Investigation of Laser Grooving Process on Copper Tin Sulfite Thin Films

Zaid L. Hadi 1, Bahaa T. Chiad 2

1 Ministry of Education, General Directorate of Education of Babylon.
2 Department of Physics, College of Science, University of Baghdad

Corresponding Author E-mail: zaid.altai@scbaghdad.edu.iq

Abstract Spray pyrolysis deposition has been successfully applied to fabricate CTS thin films onto glass substrates that maintained at 300°C, via the homemade fully computerized system. A mixture aqueous solution of thiourea and dihydrate chloride of Sn (II) and Cu (II) were used for the spraying process. Structural, optical, and morphological properties of CTS films were examined. XRD endorses a monoclinic crystallinity. XRD pattern has diffraction peaks at 2θ = 28.39°, 33.02°, 47.34° and 56.39°, respectively. The FTIR examination certified the vibration mode of Cu-S and Sn-S bonds. The crystallite size was noted about 78 nm, where measured by debye-Scherrer’s formula. Both absorption and transmission spectra were recorded in the wavelength range of 300-800 nm. The surface morphology of the fabricated CTS films exposed a uniform coating on the substrate with an applicable distribution. Laser grooving process was applied to grove the fabricated film. The groove width was found about 37 µm, etched via 500 mW blue laser source.

Keywords: Fully computerized Spray pyrolysis, CTS, Laser grooving.

1. Introduction
Spray pyrolysis technique (SPT) has been successfully employed to deposit a wide variety of thin films. These films were used in various devices such as solar cells, sensors, and solid oxide fuel cells [1]. SPT can be considered as a cost-effective and eco-friendly technique which used for thin film production [2]. Copper tin sulfide (CTS) thin films were prepared with different methods such as solid-state reaction [3], co-evaporation [4], solvothermal [5], sulfurization [6], chemical bath deposition [7], in addition, the famous one which is spray pyrolysis technique [8] and so on. Fewer elements (Cu, Sn, S) were used in CTS, which would reduce the cost of fabrication and simplify the manufacturing process [9]. Thin films of ternary chalcogenide materials like Cu2SnS3 were successfully deposited by SPT [10]. CTS was attracted a great deal of attention as excellent absorber materials [11]. Many of CTS phases have been reported in literatures, such as Cu2SnS4, Cu3SnS4, Cu3SnS5, and Cu4Sn7S16 [12]. Cu2SnS3 is the most promising phase for applications in solar cell field [13]. Because of their high absorption coefficient and their optimal direct band gap for solar energy conversion [3]. Important and influential factors in determining and selecting a chemical compound are the low cost of manufacturing, the adoption of a simple and uncomplicated system that used to prepare layers which are suitable for solar applications [14]. Recently, lasers have employed in a number of common manufacturing applications, such as welding, drilling, cutting, and grooving processes [15].

2. Experimental
CTS thin films have been magnificently deposited onto glass substrates by SPT. The deposition process was applied a homemade fully computerized CNC spray pyrolysis system. Where system design consists of mechanical, electrical, and electronic parts which controlled by program C
languages [16]. Copper (II) chloride dihydrate \([\text{CuCl}_2 \cdot 2(\text{H}_2\text{O})]\), Tin (II) chloride dihydrate \([\text{SnCl}_2 \cdot 2(\text{H}_2\text{O})]\), and thiourea \([\text{CS(NH}_2\text{)}_2]\) were used as a row of chemical reactant. These chemicals manufactured by Sigma-Aldrich with 99% purity. An aqueous solution of equimolar concentration has mixed in a volumetric ratio (1:1:2), for starting the spraying process. After mixing, the solution was stirred without heating for 15 min. Moreover, whole chemicals that used for the deposition process were dissolved in distilled water. The pH value of the solution adjusted to be 1.2, where a few droplets of hydrochloric acid were added. Before starting deposition, the glass substrates were ultrasonically cleaned for 30 min by immersing it in a distilled water that heated up to 70 °C. The aqueous solution sprayed with the rate around 0.24 mL/sec through a metallic nozzle with a radius of 0.35 mm onto preheated substrates held at 310 °C±5, for concerning uniformity thin films. The chemical reaction of row precursors on the substrate could be depicted as the following chemical equation.

\[
\text{SnCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{CuCl}_2 \cdot 2\text{H}_2\text{O} + 3\text{CS(NH}_2\text{)}_2 \rightarrow \text{Cu}_2\text{SnS}_3 + 6\text{HCl} \uparrow +3\text{CO}_2 + 3\text{N}_2 + 9\text{H}_2
\]

Therein, 30 cm was the nozzle to substrate distance in present optimum condition. Whereas, a compressed ambient air was used as a carrier gas, which governed by a variable flowmeter. After which, a blue laser source (pointer) of wavelength 410 nm at 500 mW of power has used in grooving process. In the present research, the laser source was attached to CNC at a finest height to obtain the best intense spot size. Grooving process was employed for increasing the surface area of CTS thin films. Whereas, the absorption is enhanced as groove depth from increased.

### 3. Instrumentations

The crystal structural was investigated using X-ray diffractometer (D2 PHASER, by BRUKER, Germany), the wavelength of CuK\(\alpha\) \(\lambda=1.54056\) Å. Meanwhile, the crystallite size calculated via Debye-Scherer’s formula as in (eq.1)

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

(1)

The thickness of CST thin films measured using optical interferometer method, employing a green laser with a wavelength of 532nm. It is worth mentioning that, this method of interference depends on the light beam that reflected from the thin film surface and its substrate. Whereas, the thickness has been determined using the formula (eq.2) [17].

\[
t = \frac{\lambda}{2} \times \frac{\Delta x}{x}
\]  

(2)

FTIR spectrum was verified using IR Prestige-21, by Shimadzu (Japan). The UV-Vis spectroscopy was achieved at room temperature via K-MAC SV2100 spectrophotometer (Korea Material & analysis, Korea). In addition, the surface morphology of deposited film was carried out using the AFM system (SPM AA3000 from Angstrom advanced Inc. USA). For the optical microscopic investigation, a digital camera of 5MB resolution used as the eye of MOTIC-B microscope (Malaysia).

### 4. Results and Discussion

Crystal structural of CTS thin film has examined using XRD. That reveals the variations of the crystallinity. XRD patterns of CTS thin films displayed in figure 1.

It has noticed that the CTS sample is polycrystalline with a monoclinic phase. The scattered X-ray peaks were noticed at angles of 2θ = 28.39°, 33.02°, 47.34° and 56.39°, respectively. Whereas, the strongest reflection intensity was observed at the first one. These patterns such referred to ICDD card no. (27-0198) [18].

When the CTS film identity has certified, there is a good agreement between the experimental and standard values for scattering angles and d-spacing. In addition, about 99.5% accuracy in the matching of d-spacing. While there is an error ratio of 0.27% in matching values of 20. According to Debye-Schererer’s formula [19], the crystallite size was found to be nearby 78nm. The average thickness of the sample was measured to be about 173 nm. FTIR spectrum of \(\text{Cu}_2\text{SnS}_3\) was displayed in figure 2. One can observe that, a narrow band at 450 cm\(^{-1}\) assigned to Cu-O vibrations bond in copper oxides such as
Cu$_2$O and CuO. Meanwhile, the vibrations frequencies in the range 500-750 cm$^{-1}$ were accorded to Cu-S, Sn-S, Sn (IV)-O and Sn(II)-O bonds, as mentioned in reference [20]. In range 2000-2300 cm$^{-1}$, weak bands that could be assigned to C = S and nitrile bond C ≡ N as mentioned in previous researches [21]. In addition, theirs are another vibrations of Amide N-H, Alcohol O-H, and Alkynes C-H bonds which clearly shown in region 3500-3350 cm$^{-1}$ [22].

The UV–Vis spectrum of CTS thin film was displayed in Figure 3. That illustrated both absorption and transmission which are in a good agreement with [23]. This spectrum was measured before grooving process. Where the absorbance data were calibrated by dividing its column on the greatest value.

Atomic force microscope was employed to achieve the surface roughness of the CTS thin film. Figure 4 illustrates that the 2D, 3D and grain size distribution of deposited CTS thin film. AFM micrographs discovered that the surface was uniformly covered with grains within scale (4×4) µm of the micrographic area. The average grain size was noted about 119 nm, with 40nm of surface roughness. Absorbance enhanced with roughness increased since the surface area enlarged.

Laser grooving process was employed for enhancing the CTS absorption by increasing the thin film surface area. Figure 5 shows the optical microscopic image of groove lines. Image processing programs were used for enhancing the optical microscopic images, like imageJ (ver.152e) and OriginLab Pro (ver.9.5.1). As mentioned in figures 6, 7 and 8, the optical image is (850×680) µm. This could prove that the groove width is around 37 µm. Figure 8 gives an obvious view of the groove line on the CTS thin film. Figure 8a displayed the groove depth on the surface. Figure 8b has been clearly shown with a colour map distribution of the CTS thin films.

5. Conclusions

Spray pyrolysis parameters have been optimized for depositing films of CTS. The prepared films were in good adhesion with glass substrates. The monoclinic crystal structure has been observed from XRD investigation. Nano-sized grains were carried out. FTIR investigation have observed bonds like Cu-S, and Sn-S. Film thickness was in nanoscale. Laser beam grooved lines in microscale (about 37 µm), such increased the deposit layer surface area, and that absorption has enhanced too.

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Figure 1: XRD pattern of CTS thin film

Figure 2: FTIR spectrum of prepared CTS Thin Film
Figure 3: UV-vis spectrum of CTS

Figure 4: AFM of CTS Thin Film
Figure 5: Microscopic image of CTS thin film surface

Figure 6: selective section of the groove line of the CTS thin film

Figure 7: the 3D image of Groove lines of CTS thin films
Figure 8: (a) Grooves homogeneity, (b) Distribution of the CTS film surface in 2D color surface map