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## The Influence of Concentration on the Formation of Chemical Bath Deposited Copper Tin Sulphide Thin Films: SEM and EDX Studies

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### ABSTRACT

Nanostructured copper tin sulphide films have been deposited on the substrate (soda lime glass) via an economical chemical bath deposition method. The scanning electron microscopy (SEM) technique and energy dispersive X-ray analyzer (EDX) method were employed in this work to study the films' morphology and composition. The EDX data and SEM images confirmed that the content of elements (sulfur, tin, and copper), the shape, and the grain size strongly depended on the concentration of the precursors during the formation of films. Experimental results revealed that a higher atomic percentage of the element could be observed for the films prepared using a higher concentration of solution during the experiment.

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## 1. Introduction

Thin films have attracted lots of attention because of their unique properties. The thin films could be divided into several groups such as binary (2 elements), ternary (3 elements), quaternary (4 elements), and pen ternary (5 elements). These compounds contained at least one chalcogen anion (sulfide, telluride, selenide ion) and one more electro-positive metal element. Currently, several efforts are made to produce ternary chalcogenide metal thin films because of huge applications, including sensors [1], supercapacitors, solar cells [2,3], optoelectronic devices, and laser devices. As highlighted by many researchers, physical methods [4-6] and chemical deposition techniques [7-9] could be used to produce nanostructured thin films onto specific substrates. The obtained samples were characterized using common techniques such as scanning electron microscopy, TEM, AFM, XPS, Raman spectroscopy, XRD, FTIR, and energy dispersive x-ray analysis. The selection of these techniques mainly depended on several conditions such as availability in the laboratory [10], economic aspects [11], operating requirements, service support, and analysis cost [12]. Table 1 shows the ternary thin films produced using various deposition techniques and highlights experimental results that were studied using different instruments.

The chemical bath deposition method has many advantages, such as a low-cost technique, a very simple deposition process with little infrastructure, and depositing thin films onto the substrate using low temperatures. In terms of economic benefits, this deposition method can produce homogenous films and stoichiometric materials with little money and less production cost. In this work, the chemical bath deposition method used to produce nanostructured thin films onto soda lime glass was reported for the first time. The main goal of this work was to investigate the morphology and composition of the obtained thin films prepared under various concentrations of precursors.

## Method and Materials

All the solutions were produced by using analytical grade reagents (copper sulfate, tin chloride, and sodium thiosulfate) and deionized water (Alpha-Q Millipore). Before the deposition process, the soda lime glass was degreased with the ethanol solution (15 minutes), then ultrasonically cleaned with distilled water (12 minutes). Thin films could be formed at 65°C onto the substrate for under 95 minutes. The concentration of the solution (molarity (M)) for each precursor is highlighted in Table 2. Generally, 15 ml of  $\text{CuSO}_4$ , 15 mL of  $\text{SnCl}_2$ , and 15 ml of  $\text{Na}_2\text{S}_2\text{O}_3$  were added slowly to a beaker. In order to prepare acidic conditions during the formation of films, hydrochloric acid (HCl) was used to adjust the pH value (pH=1.3). The cleaned soda lime glass substrate was vertically immersed in the beaker. After completion of film deposition, the sample was removed, washed (with distilled water), dried (desiccator), and kept for further characterization.

The obtained films were studied (morphology properties) by scanning electron microscopy (JEOL, JSM-6400), under specific conditions such as 20 kV with 1000 X magnification. The composition of the sample was investigated via energy dispersive analysis X-ray technique. The composition of the sample was investigated via energy dispersive analysis X-ray technique.

## Results and Discussion

Based on the literature review, scanning electron microscopy (SEM) and the energy dispersive analysis of X-ray (EDX) analyzer have been used by many researchers to study the properties of thin films. The advantages of SEM include higher resolution [36], very clear images that can be generated [37], and significant depth of the field if compared to other microscopes [38]. The benefits of energy dispersive X-ray analysis such as data collection rapidly [39], the ability to scan areas [40], and higher production yield [41].

Sample 1 was prepared using 0.01M tin chloride, 0.07M sodium thiosulfate, and 0.085M copper sulfate via the chemical deposition method. The morphology of Sample 1 was studied by using SEM. The well-formed grains with varying grain sizes (6-8  $\mu\text{m}$ ) and nearly uniform shapes as shown in Figure 1. Also, it revealed that the majority of the grains were small in size. The energy dispersive x-ray analysis (EDX) confirmed the presence of copper, tin, and sulfur in the sample (Table 3). The maximum and minimum atomic percentages of tin were 1.6% and 1.02%,

respectively, for the films prepared using 0.01M tin chloride. Experimental results revealed a higher atomic percentage in copper and sulfur due to the addition of higher concentrations of copper sulfate and sodium thiosulfate in the chemical bath during the formation of thin films.

**Table 1: Ternary thin films prepared via different deposition methods and related highlighted experimental results.**

Thin Films	Deposition Technique	Results
Cu <sub>2</sub> SnS <sub>3</sub>	Spray pyrolysis	XRD: tetragonal phase [13] AFM, SEM: smooth morphology without pinholes UV-visible spectroscopy: band gap was 1.6 eV
Cu <sub>2</sub> SnS <sub>3</sub>	Magnetron sputtering	XRD: monoclinic structure [14] UV-visible spectroscopy: 0.91 eV
Cu <sub>2</sub> SnS <sub>3</sub>	Spray pyrolysis	XRD: tetragonal phase [15] SEM: small grain without pinholes
MoBi <sub>2</sub> Se <sub>5</sub>	Arrested precipitation method	UV-visible spectroscopy: band gap was 1.78 eV XRD: orthorhombic phase [16] SEM: porous layer with high surface area
Mo(S <sub>1-x</sub> Se <sub>x</sub> ) <sub>2</sub>	Arrested precipitation method	EDX: confirmed stoichiometry films [17]
AgIn <sub>5</sub> S <sub>8</sub>	Chemical bath deposition	UV-visible spectroscopy: 1.7 to 1.97 eV SEM: Uniform and adherent films onto the surface of the substrates [18]
CuInSe <sub>2</sub>	Electro deposition method	XRD: Chalcopyrite phase has been changed to sphalerite depending on experimental conditions [19] SEM: grain sizes of 0.6 μm were observed
CuInSe <sub>2</sub>	Metal Organic Chemical Vapor Deposition	EDX: stoichiometry layers [20] UV-visible spectroscopy: band gap was 1 eV
BiSbSe <sub>2</sub>	Arrested precipitation technique	EDX: confirmed BiSbSe <sub>2</sub> phase [21] XRD: polycrystalline phase
CuGaTe <sub>2</sub>	Co-evaporation method	XRD: major peak corresponding to (112) plane [22] PL measurement: peaks at 650 nm and 1030 nm SEM: good grain growth EDX: 18.31-30.33% Cu, 24.41-27.59% Ga, 45.06-57.29% Te could be observed in all samples. TEM: polycrystalline nature UV-visible spectrophotometer: band gap was 1.24 eV
CuInTe	Flash evaporation	XRD: confirm the chalcopyrite phase [23] UV visible spectrophotometer: 0.94 eV
Copper indium telluride films	Pulse electro-deposition	AFM: grain sizes (15 to 30 nm) and surface roughness (1 to 1.5 nm) were reported [24] UV-visible spectrophotometer: band gap values (0.98 eV to 1.02 eV) XRD: single phase
CuInTe <sub>2</sub>	Electro deposition method	XRD: showed good crystallinity when the films were produced at 65 °C SEM: Films indicated smooth, spherical grains and uniform morphology for the films deposited at -900mV versus SCE (deposition potential). UV-visible spectroscopy: direct band gap was 1.04 eV [25]
CuInSe <sub>2</sub>	Vacuum evaporation	UV-visible spectroscopy: band gap and absorption coefficient were 1.018 eV and 10 <sup>4</sup> cm <sup>-1</sup> , respectively [26]. XRD: polycrystalline with the most intense peak corresponding to the (112) plane.
CuInSe <sub>2</sub>	Vacuum co-evaporation	XRD: the strongest peak contributed to (112) plane, with chalcopyrite phase [27]. UV-visible spectroscopy: band gap was 0.99 eV
CuInSe <sub>2</sub>	Chemical bath deposition	UV-visible spectroscopy: 1.1 eV Electrical resistivity: 10 <sup>2</sup> Ωcm [28]

Table 1 (contd....)

Thin Films	Deposition Technique	Results
CuInSe <sub>2</sub>	Chemical bath deposition	EDX: near stoichiometric films XRD: tetragonal unit [29] AFM: grains and coalescence between them SEM: All the grains covered the surface of the substrate. UV-visible spectroscopy: The band gap was 1.39 eV
CuInS <sub>2</sub>	Spray pyrolysis	TG and DTA: Confirmed that a complex process was observed in thermal degradation of the precursors [30] RBS: the films produced at 320 °C showed stoichiometry
Ag <sub>33</sub> Sb <sub>31</sub> Se <sub>36</sub>	Thermal evaporation	XRD: Amorphous phase and polycrystalline structure could be observed in as-deposited films and annealed films, respectively [31]. UV-visible spectroscopy: indirect band gap in both samples.
CuInS <sub>2</sub>	Spray pyrolysis	SEM: Average grain size (100-800 nm) Band gap =1.48eV EDX: stoichiometric ratio of 1.14:1:1.88 (CIS) XRD: chalcopyrite phase [32]
CuIn <sub>2</sub>	Successive ionic layer adsorption and reaction method	TEM, XRD: well-crystallized films could be observed in annealed films [33]. UV-visible spectroscopy: Band gap increased (1.32 to 1.58eV) with annealing time (0.5 to 2 hours).
CuInS <sub>2</sub>	Successive ionic layer adsorption and reaction method	EDX: confirmed copper rich in the obtained films [34] XRD: crystallite size (10-84 nm) UV-visible spectroscopy: The band gap was 1.5 eV when the films were prepared at 60 °C
CuInS <sub>2</sub>	Magnetron sputtering	UV-visible spectroscopy: The band gap was 1.48 to 1.5 eV [35] SEM: Spherical grains with nanosized (2-5 μm) Raman: Confirmed that the crystals regrow during the sulfurization process.

Table 2: Concentration of copper sulfate, tin chloride, and sodium thiosulfate during the formation of thin films.

Sample Description	Concentration of Copper Sulfate	Concentration of Tin Chloride	Concentration of Sodium Thiosulfate
Sample 1	0.085 M	0.01 M	0.07 M
Sample 2	0.01 M	0.075 M	0.075 M
Sample 3	0.015 M	0.08 M	0.08 M

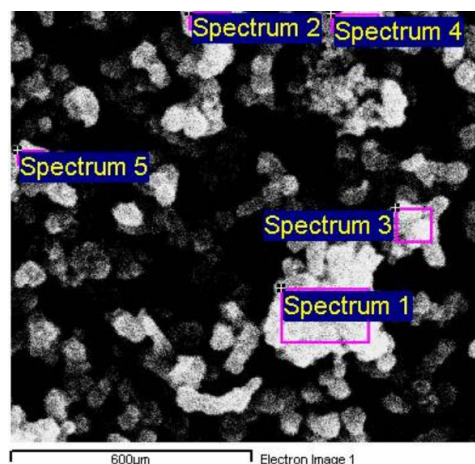
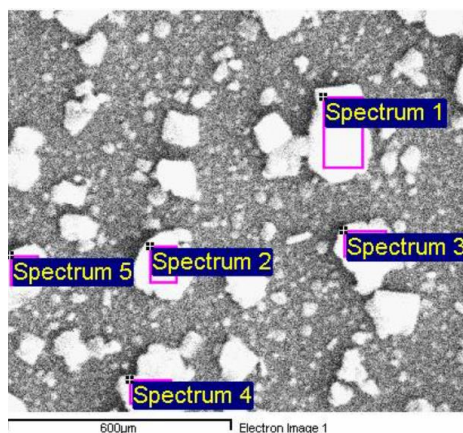


Figure 1: SEM image of the sample 1.

**Table 3: EDX analysis of the sample 1.**

Spectrum	Sulphur (%)	Copper (%)	Tin (%)
Spectrum 1	34.40	64.24	1.36
Spectrum 2	33.84	64.77	1.4
Spectrum 3	32.59	65.81	1.6
Spectrum 4	32.08	66.35	1.57
Spectrum 5	34.15	64.82	1.02
Maximum	34.4	66.35	1.6
Minimum	32.08	64.24	1.02

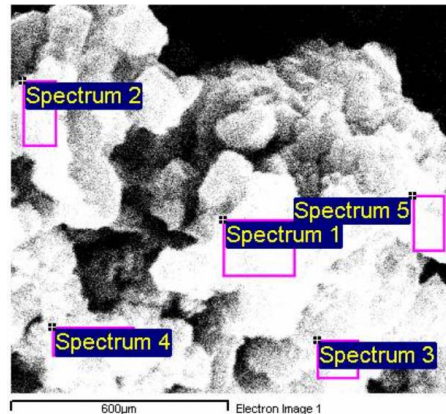
According to the SEM image, irregular-shaped [spherical and cuboidal geometry] grains covered the substrate surface in Sample 2. Non-uniform grain (3-6  $\mu\text{m}$ ) sizes could be observed, as indicated in Figure 2. The EDX data (Table 4) confirmed a higher atomic percentage in sulphur (46.81-50.56%) and tin (45.81-46.76%) if compared to copper (2.92-6.93%). Because of more diluted concentration of copper sulfate was used during the preparation of thin films onto a substrate.

**Figure 2:** SEM image of sample 2.**Table 4: EDX analysis of sample 2.**

Spectrum	Sulphur (%)	Copper (%)	Tin (%)
Spectrum 1	50.56	2.92	46.52
Spectrum 2	48.66	5.52	45.81
Spectrum 3	47.81	5.57	46.62
Spectrum 4	48.71	4.53	46.76
Spectrum 5	46.81	6.93	46.26
Maximum	50.56	6.93	46.76
Minimum	46.81	2.92	45.81

Based on the SEM analysis, the grain could grow to large agglomerates in Sample 3. As reported by Ukoba et al., an increase in grain was observed in nickel oxide films as the precursor solution was increased from 0.025M to

0.1M. This confirmed that the varying concentration of the precursors affects the NiO film morphology [42]. It is observed that almost spherical grains were distributed entirely on the substrate surface with a grain size of 600  $\mu\text{m}$ , as indicated in Figure 3. Table 5 shows the atomic percentage of copper, tin, and sulphur presented in five different spots in the sample. Here, the lowest atomic percentage of copper (1.01-14.24%) was observed than other elements such as sulphur (38.83-50.35%) and tin (46.93-51.75%).



**Figure 3:** SEM image of Sample 3.

**Table 5: EDX analysis of Sample 3.**

Spectrum	Sulphur (%)	Copper (%)	Tin (%)
Spectrum 1	50.35	1.01	48.64
Spectrum 2	50.16	2.4	47.44
Spectrum 3	49.17	2.35	48.47
Spectrum 4	42.81	5.44	51.75
Spectrum 5	38.83	14.24	46.93
Maximum	50.35	14.24	51.75
Minimum	38.83	1.01	46.93

## Conclusion

A simple and economical chemical bath deposition technique has been used to produce copper tin sulfide thin films onto soda lime glass substrate at the specific experimental conditions (65°C, 95 minutes in acidic conditions). In this work, the compositional and morphological of the obtained thin films have been studied using energy dispersive X-ray analysis (EDX) and scanning electron microscope, respectively. Experimental results revealed that a higher atomic percentage of the element could be observed for the films prepared by using a higher concentration of solution during the experiment.

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