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SYNTHESIS AND CHARACTERIZATION OF ZINC TIN SULPHIDE (ZTS) THIN FILMS VIA CHEMICAL BATH DEPOSITION ROUTE

Adeniji, Q. A. [1,2]*, Odunaike, R. K.[2], Bamijoko, B. A.[2] , Adeleke, A. T.[2] and Dahunsi, K. T.[3]

[1]Department of Physics, Federal University Kashere, Nigeria.
[2]Department of Physics, Olabisi Onabanjo University, Ago-Iwoye, Nigeria.
[3]Physics Unit, Department of General Studies, Federal College of Fisheries and Marine Technology, Lagos, Nigeria.

***Corresponding Author: qadeniji@yahoo.com**
(Tel: +2348030755031, Orcid No: 0000-0002-1970-3836)

Abstract

Zinc Tin Sulphide (ZTS) thin films were deposited on glass substrates by Chemical Bath Deposition (CBD) technique. The CBD was obtained by preparing 20 ml of 0.5M of Zinc chloride solution, 20ml of 0.5M stannum chloride ($SnCl_2$) with 3ml of Triethanolamine (TEA) ($N(CH_2CH_2OH)_3$) and 25ml of 0.5M of Thiourea as complexants. The grain size of ZTS from the SEM micrographs was spherically-shaped without visible defects like crack or peel. The SEM micrograph of the annealed ZTS thin films, however, showed a dense sponge-like structure. ZTS thin films reflectance curve exhibited average reflectance below 30% for all films. Annealed ZTS thin films (at 200 ^0C) exhibited the greatest reflectance of about 30% than all other films. Both as-deposited and annealed ZTS films exhibited transmittance above 40% for wavelength around 780 nm and above. The extrapolated band gaps energy values for ZTS for as-deposited and annealed thin films varied from the range of 3.30 to 3.40 eV. The resistivity increased with an increase in heat treatment and it ranged between, 1.83×10^{-1} Ωm to 9.71×10^{-2} Ωm.

Keywords: Characterization, Zinc Tin Sulphide (ZTS), Chemical Bath, Renewable Energy

1. Introduction

An increase in interest in thin-film photovoltaics as a result of the energy requirements and low production costs cannot be overemphasized. ZnSnS is considered to be a promising material for application in low cost and environmentally friendly thin-film solar cells (Tanusevski & Poelman, 2003). Thin-film solar cells are emerging as an alternative technology to silicon-based solar cells (Kahraman *et al.,* 2013). In comparison to another ternary, ZTS has the advantages of earth-abundant and non-toxic elements which makes it one of the promising candidates for cost-effective as well as environmentally benign devices. The conversion efficiency of CZTS-based solar cells has been improved recently from 6.7 % in 2008 to 9.7 % in 2010 and 11.1 % in 2012 indicating the promise of this new thin-film PV materials system (Katagiri *et al.,* 2008; Todorov *et al.,* 2013a). The current record efficiency of CZTS-based thin film is 12.6 % and was reported by Wang *et al.* (2014). Since 2010, the efficiency is improved by partly selenizing the CZTS thin film to have a broader spectral photoresponse. In this new record, Wang *et al*., (2014), used hydrazine pure-solution approach targeting a Cu-poor and Zn-rich condition (Todorov *et al., 2013c).* Many researchers have addressed various kinds of CZTS nanocrystals and CZTS nanocrystals with different crystalline structures and shapes had been synthesized.

2. Materials and Methodologies

The Apparatus used in this study were: Glass beakers (50 ml and 100 ml); Microscopic glass substrate; Stirring rod; Measuring cylinders (25 ml and 50 ml); Electronic weighing balance (Max.=500g; d=0.01g); Syringes (2ml, 10ml, and 20ml); Substrate holder; Hot plate with magnetic stirrer; Laboratory spoon; Petri dishes; Clip; Stopwatch; Mettler Toledo AG 8603 pH meter; Scanning Electron Micrograph (SEM) machine, Avantes UV-VIS spectrophotometer; Keithley Four Point Probe (FPP) Machine, etc. The chemical reagents were of LR grades; EDTA, Triethanolamine (TEA) ($N(CH_2CH_2OH)_3$) and sodium hydroxide NaOH($_{aq}$), which were used as complexants for Zinc Chloride ($ZnCl_2$), Stannum Chloride (SnCl) and Thiourea respectively with distilled water making up to 100ml. Ammonia (NH_3) was used to increase the pH of the mixture. The CBD method depends on the deposition of thin films from aqueous solutions by chemical reactions under appropriate conditions. Thin films were deposited on soda-lime glass (SLG) substrates (76.2mm x 2.5mm x 1.2mm) which were immersed into the precursor. To remove the organic and inorganic impurities, the glass substrates with a dimension of 76.2mm x 2.5mm x 1.2mm was cleaned with detergent and water severally, subsequently soaking them in HCl acid for 20 minutes. After that slides were thoroughly washed with distilled water several times, then rinsed with acetone, washed with deionized water, and air-dried. The chemical bath solution was obtained by preparing 20 ml of 0.5M of Zinc chloride solution, 20ml of 0.5M stannum chloride ($SnCl_2$) with 3ml of Triethanolamine (TEA) ($N(CH_2CH_2OH)_3$) and 25ml of 0.5M of Thiourea was placed into 100ml beaker, NaOH(aq) which was added in until a pH of 9 and temperature of the mixture was monitored with the aid of Mettler Toledo AG 8603 pH meter. Then, 30ml of distilled water was added to the solution to make a final volume of 100ml in the beaker. The mixture was gently stirred at the temperature to obtain a homogenous solution. The colour changes of the solution were noticed during the measurement/preparation and the experiment at large. The substrates were kept vertically and at the center of the water bath to prevent the substrates from leaning against one another and the walls of the bath. The deposition was carried out for 5 hours at about 80 ^oC.

3. Results

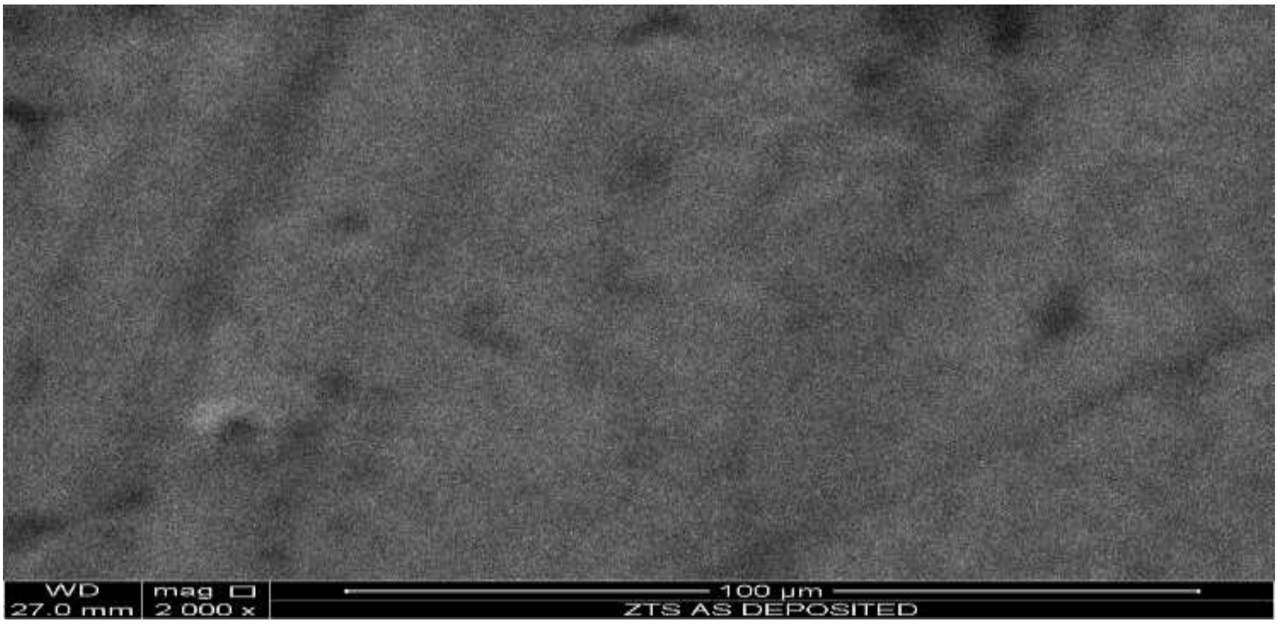

Figure 1a: SEM image of ZTS as deposited

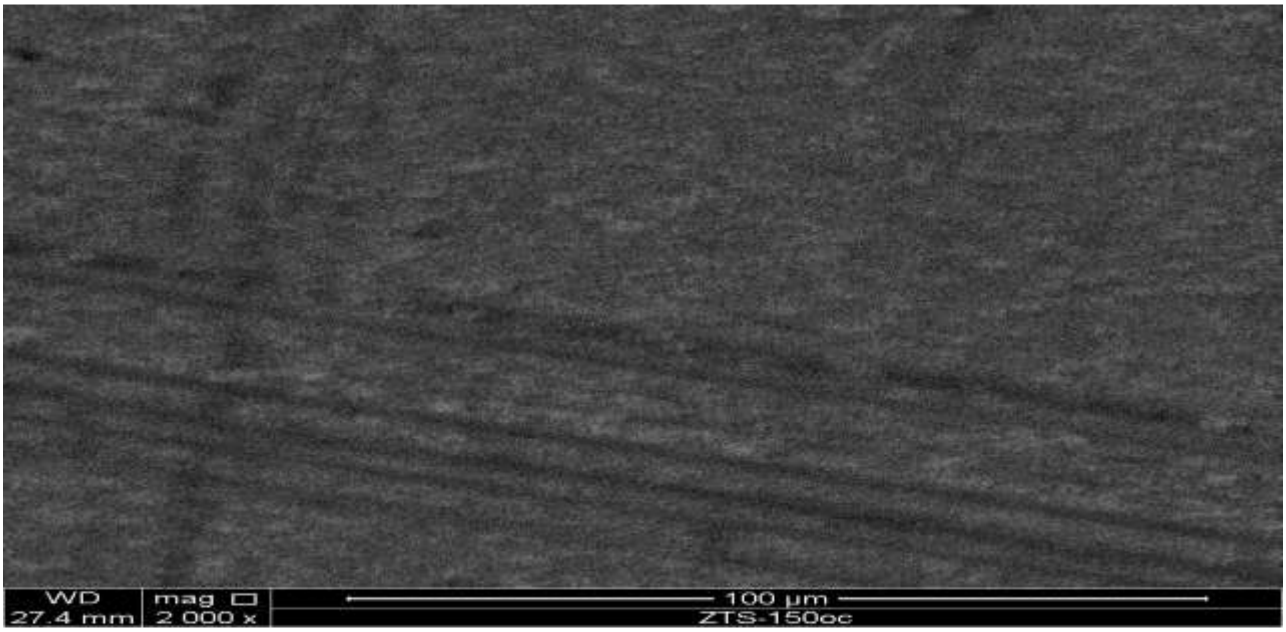

Figure 1b: SEM image of ZTS annealed at 150 ^{0}C

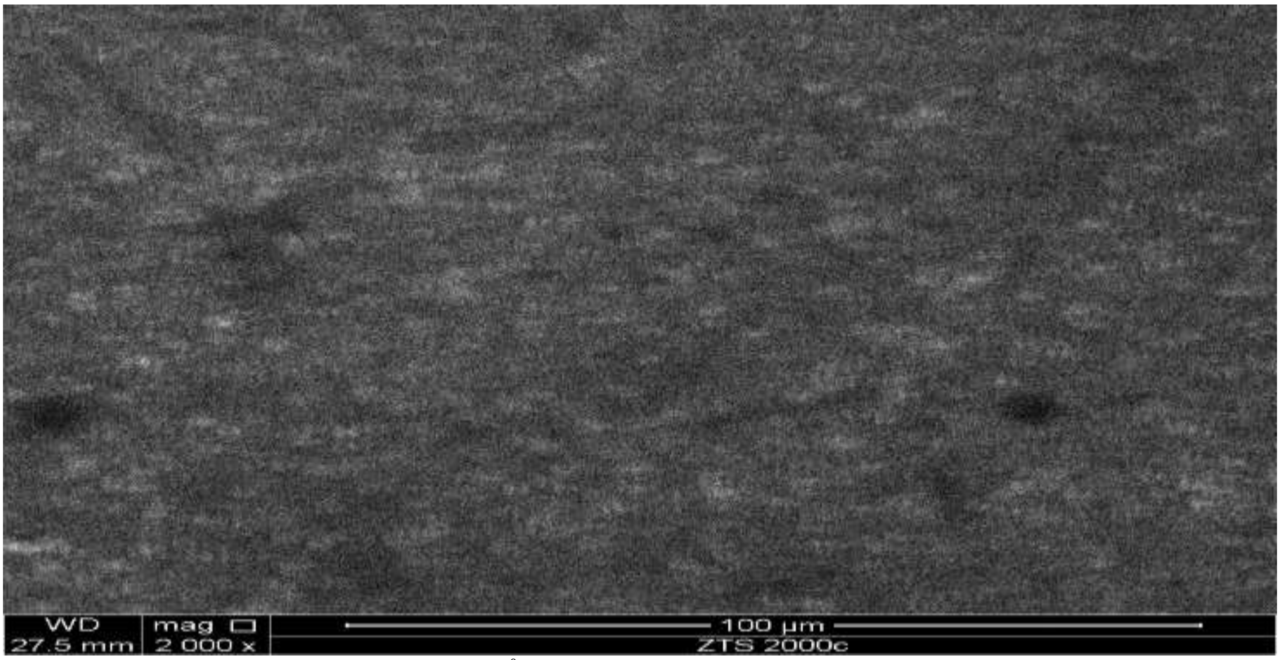

Figure 1c: SEM image of ZTS annealed at 200 ^{0}C

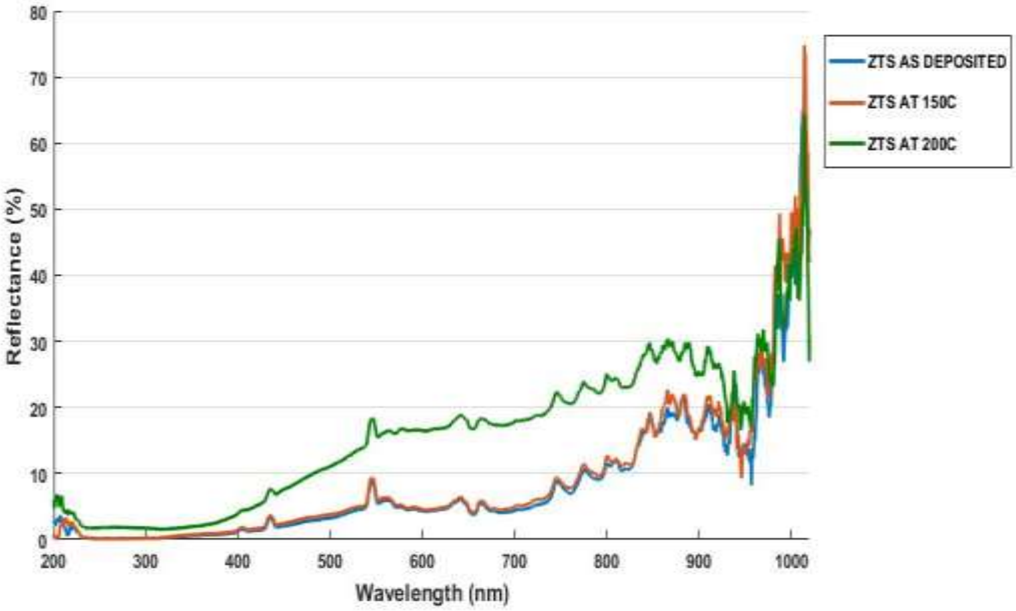

Figure 2: Graph of reflectance against wavelength for ZTS

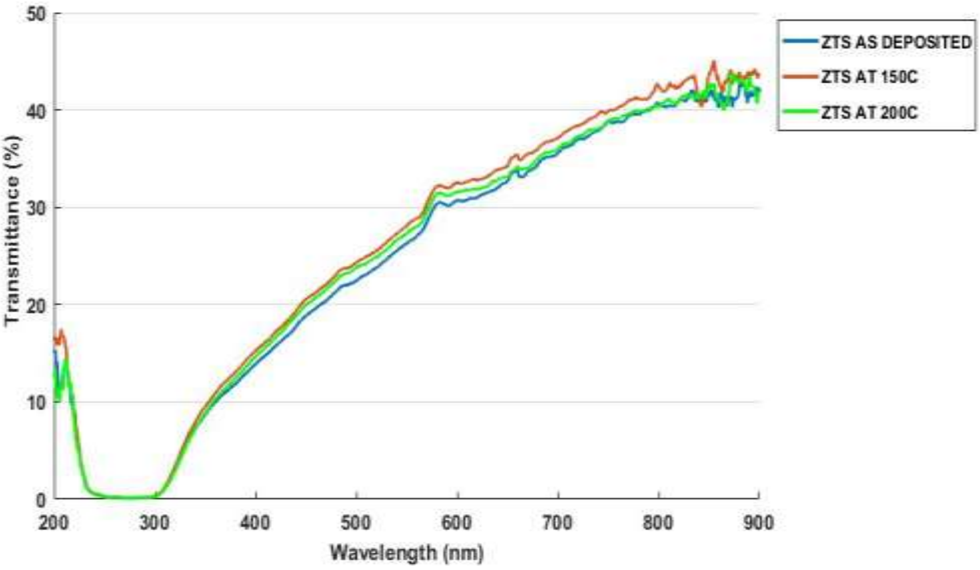

Figure 3: Graph of Transmittance against wavelength for ZTS

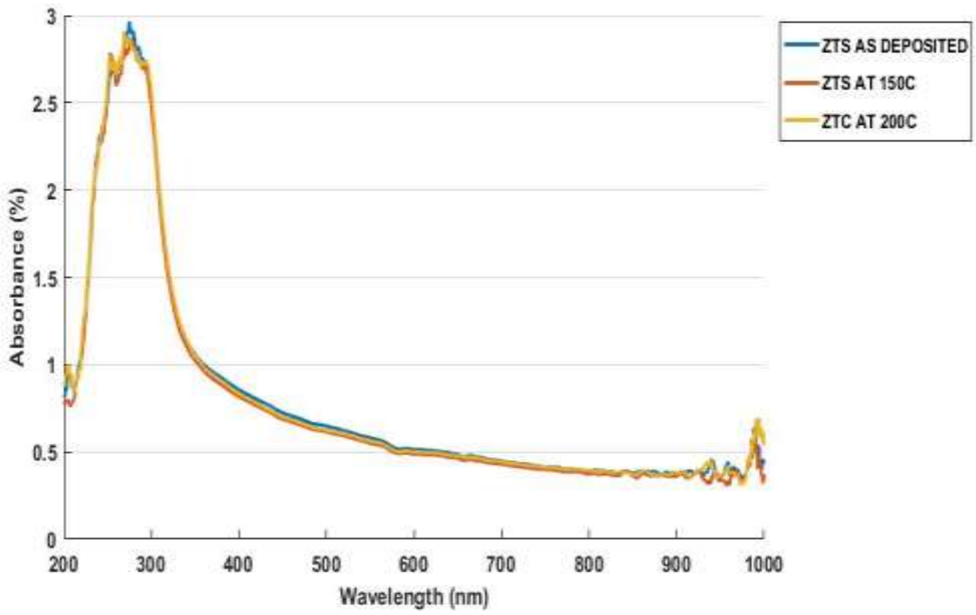

Figure 4: Graph of absorbance against wavelength for ZTS

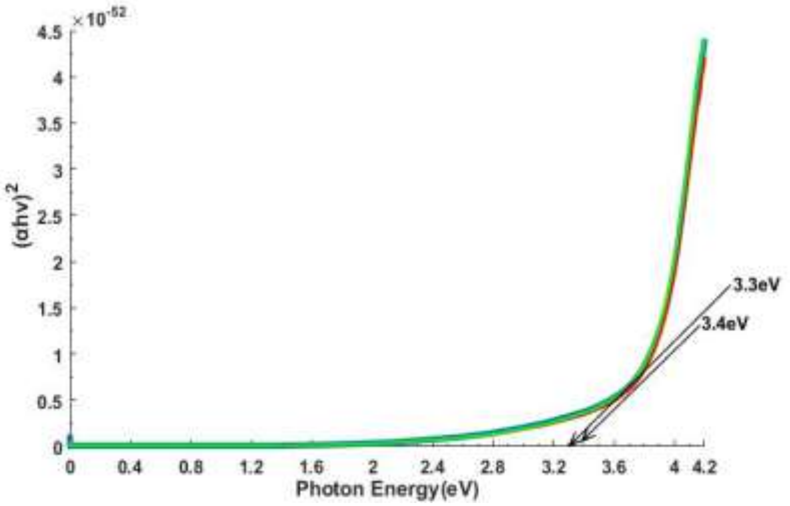

Figure 5: Graph of $(\alpha hv)^2$ against Photon Energy in eV for ZTS

Table 1: **Electrical Properties of ZTS**

Samples	**Voltage (v)**	**Current (A)**	**Resistivity (Ωm)**	**Conductivity (Ωm^{-1})**	**Sheet resistance, R_s (Ω/m^2)**
ZTS as deposited	1.25×10^3	3.1×10^4	3.66×10^{-2}	2.73×10^1	1.83×10^{-1}
ZTS annealed at 150 ^{0}C	1.08×10^3	2.75×10^4	3.56×10^{-2}	2.81×10^1	1.78×10^{-1}
ZTS annealed at 200 ^{0}C	4.50×10^2	2.10×10^4	1.94×10^{-2}	5.15×10^1	9.71×10^{-2}

4. Discussion

4.1 Morphology Properties

Figure 1 showed that the films look highly smooth and homogenous with densely packed and spherically-shaped grains, well distributed over the entire substrate which revealed that the films adhere to the substrate without crack, peel, or pinhole. The high magnifications (Figures 1a, b, and c) of the SEMs exhibited nano-crystallinity with the formation of a textured surface. This result made the effectiveness of the Chemical Bath Deposition (CBD) technique in the growth of nanocrystalline films of high quality.

4.2 Optical Properties

The optical analysis data were obtained from Avantes UV-VIS-NIR spectrophotometer in the range of 200-900nm. The reflectance graphs of ZTS thin films are shown in Figure 2 they are found to be varied from 4-8% at initial for as-deposited, annealed at 150^0 C, and annealed at 200^0 C. It was observed that ZTS annealed at 200 ^{0}C thin films had the greatest reflectance of about 30% than all other films. This is in agreement with Wanjala *et al.* (2016). Figure 3 shows the transmittance for ZTS thin films. All films exhibited transmittance above 40% for wavelength above 780 nm. The optimized transmittance at λ=900 nm was found to be 48%. This transmittance value of the thin film is fairly good for the window material to be used in solar cells. Figure 4 shows that ZTS films have good absorption in a short wavelength region, the absorption decreased with the increasing wavelength of solar radiation. From the figure there was a decrease in absorbance up to a wavelength, λ=990nm, then a slight increase in absorption. ZTS Thin films annealed at 150 ^{0}C had the lowest absorbance of 0.4% at wavelength 950 nm whereas as-deposited ZTS thin film has the highest absorbance of 3.0% at wavelength 300 nm. The extrapolated band gaps energy values for ZTS for as-deposited and annealed thin films vary from the range of 3.30eV - 3.40 eV respectively as seen in Figure 5. These Band gap values were in agreement with the study of Rahdar *et al.* (2012) who obtained the energy bandgap on the determination of optical properties of ZnS thin films in the range 3.64eV-4.00eV.

4.3 Electrical Properties

Table 1 shows ZTS as-deposited, annealed at 150 ^{0}C and 200 ^{0}C with resistivities values of 2.05×10^{-3} Ωm and 4.37×10^{-4} Ωm respectively. From Table 1, it was observed that sheet resistivity decreases with an increase in heat treatment and it ranged between, 1.83×10^{-1} Ωm to 9.71×10^{-2} Ωm. The decrease in film resistivity makes it very useful for photovoltaic applications. Similar sheet resistivity measurements for ZnS were obtained using Van der Pauw technique in the order of 10^2 Ω-cm to 10^1 Ω-cm and electrical conductivity of 10^{-3} to 10^{-2} $(\Omega\text{-cm})^{-1}$ by Shinde *et al*. (2011). Adeniji *et al*. 2020 reported that when conductivity increases as the heat treatment increases, it enhances the electrical properties of ZTS thin films and this made the ZTS a good candidate for solar cell fabrication.

5. Conclusions

ZTS thin films have been successfully deposited on glass substrates by Chemical Bath Deposition (CBD) technique. Thin films deposited through chemical bath deposition technique (CBD) were found to have high absorbance in UV-VIS-NIR regions while the film's absorbance increases as the thickness increased, thus they could find applications in solar radiation absorbers for solar cell applications. The high bandgap properties indicate that the films can be used as a window layer in the fabrication of thin-film heterojunction solar cells and other optoelectronic devices. Conversely, their low reflectance properties make them good materials for antireflection coatings, solar cell absorbers, thermal control, and photosynthetic coatings.

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Conflicts of Interest

The authors declare no conflict of interest.

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