**Preparation of nanocrystalline SnS thin film by silar**

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**ABSTRACT**

Nanocrystalline tin sulphide (SnS) thin films has been synthesized using successive ionic layer adsorption and reaction (SILAR) technique. The films are phase pure and polycrystalline with crystallite size approximately ranging between 8-11 nm. The crystallite size was measured using X-ray line broadening method. The variation of structural property with increasing thickness has been studied. Complete oxidation to tin oxide was found due to heat treatment at 400°C for one hour. The electrical characterization was carried out using conventional DC two-probe technique. An activation energy barrier value of 0.28 eV was observed, which can be associated with deep acceptor levels due to excess tin atoms.

**Key words:** Tin sulphide, nanocrystallin thin film, SILAR.

**INTRODUCTION**

The synthesis and characterization of tin sulphide via different techniques have attracted considerable attention due to their application prospects. This binary compound has potential applications in current controlled devices, sensor and laser devices, switching devices and photovoltaic devices. Particularly in thin film form the material is reported to be suitable for photovoltaic and photoelectrochemical devices. Like other metal chalcogenides, different physical and chemical techniques have been utilized to grow tin sulphide thin films. These include vapor transport, vacuum evaporation, chemical vapor deposition, chemical bath deposition, electrodeposition, electroless deposition, Chemical melt growth and spray pyrolysis. One of the relatively less used and less studied techniques is SILAR (Successive ionic layer adsorption and reaction) In SILAR technique thin films are obtained by immersing the substrate into separately placed cationic and anionic precursors. Although many workers have carried out deposition of CdS and ZnS by SILAR, that on tin sulphide (SnS) is almost nonexistent. Reports on characterization of SILAR deposited SnS, to the best of our knowledge are almost nonexistent barring first reported by Ristov et al. Sankapal et al. reported preparation of tin disulphide (SnS₂) by this technique.

The SILAR deposition of thin films from an aqueous solution is a very promising method because of its simplicity and economy. In this technique a substrate can be introduced into beakers containing cationic or anionic precursors for reaction at chosen temperatures. The substrate can be introduced into various beakers for a specific interval, withdrawn and reintroduced into another beaker for reaction. The immersion-reaction cycle can be repeated for any number of times. The different parameters that can affect the film growth process are the nature of the bath solution, concentration of the bath solution and its pH value, nature of the substrate and temperature of deposition. By proper optimisation of the deposition parameters, good quality film can be achieved. Since in SILAR technique, the deposition is carried out in
ambient air, the microstructure of the SILAR deposited films are expected to be different from sophisticated physical techniques where the deposition is carried out in vacuum. They are expected to have different properties from chemical techniques as well.

During the last few decades, there has been increasing interest in fabricating the oxide materials by different chemical methods since they are relatively low cost processes and can be easily transferred to industry. Conventional physical techniques generally produce good quality transparent films. However they are very expensive and are difficult to carry out in the industrial level. Different chemical techniques include spray pyrolysis, sol-gel, electro less deposition, chemical deposition etc. While spray pyrolysis has the disadvantage of non-uniform film deposition, sol-gel requires costly chemicals. Electro less deposition is characterized with films, which are mechanically poor. The aim of the present work is to promote interest in the SILAR method as applied to tin sulphide thin films. A solution of stannous chloride (SnCl₂, 2H₂O) was used as source of tin (Sn²⁺) ions and solution of sodium sulphide (Na₂S) was used as source of sulphur (S²⁻) ions. The studies include preparation of films under optimised conditions, the structural characterization of the film, stability against temperature and electrical characterization.

EXPERIMENTAL

Material and methods
Tin sulphide film was deposited on glass substrates (commercially available microscope slides) by alternate dipping in SnCl₂ and Na₂S baths. The temperature of SnCl₂ bath was varied between room temperature up to 80°C and the Na₂S bath was kept at room temperature. The glass substrate was cleaned, before deposition, by chromic acid followed by distilled water rinse and ultrasonic cleaning with acetone and alcohol. The cleaned substrate was tightly held in a holder so that only a requisite area for film deposition was exposed. Thus, the film deposition area could be easily varied by adjusting the holder arrangement. The film thickness was determined gravimetrically by measuring the change in weight of the substrate due to film deposition, the area of deposition and using the known density of SnS. Fig. 1 shows the schematic diagram of the deposition process for SnS thin film.

X-ray diffraction (XRD) with CuKα radiation (λ=1.5418 Å) was used for structural characterization and phase identification of the deposited SnS films in a Philips PW 1830 XRD-system. Scanning electron microscopy (SEM) was used to illustrate the formation of crystallites on the film surface.

![Schematic diagram for chemical deposition process for SnS deposition](image_url)
The electrical characterization of the deposited films was carried out in a closed quartz tube furnace by monitoring the variation of electrical resistance (R) as a function of temperature (T) using the conventional DC two-probe technique. The temperature was controlled using a temperature controller and the resistance values were measured using system electrometer (Keithley 6514). The range of temperature investigated was room temperature to 200°C with a control accuracy of (±)1°C. Approximately 20 mm long silver (Ag) contacts, separated by 5 mm, were made on SnS films (30 mm × 25 mm) for electrical measurements. The width of the electrodes was approximately 1 mm. The conducting silver paste was cured at 200°C for this purpose. The data were recorded during heating only and an uniform heating rate (~3°C/minute) was maintained during heating. Copper (Cu) wires were connected from the electrodes to the resistance-measuring instrument.

RESULTS AND DISCUSSIONS

Film deposition

The stannous chloride bath, used for deposition of SnS was prepared by adding SnCl₂ (Merck) in deionized water. Similarly sodium sulphide flakes (Merck) was added in deionized water to prepare the Na₂S bath. One of the problems with stannous chloride solution is that it does not dissolve completely. So during preparation of films, the SnCl₂ bath was continuously stirred using a magnetic stirrer. The solution of sodium sulphide was stable and no stirring was required.

The film deposition process consisted of the following steps: (i) dipping of the pre-cleaned substrate in the hot SnCl₂ which carries a thin layer of tin ion adhered to the surface of the substrate and (ii) introduction of the substrate into Na₂S bath kept at room temperature. The reaction between tin ions and sulpher ions leads to the formation of SnS. Thus one complete dipping cycle involves dipping the substrate into SnCl₂ bath, its withdrawal from the bath followed by dipping into the Na₂S bath. The dipping time in each bath was 2 seconds. The film thickness can be built up by increasing the number of dipping cycles and/or bath concentrations.

The deposition was carried out for SnCl₂ bath pH of approximately 3.0. This was found to be the optimised pH value for getting good adhesion. Decreasing or increasing of pH leads to nonadherent poor quality films that could be easily rubbed away. Efforts to increase the pH (in order to completely dissolve SnCl₂ in deionized water so that continuous stirring can be avoided) also result in extremely slow growth rate. The pH of Na₂S bath was approximately 10.0. The concentration of both the bath solutions was 0.1 M.

The film thickness increases slowly as the SnCl₂ bath temperature increases in the range 50°-80°C. However below 50°C, the growth rate is extremely slow and almost no film deposition occurs at room temperature. Above 80°C, the effective concentration of the SnCl₂ bath changes due to quick evaporation of water and therefore changing the effective bath concentration. Thus the temperature of SnCl₂ bath was optimized at 80°C.

It was observed in the present work that above 0.1 M concentrations of the baths, powder like precipitates appears on the film surface resulting in a poor quality film. For still higher concentrations (greater than 0.15 M), film detachment from the substrate surface took place and no layer could be deposited. Thus the concentration of the baths was fixed at 0.1 M. For lower concentrations the growth rate is very slow. It appears that for higher concentrations, nucleation process is affected possibly due to presence of higher amount of reactant (i.e. large number of ionic species) at the substrate-solution interface.

Upon dipping in sodium sulphide bath, a brown adherent precipitate of tin sulphide is thus formed on the substrate. A part of the SnS so formed on the substrate remains as a strongly adherent film and a part of it forms precipitate in the bath solutions. It is believed that Sn₂⁺ ions are adsorbed on the substrate when it is dipped in stannous chloride bath (cationic bath). Upon immersion into Na₂S bath, where S²⁻ ions (anions) are available, reaction between anionic and cationic species gives rise to formation of SnS.

A part of the SnS so formed was deposited onto the substrate as a strongly adherent film and
another part of it forms precipitate in the bath solutions. Thus the bath solution needs to be changed at regular intervals. After every ten (10) dipping, the bath solutions were changed. Thus, only the strongly adherent microcrystals remained on the surface. These crystals then served as nuclei for further growth during subsequent dipping. It was observed that when the number of dipping exceeds 50 (keeping the bath concentrations fixed at 0.1 M), powder like precipitates appears on the surface. Thus more than 50 dipping was not performed in the present work. It seems that it is preferable to change the bath solutions for even lower number of dipping. Possibly use of intermediate rinsing in deionized water after every dipping can improve film quality and can also promote higher thicknesses. Experiment in this direction is in progress.

The film thickness was measured gravimetrically\textsuperscript{24} by weighing the substrate before and after deposition in an electronic balance and taking the theoretical density of the material. Thus, if \( W_1 \) and \( W_2 \) be the weights of the substrate before and after film deposition in gm. \( A \) is the area of film deposition in cm\textsuperscript{2} and \( \rho \) be the theoretical density of, then the film thickness was evaluated as following:

\[
d = \frac{(W_2 - W_1)}{A \rho} \times 10^{-4} \mu m
\]

The film thickness was found to be approximately 0.35 mm for 30 dipping and approximately 0.6 mm for 50 dipping. This indicates linearity of growth rate up to 50 dipping above which film quality starts degrading.

Structural characterization

\fig{2: XRD patterns of (a) 15 dip SnS, (b) 30 dip SnS and (c) 50 dip SnS}
Fig. 2 shows the XRD patterns of the as-deposited films. The material was scanned in the range 20-40°. Figure 2(a) shows the XRD pattern for 15 dipping film, which shows no diffraction peaks. This might be due to nonuniform coverage of the film on the substrate or due to amorphous nature for such low dipping. Fig. 2(b) shows the XRD pattern for 30 dipping film, which corresponds to approximately 0.35 µm thickness. Fig. 2(c) on the other hand shows the XRD pattern for 50 dipping film corresponding to approximately 0.6 µm thickness.

The peaks at 26.62°, 30.94° and 31.62° are in good agreement with the Joint committee on powder diffraction standard (JCPDS) data belonging to orthorhombic SnS. The corresponding reflecting planes are (120), (101) and (111). The relative intensity of the peaks from (120) and (101) planes are 57 and 59 respectively for 30 dipping film and their intensity increases with increasing number of dipping.

The crystallite size was calculated by the X-ray line broadening method using the Scherrer formula [26]:

$$D = \frac{K \lambda}{\beta \cos \theta}$$

where \(\lambda\) is the wave length of radiation used (CuK\(\alpha\) in this case), \(k\) is the Scherrer constant, \(\beta\) is the full width at half maximum (FWHM) intensity of the diffraction peak for which the particle size is to be calculated, \(\theta\) is the diffraction angle of the concerned diffraction peak and \(D\) is the Crystallite dimension (or particle size). Assuming \(k = 0.89\), which corresponds to spherical crystallites, the average particle size calculated using Scherrer formula for 30 dipping film (i.e. ~0.35 µm thick film) is approximately 10.2 nm, whereas it is approximately 8.2 nm for 50 dipping film (i.e. ~0.5 µm thick film).

While calculating the particle size, the instrumental broadening was taken into account. The instrumental broadening (\(\beta_i\)) also contributes to the observed broadening (\(\beta_o\)). This arises from various factors such as non-parallelism of incident x-ray beam, presence of other wavelength apart from CuK\(\alpha\) etc. and it is a constant for a particular experimental setup. Thus the observed broadening is generally represented as \(\beta_o = \beta_i + \beta_s\), where \(\beta_s\) is the actual broadening arising solely from particle size. In other words, is the corrected line width at half-peak intensity. Diffraction data from silicon (Si) powder was used to measure the instrumental broadening. The broadening in this case is due to instrument and crystallite broadening is almost negligible. This value is then deducted from observed broadening to get the particle size broadening [26-27].

Fig. 3 (a) shows the XRD pattern of 0.35 µm thick SnS film heat treated at 200°C for 1 hour. Figure 3(b) shows the XRD pattern of the film heat treated at 300°C for 1 hour. The SnS peaks at 30.94° and 31.62° decreases in intensity and a peak at 33.84° appears indicating formation of SnO\(_2\). Heat treatment at 400°C for 1 hour results in complete conversion to SnO\(_2\). The peaks at 26.34° and 33.84° corresponding to reflections from (110) and (101) plane are in agreement for SnO\(_2\) [28].

It is seen from the XRD pattern that the SnO\(_2\) film is phase pure with (110) plane having maximum intensity as expected for a cassiterite crystal structure [27]. Thus the structure seems to be stable up to 200°C (although the effect of prolonged heating at this temperature was not checked) and thermal oxidation of the SnS layer in air at 400°C for one hour directly leads to the formation of SnO\(_2\).
Fig. 3: XRD patterns of (a) as-deposited SnS; (b) heat treated SnS (300°C, 1 hr.); (c) heat treated SnS (400°C, 1 hr.) leading to complete conversion to SnO₂

Fig. 4: Scanning electron micrograph of SnS film deposited on glass substrate
evidenced from SEM), the value is slightly higher than 0.89 and accordingly the crystallite size will be slightly higher than that we calculated.

**Electrical resistance vs. temperature for SnS thin film**

The dark electrical resistance measurement was carried out in the temperature range room temperature to 200°C using the DC two-point probe method. Fig. 5 shows the variation of resistance with temperature. Resistance in kilo-ohms is plotted against temperature in °C. It is observed that resistance decreases with increasing temperature, suggesting the semiconducting behavior of SnS film.

The activation energy was determined by sing the equation

\[ R = R_0 e^{E_a/kT} \]

where \( R \) is the resistance at temperature \( T \), \( R_0 \) is a constant, \( E_a \) is the activation energy and \( k \) is the Boltzmann constant.

The activation energy value for the present SnS film is 0.28 eV. Lokhande\(^29\) has reported the activation energy of SnS\(_2\) to be 2.18 eV. For SnS, Pramanik et al. [30] reported a value of 0.74 eV. Lopez et al. reported an activation energy value of 0.54 eV for SnS and associated the value with deep acceptor states arising from excess tin atoms\(^18\). Engeken et al. obtained an activation energy value of 0.3 eV, which is associated with deep acceptor levels due to excess tin atoms\(^6\). Ortiz \textit{et al.},\(^31\) reported a value of 0.30-0.31 eV for plasma-CVD deposited SnS thin films and attributed the value to existence of excess tin atoms over the incorporated sulphur. Thus the observed value of 0.28 eV for our sample also matches well with those reported\(^8,31\). Such differences in activation energies may be due to varying preparative parameters giving rise to variation of the relative chemical composition and the crystallography of the films. The variation of relative chemical composition introduces defect states to different extent.

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