

Ibn Al-Haitham Journal for Pure and Applied Sciences

Journal homepage: jih.uobaghdad.edu.iq



The Effect of substrate Nature on the properties of Tin Sulfide Nanostructured Films Prepared by chemical bath deposition

Zahra'a A.Abood™ Department of Physics, College of Education, University of Mustansiriyah, Baghdad, Iraq. Mohamed S. Mahdi^{*} Ministry of Science and Technology, Renewable Energy Directorate Baha'a A.M.Al Hilli Department of Physics, College of Education, University of Mustansiriyah , Baghdad, Iraq.

*Corresponding author: <u>msaleh196730@gmail.com</u>

Article history: Received 17 September 2022, Accepted 27 November 2022, Published in July 2023.

doi.org/10.30526/36.3.3020

Abstract

The substrate's nature plays an important role in the characteristics of semiconductor films because of the thermal and lattice mismatching between the film and the substrate. In this study, tin sulfide (SnS) nanostructured thin films were grown on different substrates (polyester, glass, and silicon) using a simple and low-cost chemical bath deposition technique. The structural, morphological, and optical properties of the grown thin films were investigated using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy. The XRD and FESEM results of the prepared films revealed that each film is polycrystalline and exhibits both orthorhombic and cubic structure types. In addition, the deposited films on polyester and glass showed good absorption in the UV-Vis-NIR range.

Keywords: Tin sulfide; Chemical bath deposition; Polyester; glass, nanostructure.

1. Introduction

Recently, significant attempts have been made to synthesize and characterize nanostructured semiconductor materials owing to their unique properties, as well as their performance in a variety of applications, notably sensing, i.e., their ability to sense gas and light [1]. Researchers are increasingly interested in IV-VI semiconductors such as SnS, GeSe, and PbS because of their numerous applications, such as photovoltaic devices and near-infrared detectors [2]. Among these semiconductors, SnS has advantages, including abundance, low toxicity, and a high absorption coefficient (10⁴ cm⁻¹) [3–5]. SnS nanostructure films can be deposited through different techniques, such as electrodeposition [6], spray pyrolysis [7], radio frequency sputtering [8],

IHJPAS. 36 (3) 2023

thermal evaporation [9], and chemical bath deposition (CBD)[10-14]. The CBD technique is simple, low-cost, and uses low-temperature deposition (<100 °C) compared to other techniques. Additionally, it can be used for continuous deposition. Moreover, the substrate's nature plays a crucial role in the characteristics of SnS film because of the thermal and lattice mismatching between the film and the substrate. Therefore, in this work, the nanostructured SnS films were deposited using the CBD method on different substrates (polyester, glass, and silicon).

2. Experimental part

The CBD technique was used to synthesize SnS films on different substrates (glass, polyester, and Si). The procedure consists of 1.12 g dihydrate tin chloride, 3.234 g complex agent tri-sodium citrate, and 0.56 g thiocetamide. All chemical materials were dissolved in 50 ml of deionized water. Aqueous ammonia was added drop by drop, and the pH of the solution was adjusted to 6.5. The mixture was stirred well using a magnetic stirrer at room temperature. Substrates were ultrasonic cleaned in acetone, methanol, and deionized water, respectively, for 30–40 minutes before film deposition. Then, the substrates were immersed in the mixture. The deposition was carried out at 80 °C for 4 h. The substrates were removed from the beaker, washed with deionized water, and dried naturally. The structural, morphological, and optical properties of the grown thin films were examined using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy.

3. Results and discussion

3.1 Structural properties

Figure 1 shows the X-ray diffraction patterns of grown SnS films on polyester, glass, and silicon substrates. These patterns showed two peaks in the area around $2\theta = 31.9$ and 39.7, which can be indexed to the orthohombic structure of SnS (ICDD Card: 39-0354) [4, 5, 15]. Moreover, the XRD patterns of the deposited films on the glass and silicon substrates exhibit additional peaks around $2\theta = 26.85$ and 31.1, which can be indexed to the cubic structure of SnS [15,16]. In addition, the peaks of polyester, and silicon substrates were observed. The high, intense, and wide peak of the polyester substrate at $2\theta = 26.3^{\circ}$ may be responsible for the absence of peaks of the cubic structure in the pattern of the deposited film on polyester.



Figure 1. XRD patterns of grown SnS films on various substrates, polyester, (b) Si, (c) glass

The average crystalline size (D) was calculated from the XRD pattern using Scherrer's formula, which is expressed as follows [5, 17, 18]:

IHJPAS. 36 (3) 2023

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the x-ray wavelength, β is the full width at half maximum of the XRD peak, and θ is the Bragg angle. The D values for (111) orientation were found to be 223 A°, 172 A°, and 295 A° for deposited films on glass, Si, and polyester, respectively. The strain (ϵ) values of the grown films were calculated using the following equation [19]:

$$\epsilon = \frac{\beta}{4tan\theta} \tag{2}$$

The ϵ values for (111) orientation are 5.64x10⁻³, 7.34 x10⁻³, and 4.24 x10⁻³ for grown films on glass, Si, and polyester, respectively. Comparative analysis of the XRD findings for the films is shown in **Table 1**.

 Table 1: XRD findings of deposited SnS films on different substrates.

substrate	(h k l)	D (Å)	ε x 10 ⁻³
Polyester	(111)	295	4.24
Glass	(111)	223	5.64
Silicon	(111)	172	7.34

3.2 Surface Morphology

Figure 2 shows FESEM images of deposited films on various substrates. It is obvious that the grown films on polyester and glass substrates comprise many flower-like nanostructures agglomerating for SnS orthorhombic structure, as well as beneath a layer of spherical grains for cubic SnS [16, 20,21]. While the grown film on the glass substrate comprised distributed and uniformly many flower-like nanostructures for orthorhombic structure SnS, as well as a beneath layer of spherical grains for cubic SnS, The presence of two morphologies that relate to orthorhombic and cubic structures agrees with the XRD analysis of **Figure 1**.



Figure 2. FESEM images of prepared films on different substrates, (a) polyester (b) glass (c) silicon

IHJPAS. 36 (3) 2023

3.3 Optical properties

The absorbance spectra of deposited films on polyester and glass substrates in the range of (350 -1100 nm) are shown in **Figure (3)**. According to the spectra, the absorption in the visible and near-infrared wavelengths is generally good. Additionally, the deposited film on glass has a larger absorbance value than the film on polyester in the range of (550 -1100 nm). While the spectra behave differently in the range of (350 - 550 nm), the film deposited on polyester has a higher absorbance value than the film deposited on glass.



Figure 3. The absorbance spectra of deposited films on polyester and glass substrates.

The nature of the energy gap optical transmission can be determined using the relation [5, 22]:

$$\alpha h \upsilon = A(h \upsilon - E_q)^n \tag{3}$$

where A is constant, h is Planck constant, υ denots frequency, E_g is the energy gap, and α is absorption coefficient. Figure (4) illustrates plotting $(\alpha h \upsilon)^2$ versus $(h \upsilon)$ curves for films deposited on two different substrates. The equation (3) is matched with n = 1/2, which indicates permissible transitions. The E_g value can be determined by extrapolating the straight line of $(\alpha h \upsilon)^2$ versus the hu curve to intercept the horizontal hu axis. From Figure (4), the E_g values were found to be 1.38 and 1.02 eV for grown films on polyester and glass substrates, respectively.



Figure 4. Energy gap of grown films on (a) polyester (b) glass

4. Conclusion

In this work, the nanostructure of tin sulfide (SnS) thin films was successfully grown by simple and low-cost chemical bath deposition on different polyester, glass, and silicon substrates. The obtained results showed that the substrate nature had significant effects on the structural, morphological, and optical properties of the deposited films.

Acknowledgment

The authors extend their thanks and gratitude to the Ministry of Sciences and Technology for its great support in completing the research, as well as the Mustansiriya University - College of Education.

References

- 1. Law. M.; Goldberger. J.; Yang. P.; Semiconductor nanowires and nanotubes, *Annu. Rev. Mater. Res.* 2004. *34*, 1, 83–122.
- 2. Xiao. G.; Recent advances in IV–VI semiconductor nanocrystals: synthesis, mechanism, and applications, *RSC Adv.* 2013. *3*, 22, 8104–8130,
- **3.** Greyson. E. C.; Barton. J. E.; Odom. T.W.; Tetrahedral Zinc Blende Tin Sulfide Nano- and Microcrystals, *Small.* **2006.** *2*, 368-375.
- **4.** Gao, C.; Shen, H.; Sun, L.; Preparation and properties of zinc blende and orthorhombic SnS films by chemical bath deposition. Appl. Surf. Sci. **2011.** *257*, 67-78.
- Mahdi. M. S.; Latif, K. H.; Jabor, A. A.; Ibrahim, K.; Ahmed, N. M.; Hmood, A.; Mustafa, F. I.; Bououdina, M.; Tin Sulfide Flower-Like Structure as High-Performance Near-Infrared Photodetector, *Journal of Electronic Materials*. 2020. 49, 5824–5830.
- **6.** Yue, G. H.; Peng, D. L.; Yan, P.X.; Wang, L.S.; Wang, W.; Luo, X. H.; Structure and optical properties of SnS thin film prepared by pulse electrode position. *Alloys Compd.* **2009**. *468*, 254-266.
- 7. Patel, M.; Mukhopadhyay, I.; Ray, A.; Annealing influence over structural and optical properties of sprayed SnS thin films. *Opt. Mater.* **2013**. *35*, 93-104.
- 8. Hartman, K.; Johnson, J. L.; Bertoni, M. I.; Recht, D.; Aziz, M. J.; Scarpulla, M.A.; Buonassisi, T.; SnS thin-films by RF sputtering at room temperature. *Thin Solid Films*. 2011. *519*,74-88.
- **9.** Cheng. S.; Conibeer, G.; Physical properties of very thin SnS films deposited by thermal evaporation, *Thin Solid Films*. **2011.** *520*, 83-95.
- **10.** Guneri, E.; Ulutas, C.; Kirmizigul, F.; Altindemir, G.; Gode, F.; Gumus, C.; Effect of deposition time on structural, electrical, and optical properties of SnS thin films deposited by chemical bath deposition, *Appl. Surf. Sci.* **2010**. *257*, 118-128.
- **11.** Mohamed, S.; Mahdi, K.; Ibrahim, A.; Hmood, N. M.; Ahmed, Mustafa, F.I.; Control of Phase, Structural and Optical Properties of Tin Sulfide Nanostructured Thin Films Grown via Chemical Bath Deposition *J. Electron. Mater.* **2017**.*46*, 42-57.
- 12. Gode, F.; Guneri, E.; Baglayan, O.; Effect of tri-sodium citrate concentration on structural, optical and electrical properties of chemically deposited tin sulfide films, *Appl. Surf. Sci.* 2014.318, 227-235.

- **13.** Jayasree, Y.; Chalapathi, U.; Raja, V. S., Growth and characterization of tin sulphide thin films by chemical bath deposition using ethylene diamine tetra-acetic acid as the complexing agent, *Thin Solid Films*, **2013.** *537*, 149-166.
- **14.** Avellaneda, D.; Delgado, G.; Nair, T. S.; Nair, P. K.; Structural and chemical transformations in SnS thin films used in chemically deposited photovoltaic cells, *Thin Solid Films*. **2007.** *515*, 57-71.
- 15. Mohamed, S.; Mahdi, K.; Ibrahim, A.; Hmood, Naser. M.; Ahmed, Falah. I.; Mustafa, Shrook A.; Azzez. High performance near infrared photodetector based on cubic crystal structure SnS thin film on a glass substrate. *Materials Letters*. 2017 200, 10-13.
- Márquez, I. G.; Romano-Trujillo, R.; Gracia-Jiménez, J. M.; Orthorhombic and amorphous SnS thin films on flexible plastic substrates by CBD, *J. Mater Sci: Mater Electron.* 2021. 32, 15898–15906.
- **17.** Tauu, J., Optical Properties and Electronic Structure of Amorphous Semiconductor in Optical Properties of Solid, *Plenum, New York*, **1969**.
- **18.** Saima, M.; Bushra I.; Misbah, A.; Zeb, N. J.; Suthan K.; Aurang. Z.; Low-temperature synthesis and characterization of Sn-doped Sb2S3 thin film for solar cell applications. *Journal of Alloys and Compounds*. **2015**. *632*, 723-728.
- **19.** Boughalmi, R.; Boukhachem, A.; Kahlaoui, M.; Maghraoui, H.; Amlouk, M.; Physical investigations on Sb2S3 sprayed thin film for optoelectronic applications. *Materials science in semiconductor processing*. **2014.** *26*, 593-602.
- **20.** Mohamed, S.; Mahdi, Husam S.; Hmood, A.; Bououdina. M.; Structure, morphology, and photoresponse characteristics dependence on substrate nature of grown π -SnS films using chemical bath deposition. *Optical Materials*. **2022.** *123.* 111-122.
- **21.** Mohamed, S.; Mahdi. Naser. M.; Ahmed, A.; Hmood, K.; Ibrahim, M.; Bououdina. Comprehensive photoresponse study on high performance and flexible π -SnS photodetector with near-infrared response. *Materials Science in Semiconductor Processing*. **2019**.100. 270-274.
- 22. Akkari, A., Guasch, C. Kamoun Turki, N.; Chemically deposited tin sulphide. *Journal of Alloys and Compounds*. 2010. 490, 180-183.