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ELECTRODEPOSITION OF SnS THIN FILMS FROM AQUEOUS MEDIUM

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Tin sulphide (SnS) films have been electrodeposited and the materials properties are reported. The potential-*p*H diagram of Sn and S in aqueous medium are superimposed to obtain the common immunity domains which predicts a *p*H value 1.5 and deposition potential of -1.0 V_{SCE} for the stoichiometric deposition. Films are cathodically deposited on SnO_2 coated conducting glass substrates at bath temperatures 303-353 K. XRD studies show the polycrystalline nature with orthorhombic structure. The optical band gap of the SnS film is 1.1 eV from the absorption studies. ESCA spectrum confirms the presence of Sn and S on the grey black sample. Uniform, smooth and pin hole free surface morphology is observed by SEM.

Keywords: Electrodeposition, cathodic deposition, tin sulphide, semiconductor thin film

INTRODUCTION

The systematic investigations have been made of IV-VI semiconducting layer type tin chalcogenides compounds in respect of optical and structural properties. Layer compounds are characterized by their anisotropic properties along different crystallographic directions. An interesting feature is that they crystallize as thin plates, a form suitable for the investigation of the optical and electrical properties. In chalcogenides, within each layer, the atoms are bound together by predominantly covalent forces. The bonds between the layers are extremely weak due to van der Waal's forces [1]. Photoelectrochemical cells have received much attention as an alternative to solid state for solar energy conversion [2]. The conversion of solar energy to the chemical form depends mainly on the physical and electrochemical properties of semiconductor materials. The chalcogenides of Sn is cheaply available and have band gaps in the region 1.0 to 1.2 eV, matching the highest intensity of the solar spectrum. Hence, studies are made with SnS and SnSe to use them in the PEC cells.

SnS has the orthorhombic structure. This structure, which is psuedo tetragonal, may be thought of as a rather strongly distorted sodium chloride structure. The crystal consists of double layers perpendicular to the c-axis in which the Sn and S atoms are tightly bound. The bonding between these layers is much weaker as shown by larger interatomic distances and by a (001) cleavage plane [3]. SnS is chosen which has great potential in solar energy conversion and in optoelectronic devices. Electron probe microanalysis and X-ray photoelectron spectroscopy of SnS was studied by Mishra et al [4]. The optical studies were performed by Nair and Nair [5]. SnS has been grown as thin films by chemical deposition [6]. The detailed report on photoelectrochemistry of layered semiconductors is given by Levy-Clement and Tenne [7]. Electrodeposition is more attractive to produce large area thin films and several experimental parameters can be controlled more precisely. Metal chalcogenides have been electrodeposited either by an anodic technique [8] or by the cathodic co- reduction of the metal and chalcogenide ions [9]. The compound semiconductor is electrosynthesized by either the chemical reaction of the chalcogen (X) with the metal adatoms (M) or by in situ precipitation of the metal ions with the electroreduced chalcogenide anions.

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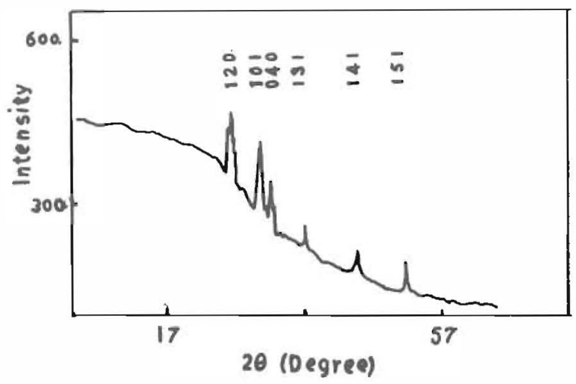

Fig. 1: X-ray diffractogram of SnS thin film

Preliminary results on SnS electrodeposition process has been discussed by Engelken et al [10]. We have carried out an elaborate study of the cathodic deposition mechanism of Sn, S and SnS. The film preparation and characterization are reported.

EXPERIMENTAL

The SnS films were deposited on tin oxide coated glass substrates with exposed area ranging between 0.5 and 2.5 cm^2. The electrodeposition bath considered of 5 mM of $SnCl_2$, 0.01 *M* of $Na_2S_2O_3$ and few drops of HCl. *p*H of the bath was kept at 1.5 Saturated Calomel Electrode (SCE) and platinum electrode were employed as the reference and counter electrodes respectively. The experiments were conducted at temperatures in the range of 303-353 K. The SnS films so formed were characterized by X-ray diffraction for structural analysis using JEOL JDX 803a X-ray diffractometer with CuK_α radiation (λ=1.5418Å).

A Cary-5E UV-VIS-NIR spectrophotometer was used to carry out the optical studies in the range 400-1500 nm for the determination of the optical band gap. A blank SnO_2 coated glass slide was used in the reference beam. The surface morphology was studied using the JSM 35CF JEOL reflection scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Initially, several attempts were made to select the composition of the electroplating bath to obtain p-type SnS films. The control of the chemistry in the bath was aimed at producing ultimate films containing tin and sulfur in a ratio reasonably close to unity. A Pourbaix diagram [11] has been used as a guide to fix the preliminary electrodeposition conditions particularly the *p*H of the electrolyte. For a single metal deposition the parameters like current density, electrode potential, concentration, *p*H of the solution etc can be easily optimized. However, the binary compound deposition is quite difficult because the conditions favourable for deposition of one of the metals may differ with that necessary for the other metals/constituents. The governing factors in the deposition of binary compounds are (i) electrode potential of individual ions of the electrolyte, (ii) cathodic polarization caused by difference in deposition potential and (iii) relative ion concentrations in the electrolyte.

The basic individual electrochemical reactions of Sn and S and their corresponding Nernst equation are given below.

$$Sn^{2+} + 2e^- \Leftrightarrow Sn(s)$$

$$E = E^0\,(\,Sn^{2+}/\,Sn \;+\; (RT\,/\,2F)\ \ln\ (a_{Sn^{2+}}/a_{Sn})$$
$$= -0.38\ V_{SCE} + 0.0295\ \ln\,(\,a_{Sn^{2+}}/a_{Sn})$$

$$(S_2O_3)^{2-} + 6H^+ + 4e^- \Leftrightarrow 2S(s) + 3H_2O$$

$$E = E^0\,(S^{2+}/S) + (RT/4F)\ \ln\,(a_{S_2O_3^{2-}}/a_s)$$
$$(3RT/6F)\ \ln\ OH^+ = +0.26\ V_{SCE} + 0.0148$$

Here, E^0 is the equilibrium electrode potential expressed with reference to SCE, 'a' are activities of ions in the bulk solution and the deposit (a = 1, for an ion in the solid deposit) and C_{H^+} is the concentration of hydrogen ions, Sn(s) and S(s) are the respective species in the deposition.

For simultaneous deposition of Sn and S, the concentration and *p*H of the electrolyte should be adjusted such that the electrode potentials of the individual deposits come closer to each other. This has been achieved by varying the potential linearly in the cathodic direction. Linear sweep voltammetry was performed from +0.5 V to -1.1 V using SnO_2 working electrode. Concentration of Sn^{2+} was varied in the range of 1 to 10 mM and that of $Na_2S_2O_3$ in the range of 5 to 50 mM. When the *p*H was 1.5, maximum reduction current was observed for a bath composition of 5 mM $SnCl_2$ and 10 mM of Na_2O_3. For higher molar concentration of these species in the bath, the reduction current becomes saturated without any further increase thereby showing this limiting

TABLE I: Comparison of d values with standard ASTM data

$d_{observed}$(Å)	d_{ASTM}(Å)	h	k	l
3.336	3.423	1	2	0
2.910	2.931	1	0	1
2.769	2.797	0	4	0
2.384	2.305	1	3	1
2.030	2.024	1	4	1
1.763	1.779	1	5	1

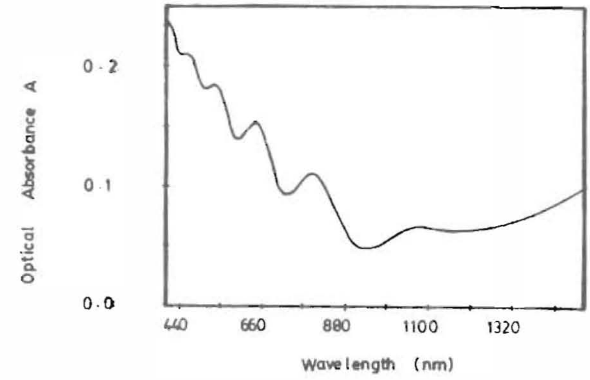

Fig. 2: Optical absorption spectrum of SnS thin film

concentrations of Sn^{2+} and S^{2-} ions as the optimum concentrations for deposition of SnS films in this study.

The X-ray diffraction pattern of the typical as-grown film is shown in Fig.1. The diffractogram indicates the polycrystalline nature of the film with all the major peaks corresponding to the orthorhombic structure. The lattice parameter values observed are a = 0.403 nm, b = 1.145 nm and c = 0.399 nm. They compare well with the reported values [4]. The calculated inter-planar spacing (d values) from these patterns were found to agree well with that ASTM data (Table I).

Fig. 2 shows typical optical absorbance vs wavelength obtained for the deposit on SnO_2 coated glass plates. The absorption edge is prominent around 750 nm. This optical data was analysed in terms of the express for near edge optical absorption α [12], in semiconductors

$$\alpha = k\,(h\nu - E_g)^{n/2}/h\nu$$

where k is a constant, E_g is the semiconductor band gap and n is a constant equal to 1 for a direct band gap material and 4 for an indirect band gap material. Fig. 3 shows the plot of $(\alpha h\nu)^{1/2})$ vs hv and yields a straight line. The extrapolation of linear part to x-axis gives a band gap of 1.1 eV and in agreement with the early reports value of 1.0 eV [4].

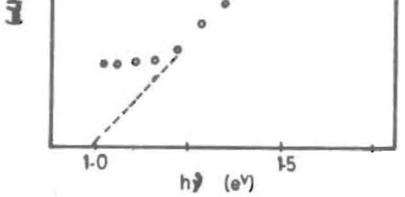

Fig. 3: Plot of $(\alpha h\nu)^{1/2}$ vs hν

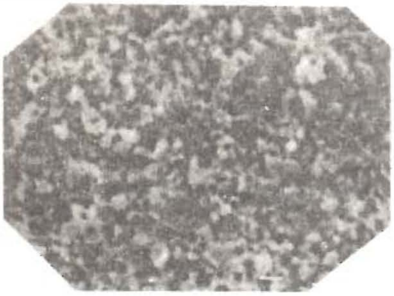

Fig. 4: Scanning electron micrograph of SnS thin film

Scanning electron microscopy is used in studying the microstructure of the film. The properties like thermal, electrical,magnetic and thermoelectric etc depend to a considerable extent on thin film microstructure and that microstructure has important aspects like porosity, number of phases, the size of constituent crystallites, the boundaries between them and texture. Surface morphology of SnS films deposited onto tin oxide coated glass substrates has been studied. Prior to SEM analysis, all the films were sputter-coated with a thin film of gold to enhanced their electrical conductivity. The deposits, in general were good .in appearance. The film is uniform and well adherent to the substrate. A careful inspection at a magnification of 5000X shows loose packing and random distribution of grains as shown in Fig. 4.

CONCLUSION

Electrodeposition of a compound semiconductor SnS exhibiting p- type conductivity confirmed by hot probe technique has been studied under potentiostatic condition in an aqueous bath containing $SnCl_2$, $N_2S_2O_3$ and few drops of HCl. A stoichiometric SnS was deposited at -1.0 V_{SCE} keeping the *p*H = 1.5 and bath temperature at 333 K. This film so obtained has a band gap of 1.1 eV and possess orthohombic structure.

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