

THE INFLUENCE OF THE TREATMENT OF SnS THIN FILMS WITH ALCOHOLIC SOLUTION, FOLLOWED BY ANNEALING

Beltina OSMANI, Atanas TANUSEVSKI¹, Ahmed JASHARI²

¹Department of Physics, Faculty of Natural Sciences and Mathematics, Ss. "Cyril and Methodius University in Skopje"

²Department of Chemistry, Faculty of Natural Sciences and Mathematics, University of Tetovo

*Corresponding author e-mail: atanas@pmf.ukim.mk

Abstract

Tin(II) sulfide (SnS) is a promising semiconductor material for photovoltaic and optoelectronic applications due to its suitable band gap, high absorption coefficient, non-toxicity, and abundance in nature. In this work, SnS thin films were deposited on glass substrates using the chemical bath deposition (CBD) technique. The deposition bath contained $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, NH_4F , NH_4OH , and $\text{Na}_2\text{S}_2\text{O}_3$ solutions at $\text{pH} = 7$. After deposition, the films were treated in an alcoholic SnCl_2 solution for different immersion times and annealed at 300°C . Structural properties of the films were investigated using X-ray diffraction (XRD). The analysis confirmed the formation of polycrystalline orthorhombic SnS. Crystallite size was estimated using the Scherrer equation and increased from 34 nm for untreated films to 50 nm after repeated treatment and annealing. The reduction in diffraction peak broadening indicates improved crystallinity and grain growth. Untreated films exhibited p-type conductivity, while longer treatment in SnCl_2 solution resulted in conversion to n-type conductivity. The results demonstrate that post-deposition treatment significantly affects the structural and electrical properties of SnS thin films and may improve their suitability for thin-film solar cell applications.

Keywords: Tin(II) sulfide (SnS), chemical bath deposition, thin films, X-ray diffraction, crystallite size, photovoltaic materials.

Introduction

Tin(II) sulfide (SnS) is a semiconductor material belonging to the IV–VI chalcogenide group that has attracted considerable scientific attention due to its potential applications in photovoltaic and optoelectronic devices (Banai et al.2016,Hedge et al.2011,Norton et al.2021). The increasing demand for renewable energy sources necessitates the development of efficient, low-cost, and environmentally friendly materials (Han et al.2026). In this context, SnS represents a promising candidate for the absorber layer in thin-film solar cells because of its high absorption coefficient in the visible spectrum ($>10^4 \text{ cm}^{-1}$), suitable band gap energy ($E_g \approx 1.1\text{--}1.5 \text{ eV}$), and good chemical and thermal stability (Banai et al.2016,Di Mare et al.2017,Norton et al.2021).

Unlike materials such as CdTe and CIGS, SnS does not contain toxic elements and is composed of earth-abundant raw materials, making it suitable for large-scale production. However, the properties of SnS thin films strongly depend on the preparation method and post-deposition treatments; therefore, detailed structural, optical, and electrical characterization is essential for optimizing their applications.

SnS crystallizes in an orthorhombic structure (Herzenbergite phase) with a layered crystal lattice, resulting in anisotropic electrical and optical properties. The material naturally exhibits p-type conductivity due to defects such as sulfur vacancies and tin interstitial atoms, which act as acceptor centers and generate holes as the dominant charge carriers.

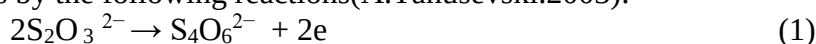
The band gap energy of SnS depends on the deposition method, grain size, and the presence of defects. Structural imperfections may create localized energy states within the forbidden band, affecting both the absorption spectrum and electrical conductivity. Therefore, controlling defects and improving the crystal structure are crucial for enhancing material performance.

Chemical Deposition of SnS

Chemical bath deposition (CBD) is a simple, low-cost, and low-temperature technique for obtaining thin films, enabling direct deposition of the material onto the substrate through controlled chemical reactions in solution. This method is particularly suitable for the deposition of chalcogenide semiconductors such as SnS (Dekhil et.al 2023, Sajeesh et al.2010).

In this study, SnS thin films were deposited using the chemical bath deposition method. The composition of the deposition bath was as follows: 30 mL of distilled water, 0.8 g NH₄F, 1.125 g SnCl₂·2H₂O, 6 mL of 0.25% NH₄OH, and 5 mL of 2 M Na₂S₂O₃. Distilled water was added to obtain a total volume of 100 mL (A.Tanusevski.2003).

The deposition of SnS films, described in this paper, was based on the reducing ability of thiosulfate ions by the following reactions (A.Tanusevski.2003):



Ammonium fluoride was used as the complexing agent and also served to control the pH value of the solution. The films were deposited at pH = 7 using a thiosulfate bath as the source of S²⁻ ions.

Microscope glass slides were used as substrates. Prior to deposition, the substrates were cleaned in chromosulfuric acid and rinsed thoroughly with distilled water. The cleaned substrates were then immersed vertically along the walls of the reaction beaker.

During deposition, the color of the solution gradually changed from yellow to yellow-brown and finally to black, indicating the formation of SnS thin films. After 18 hours of deposition, thin films with a thickness of approximately 0.34 μm were deposited on both sides of the glass slides (75 × 25 × 1 mm³), while additional precipitate accumulated at the bottom of the beaker. For all measurements, the films deposited on the side facing the beaker wall during deposition were used. The layers formed on the opposite side of the slides were removed using a cotton swab soaked in diluted HCl solution. The obtained films exhibited a dark red color and showed p-type semiconductor behavior.

Following deposition, the films were immersed in an alcoholic SnCl₂ solution for 1 minute, 2 minutes and 3 minutes, respectively. Subsequently, the films underwent thermal treatment at 300 °C.

Film Treatment

SnS is naturally a p-type semiconductor, mainly due to the presence of defects in the crystal lattice such as sulfur vacancies and tin interstitial atoms (Dahule et al.2022, Norton et al.2021). In order to achieve a transformation from p-type to n-type conductivity, the SnS films were treated with a SnCl₂ solution followed by thermal annealing at 300°C.

During this process, some sulfur atoms in the lattice may be substituted by chlorine ions, which act as donor impurities and provide free electrons. The thermal treatment enables the diffusion of chlorine and sulfur ions into the interior of the film and simultaneously contributes to recrystallization, grain growth, and reduction of defect concentration (Pandey et al.2021, Yanagi et al. 2016).

In this study, four samples were characterized:

0 min – as-prepared p-type film

2 min – treated once for 2 minutes, p-type

3 min – treated once for 3 minutes, n-type

2×3 min – treated twice for 3 minutes, n-type

Structural Analysis by XRD and Grain Size Determination

X-ray diffraction (XRD) was used to determine the crystalline phase and degree of crystallinity of the films. The analysis is based on Bragg's law, which relates the wavelength of X-ray radiation to the interplanar spacing in the crystal lattice (Freund et al.2021,Pope C.G 1997). Figure 1, shows the diffraction patterns obtained from the XRD analysis of the investigated samples.

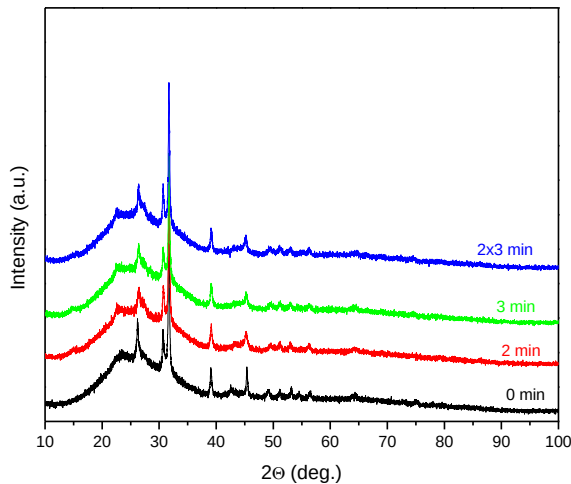


Figure 1. X-ray diffraction analysis (XRD) of the investigated SnS thin films.

The crystallite size was estimated using the Scherrer equation, which relates the broadening of diffraction peaks to grain size (Balaz et al.2013,Howarth et al.2016):

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (5)$$

Where:

$\lambda = 0.154$ nm (X-ray wavelength)

β = full width at half maximum (FWHM)

θ = Bragg angle

$K = 0.94$ (shape factor constant)

A decrease in the full width at half maximum after treatment indicates an increase in grain size and improved crystal ordering.

The grain sizes calculated for the analyzed samples are presented in Table 1.

Table 1. Crystallite size of the analyzed samples determined using the Scherrer equation.

Sample	D (nm)
0 min (p-type)	34
2 min (p-type)	35
3 min (n-type)	41
2×3 min (n-type)	50

From Table 1, it can be observed that treatment of the films in SnCl_2 solution followed by heating at 300°C leads to an increase in grain size. Larger grains imply fewer grain boundaries, resulting in reduced scattering of charge carriers and improved electrical properties.

Discussion

The obtained results demonstrate that post-deposition treatment significantly affects the structural and optical properties of chemically deposited SnS thin films. XRD analysis confirmed the polycrystalline nature of the films and revealed improved crystallinity after treatment with SnCl₂ solution and thermal annealing.

The increase in crystallite size from 34 nm for the untreated sample to 50 nm for the twice-treated sample indicates enhanced recrystallization and grain growth during thermal treatment. Larger crystallites reduce the density of grain boundaries, which in turn decreases charge carrier scattering and improves electrical transport properties.

The conversion from p-type to n-type conductivity after longer treatment durations indicates successful incorporation of sulfur or chlorine donor impurities into the SnS lattice.

Overall, the results demonstrate that SnCl₂ treatment combined with thermal annealing effectively modifies the structural and optical properties of SnS thin films and improves their suitability for photovoltaic and optoelectronic applications.

Conclusion

SnS thin films were successfully deposited by the chemical bath deposition method using a thiosulfate bath at pH = 7. The deposited films exhibited a polycrystalline orthorhombic structure and p-type semiconductor behavior.

Post-deposition treatment in alcoholic SnCl₂ solution followed by thermal annealing at 300 °C significantly influenced the structural and optical properties of the films. XRD analysis showed an increase in crystallite size and improved crystallinity after treatment.

Furthermore, the treatment process enabled the transformation of conductivity from p-type to n-type, indicating successful donor doping through chlorine incorporation. These findings suggest that chemically deposited SnS thin films possess promising structural and optical properties for potential application in thin-film solar cells and other optoelectronic devices.

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