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Properties of Bi₂O₂S Thin Films Produced by Chemical Bath Deposition at Different Immersion Bath Numbers

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Received: 14 May 2026; Accepted: 10 June 2026; Published: 02 July 2026

ABSTRACT: The major challenge in developing efficient photovoltaic devices is achieving highlight absorption, optimal charge transport, and low recombination losses. In this work, the effect of the immersion bath numbers in the chemical bath deposition (CBD) technique on the properties of bismuth oxysulfide (Bi₂O₂S) thin films, as emergent materials, was studied. The films were synthesized under eco-friendly conditions, using a low-concentration bismuth nitrate precursor and thioacetamide as the sulfur source, and under basic conditions at moderate temperature, with a reaction time of 3 h. X-ray diffraction demonstrated the formation of a crystalline Bi₂O₂S phase, and the morphological analysis showed a uniform film coverage with flower-like morphology, indicating anisotropic growth. XPS verified the coexistence of bismuth, oxygen, and sulfur, confirming the formation of the oxysulfide compound. Results demonstrated that absorbance increased as the number of immersion bath numbers increased. Indeed, structural analysis established that the number of immersion baths critically influences crystallite size, interlayer spacing, and crystallinity of Bi₂O₂S nanosheets. Finally, a formation mechanism is proposed for these Bi₂O₂S thin films for the one-, two-, and three-immersion bath. This study demonstrates that CBD processing parameters critically influence film quality and phase purity, offering an effective and low-cost route to produce Bi-based thin films with potential applications in photovoltaic devices.

KEYWORDS: Bismuth oxysulfide; Bi₂O₂S; chemical bath deposition; immersion bath numbers; thin film; semiconductor

1 Introduction

Bi₂O₂S (bismuth oxysulfide) is an emerging semiconductor material distinguished by its tetragonal layered crystal structure characteristic of the Sillén phase family, which consists of alternating [Bi₂O₂] layers and sulfur planes. The optimal band gap value for visible light absorption is approximately 1.5 eV, making

$\text{Bi}_2\text{O}_2\text{S}$ an excellent candidate for efficient photon harvesting with reduced thermal losses, positioning it as a promising material for photovoltaic applications. The Sillén structure represents a unique family of layered crystal architectures typically observed in bismuth oxychalcogenides such as $\text{Bi}_2\text{O}_2\text{S}$. It features alternating layers of Bi_2O_2 units and chalcogen atoms (S, Se, or Te), arranged in a tetragonal lattice system. In this laminar arrangement, bismuth and oxygen atoms form robust Bi_2O_2 layers, where Bi is typically coordinated to oxygen in a square pyramidal environment, while sulfur atoms constitute planar layers that interact weakly through electrostatic forces with the bismuth-oxygen layers [1–3].

The exploration and validation of $\text{Bi}_2\text{O}_2\text{S}$ for developing functional solar cell prototypes present both significant challenges and opportunities. Chemical bath deposition (CBD) provides an economical, scalable, and controllable method for producing high-quality $\text{Bi}_2\text{O}_2\text{S}$ thin films. By adjusting growth parameters such as precursor concentration and bath temperature, CBD enables precise control over film thickness, morphology, and crystallinity, directly influencing device performance.

Furthermore, it is critical to conduct comprehensive studies on solar cell prototypes incorporating one, two, or three immersion baths during the synthesis of $\text{Bi}_2\text{O}_2\text{S}$ films to clarify how film architecture affects light absorption, charge transport, and overall efficiency. While a single immersion bath may not suffice for complete light harvesting, multilayer films can enhance absorption at the potential cost of mechanical challenges and increased recombination losses [4]. Thus, optimizing the balance between optical and electronic properties is essential for improving both performance and reliability.

It is equally important to distinguish $\text{Bi}_2\text{O}_2\text{S}$ from chemically related compounds such as Bi_2S_3 and Bi_2O_3 , which exhibit substantially different band gaps and electronic properties. For example, Bi_2O_3 , with a band gap around 2.8 eV, tends to limit light absorption, while Bi_2S_3 has a narrower band gap near 1.3 eV [5–7]. Accurate phase identification is therefore vital to ensure targeted material properties in photovoltaic applications. Other interesting research are referent to BiI/BiOI thin films also obtained by CBD technique [8].

This study aims to synthesize multilayer $\text{Bi}_2\text{O}_2\text{S}$ thin films via the CBD technique, by varying the number of immersion baths, and to evaluate their structural, morphological, and photovoltaic properties. CBD was implemented to produce Bi-based thin films due to its simplicity and low operational expense. The findings contribute foundational knowledge for the development of future renewable energy devices leveraging abundant and environmentally friendly bismuth oxysulfide materials.

2 Materials and Methods

2.1 Materials and Reagents

Bismuth (III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O} \geq 98\%$) from SIGMA-Aldrich (USA), triethanolamine (TEA, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ 97%), and thioacetamide (TA, CH_3CSNH_2 99%) from Alfa Aesar (UK); ammonium hydroxide (NH_4OH 29%), and NH_3 from Fermont (MX). All analytical-grade chemicals were utilized, without any purification. Microscope glass slides (25×75 mm) were used as substrates to synthesize the different thin films.

2.2 Synthesis of Bi-Based Thin Films

Bi-based thin films were synthesized by CBD, varying the number of immersion baths. The first step in the deposition process involved a surface treatment of the microscope glass slides used as substrates. For that, glass slides were immersed in 10% HNO_3 (v/v) for 48 h and washed with deionized water to eliminate impurities and activate the surface, dried at room temperature, and carefully stored.

The bath solution is a mixture of an aqueous solution of bismuth (III) nitrate pentahydrate (0.01 M, 10 mL), triethanolamine (1 M, 5 mL), ammonium hydroxide (1 M, 1 mL), and thioacetamide (0.1 M, 2 mL) in deionized water to get a final volume of 100 mL.

For producing Bi-based thin films, the surface-activated glass substrates (two substrates in each bath) were immersed in the bath solution and placed in a water bath at 60°C for 3 h, as represented in Fig. 1. After completing the deposition period, the films were rinsed with deionized water and allowed to dry in the air at room temperature. To investigate the effect of different deposition layers, this procedure was consistently executed for the CBD technique's one-immersion bath, two-immersion bath, and three-immersion bath, each time in fresh bath solutions. Throughout each immersion, the pH of the final volume was maintained at 9.

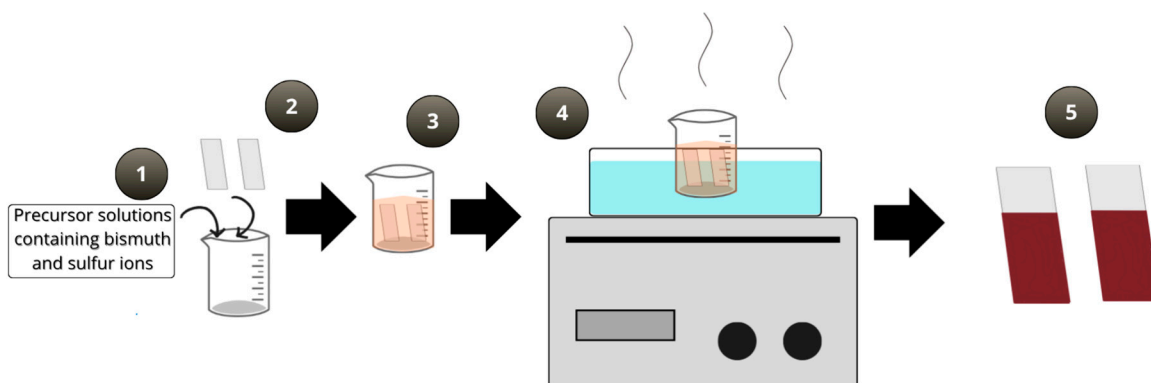


Figure 1: Flowchart of the synthesis process of Bi-based thin films by the CBD technique.

2.3 Bi-Based Thin Films Characterization

The UV-Vis technique was employed to characterize the Bi-based thin films across the 200–900 nm range using a Perkin Elmer Lambda 19 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was implemented to perform chemical analysis using a Perkin Elmer Phi 5600 ESCA system that was equipped with a magnesium (Mg) X-ray source. The X-ray diffractograms (XRD) were acquired using a Bruker D8 Advance X-ray diffractometer with CuK α radiation (1.5418 Å) with Bragg–Brentano geometry. A HITACHI TM3030Plus system was implemented to acquire the SEM micrographs and energy-dispersive X-ray spectroscopy (EDS) for the determination of the elemental composition. The surface morphology of all Bi-based thin films synthesized was analyzed using scanning electron microscopy (SEM) with a FEI model Scios operating at 10 kV. To enhance conductivity, all samples were sputter-coated with a thin gold layer before imaging. Both secondary electron (SE) and backscattered electron (BSE) modes were employed to reveal surface texture and compositional contrast.

3 Results and Discussion

3.1 Optical Characterization of the Bi-Based Thin Films

Fig. 2 depicts the optical properties of Bi-based thin films fabricated by the CBD method with one, two, or three immersion baths. UV-Vis spectroscopy was measured in the wavelength range of 200–900 nm. The optical band gap energy (E_g) and absorption coefficient (α) were calculated from the transmittance data region. The Tauc plot $(\alpha h\nu)^2$ versus photon energy ($h\nu$) was obtained by analyzing the UV-Vis absorption spectra. The linear region of the plot was extrapolated to determine the optical band gap of the Bi-based thin films.

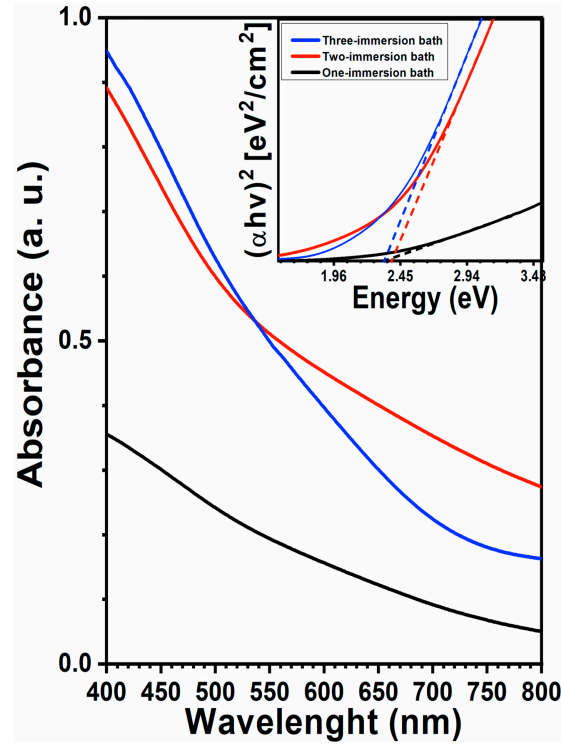


Figure 2: Absorption of $\text{Bi}_2\text{O}_2\text{S}$ thin films for one-, two-, and three-immersion bath. In the inset, the Tauc method for the bandgap determination is shown.

When comparing the results obtained for the one-, two-, and three-immersion bath thin films, a considerable absorbance increase was observed as the number of immersion baths increased. The three-immersion bath thin film exhibited the highest absorbance across the visible range, indicating a high light absorption, with a sharp absorption edge observed around 500–600 nm, as depicted in Fig. 2. These results indicate the influence of different refractive indices for phases present related to optical properties. Absorption coefficient is highly related to optical properties as absorption index and extinction coefficients, which are also influenced by thin-film fabrication method and structural characteristics of microstrain, interplanar spacings, phase, defects, and crystalline symmetry. It is evident that three-immersion bath thin film showed higher absorbance in the visible region compared to one- and two-immersion bath thin films, as depicted in Fig. 2.

To determine the band gap, the linear region of the plot was extrapolated to intersect the energy axis, (Fig. 2 (inset)), yielding an E_g value of approximately 2.07 eV and 2.3 eV, for the three- and two-immersion bath, respectively. These E_g values obtained for $\text{Bi}_2\text{O}_2\text{S}$ thin films confirm its semiconductor nature [9]. These results indicate that the band gap decreases while the number of layers increases. This behavior suggests an influence of the crystal structure or electronic structure of the thin films, or an increase in defects of sites or oxygen vacancies, which in turn could influence the absorption properties. These results demonstrated that controlling the number of layers deposited effectively tunes the optical properties of Bi-based thin films, in this case, thin films of $\text{Bi}_2\text{O}_2\text{S}$, as demonstrated in Section 3.2, which is critical for optimizing performance in optoelectronic devices. From our findings, we demonstrate that the $\text{Bi}_2\text{O}_2\text{S}$ thin films possess favorable optical properties, making them promising candidates for use in photovoltaic devices.

3.2 X-Ray Diffraction Analysis

Fig. 3 depicts the XRD patterns of the Bi-based thin films prepared by chemical bath deposition with one-, two-, and three-immersion bath. The crystallinity and phase purity of the film were confirmed by distinct diffraction peaks corresponding to the orthorhombic phase of $\text{Bi}_2\text{O}_2\text{S}$ (space group Pnnm 58), consistent with the standard JCPDS card No. 34-1493 and previous literature. Secondary phases of Bi_2O_3 and Bi_2S_3 were also detected, as evidenced by additional distinguishable peaks. Phase quantification based on rigorous peak deconvolution allowed the determination of the relative amounts of $\text{Bi}_2\text{O}_2\text{S}$, Bi_2O_3 , and Bi_2S_3 present.

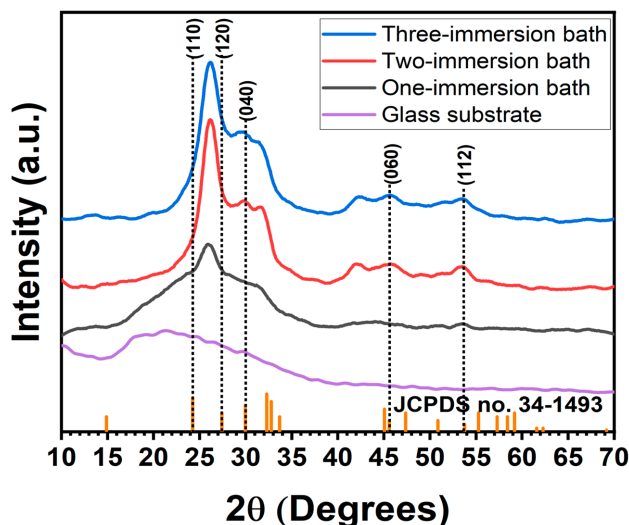


Figure 3: XRD patterns of Bi-based thin films with one-, two-, and three-immersion bath.

Table 1 summarizes the diffraction peak position (2θ), full width at half maximum (FWHM), and crystallite sizes calculated using the Scherrer equation. The main peaks observed at approximately $2\theta = 22.21^\circ, 25.74^\circ, 31.23^\circ, 43.79^\circ, 52.67^\circ$, and 66.96° correspond to the (220), (310), (040), (520), (351), and (470) crystal planes of the Bi_2S_3 mixed with the Bi_2O_3 phase in the one-immersion bath thin film. Similarly, in the two-immersion bath thin film, peaks at $2\theta = 24.91^\circ, 31.29^\circ, 46.16^\circ$, and 53.24° that correspond to the (110), (040), (060), and (112) crystal planes, confirming $\text{Bi}_2\text{O}_2\text{S}$ formation. In the three-immersion bath thin films, the peaks at $2\theta = 25.85^\circ, 29.91^\circ$, and 53.45° well correspond to the (110), (040), and (112) crystal planes of $\text{Bi}_2\text{O}_2\text{S}$ [6,10–12]. Notably, the $\text{Bi}_2\text{O}_2\text{S}$ phase was absent in the one-immersion bath thin film, indicating that at least two immersion baths are required to induce the crystallization of this phase. These results demonstrate the successful formation of crystalline $\text{Bi}_2\text{O}_2\text{S}$ by chemical bath deposition after two or more immersion baths.

The main diffraction peak corresponding to the (040) plane remains consistent for the two- and three-immersion bath thin film samples, appearing at approximately 30° (2θ). This consistency suggests that the underlying $\text{Bi}_2\text{O}_2\text{S}$ crystal structure is stable across these deposition conditions. However, a significant decrease in full width at half maximum (FWHM) values was observed as the number of immersion baths increased, indicating improved crystallinity and grain growth. Additionally, as the immersion baths increase from two to three, the main diffraction peak shifts slightly toward lower 2θ angles, implying a slight expansion in the interlayer spacing. This shift may arise from interlayer interactions or strain induced by the stacking of layers. Furthermore, peak intensities become sharp and more pronounced with

the increasing number of layers, reflecting larger average crystallite sizes and enhanced crystallinity in thicker films (Table 2). The average crystallite size increases from the two- to the three-immersion bath samples from approximately 19.33 nm to 48.27 nm as revealed by the Scherrer analysis of the (040) peak. These results suggest that grain growth improves as the number of layers increases. This is in accordance with the agglomeration of nanosheets observed in vacuum-dried samples of $\text{Bi}_2\text{O}_2\text{S}$ and is correlated with a decrease in peak broadening in the two-immersion bath thin film (for additional details, refer to the Supplementary Materials (Figs. S1 and S2)) [13].

Table 1: Lattice parameters for samples prepared by varying the number of immersion baths.

	One-Immersion Bath		Two-Immersion Bath			Three-Immersion Bath		
Representative phase	Bi ₂ S ₃	Bi ₂ O ₃	Bi ₂ S ₃	Bi ₂ O ₃	Bi ₂ O ₂ S	Bi ₂ S ₃	Bi ₂ O ₃	Bi ₂ O ₂ S
Unit cell type	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Lattice parameters	a = 11.06 Å	a = 6.89 Å	a = 10.90 Å	a = 4.33 Å	a = 17.90 Å	a = 11.07 Å	a = 34.17 Å	a = 3.60 Å
	b = 11.34 Å	b = 10.30 Å	b = 11.30 Å	b = 7.00 Å	b = 17.14 Å	b = 9.56 Å	b = 7.54 Å	b = 11.94 Å
	c = 3.96 Å	c = 6.92 Å	c = 4.12 Å	c = 6.35 Å	c = 4.29 Å	c = 4.13 Å	c = 8.44 Å	c = 3.95 Å
Interplanar spacing	3.46 Å	1.40 Å	3.11 Å	1.965 Å	3.57 Å	3.44 Å	2.158 Å	3.44 Å
Unit cell volume	497.10 Å	465.57 Å	508.91 Å	192.07 Å	1317.07 Å	437.59 Å	1280.42 Å	169.58 Å
Stoichiometric ratio	BiS _{1.5}	BiO _{1.5}	BiS _{1.5}	BiO _{1.5}	Bi ₂ O ₂ S	BiS _{1.5}	BiO _{1.5}	Bi ₂ O ₂ S

Table 2: Crystallinity index of Bi-based thin films.

Immersion Baths Number	Bismuth Oxysulfide Structural Parameters		
	Microstrain (ϵ)	Density Dislocations	Crystallite Size (nm)
1	3.705E−2	2.307E−1	2.08
2	5.97E−3	2.675E−3	19.33
3	1E−3	4.291E−4	48.27

The occurrence of mixed phases such as Bi_2O_3 and Bi_2S_3 introduces heterointerfaces and lattice mismatches known to serve as recombination centers, which could be responsible for potentially reducing photovoltaic efficiency. Each phase exhibits a distinct electronic bandgap (Bi_2O_3 : 2.6–3.0 eV, Bi_2S_3 : 1.56–2.10 eV, $\text{Bi}_2\text{O}_2\text{S}$: 1.12–2.5 eV), which modifies optical absorption edges and carrier dynamics, thereby influencing device optimization [14–19]. In photovoltaic applications, phase purity and microstructural quality directly influence charge separation and transport [20,21]. Therefore, Williamson-Hall analysis is essential for precise structural understanding and elucidating stress-induced modifications in band structure and defect recombination pathways, which significantly affect device performance.

The appropriate bandgap of Bi-based thin films (1.5 to 3.0 eV) has garnered significant research interest as a promising semiconductor for solar energy conversion, enabling efficient absorption of visible light. The layered structure of $\text{Bi}_2\text{O}_2\text{S}$ facilitates effective charge separation and transport, thereby enhancing photo-response and photovoltaic efficiency [22,23]. Moreover, $\text{Bi}_2\text{O}_2\text{S}$ exhibits exceptional charge carrier lifetimes and high chemical stability, both critical for the long-term operation of solar devices [24,25]. Recent studies have demonstrated that prototype $\text{Bi}_2\text{O}_2\text{S}$ -based solar cells and photodetectors can achieve high photocurrent densities and rapid response times, attributed to the material's favorable optoelectronic

properties and crystalline quality [26]. In this study, structural characterization of the synthesized Bi-based thin films was performed by integrating unit cell volume calculations derived from X-ray diffraction (XRD) data with stoichiometric and oxidation state information obtained through X-ray photoelectron spectroscopy (XPS, in Section 3.3). Unit cell volumes were calculated for the three phases present Bi_2O_3 , Bi_2S_3 , and $\text{Bi}_2\text{O}_2\text{S}$, in all the thin films synthesized (one-, two-, and three-immersion bath), using lattice parameters and crystal symmetries appropriate to each phase. These calculations allowed accurate estimation of phase-specific structural parameters (Table 3). Variations in unit cell volumes correlated subtly with the number of immersion baths, reflecting lattice expansions or contractions associated with phase growth dynamics.

Table 3: Stoichiometry and ratio calculated from XRD and XPS for: bismuth (3+), bismuth (5+), and sulfur (2−) in thin films for different numbers of immersion bath.

	Bi^{3+}	Bi^{5+}	$\text{Bi}^{5+}/\text{Bi}^{3+}$	$\text{Bi}^{3+}/\text{S}^{2-}$	$\text{Bi}^{3+}/\text{O}^{2-}$
One-immersion bath	$\text{Bi}_1\text{S}_{0.94}\text{O}_{1.62}$	$\text{Bi}_1\text{S}_{0.72}\text{O}_{1.23}$	1.2103	1.0597	0.6167
Two-immersion bath	$\text{Bi}_1\text{S}_{2.02}\text{O}_{1.11}$	$\text{Bi}_1\text{S}_{1.53}\text{O}_{0.84}$	1.0033	0.4954	0.9007
Three-immersion bath	$\text{Bi}_1\text{S}_{0.63}\text{O}_{6.06}$	$\text{Bi}_1\text{S}_{1.15}\text{O}_{11.10}$	3.2115	1.5951	0.1649

As the number of immersion baths increases, distinct volumetric behaviors emerge, linked to atomic arrangements and bonding environments. Bi_2O_3 exhibits substantial unit cell volume expansion up to approximately 1280 Å after three immersion baths, likely driven by structural defects, internal stresses, and interlayer interactions during film growth. It is conceivable that Bi_2O_3 serves as a template for $\text{Bi}_2\text{O}_2\text{S}$ formation in the two- and three-immersion bath thin films, where the ordered Bi_2O_2 base promotes the oriented growth and crystallinity of $\text{Bi}_2\text{O}_2\text{S}$. The unit cell volume of $\text{Bi}_2\text{O}_2\text{S}$ after two immersion baths (~1317 Å) signifies notable lattice expansion at this stage.

Further stabilization in three-immersion bath samples may arise from a passive Bi_2O_2 layer (~169 Å), acting as a protective barrier that mitigates mechanical stress and degradation while enhancing adhesion and structural integrity. This templating and passivation mechanism aligns with phenomena in oxides and oxychalcogenides where hydroxylated intermediate phases encourage ordered growth and improved stability. So, the physical properties and structural stability of these bismuth-based compounds are significantly influenced by crystal structure and the number of immersion baths.

In comparison, Bi_2S_3 demonstrated a more moderate volume increase (~437 Å after three immersion baths), maintaining better dimensional integrity, likely due to reduced lattice distortion or stronger atomic bonding. $\text{Bi}_2\text{O}_2\text{S}$, crystallizing orthorhombically, exhibits the smallest unit cell volumes among the phases, with a dense layered architecture (~169 Å after three immersion baths) that supports efficient growth with minimal expansion. These structural characteristics underpin superior stability and reduce susceptibility to stress-induced lattice distortions of $\text{Bi}_2\text{O}_2\text{S}$. While all three compounds undergo volume increases with the number of immersion baths increases, the magnitude and growth patterns differ by crystallographic symmetry and atomic configuration, impacting their electronic and mechanical properties.

These volumetric trends robustly indicate phase stability and structural evaluation during film deposition. Simultaneously, as shown in Section 3.3, XPS-derived stoichiometric ratios (Bi:O:S) enabled empirical formula calculation for each phase (Table 3) confirming their presence and relative abundance. The oxidation states resolved from XPS core-level spectra correlated strongly with stoichiometric shifts, reflecting phase transformations-Bi (III) states aligned with oxygen-rich phases (Bi_2O_3 , Bi_2S_3 , $\text{Bi}_2\text{O}_2\text{S}$), while sulfur states correlated to sulfide phases.

The Sillén structure of $\text{Bi}_2\text{O}_2\text{S}$, characterized by alternating $[\text{Bi}_2\text{O}_2]$ layers and sulfur planes, directly influences the material's crystallographic and morphological properties as revealed by X-ray diffraction (XRD) and scanning electron microscopy (SEM, in Section 3.4) analyses. XRD patterns confirm the presence and evolution of the Sillén phase, showing progressive sharpening and intensification of diffraction peaks as the number of immersion baths increases, indicating enhanced crystallinity and lattice ordering. Complementary, SEM images illustrate the morphological transformation from isolated and scattered structures in the initial deposition stages to densely packed and well-aligned nanostructures upon completion of multiple immersion baths. This morphological evolution correlates with the layered crystal framework of the Sillén phase, which promotes anisotropic growth and directional assembly of nanostructures. Together, XRD and SEM analyses validate the growth mechanism rooted in the Sillén structure, providing a comprehensive understanding of the structural and morphological properties essential for optimizing $\text{Bi}_2\text{O}_2\text{S}$ thin films in photovoltaic applications.

This comprehensive structural analysis established that the number of immersion baths critically influences crystallite size, interlayer spacing, and crystallinity of $\text{Bi}_2\text{O}_2\text{S}$ nanosheets, with implications for their optoelectronic properties. To optimize photovoltaic efficiency, controlling phase purity is essential, as secondary phase formation introduces detrimental electronic and optical heterogeneities.

3.3 X-Ray Photoelectron Spectroscopic Measurements

The XPS measurements provide important information on the oxidation state of Bi in the bismuth-based thin films. The XPS signals were calibrated using the C 1s peak of the adventitious carbon at 285 eV, and the signals were deconvoluted using the Shirley method. The contributions of Bi 4f are identified at different energies (BE) and have distinctly different features as shown in Fig. 4a–c. The elemental composition and chemical states of the elements present in the Bi-based thin films were determined. The XPS survey showed the occurrence of Bi 4f, S 2p, and O 1s core-level (for additional details, refer to the Supplementary Materials, Fig. S3). High-resolution spectra of Bi exhibited the characteristic peaks corresponding to Bi 4f_{5/2} and Bi 4f_{7/2} spin-orbit doublet. These peaks are indicative of Bi +3 and +5 oxidation states, consistent with the formation of Bi-based compounds [24].

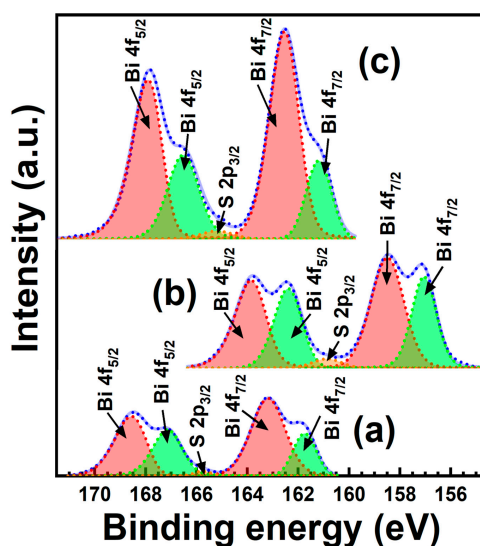


Figure 4: XPS spectra of Bi4f and S2p regions for Bi-based films deposited with one-immersion bath (a), two-immersion bath (b), and three-immersion bath (c).

The O 1s spectrum showed a peak around 530 eV, attributed to lattice oxygen in the bismuth oxide structure. No signals related to metallic bismuth were found, indicating a predominantly oxidized surface layer. Quantitative analysis revealed a Bi:O atomic ratio close to the stoichiometric ratio expected for bismuth oxide and bismuth oxysulfide. The S 2p feature of sulfur in the S^{2-} oxidation state confirmed the sulfide ions for forming the Bi-based film formation. He et al. reported that the spectra for Bi^{3+} are characterized by a narrow, single line around 158.38 eV and 163.75 eV, which can be used to confirm the presence of Bi (III) oxidation state from the Bi_2S_3 and Bi_2O_3 . These XPS results complement structural analysis performed by X-ray diffraction [27].

For the one-immersion bath thin film, the high-resolution spectra of Bi $4f_{5/2}$ corresponding to Bi^{5+} exhibited two peaks at 168.56 eV and 163.19 eV, respectively. Also, the Bi $4f_{7/2}$ attributed to Bi^{3+} , exhibited two peaks 167.14 eV and 161.75 eV, with a spin-orbit of 5.37 eV. This peak corresponds to Bi in the 3+ oxidation state and is consistent with the occurrence of oxidized bismuth in the film [28]. The O 1s spectrum shows a single feature centered at 534.86 eV, oxygen bonded in a Bi-O structure, and oxygen vacancies [29]. The S 2p spectrum has a peak at 165.76 eV characteristic of S^{2-} oxidation state, which confirms the incorporation of sulfur into the lattice.

For the two-immersion bath thin film, the high-resolution spectra for Bi $4f_{5/2}$ corresponding to Bi^{5+} exhibited two peaks at 163.86 eV and 158.49 eV, respectively. The O 1s spectrum shows a single feature centered at 531.85 eV, attributed to oxygen vacancies within the lattice oxygen bonded in the Bi-O structure. The S 2p spectrum has a peak at 160.87 eV characteristic of S^{2-} oxidation state, which confirms the incorporation of sulfur into the lattice.

For the three-immersion bath thin film, the high-resolution spectra of Bi $4f_{5/2}$ corresponding to Bi^{5+} exhibited two peaks at 167.92 eV and 162.4 eV, respectively. Also, the Bi $4f_{7/2}$ attributed to Bi^{3+} exhibited two peaks at 166.54 eV and 161.2 eV. The S 2p spectrum has a peak at 165.21 eV characteristic of S^{2-} oxidation state, which confirms the incorporation of sulfur into the lattice. The O 1s spectrum shows a single feature centered at 529.27 eV, attributed to lattice oxygen bonded in the Bi-O structure and oxygen vacancies. XPS confirmed the oxidation states of bismuth, with in the case of Bi_2O_3 , Bi_2S_3 , and Bi_2O_2S , the Bi 4f spin-orbit doublet was successfully assigned to Bi 4f. Further deconvolution of each of the Bi 4f doublet peaks for one, two, and three immersion baths allows us to assign these features to the Bi (III) state. The results are consistent with those reported by Samanta and Biswas [30] in the case of homologous $(Bi_2)_m(Bi_2S_3)_n$ heterostructures.

When comparing the XPS signals of the three types of synthesized thin films, a notable shift is observed in the bismuth doublet (Bi 4f), strongly dependent on the number of immersion baths performed using the CBD technique. However, the most critical shift corresponds to the film obtained after two immersion baths. The binding energy shift to lower values (~158 eV) observed in the two-immersion bath thin film can be attributed to Bi^{3+} state coordinated with sulfur, confirming the successful crystallization of the bismuth sulfide Bi_2S_3 in the bismuthinite phase. Thermodynamically, the second immersion cycle promotes the lateral coalescence of initial isolated islands into a continuous and highly homogeneous layer. From an electronic perspective, replacing lattice oxygen with the less electronegative sulfur increases the electron density shielding around the bismuth atomic cores, which effectively decreases the binding energy associated with the core electrons. On the other hand, the pronounced shift toward higher binding energies exceeding 163 eV in the one-immersion bath sample is intrinsically linked to its discontinuous, ultrafine morphology. In this initial stage, nucleated islands leave exposed substrate areas, leading to a highly de-shielded electronic environment. This effect is driven by the strong electron-withdrawing nature of oxygen and the stabilization of higher oxidation states (such as Bi^{5+}) within the uncoalesced Bi_2O_3 network [31].

Furthermore, a distinct intermediate trend at 162 eV appears for the three-immersion bath thin film. At this stage, the over-deposition of material shifts the growth vertically, increasing surface roughness and grain size. This thicker film introduces mass diffusion limitations for the incoming sulfur species, restricting a complete topotactic anion exchange down to the deepest layers and forcing the coexistence of both, where the binding energy difference (see Table 4) is attributed to the bismuth, which is predominant in the +3 oxidation state in the successful formation of the $\text{Bi}_2\text{O}_2\text{S}$ phase [32].

Zatsepin et al. reported the study of solid-state interactions between Bi and the oxygen sublattice by Bi-implanted samples against those of the native metal and stable metal oxide phases, specifically examining the Bi 4f core-level spectra [33]. As is well known, XPS core-level spectra of not oxidized metals have strong asymmetrical line shapes, which is a key signature to identify the metal phase in thin films. The formation of oxidized bismuth species occurs when bismuth is fully oxidized to the +3 oxidation state and can be produced from bismuth in its metallic state. At this stage, several polymorphs of Bi_2O_3 exist, with their stability dependent on temperature and synthesis conditions. A partially oxide state will depend on spatial constraints due to ionic radius mismatch in Bi_2S_3 or $\text{Bi}_2\text{O}_2\text{S}$. The formation of oxidized bismuth species implies enough oxygen availability for oxygen and Bi atoms that can occupy substitutional or interstitial sites, allowing full oxidation and crystal restructuring. The formation of $\text{Bi}_2\text{O}_2\text{S}$ requires sulfur incorporation in addition to oxygen, and the existence of oxidized Bi is detected by XPS.

The valence states of Bi, S, and O detected by XPS are consistent with Bi^{3+} , S^{2-} , and O^{2-} , confirming the formation of the $\text{Bi}_2\text{O}_2\text{S}$ compound. Observed shifts in BE values are attributed to the lattice changes due to sulfur incorporation and consequent variations in local chemical environment and electric potential. Rong et al. [28]. reported the formation of $\text{Bi}_2\text{O}_2\text{S}$ flowers, and from their XPS findings, it was possible to corroborate the production of $\text{Bi}_2\text{O}_2\text{S}$ flowers-like structures in our results. As can be seen from Fig. 4b, the peak at approximately 162.40 eV and 157.06 eV with spin-orbit splitting of 5.34 eV well corresponds to the binding energy of Bi 4f_{7/2} and Bi 4f_{5/2}, respectively, and are assigned to the Bi^{3+} . It is evident from the O 1s spectrum that oxygen is part of the lattice oxygen. The S 2p in Fig. 4 depicts a peak at 160.87 eV that is in good agreement with the S^{2-} oxidation estate, see Table 4 for the corresponding values of one-, two-, and three-immersion bath thin films.

Table 4: XPS core-level Bi 4f, S 2p and O 1s BE (eV) for one-, two- and three-immersion bath thin films.

Number of Immersion Baths	Core-Level Binding Energy					O 1s
	Bi 4f _{5/2} (Bi^{5+})	Bi 4f _{7/2} (Bi^{5+})	Bi 4f _{5/2} (Bi^{3+})	Bi 4f _{7/2} (Bi^{3+})	S 2p _{3/2}	
One	168.56 eV	163.19 eV	167.14 eV	161.75 eV	165.76 eV	534.86 eV
Two	163.86 eV	158.49 eV	162.40 eV	157.06 eV	160.87 eV	531.85 eV
Three	167.92 eV	162.55 eV	166.54 eV	161.20 eV	165.21 eV	529.27 eV

3.4 Scanning Electron Microscopy Analysis

Fig. 5a–c, corresponding to the SEM analysis, depicts the evolution of Bi-based thin films. In the case of the one-immersion bath thin film, the surface morphology displays small and discontinuous features, with sparse nucleation sites observed as irregular aggregates. Distinct nucleation centers create flower-like structures. A partial substrate coating and minimal growth are suggested by the absence of continuous coverage. Contrastingly, the two-immersion bath sample exhibits a significant morphological transformation. The hierarchical, porous, and high-surface-area structures observed are associated with the formation of the $\text{Bi}_2\text{O}_2\text{S}$ phase. These results are consistent with those obtained by X-ray diffraction (XRD). The preferential growth along defined crystallographic directions is facilitated by the layers of

$\text{Bi}_2\text{O}_2\text{S}$, which leads to a more uniform and anisotropic morphology. Concerning the three-immersion bath sample, a denser and more compact film was obtained. Nanostructures coalesce to diminish the definition of flower-like structures and enhance the uniformity of surface coverage. Compared to the two-immersion bath sample, this evolution results in a smoother topography with reduced porosity. According to the XRD analysis, the three-immersion bath sample is mainly composed of an oxidized bismuth phase that is distinctive from $\text{Bi}_2\text{O}_2\text{S}$. This phase is likely responsible for the denser particle growth and morphological changes that were observed.

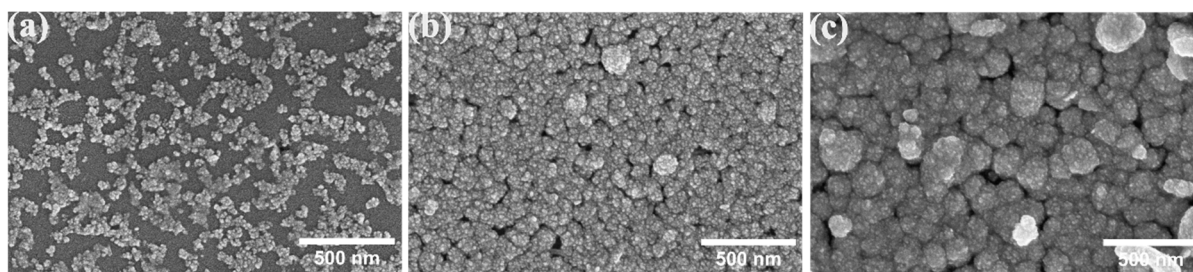


Figure 5: SEM micrograph of (a) one-, (b) two-, and (c) three-immersion bath thin films of bismuth oxysulfide.

At last, the deposition cycle number significantly impacts the morphology of the film, progressing from sparse nucleation (one-immersion bath) to hierarchical growth (two-immersion bath) and compact films (three-immersion bath). XRD results are consistent with these morphological transitions, which have the potential to remarkably influence the optical and electronic properties of the films. Due to its uniformity and phase purity, the two-immersion bath $\text{Bi}_2\text{O}_2\text{S}$ phase thin film exhibits promising characteristics for photovoltaic applications.

The growth mechanism of $\text{Bi}_2\text{O}_2\text{S}$ thin films is intrinsically linked to the Sillén phase crystal structure, which consists of alternating layers of Bi_2O_2 units and sulfur planes arranged in a tetragonal lattice. This distinctive layered architecture facilitates a layer-by-layer growth process, where the initial formation of a metastable oxide-rich layer transitions into a well-ordered $\text{Bi}_2\text{O}_2\text{S}$ phase upon progressive sulfur incorporation. The strong coordination within the Bi_2O_2 layers and the weak electrostatic interactions with the sulfur planes enable anisotropic crystal growth and lattice ordering characteristic of the Sillén structure. This layered framework acts as a structural template that governs the phase transformation and the morphological evolution observed experimentally by XRD and SEM, promoting the formation of nanoneedle arrays with enhanced crystallinity and reduced defects. Thus, the unique features of the Sillén phase are crucial for understanding and controlling the growth dynamics, as well as optimizing the properties of $\text{Bi}_2\text{O}_2\text{S}$ thin films for high-performance optoelectronic applications.

Fig. 6 shows a comparison of the measurements of SEM and EDS for the cross-section of the three-immersion bath thin film, prepared by the CBD technique. The visualization of the sample undergoes significant changes. It is possible to precisely determine their widths of 35 to 53 nm. However, it was impossible to distinguish all the individual layers.

3.5 Mechanism of $\text{Bi}_2\text{O}_2\text{S}$ Thin Film Formation

In this study, a sequential, number of immersion baths dependent transformation process is facilitated by a metastable intermediate phase during the chemical bath deposition (CBD) of Bi-based thin films. As shown in the sections described above, this multistep evolution is evidenced by structural, morphological, and microstructural changes detected through complementary techniques, including X-ray diffraction (XRD),

X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The growth mechanism is driven by progressive sulfur incorporation, increased crystallinity, and morphological refinement induced by successive immersion baths. Initially, the high oxygen activity in the chemical bath promotes nucleation of a metastable Bi_2O_2 phase during the initial deposition stage. Early SEM observations display isolated, short $\text{Bi}_2\text{O}_2\text{S}$ flower-like structures randomly distributed on the substrate, see Fig. 5a, characteristic of initial nucleation with limited surface coverage and connectivity, reflective of a porous early-stage film morphology. Backscattered electron imaging, see Fig. 7, enhances compositional contrast, confirming the bismuth-rich nature of these flower-like structures. This phase seems to act as a structural intermediate, alongside transient secondary phases of Bi_2O_3 and Bi_2S_3 , facilitating sulfur incorporation to form $\text{Bi}_2\text{O}_2\text{S}$. The Bi_2O_2 lattice offers a compatible environment, minimizing disruption during anion exchange and enabling transition to the $\text{Bi}_2\text{O}_2\text{S}$ structure.

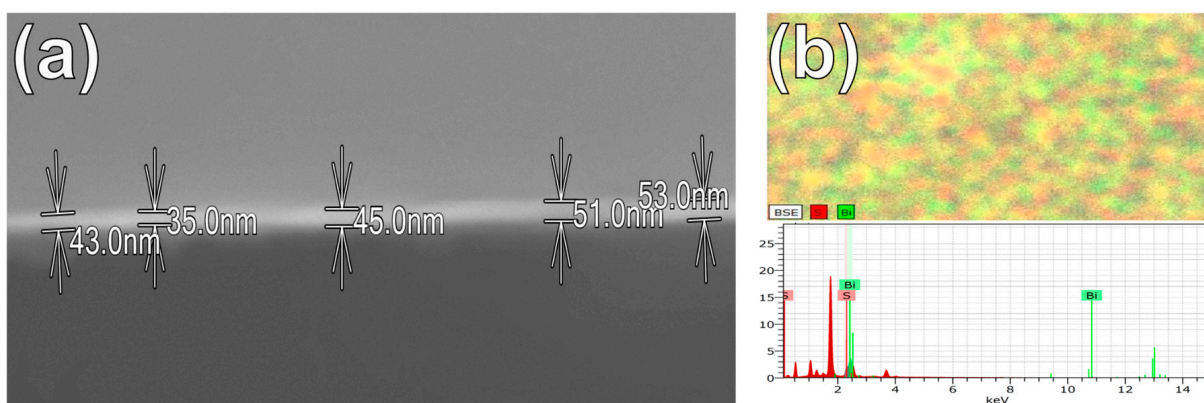


Figure 6: (a) SEM micrograph showing measurements in several regions along the film, and (b) EDS elemental mapping of the cross-section of the three-immersion bath thin film.

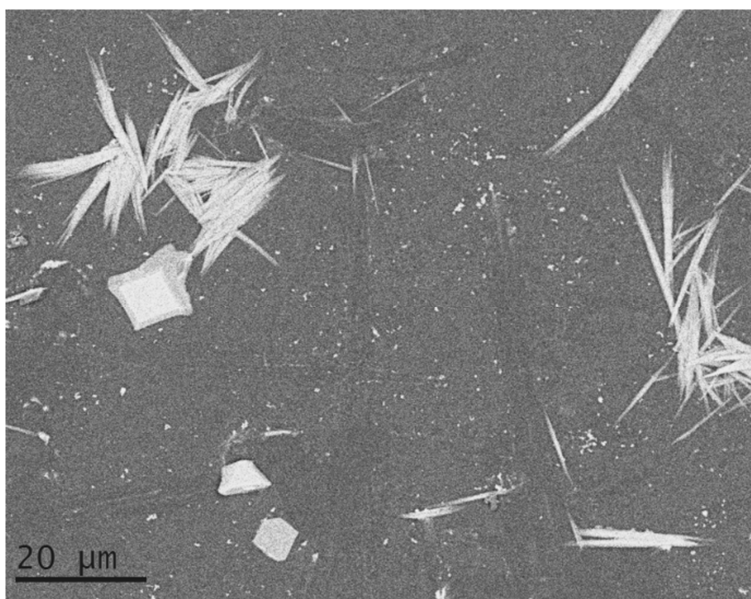


Figure 7: SEM micrograph where the flower-like structures are shown with backscattered electrons for one-immersion bath thin film.

The first immersion bath occurs in an oxygen-rich environment, resulting in the formation of a laminar, metastable Bi-based oxide phase, likely $\text{Bi}_2\text{O}_2(\text{OH})_2$ and/or Bi_2O_2 , arising from partial hydrolysis of Bi^{3+} ions as confirmed by XPS. This phase serves as a structural template for subsequent sulfur incorporation. XRD patterns at this stage exhibit broad, low-intensity reflections corresponding to the (040) and (112) planes of $\text{Bi}_2\text{O}_2\text{S}$, suggesting poor crystallinity and incomplete sulfurization. Residual Bi_2O_3 may also be present as a secondary phase. SEM images reveal isolated, short nanoneedle-like structures randomly distributed on the substrate, characteristic of initial nucleation with limited surface coverage and connectivity, typical of early-stage, porous film morphology.

During the second immersion bath, the $\text{Bi}_2\text{O}_2(\text{OH})_2$ scaffold undergoes a topotactic transformation driven by the increased availability of sulfide ions (S^{2-}) released from thiosulfate or thiourea precursors in the chemical bath, as supported by XPS evidence indicating progressive sulfur incorporation replacing hydroxide or oxygen anions within the interlayer space. This substitution occurs while maintaining the underlying crystallographic orientation, facilitating the transition to the crystalline $\text{Bi}_2\text{O}_2\text{S}$ phase.

The XRD patterns of two-immersion bath films exhibit more distinct and sharper peaks indexed to the (040), (060), and (112) planes of $\text{Bi}_2\text{O}_2\text{S}$, confirming improved crystallinity. Minor Bi_2S_3 phases may coexist, indicating ongoing competition between sulfide and oxide phase formation. SEM analysis, see Fig. 5b, shows that the nanoneedles become longer, more aligned, and more densely packed, reflecting enhanced anisotropic growth and grain connectivity. This intermediate stage is thus characterized by partial phase conversion and increased structural ordering.

The incorporation of sulfur is completed upon the third immersion bath, favoring the formation of well-crystallized orthorhombic $\text{Bi}_2\text{O}_2\text{S}$. The partially formed $\text{Bi}_2\text{O}_2\text{S}$ layers act as a structural template, facilitating epitaxial-like or oriented growth during subsequent deposition. At this stage, XRD patterns exhibit sharp, intense reflections at 2θ values of approximately 30.46° , 45.23° , and 58.11° , corresponding to the (040), (414), and (132) crystallographic planes, respectively, indicative of the dominant $\text{Bi}_2\text{O}_2\text{S}$ phase presence. A systematic shift toward higher angles, alongside a pronounced reduction in peak full width at half maximum (FWHM), suggests enhanced crystalline, decreased interplanar spacing, and reduced lattice strain.

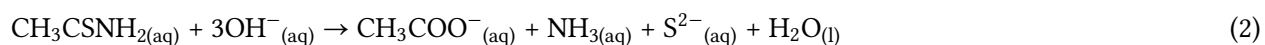
SEM images, see Fig. 5c, reveal a continuous, interconnected network of elongated, densely packed nanoneedles. The Williamson-Hall analysis confirms a reduction in microstrain and dislocation density consistent with the dense morphology and anisotropic growth. The film thus becomes more compact, uniform, and structurally coherent following three immersion baths.

A step-by-step reaction mechanism is proposed as follows:

- (1) The initial hydroxylation of the bismuth precursor and the formation of the bismuth oxide (Eq. (1))



- (2) On the other hand, the chemical decomposition of the sulfur source (ionic hydrolysis of thioacetamide) in the bath to yield active ions (Eq. (2))



- (3) Then, the subsequent topotactic anion exchange leading to the formation of crystalline bismuth oxyhydroxide (Eq. (3))



- (4) Alternatively, the formation of the bismuth sulfide (Eq. (4)), and finally



(5) The formation of the bismuth oxysulfide (Eq. (5))



A clear phase transformation mechanism is evidenced by the gradual transition from a disordered, oxide-rich initial layer to a well-defined $\text{Bi}_2\text{O}_2\text{S}$ nanoneedle array with successive immersion baths. Each additional immersion bath promotes morphological refinement, lattice ordering, and improved phase purity. These progressive enhancements culminate in nanostructured films that exhibit optimized morphologies, reduced lattice defects, and superior crystallinity. Such structurally coherent films are highly promising for optoelectronic applications, particularly in solar energy conversion, where their enhanced electrical and optical properties can significantly improve device performance.

The combined analysis of XRD and SEM results supports the proposed phase transformation and growth mechanism of $\text{Bi}_2\text{O}_2\text{S}$ thin films with increasing immersion baths. XRD patterns reveal a progression from broad, low-intensity peaks in early immersion bath, indicating poor crystallinity and incomplete sulfur incorporation to the structure, intense reflections characteristic of well-crystallized orthorhombic $\text{Bi}_2\text{O}_2\text{S}$ at higher immersion baths, confirming improved lattice ordering and purer phase. These structural improvements coincide with SEM observations, which show an evolution from isolated, short, flower-like structures with low surface coverage to densely packed, elongated, and interconnected nanoneedles forming a uniform network. This morphological refinement reflects anisotropic grain growth and coalescence, consistent with reduced lattice strain and defect densities evidenced by Williamson-Hall analysis. Together, the structural and morphological data elucidate a immersion baths-dependent growth pathway wherein a metastable oxide-rich phase serves as a template that transforms via sulfur incorporation into a well-ordered $\text{Bi}_2\text{O}_2\text{S}$ array. This sequential transformation is directly linked to improved crystallinity, reduced microstrain, and the formation of a compact, uniform film morphology suitable for high-performance optoelectronic applications.

4 Conclusions

In this study, semiconducting emerging chalcogenide $\text{Bi}_2\text{O}_2\text{S}$ thin films were successfully synthesized via an eco-friendly chemical bath deposition (CBD) method. The number of immersion baths was established as a critical governing parameter for both phase evolution and film morphology. Results shown a considerable absorbance increase as the number of immersion baths increased. Physical characterization revealed an immersion bath-dependent growth pathway, transitioning from a disordered, oxide-rich initial layer at one-immersion bath to a well-ordered nanoneedle array at three-immersion baths. A minimum of two immersion baths was found to be necessary to induce the crystallization of the phase. This sequential structural ordering and subsequent reduction of lattice defects allowed for precise tuning of the optical properties. Specifically, the optical band gap decreased from the two-immersion bath thin film, directly correlated with improved crystallinity and reduced microstrain. Ultimately, these findings demonstrate that controlling the number of immersion baths during thin film synthesis by the CBD technique effectively modulates the optoelectronic properties of Bi-based chalcogenides, in this case, thin films of $\text{Bi}_2\text{O}_2\text{S}$, which is crucial for optimizing performance in optoelectronic devices.

Acknowledgement: Edgar G. Zamorano-Noriega would like to acknowledge SECIHTI (Secretaría de Ciencia, Humanidades, Tecnología e Innovación, Mexico) for the financial support provided for his graduate studies during this study.

Funding Statement: The authors received no specific funding for this study.

Author Contributions: The authors confirm contribution to the paper as follows: Conceptualization, María E. Martínez-Barbosa, Ana B. López-Oyama and Santos J. Castillo; methodology, Edgar G. Zamorano-Noriega, Santos J. Castillo, María E. Martínez-Barbosa and Ana B. López-Oyama; formal analysis, Eugenio Rodríguez González, Edgar G. Zamorano-Noriega, Santos J. Castillo, María E. Martínez-Barbosa and Ana B. López-Oyama; investigation, Edgar G. Zamorano-Noriega, Crescencio García-Guendulain and María L. Mota; writing—original draft preparation, Edgar G. Zamorano-Noriega, Ana B. López-Oyama, María E. Martínez-Barbosa and Santos J. Castillo; writing—review and editing, María E. Martínez-Barbosa, Santos J. Castillo, Ramón Ochoa-Landín, Fernando J. Sánchez-Rodríguez and Edgar G. Zamorano-Noriega. All authors reviewed and approved the final version of the manuscript.

Availability of Data and Materials: The original contributions presented in the study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding authors.

Ethics Approval: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.

Supplementary Materials: The supplementary material is available online at <https://www.techscience.com/doi/10.32604/cl.2026.085590/s1>. Fig. S1. Peak positions, peak shift, and peak broadening for the one-, two-, and three-immersion bath thin films. The (040) plane is the preferred orientation; Fig. S2. XRD patterns of Bi-based thin films matched with the corresponding diffraction planes from Powder Diffraction File (PDF) cards No. 41-1449 (Bi₂O₃) and No. 17-0320 (Bi₂S₃) and Fig. S3: XPS survey spectrum for Bi-based thin film.

Abbreviations

The following abbreviations are used in this manuscript:

BE	Binding Energy
TEA	Triethanolamine
TA	Thioacetamide
SE	Secondary electron
BSE	Backscattered electron

References

1. Bui TK, Aravindakumar CT, Arthanareeswaran G, Van Pham V. Hydrothermal synthesis of Bi₂O₃/Bi₂O₂S heterojunctions as emerging photocatalysts for tetracycline degradation. *Mater Emerg Technol Sustain*. 2025;1:2550002. [CrossRef].
2. Berekute AK, Yu KP, Chuang YB. Enhanced photocatalytic activity of novel α -Bi₂O₃@g-C₃N₄ composites for the degradation of endocrine-disrupting benzophenone-3 in water under visible light. *Sustain Environ Res*. 2022;32(1):17. [CrossRef].
3. Chitara B, Limbu TB, Orlando JD, Tang Y, Yan F. Ultrathin Bi₂O₂S nanosheet near-infrared photodetectors. *Nanoscale*. 2020;12(30):16285–91. [CrossRef].
4. Bondarenko EA, Streltsov EA, Malashchonak MV, Mazanik AV, Kulak AI, Skorb EV. Giant incident photon-to-current conversion with photoconductivity gain on nanostructured bismuth oxysulfide photoelectrodes under visible-light illumination. *Adv Mater*. 2017;29(40):1702387. [CrossRef].
5. Linhart WM, Zelewski SJ, Scharoch P, Dybała F, Kudrawiec R. Nesting-like band gap in bismuth sulfide Bi₂S₃. *J Mater Chem C*. 2021;9(39):13733–8. [CrossRef].
6. Liu YL, Li MQ, Wang GG, Dang LY, Li F, Yan D, et al. Bi₂O₂S nanosheets anchored on reduced graphene oxides as superior anodes for aqueous rechargeable alkaline batteries. *Electrochim Acta*. 2022;427:140833. [CrossRef].
7. Tezel FM, Kariper A. Synthesis, surface tension, optical and dielectric properties of bismuth oxide thin film. *Mater Sci Pol*. 2017;35(1):87–93. [CrossRef].
8. Kariper İA. Producing BiI/BiOI thin films via chemical bath deposition. *Mat Res*. 2016;19(1):18–23. [CrossRef].

9. Strehlow WH, Cook EL. Compilation of energy band gaps in elemental and binary compound semiconductors and insulators. *J Phys Chem Ref Data*. 1973;2(1):163–200. [CrossRef].
10. Karıper İA. Synthesis and characterization Bi₂O₂S thin film via chemical bath deposition at low pH. *Spectrochim Acta Part A Mol Biomol Spectrosc*. 2016;163:102–7. [CrossRef].
11. Koyama E, Nakai I, Nagashima K. Crystal chemistry of oxide–chalcogenides. II. Synthesis and crystal structure of the first bismuth oxide–sulfide, Bi₂O₂S. *Acta Crystallogr B Struct Sci*. 1984;40(2):105–9. [CrossRef].
12. Zhang X, Liu Y, Zhang G, Wang Y, Zhang H, Huang F. Thermal decomposition of bismuth oxysulfide from photoelectric Bi₂O₂S to superconducting Bi₄O₄S₃. *ACS Appl Mater Interfaces*. 2015;7(7):4442–8. [CrossRef].
13. Al-Jawad SMH. Influence of multilayer deposition on characteristics of nanocrystalline SnO₂ thin films produce by sol-gel technique for gas sensor application. *Optik*. 2017;146:17–26. [CrossRef].
14. Ibrahim S, Minasyan L, Bonnet P, Monier G, Tomasella E, Sauvage T, et al. Photocatalytic Properties of Bismuth Oxyfluoride Thin Films Deposited by Reactive Magnetron Sputtering in Ar/O₂/CF₄ Atmosphere [Internet]. 2023 [cited 2026 Jan 1]. Available from: <https://hal.science/hal-04037069v1>.
15. Ding F, Wang Q, Zhou S, Zhao G, Ye Y, Ghomashchi R. Synthesis of Bi₂S₃ thin films based on pulse-plating bismuth nanocrystallines and its photoelectrochemical properties. *R Soc Open Sci*. 2020;7(8):200479. [CrossRef].
16. Brindha R, Renuka Devi KB. Fundamental properties of chemical bath deposited Bi₂S₃ thin films. *Int J Macro Nano Phys*. 2016;1(1):70–6. [CrossRef].
17. Moreno-García H, Messina S, Calixto-Rodriguez M, Martínez H. Physical properties of chemically deposited Bi₂S₃ thin films using two post-deposition treatments. *Appl Surf Sci*. 2014;311:729–33. [CrossRef].
18. Zhang R, Zhou Z, Qi N, Zhao B, Zhang Q, Zhang Z, et al. Significant enhancement in the thermoelectric performance of Bi₂O₂S through dimensionality reduction. *J Mater Chem C*. 2019;7(47):14986–92. [CrossRef].
19. Meng S, Zhang X, Zhang G, Wang Y, Zhang H, Huang F. Synthesis, crystal structure, and photoelectric properties of a new layered bismuth oxysulfide. *Inorg Chem*. 2015;54(12):5768–73. [CrossRef].
20. Han D, Du MH, Dai CM, Sun D, Chen S. Influence of defects and dopants on the photovoltaic performance of Bi₂S₃: first-principles insights. *J Mater Chem A*. 2017;5(13):6200–10. [CrossRef].
21. Koltsov M, Gopi SV, Raadik T, Krustok J, Josepson R, Gržibovskis R, et al. Development of Bi₂S₃ thin film solar cells by close-spaced sublimation and analysis of absorber bulk defects via in-depth photoluminescence analysis. *Sol Energy Mater Sol Cells*. 2023;254:112292. [CrossRef].
22. Jamali-Sheini F, Cheraghizade M, Heshmatynezhad L. An efficient wide range photodetector fabricated using a bilayer Bi₂S₃/SnS heterojunction thin film. *Semicond Sci Technol*. 2019;34(4):045008. [CrossRef].
23. Zhang W, Liu D, Jin W, Zhang D, Sun T, Liu E, et al. *In situ* construction of 2D/1D Bi₂O₂S/Bi₂S₃ heterojunction from the topological transformation of Bi₂O₂S with significantly enhanced photoelectrochemical performance.. *Int J Hydrogen Energy*. 2024;51:1545–57. [CrossRef].
24. Wang K, Qiao H, Li J, Qi X. A robust photoelectrochemical photodetectors based on the self-healing properties of Bi₂O₂S nanoplates. *Appl Surf Sci*. 2021;565:150444. [CrossRef].
25. Jayeola KD, Sipuka DS, Sebokolodi TI, Nkwachukwu OV, Muzenda C, Koiki BA, et al. The design and characterisation of a Z-scheme Bi₂O₂S/ZnO heterojunction photoanode for the photoelectrochemical removal of ciprofloxacin in synthetic and real wastewater. *Chem Eng J*. 2024;479:147482. [CrossRef].
26. Zhang W, Liu X, Jin W, Li Q, Sun Q, Liu E, et al. Epitaxial grown [hk1] oriented 2D/1D Bi₂O₂S/Sb₂S₃ heterostructure with significantly enhanced photoelectrochemical performance. *J Colloid Interface Sci*. 2024;654:413–25. [CrossRef].
27. He S, Bahrami A, Zhang X, Cichocka MO, Yang J, Charvot J, et al. Atomic layer deposition and characterization of Bi₁Se₁ thin films. *J Eur Ceram Soc*. 2023;43(11):4808–13. [CrossRef].
28. Rong P, Gao S, Zhang M, Ren S, Lu H, Jia J, et al. Large-area hierarchical Bi₂O₂S flowers composed of 2D ultrathin nanosheets for high performance self-powered IR photodetector. *J Alloys Compd*. 2022;928:167128. [CrossRef].
29. Yang X, Qu L, Gao F, Hu Y, Yu H, Wang Y, et al. High-Performance broadband photoelectrochemical photodetectors based on ultrathin Bi₂O₂S nanosheets. *ACS Appl Mater Interfaces*. 2022;14(5):7175–83. [CrossRef].
30. Samanta M, Biswas K. 2D nanosheets of topological quantum materials from homologous (Bi₂)_m(Bi₂Se₃)_n heterostructures: synthesis and ultralow thermal conductivity. *Chem Mater*. 2020;32(20):8819–26. [CrossRef].
31. Alessio Verni G, Long B, Gity F, Lanius M, Schüffolgen P, Mussler G, et al. Oxide removal and stabilization of bismuth thin films through chemically bound thiol layers. *RSC Adv*. 2018;8(58):33368–73. [CrossRef].

32. Hughes MA, Fedorenko Y, Gholipour B, Yao J, Lee TH, Gwilliam RM, et al. N-type chalcogenides by ion implantation. *Nat Commun.* 2014;5:5346. [[CrossRef](#)].
33. Zatsepin DA, Boukhvalov DW, Gavrilov NV, Kurmaev EZ, Zhidkov IS. XPS and DFT study of pulsed bi-implantation of bulk and thin-films of ZnO—The role of oxygen imperfections. *Appl Surf Sci.* 2016;387:1093–9. [[CrossRef](#)].