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

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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 α > 104 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 Cu2ZnSnS4 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 SnS2P 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
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 × 26 × 1 mm³) by the CBD method. Deposition of the films initiates from the following precursor solution: 0.5 g of SnCl₂·H₂O dissolved in 2.5 ml of acetone, which is then mixed in 6 ml of 3.7 M of triethanolamine [(HOCH₂CH₂)₃N]. After that, the non-toxic complexing agent tri-sodium citrate (C₆H₅Na₃O₇) 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 (CH₃CSNH₂) and 5 ml 4 M of ammonia (NH₃) 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 = 0.154049 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 × 10 mm²). 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° ≤ 2θ ≤ 40° 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 d₃₃₃ values (inter-planar spacing) for the orthorhombic structure, which is given by [25]:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

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 ≈ 0.431 nm, b ≈ 1.120 nm and c ≈ 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.](image-url)
Table 1
Comparison of XRD results for the grown SnS films with the standard values.

<table>
<thead>
<tr>
<th>Material (SnS)</th>
<th>(h k l)</th>
<th>2θ (°)</th>
<th>d (nm)</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDF no:33-1375</td>
<td>(1 1 1)</td>
<td>31.498</td>
<td>0.284</td>
<td>0.433</td>
<td>1.120</td>
<td>0.399</td>
</tr>
<tr>
<td>6.4 × 10⁻³ M TSC</td>
<td>(1 1 1)</td>
<td>31.508</td>
<td>0.283</td>
<td>0.438</td>
<td>1.132</td>
<td>0.395</td>
</tr>
<tr>
<td>7.2 × 10⁻³ M TSC</td>
<td>(1 1 1)</td>
<td>31.508</td>
<td>0.284</td>
<td>0.424</td>
<td>1.117</td>
<td>0.405</td>
</tr>
<tr>
<td>8.0 × 10⁻³ M TSC</td>
<td>(1 1 1)</td>
<td>31.508</td>
<td>0.284</td>
<td>0.433</td>
<td>1.120</td>
<td>0.399</td>
</tr>
</tbody>
</table>

Fig. 2. Two and three dimensional views of AFM images of the SnS films grown under TSC concentrations of (a, b) 6.4 × 10⁻³ M, (c, d) 7.2 × 10⁻³ M and (e, f) 8.0 × 10⁻³ M.
Fig. 1(b), (d) and (f) shows SEM micrographs of SnS films deposited at the considered TSC concentrations recorded in the backscattered mode at 30000× magnifications. It can be seen that film deposited using $6.4 \times 10^{-3}$ M TSC concentration consists of flower-like spherical grains with significant vacant space in between, Fig. 1(b). The grains start to coalesce for the film produced at $7.2 \times 10^{-3}$ M TSC concentration, Fig. 1(d). Further increase in the TSC concentration to $8.0 \times 10^{-3}$ M results in almost disappearing of the vacancies, Fig. 1(f). This is due to the fact that the porosity of the films is inversely related to the TSC concentration since larger amounts of the citrate ions hold more Sn$^{2+}$ ions, as the concentration is increased. Formation of similar grains on SnS thin film surfaces is also observed in our previous work [16].

Two-dimensional AFM images in Fig. 2(a)–(c) show that the average grain size of the SnS particles increases from approximately 345 nm to approximately 750 nm with increasing TSC concentration, as listed in Table 2. Three-dimensional AFM images in Fig. 2(d)–(f) reveal that the surface roughness decreases with increasing TSC concentration. The root mean square (RMS) roughness for SnS films decreased from 120.180 nm to 29.336 nm with increasing TSC concentration. Indeed, as shown in Fig. 2(f), the film surface becomes smoothest when the TSC concentration is $8.0 \times 10^{-3}$ M, while the mean grain size is highest as calculated from AFM data (approximately 750 nm).

To measure the film thickness by AFM, we produce a step-like structure of the films by applying scratch marks on it with a sharp tool. As the material of the film was softer compared to the substrate, we assume that the scratches completely remove the film material on the substrate and a step structure is produced at the junction of a scratched and unscratched film where the heights of the steps represent the film thickness. Several lateral AFM scans across the steps were taken and an average of them was calculated to obtain the film thickness. The film thicknesses calculated from the AFM images increased approximately from 229 nm to 500 nm, as shown in Fig. 3 and listed in Table 2. From the XRD, SEM and AFM results, the uniformity of SnS thin films is found to be improved with increasing TSC concentration and denser films could be produced by increasing the concentration.

The dependence of transmission and reflectance spectra of the SnS films is shown in Fig. 4(a) and (b), respectively. The optical absorption coefficient ($\alpha$) was calculated to be on the order of...
$10^6$ cm$^{-1}$ in the wavelength range of 400–1100 nm using the following equation [26]:

$$T = (1 - R)^2 \exp(\alpha t)$$

(2)

where $T$ is the transmittance, $R$ is the reflectance and $t$ is the film thickness. The variation of $\alpha$ with wavelength ($\lambda$) is analyzed to find out the nature of the electronic transition across the optical band gap. The nature of the transition was determined using the relation:

$$\alpha h\nu = B(\nu - E_g)^n$$

(3)

where $B$ is a constant, $h$ is the Planck’s constant, $\nu$ is the frequency of photons and $n$ equals to $\frac{3}{2}$ for direct band gap [27]. Band gap energy ($E_g$) can be obtained by extrapolating the straight line of $(\alpha h\nu)^2$ vs. $\nu$ curve to intercept the horizontal $\nu$ axis. The calculated $E_g$ values of the samples, as depicted in Fig. 5(a)–(c), for different TSC concentrations are listed in Table 2. It can be seen from Fig. 5 that the values of the optical band gap are observed to decrease from 1.40 eV to 1.17 eV as the TSC concentration increases from $6.4 \times 10^{-3}$ M to $8.0 \times 10^{-3}$ M, as shown in Fig. 5(a)–(c). The observed decrease in band gap width with increasing TSC concentration can be attributed to quantum confinement in the films. This is consistent with results reported in literature by Jakbar et al. [28] and by Jain and Arun [29]. The cross-sectional AFM images also showed that the thicknesses of the SnS thin films increased with increasing TSC concentration. The increase in film thickness of the SnS thin films is assigned to the higher concentration of Sn-complexing-agent bonded ions that may have exhibited Sn–S bonding in the reaction bath and thus increased the thickness of the SnS thin film [30]. Band gap energies of SnS films listed in Table 2 are also in good agreement with the reported data on SnS thin films [22,24,31].

Determining the refractive index of semiconductor is important for optical wave guiding in optoelectronic structures such as heterojunction laser diodes, optical amplifiers or optical fibers. Hence many attempts have been made to correlate the energy band gap to the optical refractive index of semiconductors. The reflectance ($R$), extinction coefficient ($k$) and the refractive index ($n$) of a solid at a certain constant wavelength ($\lambda$) are related through the following equations [26]:

$$k = \frac{\alpha \lambda}{4\pi}$$

(4)

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

(5)

Using these relations, the values of the refractive index and extinction coefficient are calculated from the absorbance and transmittance data. Fig. 6 shows that $n$ is found to decrease from 12.50 to 5.04 at the wavelength of 600 nm with increasing TSC concentration. Considering the spectral range of 400–1100 nm, Nwofe et al. [32] reported a refraction index variation between 6.25 and 5.49 and our results are comparable to their values. Also it can be seen from Table 2 that the refractive index was higher for lower film thickness. Such a behavior has been observed in other reported works by Swampeoal [33] and Ahmed et al. [34]. The observed extinction coefficient decreased from 0.41 to 0.09 at spectral range of 600 nm, with increasing TSC concentration, see Table 2. The real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the complex dielectric constant are given by [35]:

$$\varepsilon_1 = n^2 - k^2$$

(6)

$$\varepsilon_2 = 2nk$$

(7)

With the help of Equations (6) and (7), the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric constant decrease from 156.00 to 25.43 and from 10.36 to 0.88, respectively, with increasing TSC concentration, see Table 2. The extinction coefficients were also higher for lower film thicknesses. The present real and imaginary dielectric constants values are consistent with reported data [36].

Table 3 lists the Hall coefficients, such as carrier concentration, mobility, resistivity and conductivity of the SnS thin films with different TSC concentrations. The carrier concentration and mobility estimated by Hall effect measurements were found to increase from $1.73 \times 10^{12}$ cm$^{-3}$ to $3.59 \times 10^{12}$ cm$^{-3}$ and from 148 cm$^2$ V$^{-1}$ s$^{-1}$ to 228 cm$^2$ V$^{-1}$ s$^{-1}$ with increasing TSC concentration. Devika et al. [37] reported the use of Sb as a dopant that lowers the hole

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**Table 2**

<table>
<thead>
<tr>
<th>TSC concentration (M)</th>
<th>Thickness (nm)</th>
<th>Grain size (nm)</th>
<th>$E_g$ (eV)</th>
<th>$n$</th>
<th>$k$</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$6.4 \times 10^{-3}$</td>
<td>~229</td>
<td>~345</td>
<td>1.40</td>
<td>12.50</td>
<td>0.41</td>
<td>156.00</td>
<td>10.36</td>
</tr>
<tr>
<td>$7.2 \times 10^{-3}$</td>
<td>~286</td>
<td>~360</td>
<td>1.28</td>
<td>8.70</td>
<td>0.26</td>
<td>75.66</td>
<td>4.44</td>
</tr>
<tr>
<td>$8.0 \times 10^{-3}$</td>
<td>~500</td>
<td>~750</td>
<td>1.17</td>
<td>5.04</td>
<td>0.09</td>
<td>25.43</td>
<td>0.88</td>
</tr>
</tbody>
</table>
The concentration of SnS to be less than $10^{14}$ cm$^{-3}$. Moreover, the carrier concentration values are lower than those reported in related works ($\sim 10^{15}$ cm$^{-3}$) [38,39]. The reduction of carrier density can be attributed to the scattering agents of charge carriers, such as ionized impurities, neutral impurities (defects, vacancies and interstitials), dislocations and grain boundaries [40]. Therefore, the ability to control carrier concentration of SnS with the addition of tri-sodium citrate in reaction bath could improve SnS-based thin film solar cells and, in general, could broaden the utility of SnS as an optoelectronic semiconductor outside the field of photovoltaics. Moreover, increase in mobility can be understood by considering the increase of the grain sizes and decrease of the grain boundaries. Measured mobility values are higher than the previously reported data [38,39]. The electrical resistivity decreased from $4.71 \times 10^4$ $\Omega$ cm to $2.05 \times 10^4$ $\Omega$ cm with increasing TSC concentration. These values are lower than the reported data [41]. However, measured electrical conductivity increased from $4.51 \times 10^{-5}$ to $8.78 \times 10^{-5}$ (cm$^{-1}$) with increasing TSC concentration. The conductivity values are higher than that of other reported SnS films deposited by CBD (10$^{-6}$) [42,43], and SILAR (10$^{-7}$) [44].

4. Conclusion

SnS thin films are prepared with three different tri-sodium citrate concentration ($6.4 \times 10^{-3}$ M, $7.2 \times 10^{-3}$ M and $8.0 \times 10^{-3}$ M) on glass substrates at room temperature for 24 h by the chemical bath deposition technique. The structural, electrical and optical properties of SnS thin films deposited have been studied as a function of the tri-sodium citrate ligand concentration. The X-ray powder diffraction pattern was used to characterize SnS thin films. The parameters of the orthorhombic unit cell are found to be $a \approx 0.431$ nm, $b \approx 1.120$ nm and $c \approx 0.399$ nm. The mean grain size of the films increases with increasing tri-sodium citrate concentration, as deduced from AFM data. Optical absorption and transmission of SnS thin films are measured over the 400–1100 nm spectral region to derive the optical parameters. The band gap energy decreased from 1.40 eV to 1.17 eV with the increase in tri-sodium citrate concentration. By SEM and AFM analysis, it is indicated that an increase in tri-sodium citrate concentration leads to an improvement in the uniformity of SnS thin films, diminution of the vacancies, reduction in rms surface roughness, as well as increase in the grain size and thickness. Moreover, Hall measurements show that electrical conductivity, carrier concentration
and mobility values increase with tri-sodium citrate concentration.

To sum up, the above-mentioned results suggest that the variation in optical band gap and electrical resistivity with the addition of tri-sodium citrate in reaction bath confirms improved morphology of SnS thin films which can be utilized in solar energy conversion devices. These results may be compared with reported data by Ubale et al. [45] in which influence of the complexing agent (Na2-EDTA) on the structural, morphological, electrical and optical properties of chemically deposited FeSe thin films was investigated.

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