

Investigation of the Influence of Precursor Concentration (SbCl_3) on the Optical Properties of CuSbS_2 Thin Films As-Deposited

J.C. Echewodo, B.C. Anusionwu, E.C. Mbamala, O.K. Echendu

Department of Physics, Federal University of Technology, P.M.B. 1526, Owerri, Nigeria

Corresponding Author: J.C. Echewodo

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ABSTRACT

This research investigated the impact of different concentrations of antimony trichloride (SbCl_3) on the optical characteristics of copper antimony sulfide (CuSbS_2) thin films in their as-deposited state. These films were synthesized using the Chemical Bath Deposition (CBD) method, with precursors including $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, SbCl_3 , $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and thiourea (NH_2CSNH_2). Triethanolamine (TEA) and acetone served as complexing agents, while an $\text{NH}_3/\text{NH}_4\text{Cl}$ solution acted as the buffer. The resulting films were characterized using X-ray Diffraction (XRD), Energy Dispersive X-ray Fluorescence (EDXRF), and UV-Vis Spectroscopy. Findings revealed that increasing the SbCl_3 concentration altered the bandgap of the CuSbS_2 films, with the highest bandgap of 1.92 eV recorded at a concentration of 1.8 M. The films showed strong absorption in both the UV and visible ranges, suggesting their suitability for applications in photodetectors and solar cell absorber layers.

Keywords: Solar cells, CuSbS_2 as-deposited, Precursors, Bandgap, Thin films

INTRODUCTION

Copper antimony sulphide (CuSbS_2) has emerged as a promising p-type semiconductor material, leading to rising

attention for its potential integration into next-generation thin-film photovoltaic devices and optoelectronic applications. One of its most attractive features is its direct bandgap that is tunable, which is reported to be in the range of 1.4 to 3.0 eV, ^[1] which closely aligns with the optimal spectral window for solar energy harvesting, thus enhancing its viability in solar cell architectures. ^[2] The precise value of this band gap can be modulated by some factors, including film thickness, chemical stoichiometry, crystalline phase, and particularly, the deposition technique employed. ^[3] In addition to its tunable optoelectronic properties, CuSbS_2 is composed of earth-abundant and non-toxic elements, offering a sustainable and low-cost alternative to conventional absorber materials such as $\text{Cu}(\text{In,Ga})\text{Se}_2$ and CdTe .^[4] Its high optical absorption coefficient further underlines its potential as a strong light absorber in thin-film solar cell technologies. A variety of deposition techniques have been used for synthesizing CuSbS_2 thin films, including spray pyrolysis,^{[3],[5]} thermal annealing of sequentially deposited Sb_2S_3 - CuS layers prepared by chemical bath deposition (CBD), ^[6] and direct one-step CBD approaches.^{[1],[7]} Interest in this ternary chalcogenide has surged as researchers seek viable replacements for toxic or rare-element-based absorbers such as CdTe , CuInSe_2 , and CuGeSe_2 , within the broader

effort to develop environmentally friendly solar energy materials.^{[8]-[9]}

CuSbS₂ and related metal-metal chalcogenides are also being studied to ascertain their suitability in photoelectrochemical (PEC) solar cells, where efficient charge separation and stability under illumination are critical parameters.^[10] Among the various fabrication methods, chemical bath deposition (CBD) stands out due to its simplicity, cost-effectiveness, and compatibility with large-area substrates. CBD allows for uniform film deposition on diverse substrate types ranging from glass to flexible polymers without the need for high vacuum systems or external energy inputs, relying solely on the controlled precipitation of metal sulphides from aqueous precursor solutions.^{[11]-[12]}

Despite its widespread application in producing binary and ternary chalcogenides such as CdS, ZnS, and CuInS₂,^{[13]-[14]} the use of CBD for direct synthesis of CuSbS₂ has traditionally been limited. Instead, earlier reports have often employed two-step or multi-layer approaches, where Sb₂S₃ precursor layer is thermally treated in the presence of another copper-based compound to achieve the desired phase.^[15] In contrast to these conventional strategies, in this study, however, we report the influence of variation of precursor (SbCl₃) concentration on the optical properties of CuSbS₂ thin film gotten by direct synthesis, a single-step CBD process from precursor solutions containing copper, antimony, and sulphur ions. It is of noteworthy that this investigation has not been widely studied by researchers.

MATERIALS AND METHODS

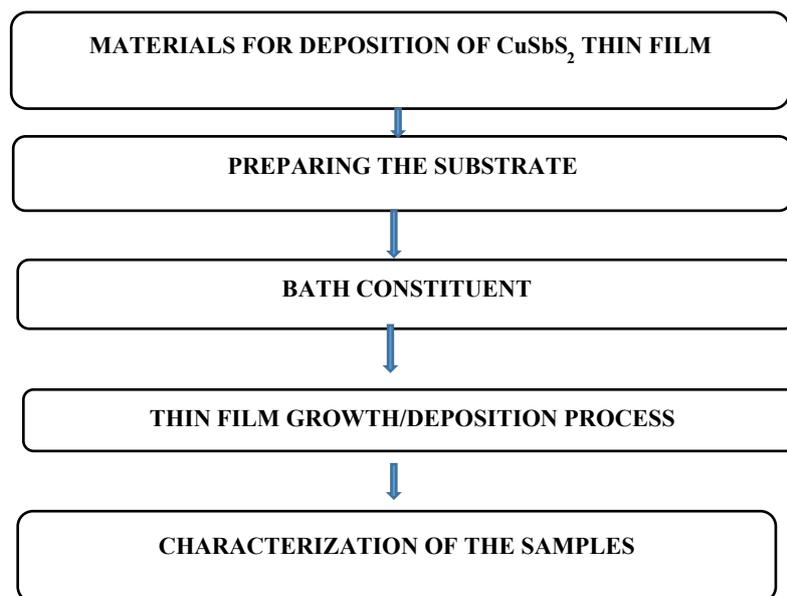


Fig1: Flow chart of Experimental design & approach

Materials

Here is the list of materials used; Chromic Acid, Glass microscope slide, Copper II Chloride, Thiourea, Triethanol amine (TEA), Ammonia Solution, Ammonium chloride, Antimony chloride, Acetone, Sodium thiosulphate, Distilled water.

Apparatus

Listed below are the apparatus used; Ultrasonic Cleanser, PH meter, Magnetic Stirrer, Thermometer, Different size of beakers, Measuring cylinder, String, clips, electronic weighing machine.

Preparing the substrate

The substrate used for thin film deposition was a glass microscope slide. Prior to

deposition, the slides underwent a thorough cleaning process, which involved degreasing in a 1:10 solution of dilute chromic acid in distilled water for 24 hours. They were then washed with a detergent solution and treated in an ultrasonic cleaner, followed by rinsing with distilled water and air-drying. This cleaning procedure was carried out to ensure the complete removal of any contaminants that could negatively impact the quality or properties of the deposited thin film.

Bath Constituent

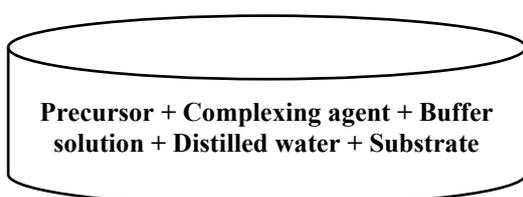


Fig 2: Schematic diagram of bath constituent

Thin film growth/deposition process

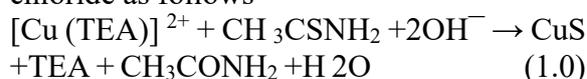
To grow CuSbS₂ we started by first growing CuS and Sb₂S₃. We obtained the optimal condition for their deposition by varying some deposition parameters; PH of bath, precursor concentration, deposition temperature and deposition time. The established condition was combined to grow CuSbS₂.

Deposition of CuSbS₂ thin film by CBD technique

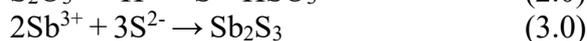
Chemical reaction 100 cm³ beaker bath (Beaker A) was set up onto which 2.0 ml of 0.5 M CuCl₂ .2H₂O solution which acts as the precursor for copper ion was added to 2.4 ml of 3.75 M TEA which acts as the complexing agent and stirred for 3 minutes using magnetic stirrer. 0.8 ml of 0.5 M thiourea which acts as sulphur precursor was added and stirred for 1 minute. Another beaker B was set up, in this beaker 0.5 g of SbCl₃ was

dissolved in 2.4 ml of Acetone and stirred for 3 minutes, 20 ml of 0.5 M Sodium thiosulphate was added and stirred for 1 minute. The solution in beaker B was mixed with the solution in beaker A and stirred for 3 minutes. 1.6 ml of Buffer solution (mixture of ammonia solution and ammonium chloride) was added and stirred for 1 minute, the buffer was used to drive the PH to 11.0, CBD performs better in alkaline medium.^[5] Distilled water was used to fill up the beaker. The prepared substrates were placed into the solution using a piece of synthetic foam positioned on top of the beaker, which both supported the slides and shielded the solution from dust. The beaker was then set on a magnetic stirrer and heated to 80°C for 90 minutes. During this process, CuSbS₂ precipitated, and the presence of complexing agents helped slow the precipitation rate to promote controlled and orderly crystal growth.

Copper ions were derived from copper chloride as follows ^[16]



Sulphur ion was derived from thiosulphate as follows ^[17];



Sb₂(CH₃COCH₃)³⁺ complex was absorbed on the surface of the glass substrate where ionic exchange with Cu²⁺ and S²⁻ resulted in a nucleation that gradually grew into the CuSbS₂ thin film.^[1]

The reaction was carried out at a temperature of 80°C for a duration of 90 minutes and repeated using different concentrations of SbCl₃ to examine how its concentration influences the optical properties of the thin film. Three distinct concentrations were tested by altering the mass of SbCl₃ used, as detailed in Table 1.

Table 1: variation of SbCl₃ concentration on CuSbS₂

Slide Number	Mass of SbCl ₃ (g)	Concentration of SbCl ₃ (M)
1	0.75	1.40
2	0.85	1.60
3	0.95	1.80

The slides were removed, rinsed in distilled water and dried in air. The as-deposited thin films were kept in slide boxes.

Crystallographic studies were done using an XRD-6000 diffractometer (Shimadzu Co., Japan) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Optical properties, including absorbance and transmittance spectra in the 200–1100 nm wavelength range, were recorded using a PerkinElmer UV-Vis-NIR Spectrophotometer. We analyzed the elemental composition using Energy

Dispersive X-ray Fluorescence (EDXRF) instrumentation from Thermo Fisher Scientific.

RESULTS AND DISCUSSIONS

There is no diffraction peaks observed from the XRD plot for the different concentrations of SbCl₃ precursor for CuSbS₂ films as-deposited indicating that the films are in an amorphous state as shown in figure 3, this is consistent with literature [5] that unannealed films of CuSbS₃ are amorphous.

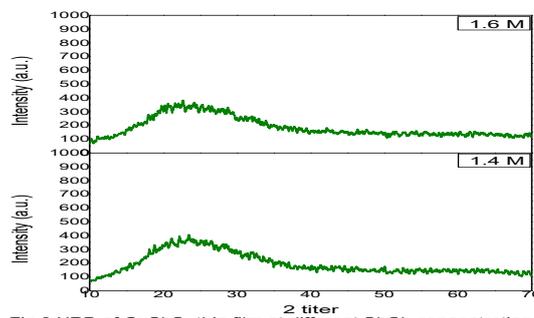


Fig 3: XRD of CuSbS₂ thin film at different SbCl₃ concentration (M)

A broad shallow hump is observed at the lower angle 15°–40°; this is due to the glass nature of the material as-deposited and glass substrate. [18]

Dispersive x-ray fluorescence (EDXRF) analysis confirmed the presence of Sb, Cu and S in the CuSbS₃ films material.

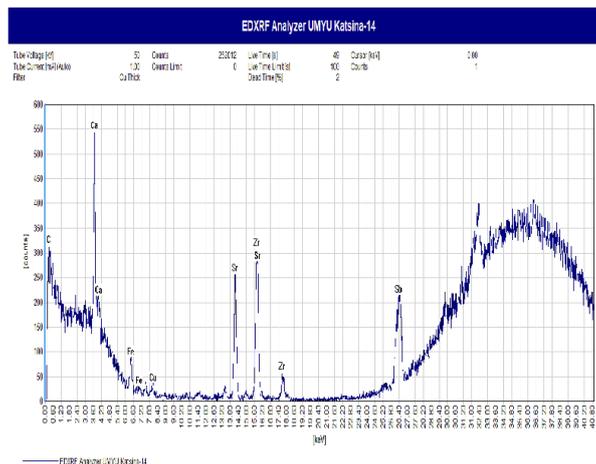


Fig 4: EDXRF of CuSbS₃ thin film material

From figure 4, Sb has a count of about 200 and Cu has a count of 50, but the the peak of Sulphur did not appear because of very low

count of sulphur this is as a result of deposition technique used (CBD). [19]

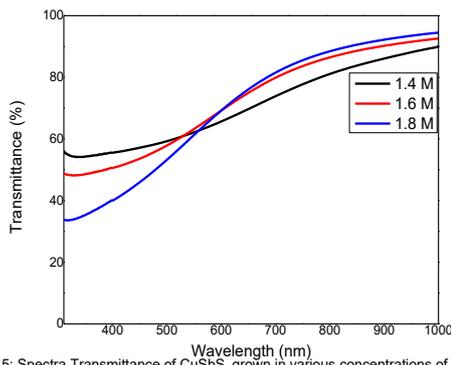


Fig 5: Spectra Transmittance of CuSbS₂ grown in various concentrations of SbCl₃

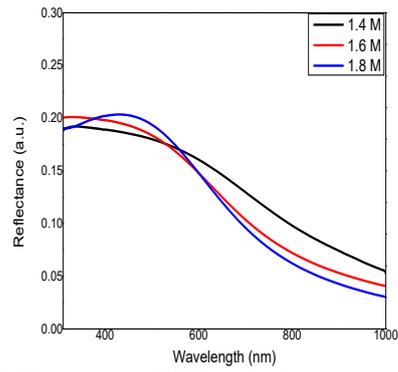


Fig 6: Spectral Reflectance of CuSbS₂ grown in various concentrations of SbCl₃

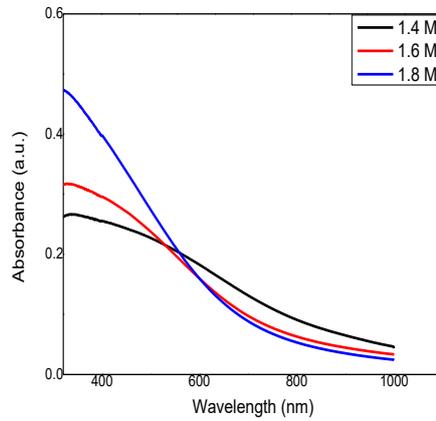


Fig 7: Spectral Absorbance of CuSbS₂ grown in various concentrations of SbCl₃

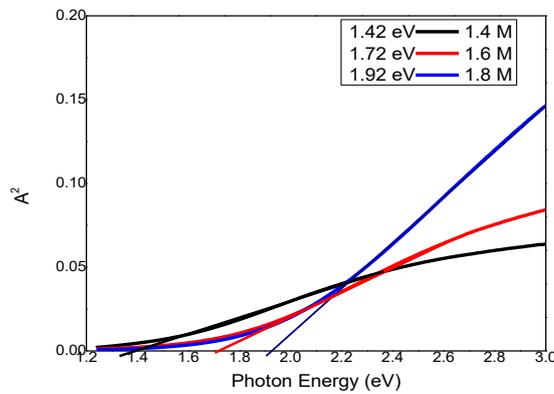


Fig 8: A² Vs Photon energy for CuSbS₂ grown in various concentrations of SbCl₃

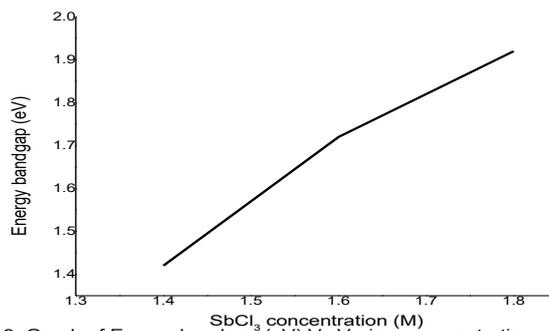


Fig 9: Graph of Energy bandgap² (eV) Vs Various concentrations of SbCl₃

Figure 5 shows the spectral transmittance of CuSbS₂ thin film grown in various concentrations of SbCl₃, 1.4 M, 1.6 M and 1.8 M. It can be seen clearly from Fig 5 that 1.8 M film has the least (34%) transmittance in the UV region but highest (94%) in the infrared region of the spectrum. 1.4 M film has the highest transmittance (56%) in UV region but least in the region with wavelength >560 nm, the highest value in visible light and infrared region is 80% and 89% respectively. Figure 6 shows the spectral reflectance of CuSbS₂ thin film grown in various concentrations of SbCl₃, 1.4 M, 1.6 M and 1.8 M. 1.4 M film has the highest reflectance of 13.5% in the infrared region while 1.8 M film has the highest value (20.5%) in the visible light region, in the UV region 1.6 M film has the highest value of 20.0%. Figure 7 shows the spectral absorbance of CuSbS₂ thin film grown in various concentrations of SbCl₃, 1.4 M, 1.6 M and 1.8 M. The absorbance for all the concentrations steadily decreased from UV to visible and maintained a relatively constant value down to near infrared region of the spectrum. The 1.8 M film exhibited the best absorbance with a value of 47.6 %, followed by 1.6 M film with a value of about 32% and finally 1.4 M film with the value of 26.4% in the UV and visible region of the spectrum. But 1.4 M film exhibited the best absorbance with a value of 13.5 % in the infrared region. Figure 8 shows the plot of Absorbance square (A²) against Photon energy (eV) of CuSbS₂ thin film grown in various concentrations of SbCl₃, 1.4 M, 1.6 M and 1.8 M. Direct energy bandgap was confirmed by the graph and energy bandgap for different concentrations of SbCl₃ were estimated by extrapolating the linear part of the curve to the energy axis. This method has been reported by several literatures.^{[20]-[21]} From the plot the 1.4 M film was estimated with a value of 1.42 eV, followed by the 1.6 M grown film with a value of 1.72 eV and finally 1.8 M film with a value of 1.92 eV. These values are in agreement with reported values for direct bandgaps 1.4 eV to 3.0 eV.^[1] The variation in energy bandgap can be

linked to the deposition method and the presence of grain boundaries. Specifically, factors such as temperature, film thickness, crystallinity, grain size, and defect states influence the band gap.^[22] Increase in concentration of SbCl₃ led to increase in the band gap of the film and this is in line with literature,^[5] this can be seen clearly in figure 9 which shows variation. The materials have a suitable bandgap for absorption of photon energy right from the infrared region of the solar spectrum hence good candidate for application in solar cell.

CONCLUSION

This study explored how varying the concentration of the precursor SbCl₃ affects the optical characteristics of CuSbS₂ thin films synthesized via the Chemical Bath Deposition (CBD) method an area that remains relatively under-researched. The deposition process utilized CuCl₂·2H₂O, SbCl₃, and thiourea (H₂SNH₂) as precursors, with NH₃/NH₄Cl serving as the buffer solution, and triethanolamine (TEA) along with acetone as complexing agents. SbCl₃ was tested at concentrations of 1.4 M, 1.6 M, and 1.8 M. X-ray diffraction (XRD) analysis revealed that the films retained an amorphous structure across all SbCl₃ concentrations. Optical characterization using UV-Vis spectroscopy indicated high absorption in the ultraviolet and visible regions, with minimal absorption in the infrared region of the solar spectrum. The material displayed a direct bandgap, which widened with increasing SbCl₃ concentration: 1.42 eV at 1.4 M, 1.72 eV at 1.6 M, and 1.92 eV at 1.8 M. Energy Dispersive X-ray Fluorescence (EDXRF) confirmed the elemental presence of copper (Cu), sulfur (S), and antimony (Sb). The pronounced absorption in the UV and visible ranges suggests the material's suitability for applications in photodetectors and solar cell absorber layers.

AUTHORS' CREDIT STATEMENT

J.C. Echewodo: Experimental Design, Material Synthesis, Result analysis, Writing Original draft. B.C. Anusionwu: Supervision

E.C. Mbamala: Experimental Design, Result Analysis, Manuscript Writing

O. K. Echendu: Experimental Design, Result Analysis, Manuscript Writing.

Declaration by Authors

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Conflict of Interest: I declare no known competing interest or personal relationship that could influence the work reported in this paper

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