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Electrodeposited SnS film for photovoltaic applications

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ABSTRACT

SnS film has been produced by electrodeposition technique onto ITO (indium-tin-oxide) coated glass substrates using aqueous solution containing $SnCl_2$ and $Na_2S_2O_3$. The pH of the solution was adjusted to 1.8 by drop-wise addition of 0.1 M HCl before the deposition. The SnS films were electrodeposited at constant potential value (−1.0 V relative to the saturated calomel electrode) in this study. The electrodeposition was carried out at 20 °C under constant stirring at 60 rpm in the bath. The deposition time was 30 min. The deposited film was uniform, well adherent and dark brown in colour. The SnS film has been characterized by X-ray diffraction (XRD) and Fourier transform infrared (FTIR). The sample is polycrystalline in nature with orthorhombic phase having (101) and (040) preferential orientations. The crystallite size, texture coefficient, lattice parameters, strain and dislocation density were estimated from XRD results. Surface morphological studies were carried out by using Field Emission Scanning Electron Microscopy (FESEM). The band gap of the SnS film has been studied using the optical absorbance measurement as a function of wavelength between 200 and 3000 nm. The direct band gap of the sample is calculated to be 1.1 eV. The conductivity type of the sample was determined as p-type by using the Hall effect measurement. The Hall mobility of the sample had also been measured with temperature by means of the Hall effect.

1. Introduction

Tin sulfide films, as one of the important IV–VI group semiconductors, have attracted considerable attention in recent years as low-toxicity and cost-effective materials for use in solid state device fabrication like photoconductors [1], photovoltaic conversion [2–5], holographic recording media [6], solar control device [7], near-infrared detector [8] etc. SnS is a layered semiconductor compound. In layered type chalcogenides, within each layer, the atoms are predominantly bound together by covalent forces. The bonds between the layers are weak due to the Van der Waals forces [9]. SnS has an orthorhombic-herzenbergite structure which is pseudotetragonal and may be thought of as a rather strongly distorted sodium chloride structure [10]. SnS shows a direct optical band gap between 1 and 2 eV with a high absorption coefficient at above the fundamental absorption edge depending on preparation techniques [11,12]. SnS films usually exhibit a p-type conduction and its electrical properties can be controlled by adding dopants like Al, Cu, Ag, N and Cl [13,14]. The narrow band gap and the interesting structural property of SnS make it a potential candidate for solar absorbers in thin film solar cells and near-infrared detectors as photovoltaic materials and other optoelectronic devices like holographic recording system [15]. Thus, preparing SnS films with different preparation techniques is of great importance for obtaining variation in bandgaps and also for the understanding of the dependence of absorption coefficient on photon energy [12].

SnS films have been produced by various techniques such as pulse electrodeposition [16], spray pyrolysis [17], rf sputtering [18], vacuum evaporation [19], chemical vapour deposition [20], chemical bath deposition (CBD) [15,21], cathodic electrodeposition [14] electrochemical deposition [22], thermal evaporation [23], hydrothermal method [24], solvothermal method [25], SILAR method [12] and electrodeposition method [26].

A variety of electrodeposition techniques, either single or in combination with others (i.e., direct current, pulsed current, direct plus pulsed current, electrodeless deposition, etc.), have been reported to produce better quality materials, but they have mainly been applied to the electrodeposition of metals [27] as well as binary [28], ternary [29], and even quaternary compounds [30] if the correct deposition bath and conditions are developed [31,32]. Electrochemical deposition (ECD) is one of the simplest chemical methods which produces films of good quality for device applications. In recent years, it has been used as an important tool for solar cell fabrication. ECD is a low-cost, large scale production, low material wastage, and easily expandable deposition technique with

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the possibility of using lower grade materials occurring at ambient pressure. ECD method offers excellent control over the properties of semiconductor films with the variation of process parameters, such as composition of the electrolytes, bath temperature, pH of the plating bath and deposition rate by current or potential bias [33]. On the other hand, one important disadvantage of ECD is that it requires conductive substrates. Overall, ECD seems to be an advantage method to deposit various semiconducting compound and alloy films including SnS alloys for solar cells [33–38].

In this present work, SnS film was prepared by using the electrodeposition method. A cyclic voltammetry (CV) was used to investigate the electrodeposition mechanism of SnS film. The crystallographic, Fourier transform infrared (FTIR) spectroscopic, surface morphological, optical and electrical properties of SnS film have been studied.

2. Experimental

SnS films were deposited onto indium-tin-oxide (ITO) coated conducting glass substrates ($15 \times 13 \times 1$ mm^3) by the electrodeposition method. The glass substrates were immersed in boiling water with detergent, and then cleaned using isopropyl alcohol and acetone in the ultrasonic bath, rinsed in distilled water at each step and finally dried in air before deposition. The deposition bath contained 50 ml of 0.03 M $SnCl_2.2H_2O$ and 0.1 M $Na_2S_2O_3.5H_2O$. The pH of the solution was adjusted to 1.8 by drop-wise addition of 0.1 M HCl before the deposition. Three-electrode cell, where a saturated calomel electrode (SCE) was used as a reference electrode, a spiral platinum wire as the counter electrode (anode) and an ITO coated glass substrate as the working electrode (cathode) was used in the ECD experiments. Electrochemical studies were performed by using a CHI 440B Model Potensiostat/Galvanostat. The SnS films were electrodeposited at constant potential value (−1.0 V relative to the SCE) in this study. This potential value was selected from the cyclic voltammetric (CV) results. Before the electrodeposition process N_2 gas was bubbled through the bath for 10 min to purge away the dissolved oxygen. The electrodeposition was carried out at 20 °C under constant stirring in the bath. The SnS deposition area was about 2 cm^2. The deposition time was 30 min. Following the deposition, the deposited SnS film was immersed in pure water to remove some unwanted particles, and dried in air at room temperature.

The reaction scheme for the formation of the SnS on a cathodic surface is represented by two equations as follows:

$$S_2O^{2-}_{3(aq)} + 2H^+_{(aq)} \rightarrow S_{(s)} + SO_{2(g)} + H_2O_{(l)} \quad (1)$$

$$Sn^{2+}_{(aq)} + S_{(s)} + 2e^- \rightarrow SnS_{(s)} \quad (2)$$

The first equation is representing the well known decomposition of thiosulfate in acid solution giving rise to elemental sulphur and sulphur dioxide. The decomposition of thiosulfate in acid solution is a classical example of a disproportionation reaction which is a specific type of redox reaction in which the same species is simultaneously reduced and oxidized to form two different products. In our case the two sulphur ions of starting thiosulfate having a (2+) chemical state give rise, as products of the disproportionation reaction, to one atom of elemental sulphur, having zero as chemical state, and one sulphur ion of the sulphurous acid having a (4+) chemical state, thus perfectly balancing the electron exchange between the sulphur species.

Although the second reaction does not clearly indicate which species is reduced to allow SnS precipitation, but we suppose that the reduction of Sn^{2+} is favourable at the cathode to form $Sn_{(s)}$ and then $SnS_{(s)}$ formation on the surface [22,39]. This is because of the fact that it is the continuation of the electrical current. Indeed this would be the case since "S" is not necessary for the continuation equation.

The thickness of the SnS film was determined to be about 1 μm by the weight difference method assuming the sample is uniform and dense as that of the bulk having a density of 5.1 g cm^{-3}. The structural characterization of the films was performed by a Bruker D8 Advance X-ray diffractometer (XRD) system using Cu Kα radiation (1.5406Å) with a scanning rate of 2°min^{-1}. The operating voltage and the current used for the XRD study are 40 kV and 30 mA, respectively. Field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX) analysis were carried out using a Zeiss Ultra Plus field emission scanning electron microscope with a magnification of 100*kx* and with an operating voltage of 15 kV. The optical band gap of the film was evaluated by means of the absorption data recorded using Shimadzu Solid Spec-3700 DUV spectrophotometer in the wavelength range 200–3000 nm with an unpolarized incident light perpendicular to the surface of the film. A rectangular-shaped sample (15×13 mm^2) having Van der Pauw geometry with 2×2 mm^2 square-shaped gold electrodes on top was used for Hall effect measurements as shown in Fig. 1 [40–42]. For the measurement of the sheet resistance of the sample, a constant current was fed into the adjacent electrodes (A–C) and potential difference was measured across between the other adjacent electrodes (B–D). This is repeated four times by changing the electrodes. For the measurement of the Hall voltage, a constant current was fed into the diagonal electrodes (A–D) and the potential difference was measured across between the other diagonal electrodes (B–C). This is repeated two times by changing the electrodes. These measurements were performed in a cryogen-free superconducting magnet system (Cryogenics Ltd.) using a conventional DC technique in combination with a constant current–voltage source Keithley 2400, switch system Keithley 7100, nanovoltmeter Keithley 182 A and temperature controller Lakeshore 340. The current flow was in a plane. A static magnetic field ($B = 1$ T) was applied to the sample normal to the plane. The sheet resistance (R_s) along the applied current and the Hall resistance (R_H) were measured as a function of temperature from 2 to 275 K. The voltage applied to the sample was kept low enough to avoid heating of the sample as well as to ensure the ohmic conduction. All of the measurements were carried out in dark.

3. Results and discussion

The electrochemical behaviour of 0.03 M $SnCl_2.2H_2O$ was investigated in aqueous solution of 0.1 M NaCl using potential cycling between 0 and −1.1 V (relative to the SCE) at a scan rate of 50 mV/s as shown in Fig. 2(a). In the forward scan, the cathodic current remains approximately constant up to a potential value

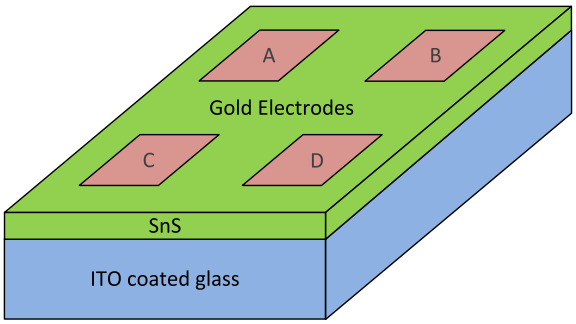

Fig. 1. Schematic diagram of a Van der Pauw geometry used in Hall effect measurements.