Ternary Cu$_2$SnS$_3$ Thin Films Deposited by Fully Controlled System of Spray Pyrolysis

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Abstract. A fully computerized system of spray pyrolysis was employed for fabricating copper tin sulphite ternary thin film onto glass substrates. During deposition process, the glass substrate was maintained at 310±10 °C. After dissolving the raw chemicals, a mixture of their aqueous solutions was used for spraying process. The optimum solution mixture at the volumetric ratio [S/(Cu+Sn)=1] at 1.5 of pH. XRD investigation was approved a monoclinic phase of CTS. A number of different platform speed was tested in the deposition process. XRD diffraction peaks were described at 2θ = 28.39°, 33.02°, 47.34°, and 56.39° corresponding to the (2 2 0 6), (2 0 1 0), and (3 2 1 0), respectively. These are crystal planes of monoclinic copper tin sulphide. The FTIR study certified a number of the chemical bond of Cu-, Sn- and S-. The grain size was observed in the range of nano using Scherrer formula. Studying surface morphology of CTS films reveals a uniform coating on the substrates which approved by SEM investigations.

Keywords: CTS, Cu$_2$SnS$_3$, Computerized Spray Pyrolysis system, Solar Absorber.

1. Introduction

Spray pyrolysis technique (SPT) is one of the simplest non-vacuum techniques starting with an aqueous solution for fabricating variety materials in thin film form [1]-[2]. In addition, it was classified as a low-cost and eco-friendly technique in fabricating thin films for different applications such as semiconductor [3] and solar absorbers [4]. In fact, the investigations on the properties of spray deposited Copper tin sulfide (CTS) thin films are really inadequate in recent decades [5]. CTS thin films were prepared with different methods such as solid-state reaction [6], co-evaporation [7], solvothermal [8], sulfurization [9], chemical bath deposition [10], chemical bath [11], electro deposition [12], and the famous one, spray pyrolysis [13]. CTS has many chemical phases such as Cu$_4$SnS$_4$[14], Cu$_2$SnS$_3$[13], Cu$_3$SnS$_4$ [15], Cu$_2$Sn$_3$S$_7$ [16], and Cu$_4$Sn$_7$S$_{16}$[17]. Among these ternary sulfide phases, Cu$_2$SnS$_3$ is the most auspicious compounds in solar cell applications, because of its high absorption coefficient, and a direct band gap [6]. In the present research, CTS absorption layers were deposit via home-made fully computerized chemical spray pyrolysis deposition system (FCSPD) [18]. It has been sprayed a liquid solution onto moving hot plat in x-y plane. FCSPD also monitored the substrate temperatures during the deposition process. The thermal energy of handmade heating element and temperature are homogeneity on the moveable hot plate [19]. The aim of the present work is to fabricate the ternary Cu$_2$SnS$_3$ to be
employed later as a solar absorber. Moreover, investigation the effect of platform speed (mm/sec) on the crystal structure of the product.

2. Experimental

The present section was divided into three parts. The first one, a brief idea about the computerized system of spray pyrolysis. The second, is about sample preparation for starting the process. While the third is about measurements and characterization of the prepared CTS sample.

2.1. Computerized Deposition System

Fully controlled spray pyrolysis system was employed in the present research for CTS thin film deposition. The FCSPD has a 3D moving ability, where the platform of the hotplate can move in x-y dimension for coating areas larger than lab scale of micro slides. Moreover, the nozzle holder moves vertically in z-axis that can precisely change the nozzle to substrate distance (NSD). The computerized setup can monitor and control the substrate temperature even at 0.25 °C of variation. Figure (1) displayed the FCSPD technique [20].

![Figure 1: Schematic diagram of chemical spray pyrolysis](image)

2.2. Sample Preparation

In predisposition of the deposition process, the glass substrate was ultrasonically cleaned by hot distilled water. Then it was washed using ethanol, finally, the glass slide was dried using hot air jet. For the present deposition process, a mixed solution of tin chloride dihydrate (SnCl\(_2\).2H\(_2\)O) and copper chloride dihydrate (CuCl\(_2\).2H\(_2\)O) in addition to thiourea (CS(NH\(_2\))\(_2\)). All of these three solutions were mixed in equimolar concentration at the optimum volume ratio was found to be [S/(Cu+Sn)=1], at 1.5 of pH, as the measured value. The mixed precursor solution was sprayed onto the preheated substrate at 310±10 °C, where the NSD was 30 cm, with standardized carrier gas pressure. The aqueous solution was sprayed with flow rate around of 0.2 mL/sec through a metallic nozzle with radius of 0.35 mm onto preheated substrates. The chemical reaction of row chemicals on the substrate can be depicted below [21], where all of the reactants are in aqueous phase:

\[
\text{SnCl}_2\cdot 2\text{H}_2\text{O} + 2\text{CuCl}_2\cdot 2\text{H}_2\text{O} + 3\text{CS(NH}_2\text{)}_2\rightarrow \text{Cu}_2\text{SnS}_3 + 6\text{HCl} \uparrow + 3\text{CO}_2 \uparrow + 3\text{N}_2 \uparrow + 9\text{H}_2 \uparrow
\]
It’s worth mentioning that, at NSD = 30 cm, there are seven different platform speeds (3, 4, 5, 6, 7, 8, and 9 mm/sec) were employed in the deposition process. Whereas, all of the other parameters were kept unchanged.

2.3. Sample Analysis

X-ray diffraction (XRD) was employed for verifying the crystal structure and crystal phase of the deposit CTS thin films. X-ray diffractometer was (D2 PHASER, by BRUKER, Germany), with CuKα₁ radiation at λ=1.54056 Å. Each CTS samples were recorded in the range 20-80 ° of 2θ diffraction angle, with speed scan 6 deg per min. The average crystallite size was premeditated on the full width at the half-maximum (FWHM) of the peak (β), by applying the Debye-Scherer’s formula of as follows in equation (1):

\[ D = \frac{K \lambda}{\beta \cos(\theta)} \]  

where \( \lambda \) is XRD radiation, \( \beta \) is the full width at half maximum (FWHM) of the peak position in radians and \( \theta \) is Bragg’s diffraction angle at the peak position.

Fourier transform infrared spectra (FTIR) were acquired to confirm the chemical bonding and vibrations. Electron microscopes are scientific instruments that use a beam of energetic electrons to examine objects on a very fine scale. Scanning electron microscopy (SEM) of the model (Inspect S50, FEI Company, Netherlands) equipped with an energy dispersive X-ray (EDX) detector (Bruker Company, Germany) were employed for scrutinizing the surface topography of the arranged thin films.

3. Results and Discussion

Structural properties of CTS thin film were investigated via XRD technique. A stack of XRD patterns of the fabricated CTS thin films that deposited at multiple platform speed was displayed in figure 2.

**Figure 2:** Stack of XRD patterns of CTS thin films deposited at multiple platform speed
As mentioned in the figure above, a brief detail can be listed in Table 1, which explains the curve line color refers to what, and the crystal structure of the obtained films. All of these data were recorded plotted in range 20-60° with the same scale of intensity, to clarify differences of the plotted patterns.

| Line Color | Deposition Platform Speed (mm/sec) | Produced thin film | JCPDS-ICDD card | Crystal Structure |
|------------|-----------------------------------|--------------------|-----------------|------------------|
| Orange     | -                                 | Glass- substrate   | -               | Amorphous        |
| Blue       | 3                                 | Cu₄SnS₆            | 36-0053         | Trigonal         |
| Black      | 4                                 | -                 | -               | Not matched      |
| violet     | 5                                 | SnS               | 39-0354         | Orthorhombic     |
| pink       | 6                                 | Cu₂SnS₃           | 27-0198         | Monoclinic       |
| Green      | 7                                 | Cu₂SnS₃           | 27-0198         | Monoclinic       |
| brown      | 8                                 | Cu₂SnS₃           | 27-0198         | Monoclinic       |
| Red        | 9                                 | SnS₂              | 21-1231         | Trigonal         |

As listed table, the CTS layers films appeared at platform speeds (6, 7, and 8 mm/sec), where the fine crystal structure at 7 mm/sec. Whereas, all other parameters such as nozzle height, volumetric ratio, concentration, etc. were kept unaltered. Moreover, XRD patterns were revealed number of phases with various crystal structure that listed in Table 1 such as; Cu₄SnS₆ [22], SnS [23], CuS [24], Cu₂SnS₃ [25], SnS₂ [26].

There are three patterns of XRD depicted in figure 3, which displayed the approximate variation of platform speed in the deposition process.

![Figure 3: XRD patterns of CTS at three different platform speed](image)

It has noticed that the CTS fair sample has a polycrystalline structure in a monoclinic phase. The obtained peaks of X-ray diffraction were nominated at angles of 2θ = 28.39°, 33.02°, 47.34°, and 56.39°, respectively as displayed in figure 4. These diffraction angles were corresponding to the (2 1 1) (2 0 6), (2 0 10), and (3 2 10), of the crystal planes of monoclinic copper tin sulfite. These patterns corresponding the JCPDS-ICDD card (27-0198) of XRD reference data [25].
As the CTS film identity was certified, a good agreement in matching the investigational and typical values of diffraction angles could be about 99.5% of accuracy. According to Debye-Scherer’s formula [27], the grain size of the selected sample was found to be nearby 80 nm.

Figure 5 showed the FTIR spectrum of Cu$_2$SnS$_3$ thin film. There is a narrow band around 450 cm$^{-1}$ that assigned to Cu-O vibrations bond in copper oxides such as CuO and Cu$_2$O. Whilst, the vibrations energies in the range 500-750 cm$^{-1}$ were accorded to Cu-S, Sn-S, and S-oxides bonds [28]. In the range of range 2000-2300 cm$^{-1}$, there is a weak bond that assigned to C ≡ S and nitrile bond C ≡ N [29]. In addition, other bonds such as N-H, O-H, and C-H were vibrated in region 3500-3350 cm$^{-1}$ [30].

The chemical elements of CTS were examined by DEX. As illustrated in figure 6, EDX was displayed Cu-Sn-S individually in the selective sample. Where, Si definitely referred to the glass
substrate, while, the oxygen gives an indication of metal oxides such (Sn, and Cu oxides) that externally formed during the thermal chemical reaction. Moreover, there is no doubt that (Cu-Sn-S) are referred to the ternary compound “Copper Tin Sulfide” that successfully fabricated as a thin film.

Figure 6: EDX of the prepared CTS sample

The surface morphologies and compositions of the deposited metal oxide films have been analyzed using a scanning electron microscope SEM. Figure 7 showed the SEM imaging of the CTS thin films on different zoom scale.

Figure 7: SEM of CTS thin film on a different zooming scale
SEM investigations showed a fine distribution of CTS, where it is one of the best features of spray pyrolysis deposition. The surface distribution profile of an arbitrary selective area with dimensions (20×20) µm in image scale (1 µm) was plotted as in figure 8. This profile can describe the morphology of the film surface within range about 40 nm.

Figure 8: Surface distribution profile of CTS thin film

4. Conclusions
Spray pyrolysis technique was employed by a computerized system with parameters optimization in CTS fabrication. Platform speed has direct effects on the film formation on the substrate. The ternary CTS films have a good adhesion to glass substrates. The crystal structure was examined via XRD studies to be monoclinic. FTIR investigations were revealed the chemical vibrating bonds of elements Cu-, Sn-, and S- in different binding forms. Thin films have a fine roughness of surface morphology.

5. References
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