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Effect of tri-sodium citrate concentration on structural, optical and electrical properties of chemically deposited tin sulfide films

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ABSTRACT

Tin sulfide thin films were deposited onto glass substrates by chemical bath deposition. The effects of molar concentration of the complexing agent, tri-sodium citrate, on the structural, morphological, optical and electrical properties of the films were investigated. The films are characterized by X-ray diffraction, scanning electron microscopy, atomic force microscopy, optical absorption spectroscopy and Hall effect measurements. Polycrystalline film structure in orthorhombic phase was determined. Flower-like spherical grains are observed on the surface. While their average size increased from 345 nm to 750 nm when the tri-sodium citrate concentration was increased from 6.4×10^{-3} M to 8.0×10^{-3} M, the surface roughness varied in an opposite manner from approximately 120.18 nm to 29.36 nm. For these concentrations, optical band gap of the films decreased from 1.40 eV to 1.17 eV, whereas the Hall conductivity, mobility and carrier concentration of the films increased slightly from 5.91×10^{-5} to 8.78×10^{-5} $(\Omega\,\mathrm{cm})^{-1}$, from 148 to 228 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and from 1.73×10^{12} to 3.59×10^{12} $\mathrm{cm^{-1}}$, respectively.

1. Introduction

In recent years, semiconductor tin sulfide (SnS) films have attracted considerable attention because of their numerous advantageous properties. For instance, SnS thin films possess large optical absorption coefficient of $\alpha > 10^4$ $\mathrm{cm^{-1}}$ [1]; a direct energy band gap changing between 1.10 eV [2] and 2.35 eV [3], which are suitable for photovoltaic applications; its constituent elements are abundant in nature and do not give rise to any health and environmental hazards compared to similar materials [4] such as lead and cadmium compounds. The photoelectric conversion efficiency of the solar cell fabricated with Cu_2ZnSnS_4 was measured as 3.14% [5]. These properties facilitate their incorporation in applications, such as absorber layers in thin film solar cells [6], near infra red detectors [7], holographic recording systems [8], anode material in lithium ion batteries [9] and optical sensors [10].

SnS thin films have been produced by various techniques, such as spray pyrolysis [11], sputtering [12], vacuum evaporation [13], successive ionic layer adsorption and reaction (SILAR) [14], solvothermal [15] and chemical bath deposition (CBD) [16]. CBD method is a well-known prevalent low temperature aqueous method for directly depositing large-area thin films of semiconductors. It requires no sophisticated instruments, such as vacuum systems, while the starting chemicals are commonly available and inexpensive. Moreover, the preparative parameters are easily controlled.

In the production of SnS thin films, use of an appropriate complexing agent (i.e. tri-sodium citrate, TSC) is crucial. The effects of triethanolamine (TEA) as the complexing agent and tin salt concentration in the bath on the growth of SnS films by CBD were reported by Jayasree et al. [17]. Hankare et al. [18] deposited SnS films by CBD using tartaric acid. Mnari et al. [19] produced Sn_xS_y thin films using tri-sodium citrate by CBD and characterized crystallography, morphology, and chemical properties of the obtained films. Salavati-Niasaria et al. [20] prepared SnS with different nanostructure forms including nanoparticles, nanosheets and nanoflowers via a simple hydrothermal reaction using thioglycolic acid. Jayasree et al. [21] grown SnS films using ethylene diamine tetra-acetic acid (EDTA). SnS microflowers were synthesized with numerous nanoplates by using L-cysteine as the sulfur source and complexing agent by Cai et al. [15]. Although there have been a number of studies on the growth mechanism, as well as morphological and structural properties, reports on influence of the complexing agent on optical parameters (band gap, refractive index, extinction

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coefficient real and imaginary dielectric constants) and electrical properties (conductivity, carrier concentration and mobility) to date are limited.

In this work, structural, morphological, optical and electrical properties of SnS thin films grown by the CBD method using three different TSC concentrations of 6.4×10^{-3} M, 7.2×10^{-3} M and 8.0×10^{-3} M are investigated. In addition, suitability of the grown films as absorber layers for use in photovoltaic solar cell applications is discussed.

2. Experimental details

SnS thin films were deposited on glass substrates ($76 \times 26 \times 1\ mm^3$) by the CBD method. Deposition of the films initiates from the following precursor solution: 0.5 g of $SnCl_2 \cdot H_2O$ dissolved in 2.5 ml of acetone, which is then mixed in 6 ml of 3.7 M of triethanolamine [$(HOCH_2CH_2)_3N$]. After that, the non-toxic complexing agent tri-sodium citrate ($C_6H_5Na_3O_7$) was used in three different concentrations as 6.4×10^{-3} M, 7.2×10^{-3} M and 8.0×10^{-3} M. Then, 4 ml 1 M of thioacetamide (CH_3CSNH_2) and 5 ml 4 M of ammonia (NH_3) were added such that the total solution volume was completed to 50 ml by adding de-ionized water. The films were obtained at room temperature (30 °C) after 24 h. Following deposition, the SnS films were washed with de-ionized water and dried in air. The obtained films were homogeneous, and their colors changed from light to dark grey with increasing TSC concentration.

For the X-ray powder diffraction experiments, a 'Rigaku RadB' diffractometer with Cu Kα radiation (λ = 0.154 049 nm) was used at a scanning speed of 0.02° s^{-1} in 2θ ranging from 10° to 60°. The morphology of the films was characterized by using an EVO40-LEO scanning electron microscope (SEM) at a magnification of 30 000× under an operating voltage of 20 kV. The film thickness, roughness and section analysis of the samples were performed using a VEECO Multimode 8 model atomic force microscope (AFM). Transmission and absorption measurements were carried out with a 'Perkin Elmer Lambda 2S' UV–vis spectrophotometer in the 400–1100 nm wavelength region using a non-coated glass as the reference beam. Hall measurements were performed in a HS-3000 Manual Ver 3.5 system, using Van der Pauw geometry, at a constant magnetic field of 0.54 T. In order to reduce the errors in the calculations, especially for the electrical studies, the sample geometry was fixed to a symmetrical square shape ($10 \times 10\ mm^2$). Indium contacts have been introduced on film surfaces in order to carry out Hall measurements.

3. Results and discussion

The effect of TSC concentration on the structure of SnS thin films was investigated by means of XRD. Fig. 1(a), (c) and (e) shows the XRD patterns of SnS thin films deposited for three different TSC concentrations in the reaction bath. All films exhibit only one peak corresponding to the (1 1 1) plane of SnS with orthorhombic lattice structure. A broad hump between $20^\circ \leq 2\theta \leq 40^\circ$ of which is due to the amorphous glass substrate. Table 1 shows that the observed XRD data is in good agreement with standard data (PDF no. 33-1375) for SnS film and with the data reported by Subramanian et al. [22] and Ghosh et al. [23,24]. The Miller indices ($h\,k\,l$), the observed and calculated interplanar spacing (d), the Bragg angles (2θ) and the lattice parameters (a, b and c) of the diffraction lines compared with standard values are listed in Table 1. The lattice parameters of the films deposited for each TSC concentration were calculated using the $d_{h\,k\,l}$ values (inter-planar spacing) for the orthorhombic structure, which is given by [25]:

$$\frac{1}{d^2_{h\,k\,l}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (1)$$

where ($h\,k\,l$) are the Miller indices of the plane concerned, and a, b and c are the lattice parameters. These values were found to be $a \approx 0.431$ nm, $b \approx 1.120$ nm and $c \approx 0.399$ nm for the orthorhombic unit cell.

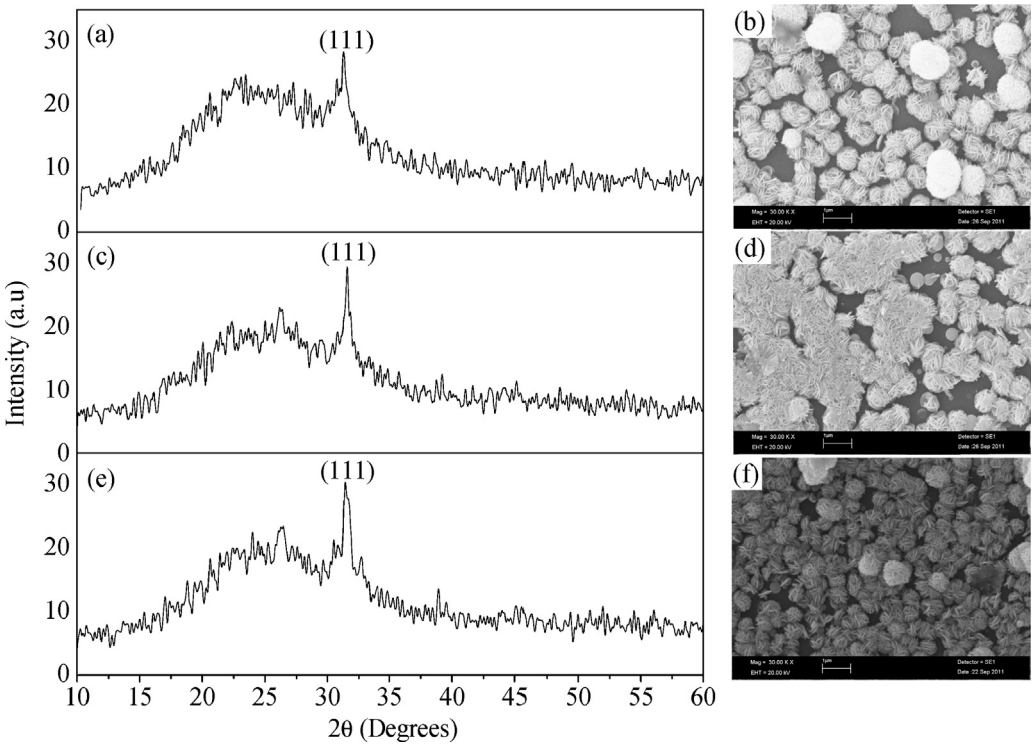

Fig. 1. XRD patterns and SEM micrographs for SnS thin films grown under different TSC concentrations: (a, b) 6.4×10^{-3} M, (c, d) 7.2×10^{-3} M, (e, f) 8.0×10^{-3} M.

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