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Chemical Bath Deposited Copper Tin Sulphide Thin Films: SEM and EDX Analysis

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ABSTRACT

In this work, the scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDX) results on the chemical bath deposited copper tin sulphide thin films were presented. Thin films were deposited on the indium tin oxide (ITO) glass substrates from aqueous solutions. The influence of the various deposition times on the morphology and the composition of the obtained films were analyzed using SEM and EDX, respectively.

KEYWORDS: Thin films, chemical bath deposition, scanning electron microscopy, Energy dispersive X-ray analysis, solar cell.

INTRODUCTION

Many efforts are currently directed to generation of ternary metal chalcogenide thin films. This is because of their potential uses in many applications such as optoelectronic devices, laser devices and solar cells. There are different syntheses of ternary metal chalcogenide thin films have been reported in the literature review including electro deposition[30,14,34,7,], chemical bath deposition[15,27,21,11,24,12,23,25,6], successive ionic layer adsorption and reaction[33], flash evaporation [13], molecular beam epitaxy [29], and atomic layer epitaxy [32]. At present, scanning electron microscopy [18,17,4,20,28,16,31,5,8]and energy dispersive x-ray analysis [10,26,3,9,22]are used in the characterization of thin films by many researchers as indicated in literature review. It is due to these techniques having emerged as simple and economical methods.

The goal of this work was to study the morphology and composition of thin films which prepared using various deposition times by using SEM and EDX, respectively. The films were deposited from aqueous solution onto ITO glass substrate.

METHOD AND MATERIALS

All the solutions were prepared from analytical grade reagents chemicals and deionized water (Alpha-Q Millipore). These chemicals included copper sulfate ($CuSO_4$), tin chloride ($SnCl_2$), sodium thiosulfate ($Na_2S_2O_3$), disodium ethylenediaminetetraacetic (Na_2EDTA) and hydrochloric acid (HCl). The copper sulfate, tin chloride and sodium thiosulfate were provided copper, tin and sulfide ions, respectively. Meanwhile, the Na_2EDTA was used as a complexing agent. The main reason Na_2EDTA was used in order to improve the lifetime of the deposition bath as well as the adhesion of deposited films on indium tin oxide glass substrate. Before deposition, the indium tin oxide (ITO) glass substrates were degreased with ethanol for 10 min and then ultrasonically cleaned with distilled water for another 15 min. The details of cleaning process can be found elsewhere[1]. Deposition of Cu_4SnS_4 thin films was carried out at 50 °C by using following procedure: 10 ml of 0.05 M $CuSO_4$ and $SnCl_2$ solutions were complexed with 10 ml of Na_2EDTA (0.1M) in separate beaker, respectively.

To this, 10 ml of 0.05 M $Na_2S_2O_3$ was added slowly to the mixture. The pH of mixture was adjusted to 1.5 by the addition of hydrochloric acid. The pH was maintained low in order to prevent the formation of hydroxyl and insoluble product. The clean ITO glass substrate was vertically immersed into beaker. After completion of film deposition (55, 80, 130 min), the ITO glass substrate was removed and washed several times with distilled water. Then the sample was dried in desiccator and was kept for further characterization.

Table 1: Atomic percentage composition of copper tin sulphide films from EDX analysis.

Deposition time (min)	Average Atomic percentage (%)		
	Copper	Tin	Sulfur
55	45.98	12.86	41.16
80	45.50	10.82	43.68
130	56.74	9.23	34.03

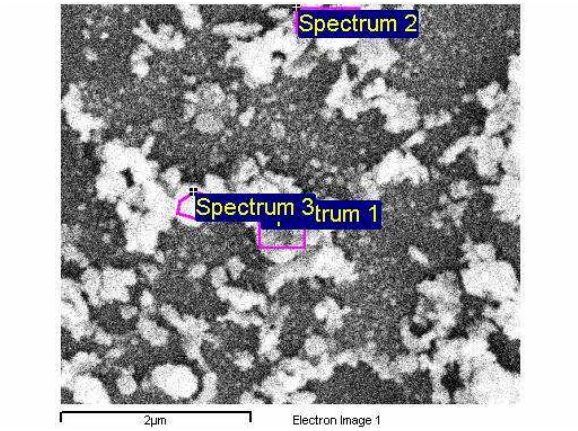

Fig. 1: Scanning electron microscopy micrograph of films prepared for 55 minutes.

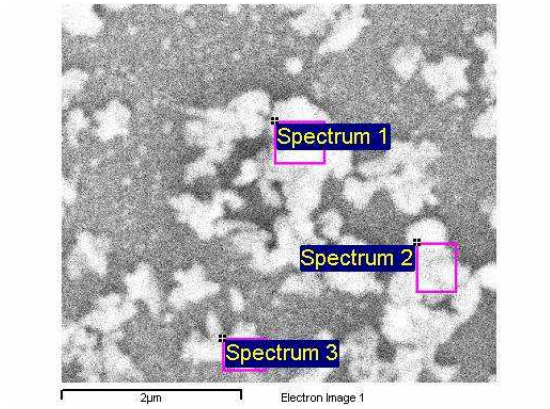

Fig. 2: Scanning electron microscopy micrograph of films prepared for 80 minutes.

The surface morphology was observed by a scanning electron microscopy (JEOL, JSM-6400), at 20 kV with a 1000 X magnification. The elemental composition of the films was studied by scanning electron microscope attached with energy dispersive analysis of X-ray (EDX) analyzer.

RESULTS AND DISCUSSION

The presence of copper, tin and sulfur ions was determined using energy dispersive x-ray analysis (EDX). The presence of Cu, Sn and S ions in the thin films were confirmed by EDX as shown in Table 1. It can be observed that the composition of the films approaches that of Cu_4SnS_4 for the deposition of 80 minutes. However, the atomic ratio of Cu:Sn:S changes to $Cu_{3.6}SnS_{3.2}$ and Cu_6SnS_4, respectively as the films were prepared for 55 and 130 minutes, respectively. There is to say the deposition time has some influence of the composition of the deposited films.

The scanning electron microscopy (SEM) studies were carried out to assess the morphology of thin films. As shown in Figure 1 and 2, there are no much different in terms of the morphology of films which prepared for 55 and 80 minutes, respectively. However, the SEM micrographs show that the grain sizes were 0.2-0.4 µm and

0.2-0.6µm respectively. Furthermore, it can be seen that the grains are packed closely and show a granular morphology without pinholes. Figure 3 indicates that the SEM micrograph for the films prepared for 130 minutes. There are very significantly that the grain size increases (0.5-0.75µm), which leading to coalescence of the grains.

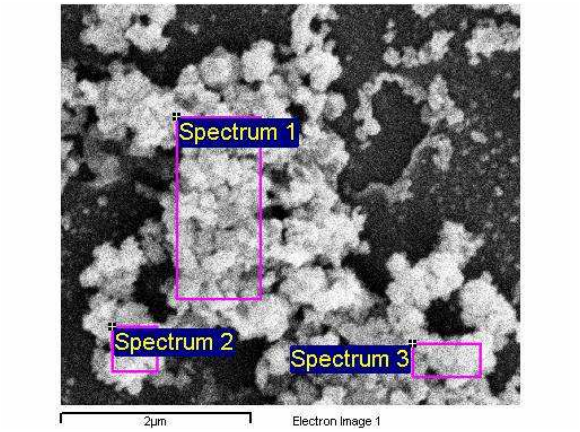

Fig. 3: Scanning electron microscopy micrograph of films prepared for 130 minutes.

1. Conclusion:

The chemical bath deposition technique has been employed to obtain ternary thin films from an aqueous solution. It could be pointed out that it was possible to grow Cu_4SnS_4 thin films onto substrate by appropriate selection of the deposition conditions. Deposition for 80 minutes favors the formation of Cu_4SnS_4 under such experimental conditions, which confirmed using EDX results.

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Authors'Contribution:

This manuscript was prepared by Dr. HO SOONMIN.

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