\nu - E_g - K\theta)^2}{1 - \exp(-\theta/T)}\right], \tag{1}$$

where E_g is the minimum energy gap, $K\theta$ the phonon energy.

Table 1.

Thin film	Conductivity (1/ohm-cm)	Mobility (cm^2/V. Sec.)	Carrier concentration (1/c.c)
$Cu_{1\cdot8}S$	4	0·58	$3\cdot57 \times 10^{20}$
TlSe	10^{-5}	0·25	$8\cdot5 \times 10^{19}$

To evaluate the band gap in $Cu_{1\cdot8}S$ at room temperature (30°C) the method used by Nakayama (1968) has been applied, where $\alpha^{1/2}$ versus $h\nu$ plot is given by two separate branches (figure 1) and from the cross point of these two lines the value of E_g is obtained. It is found to be 2·26 eV which is equivalent as Nakayama's finding. The band gap reported by Goswami and Rao (1974) of vacuum deposited $Cu_{1\cdot8}S$ thin film is 2·16 eV. The absorption measurement is done by Carry 17-D, spectrophotometer.

Optical band gap of TlSe, found to be 1·12 eV, is shown in figure 2. Mary Juliana *et al* (1969) reported the band gap and electrical resisitivity of TlSe thin film to be 0·8 eV and 2×10^{-3} ohm^{-1}. Scanning electron micrograph reveals distribution of small crystallites which is shown in figure 3. TlSe film is found to be polycrystalline nature, while x-ray diffraction data shows that $Cu_{1\cdot8}S$ films are amorphous in nature.

Acknowledgement

The authors are grateful to Prof. H N Acharya of the Physics Department for his assistance in this investigation.

References

Acharya H N and Bose H N 1971 *Phys. Status Solidi* **A6** K43
Bloem J 1956 *Appl. Sci. Res.* **B6** 92
Goswami A and Rao B V 1974 *Indian J. Pure Appl. Phys.* **12** 21 (1974)
MacFarlane G G and Roberts V 1955 *Phys. Rev.* **98** 1865 T. S. Moss: Optical Properties of Semiconductor
Mary Juliana Mangalam, Nagaraja Rao K, Rangarajan N, Siddiqui M I A and Suryanarayana C V 1969 *Jpn. J. Appl. Phys.* **8**
Nakayama N 1968 *J. Phys. Soc. Jpn.* **25** 290 (Eng.)
Pramanik P and Bhattacharya R N 1980 *J. Electrochemical Soc.* **127** 2087
Pramanik P, Bhattacharya R N and Mondal A 1980 *J. Electrochem. Soc.* **127** 1857