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Effect of Thioacetamide Concentration on the Preparation of Single-Phase SnS and SnS₂ Thin Films for Optoelectronic Applications

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Abstract: Eco-friendly tin sulfide (SnS) thin films were deposited by chemical solution process using varying concentrations of a sulfur precursor (thioacetamide, 0.50–0.75 M). Optimized thioacetamide concentrations of 0.6 and 0.7 M were obtained for the preparation of single-phase SnS and SnS₂ films for photovoltaic absorbers and buffers, respectively. The as-deposited SnS and SnS₂ thin films were uniform and pinhole-free without any major cracks and satisfactorily adhered to the substrate; they appeared in dark-brown and orange colors, respectively. Thin-film studies (compositional, structural, optical, and electrical) revealed that the as-prepared SnS and SnS₂ films were polycrystalline in nature; exhibited orthorhombic and hexagonal crystal structures with (111) and (001) peaks as the preferred orientation; had optimal band gaps of 1.28 and 2.92 eV; and exhibited p- and n-type electrical conductivity, respectively. This study presents a step towards the growth of SnS and SnS₂ binary compounds for a clean and economical power source.

Keywords: tin monosulfide; tin disulfide; chemical solution process; absorber; buffer; solar cells; renewable energy

1. Introduction

In recent years, inorganic semiconductors have been employed to generate clean energy in various optoelectronic and electrochemical fields, mainly because of their high stability under atmospheric conditions [1–5]. Among these, groups IV–VI tin-based binary sulfides such as tin monosulfide (SnS) and tin disulfide (SnS₂) have drawn much attention because of their abundance, low cost, non-toxicity, high catalytic activity, material diversity, structural multiformity, and excellent electrical conductivity [6]. SnS crystallizes in an orthorhombic structure with the Pnma space group [7] and exhibits excellent optoelectrical properties such as a strong absorption coefficient (> 10^5 cm⁻¹) with direct optical band gap energy ranging from 1.16 to 1.79 eV [8,9] and p-type conductivity with a carrier concentration of the order of 10^{11} – 10^{18} cm⁻³ [10], which are suitable for thin-film photovoltaic absorbers. In addition, maintenance of stoichiometry is simpler compared with the other conventional light absorbers [11–15]. Another tin-based binary sulfide, SnS₂, adopts a hexagonal-layered structure with the P3ml space group, similar to the structure of the CdI₂ system [16]. Moreover, SnS₂ has a relatively high optical band gap in the range of 2.04–3.30 eV [17] with direct transitions and exhibits n-type conductivity. These promising characteristics make SnS a suitable absorber candidate material



for thin-film solar cells [1]; moreover, SnS is presumably expected to be a better alternative to the already developed technologies such as Cu(In,Ga)Se₂ (23.35%) [18] and CdTe (22.1%) [19], which are limited by their toxicity, scarcity, and exorbitant cost. Similarly, the favorable electronic characteristics, excellent structural flexibility, wider spectral response, and better thermal stability of SnS₂ make it a competitive nontoxic substitute for the conventional CdS [14] and Zn(O,S) [20] buffers in thin-film solar cells [2]. Furthermore, both SnS and SnS₂ have also been applied in photodetectors [21,22], photocatalysis [23], water splitting [24], gas sensors [25,26], biosensors [27], field-effect transistors [28,29], lithium-sodium ion batteries [30,31], thermoelectrics [32], electrochemical capacitors [33], and supercapacitors [34].

Various approaches including physical and chemical techniques have been explored to deposit both SnS and SnS₂ thin films. Among these techniques, the chemical solution process (CSP) or chemical bath deposition (CBD) offers more inexpensive and flexible depositions. The preparation of single-phase SnS and SnS₂ films by CSP depends on the release and reaction rate of sulfur ions in the reaction solution, which can be controlled by the selection of a suitable sulfur precursor at a concentration, which affects not only the formation of the phase but also the growth rate, thickness, and other physical properties of the product films. Therefore, optimizing the concentration of the sulfur precursor is highly preferable to obtain high-quality SnS and SnS₂ films for the desired applications. Previous research suggests that thioacetamide (TA) and sodium thiosulfate have been mainly used as sulfur precursors since 1987 (Figure 1). Of these, thioacetamide is more preferable because it works under both acidic and alkaline bath conditions.

Therefore, a set of SnS thin films were deposited by CSP using varying thioacetamide concentrations, while the other growth parameters were maintained constant. The influence of thioacetamide concentration on the growth and physical properties of the thin films are discussed in the subsequent sections. Thus, its concentration was optimized for the preparation of pure SnS and SnS₂ films for wide applications.



Figure 1. The number of chemical bath deposition (CBD) SnS reports on the usage of different sulfur precursors from 1980 to the present.

The deposition procedure for SnS and SnS₂ films by CSP is schematically presented in Figure 2, and the process has been described in detail in our previous reports [35,36]. Analytical-grade tin chloride (SnCl₂.2H₂O, 0.1 M) and tartaric acid (C₄H₆O₆, 1.2 M) were used as a tin source and complexing agent, respectively, and 10 mL of thioacetamide (C₂H₅NS, 0.50-0.75 M) was used as the source material for the S ions. The as-prepared thin films were cleaned using deionized (DI) water and dried in a vacuum oven. By the following equations, the kinetics of SnS and SnS₂ films can be understood.



Figure 2. Schematic representation of the growth of tin sulfide films.

In an aqueous tin chloride solution, the complexation of tartaric acid is

$$SnCl_2 \cdot 2H_2O + L \Leftrightarrow Sn(C_4H_6O_6)^{2+} + 2Cl^- + 2H_2O_6$$

The free Sn^{2+} ions are slowly released by the dissociation of tin tartrate ions ($\text{Sn}(\text{C}_4\text{H}_6\text{O}_6)^{2+}$) in a controlled way, as below:

$$\mathrm{Sn}(\mathrm{C}_4\mathrm{H}_6\mathrm{O}_6)^{2+} \rightleftharpoons \mathrm{Sn}^{2+} + \mathrm{C}_4\mathrm{H}_6\mathrm{O}_6.$$

The hydrolysis of thioacetamide can produce S^{2–} ions by

$$CH_{3}CSNH_{2} + H_{2}O \rightleftharpoons CH_{3}CONH_{2} + H_{2}S,$$
$$H_{2}S + H_{2}O \rightleftharpoons H_{3}O^{+} + HS^{-},$$
$$HS^{-} \rightleftharpoons H^{+} + S^{2-},$$
$$HS^{-} + OH^{-} \rightleftharpoons H_{2}O + S^{2-}.$$

When the thioacetamide concentration is changed, multiphase or other single-phase films can be formed by the following reactions:

 $Sn^{2+} + S^{2-} \rightarrow SnS,$ $3SnS + S \rightarrow SnS + Sn_2S_3,$ $Sn_2S_3 + S \rightarrow 2SnS_2,$

The compositional, structural, optical, and electrical characteristics of the as-deposited films were analyzed using an X-ray photoelectron spectrometer (Waltham, MA, USA) (XPS: A VG Multilab 2000; Al K α radiation = 1486.6 eV), X-ray diffractometer (Almelo, Overijssel, Netherlands) (XRD: PANalytical X'Pert PRO MPD, Malvern Panalytical with Cu K α radiation, λ = 1.5406 Å), UV-Vis-NIR spectrometer (Santa Clara, CA, USA) (Aglient), and Hall measurement system (Anyang-city, Gyeonggi-do, South Korea) (ECOPIA HMS-3000VER), respectively.

3. Results and Discussion

All the deposited tin sulfide films were confirmed to be satisfactorily adherent. The films appeared in dark-brown and orange shades at TA concentration ranges of 0.50–0.65 M and 0.70–0.75 M, respectively. The effect of TA concentration on the elemental composition and chemical states of elements was investigated by XPS. The XPS survey spectrum indicated that the deposited films were mainly composed of the Sn 3d doublet along with the S 2p peaks, representing the existence of the elements Sn and S. A high-resolution scan of the Sn 3d and S 2p peaks is shown in Figure 3a,b, respectively.

The Sn 3d doublet in the films grown with lower TA concentrations (0.5–0.6 M) showed two strong peaks at about 485.6 and 494.1 eV that were related to Sn $3d_{5/2}$ and Sn $3d_{3/2}$, respectively, which are the characteristics of Sn^{2+} in SnS. The Sn $3d_{5/2}$ and Sn $3d_{3/2}$ peaks were observed to expand at a TA concentration of 0.65 M, and the deconvolution of these peaks reveals the existence of two humps in each peak, linked to the elevated intensity for Sn²⁺ and low intensity for Sn⁴⁺, indicating the coexistence of secondary Sn₂S₃ along with SnS. As the TA concentration was increased further (0.7 M), the spectra showed the binding energies for Sn $3d_{5/2}$ and Sn $3d_{3/2}$ as 486.7 (487.2) and 494.9 (495.1) eV, respectively [37,38], revealing the presence of Sn⁴⁺ produced in the SnS₂ phase. Beyond this concentration (0.75 M), the deconvolution of the broadened Sn 3d doublets suggests the presence of low intense Sn²⁺ and high intense Sn⁴⁺, confirming the formation of the Sn₂S₃ secondary phase along with SnS₂. The high-resolution XPS spectrum of S 2p for the as-prepared films exhibited single peaks related to S^{2–}–Sn²⁺ (161.3 eV) and S–Sn⁴⁺ (162.3 eV) bonds at TA concentrations of 0.5–0.6 and 0.7 M, which are characteristic of single-phase SnS and SnS₂ films, respectively [35]. The remaining core-level S 2p spectra (for TA = 0.65 and 0.75 M) showed two deconvoluted peaks related to the binding energies of both S^{2–}–Sn²⁺ (161.3 eV) and S–Sn⁴⁺ (162.3 eV) bonding, suggesting the presence of the Sn₂S₃ secondary phase. The Sn/S atomic ratio varied between 1.12 to 0.53 with the change in TA concentration. The lower Sn/S atomic ratio indicated that S is more dominant at higher TA values. This excess of sulfur probably led to the formation of the binary phases, SnS₂ and Sn₂S₃ along with the SnS phase, which were further observed in the XRD studies. The film grown at TA concentrations of 0.6 M and 0.7 M exhibited Sn/S atomic ratios of 0.98 and 0.51, indicating that the films have a clear stoichiometry for the formation of the pure SnS and SnS₂ phases, respectively.



Figure 3. High-resolution X-ray photoelectron spectrometer (XPS) scan of (**a**) Sn 3d and (**b**) S 2p core levels.

In general, the structural properties of the thin films were observed to be highly influenced by the compositional variations in the film. In this study, the structural behavior of SnS films grown using different TA concentrations was analyzed using XRD. The diffraction patterns (Figure 4) confirmed the polycrystalline nature of the as-prepared films; some of these showed various binary phases, depending upon the TA concentration: the films deposited in the TA concentration range of 0.5–0.6 M exhibited a strong peak at $2\theta = 31.6^{\circ}$, which is related to the (111) plane, along with other minor peaks at around $2\theta = 27.1^{\circ}$, 38.8° , and 51.1° , which were assigned to the diffraction from the (101), (131), and (112) planes of orthorhombic SnS (JCPDS Card No. 39-0354) [39], respectively. Moreover, the crystalline state improved with an increase in the TA concentration. As the TA concentration was increased to 0.55 M, the film exhibited additional planes of (130) and (260) related to the Sn₂S₃ binary phase (JCPDS Card No. 14-0619) [40]; as the TA concentration was further increased to 0.7 M, the film exhibited different diffraction planes of hexagonal SnS₂ (JCPDS Card No. 23-0677) [41] with (001) reflection at 15.02° as the preferred orientation; and beyond this TA concentration (0.75 M), the film

additionally exhibited (130), (260), and (540) planes of the secondary Sn_2S_3 phase along with Sn_2 . Therefore, the films deposited under TA concentrations of 0.6 and 0.7 M exhibited good crystalline and pure orthorhombic SnS (111) and hexagonal Sn_2 (001) phases, respectively. Thus, these results are observed to agree well with the XPS observations.



Figure 4. XRD patterns of the films deposited at different TA concentrations.

The average crystallite size, D, of the deposited films was estimated using the Debye–Scherrer formula [42] using the strong (1 1 1) and (0 0 1) peaks of the deposited films with a TA concentration in the range of 0.5-0.65 M and 0.7-0.75 M, respectively. It was found that the crystal size varied from

15 to 29 nm with the change of TA concentration from 0.5 to 0.65 M. In addition, a D of 26 nm was obtained for the film deposited at a concentration of 0.7 M, and it was decreased to 24 nm for a further increase in TA concentration to 0.75 M. Therefore, the D of the SnS (TA = 0.6 M) and SnS₂ (0.7 M) films was obtained as 29 nm and 26 nm, respectively. The surface morphology and surface average grain size of both SnS (TA = 0.6 M) and SnS₂ (0.7 M) films were obtained from SEM images (Figure 5). Both the films showed compact morphology without pin-holes and cracks. The SnS film showed almost elliptical-shaped grains with an average grain size of ~295 nm, whereas the SnS₂ film showed shuttle-shaped grains of nearly 272 nm in size.



Figure 5. SEM surface images of both SnS and SnS₂ films deposited at thioacetamide (TA) concentrations of 0.6 and 0.7 M, respectively.

The optical studies of the films deposited at different TA concentrations were carried out using the UV-Vis-NIR photo spectrometer. The films deposited at TA concentrations in the range of 0.5–0.6 and 0.7 M exhibited a sharp absorption edge in the absorption spectra, whereas at TA concentrations of 0.65 and 0.75 M, the films exhibited a nonlinear fall in the absorption edge, indicating the potential presence of the secondary phase of Sn₂S₃ along with either the SnS or SnS₂ phase. The band gap of the prepared films was estimated from the Tauc plots $((\alpha h\nu)^2 vs. h\nu)$ [43], as shown in Figure 6. The films deposited at concentrations of 0.6 and 0.7 M are observed to exhibit band gaps of 1.28 and 2.92 eV, respectively, corresponding to the energy gaps of the SnS and SnS₂ phases. Furthermore, the films prepared at a 0.65 M concentration exhibited two different values of band gap—specifically, ~0.94 and ~1.34 eV—that are attributed to the presence of the Sn₂S₃ secondary phase along with SnS; on the other hand, at a concentration of 0.75 M, the films exhibited band gaps of ~1.11 and ~2.53 eV, corresponding to the presence of the Sn₂S₃ secondary phase and SnS₂ phase, respectively.

Figure 7 shows the variation of the refractive index (n) and extinction coefficient (k) as a function of the TA concentration. The evaluated n value is observed to first increase and then decrease with increasing TA concentrations up to 2 M, whereas the calculated k value exhibits a reverse variation trend. The films grown at TA concentrations of 0.6 and 0.7 M exhibit n values of 3.24 and 2.63 and k values of 0.13 and 0.61, respectively. The obtained n and k values in the present study are in good agreement with the reported values [2,44].

Electrical parameters such as conductivity type, resistivity, mobility, and carrier density of the films deposited at various TA concentrations were determined using Hall effect studies. The positive sign of the Hall coefficient for the films prepared at TA concentrations in the range of 0.50–0.65 M indicates p-type electrical conductivity, whereas the negative sign for the films deposited at TA concentrations of 0.7 and 0.75 M suggests n-type electrical conductivity. Furthermore, the films deposited at concentrations of 0.6 and 0.7 M exhibited carrier densities of 4.1×10^{15} and 7.2×10^{19} cm⁻³; mobilities of 62.3 and 32.4 cm²V⁻¹s⁻¹; and resistivities of 29.2 and 17.4 Ω -cm, respectively, which are related to the SnS and SnS₂ phases. These results are in agreement with the reported data [45,46].



Figure 6. Tauc's plots of the films deposited at different TA concentrations.



Figure 7. Variation of n and k with TA concentrations.

4. Conclusions

In this study, SnS thin films were prepared using chemical solution process by varying the concentration of TA (0.5-0.75 M), while the other growth parameters were maintained constant. The films prepared at TA concentrations of 0.6 and 0.7 M exhibited Sn/S atomic ratios of 0.98 and 0.51, confirming the formation of single SnS and SnS₂ phases, respectively. The XRD studies showed that all deposited films were polycrystalline in nature and exhibited various binary phases depending upon the TA concentration. The films deposited at a TA concentration of 0.6 M exhibited a pure orthorhombic SnS phase, whereas those at 0.7 M concentration exhibited a completely hexagonal SnS₂

phase. In addition, they showed the direct optical band gap of 1.28 and 2.92 eV with p- and n-type conductivities, which confirmed the suitability of these films not only for application as solar absorbers and buffers, respectively, but also for other applications.

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