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Study of Mixing Different Volume Ratios for Preparing Cu_2SnS_3 Thin Films using Computerized Spray Pyrolysis System

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Abstract

Ternary thin films was deposited , using a fully computerized system of spray pyrolysis technique, on glass substrates at 310±5 °C. A mixture of an aqueous solution of thiourea, tin chloride dehydrate and copper chloride was used as spraying liquid. The optimum volumetric ratio of mixing was found to be [S/(Cu+Sn)=1] at pH =1.5, in the present work. XRD examination revealed CTS in a monoclinic phase.A number of platform speeds were employed in the spraying process. XRD peaks were described at 2θ = 28.39°, 33.02°, 47.34°, and 56.39° corresponding to $(\bar{2}\,\bar{1}\,1)$, $(\bar{2}\,0\,6)$, $(\bar{2}\,0\,10)$, and $(\bar{3}\,\bar{2}\,10)$, respectively. The FTIR investigations certified a numeral of the chemical bond of Cu-, Sn- and S-. The crystallite size was observed in the range of nano-sized using Scherrer formula. Studying surface morphology of CTS films reveals a uniform coating on the substrates which approved by SEM investigations.

Keywords: CTS, Cu_2SnS_3, Computerized Spray Pyrolysis system, Solar Absorber.

خلط نسب حجميه مختلفة لإعداد اغشية Cu_2SnS_3 الرقيقة باستخدام منظومة الرش الحراري المحوسبة

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الخلاصة

تم ترسيب غشاء رقيق لمادة ثلاثية باستخدام منظومة محوسبة تعمل بتقنية الرش الحراري على قاعدة زجاجية عند درجة حرارة 310±5 °C . استخدم سائل الرش خليط مائي مكون من الثايوريا و كلوريدات ثنائية جزيئة الماء لكل من النحاس و القصدير. افضل نسبة للخلط كانت [S/(Cu+Sn)=1] عند الاس الهيدروجيني 1.5 . كشفت فحوصات حيود الاشعة السينية ان المادة المنتجة هي بالطور البلوري احادي الميل. كانت زوايا الحيود هي 2θ = 28.39°, 33.02°, 47.34°, 56.39° عند المستويات البلورية $(\bar{2}\,\bar{1}\,1)$. $(\bar{2}\,0\,6)$, $(\bar{2}\,0\,10)$, $(\bar{3}\,\bar{2}\,10)$, كشفت الدراسة الطيفية لتحويلات فورير للاشعة تحت الحمراء عدد من الاواصر الكيميائية للعناصر −Cu−, Sn− , S . استخدمت معادلة شيرر لحساب الحجم الدقائقي الذي وجد ضمن المدى النانوي. تم دراسة تشكلية السطح للاغشية المرسبة والتي وضحت طلاءا منتظما على القاعدة باستخدام المجهر الالكتروني.

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Introduction

Spray pyrolysis deposition technique (SPT) is a simplewidely used technique for thin films deposition starting with an aqueous solution. SPT can be categorized as a non-vacuum and inexpensive technique for thin films. It was used for different applications such as solar absorbers [1]

As mentioned, SPT is a solution-based method [2], where its process start as droplets of the reaction precursors which are produced from the prepared liquid in a section of the apparatus and then carried by the gas flow to the other heated section where pyrolysis of the aerosol takes place [3]. Spray pyrolysis has many parts of apparatus such as spraying nozzle, liquid solution, substrate platform, heating unit, and temperature monitoring and controlling [4].

Spray pyrolysis is a non-vacuum technique that is employed in the deposition of ternary chemicals like copper tin sulfide (CTS) thin films [5]. CTS thin films have been prepared with different methods such as solid-state reaction, co-evaporation, solvothermal, sulfurization, chemical bath deposition [6], chemical bath, electrodeposition, spin coating, DC magnetron sputtering, and the famous one, spray pyrolysis [7]. CTS has quite a few chemical phases, such as Cu_4SnS_4, Cu_2SnS_3, Cu_3SnS_4, $Cu_2Sn_3S_7$, and $Cu_4Sn_7S_{16}$ [8].

Of all these ternary sulfides, Cu_2SnS_3 is the most auspicious phase that can be employed in solar cells in view of their high absorption coefficient and optimum direct band gap in applications of solar energy conversion [9]

Different crystal structures such as cubic, tetragonal, hexagonal, monoclinic, and triclinic [8] were reported in the literature for the Cu_2SnS_3 films. In the present study, CTS absorption layers were deposited by a home-made fully computerized chemical spray pyrolysis deposition system (FCSPD) [10]. The liquid solution was sprayed using an adjustable nozzle height onto a movable hot plat in x-y directions. FCSPD instantaneously monitors the substrate temperatures during the deposition process within an accuracy of about 0.25 °C. The home-made heating element distributes the thermal energy homogenously [11].

The aim of this paper is to fabricate Cu_2SnS_3 thin films to be utilized as solar absorbers. Furthermore studying the deposition speed (mm/sec) effect on the product crystal structure

Experimental

The experimental procedure has been divided into three parts. The first one a synopsis explanation of the computerized system of spray pyrolysis the second, sample preparation for starting the deposition process The third part is the measurements and characterization of the prepared CTS samples.

Computerized Spray Pyrolysis System

A homemade fully controlled spray pyrolysis deposition system (FCSPD) was used in the present work for the deposition of CTS thin films. The FCSPD setup has a hotplate platform that can be moved in x-y dimension for coating layers within or larger than micro slide lab scale. In addition, there is a vertical movement of the nozzle holder in the z-axis that can precisely change the nozzle to substrate distance (NSD). The computerized setup can instantaneously monitor and control the substrate temperature within an accuracy of about 0.25 °C using MAX6675 Arduino Type-K digital conversion Thermocouple.

Sample Preparation

The glass substrate was cleaned ultrasonically with 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 of an aqueous solution of tin chloride dihydrate $SnCl_2[H_2O]_2$ and copper chloride dihydrate $CuCl_2[H_2O]_2$ in addition to thiourea $CS(NH_2)_2$ as a source of sulfur. These chemicals were supplied by Sigma- Aldrich with a purity of about 99%.

The raw chemicals were dissolved in distilled water to prepare a fine mixture, the volumetric ratios of the prepared chloride solutions were mixed within an equimolar concentration, excepting the aqueous solution of thiourea which was in five multiple times.

A number of different volumetric ratios were mixed to be prepared as spray solution for the deposition process, as listed in Table-1

Table 1- pH value of the raw chemicals preparing solution

Concentration (M) Cu:Sn:S	Volumetric ratio (mL) Cu:Sn:S	pH
1:1:5	2:2:8	1.6
	2:1:4	2.2
	2:1:8	1.7
	4:2:6	1.5
	4:2:8	2.4
	4:4:8	1.7

The optimum volumetric ratio was found to be at [S/(Cu+Sn)=1]. The liquid mixture was sprayed on the substrate at 310±5 °C, at a nozzle height of about 30 cm, with unvarying carrier gas flow. The aqueous solution was sprayed at a rate around 0.2 mL/sec through a metallic nozzle of 0.35 mm radius onto preheated substrates. The mixture liquid solution interacted on the substrate as depicted in the chemical equation: -

$$SnCl_2.2H_2O + 2CuCl_2.2H_2O + 3CS(NH_2)_2 \xrightarrow{heat} Cu_2SnS_3 + 6HCl\uparrow + 3CO_2 + 3N_2 + 9H_2$$

At fixed nozzle height condition (30 cm), platform speeds were varied as (3, 4, 5, 6, 7, 8 and 9 mm/sec) in each run of the deposition process L1 All the other parameters were kept unchanged.

Sample Analysis

The crystal structure of the deposited CTS thin films was examined using X-ray diffraction (XRD) patterns. X-ray diffractometer (CuKα_1, λ=1.54056 Å) of the model (D2 PHASER, by BRUKER, Germany) was employed. The crystallite was determined using Scherrer equation (1) [12]:

$$D = \frac{K\,\lambda}{\beta\,\cos(\theta)} \qquad (eq. 1)$$

where λ is XRD radiation wavelength, β is the full width at half maximum (FWHM) of the peak position in radians and θ is Bragg's diffraction angle at the peak position.

Fourier transform infrared spectrum (FTIR) was used to confirm the vibrations of the chemical bonding. Scanning electron microscope (SEM) (model Inspect S50, FEI Company, Netherlands) equipped with an energy dispersive X-ray (EDX) detector (Bruker Company, Germany) was employed for examining the surface topography of the arranged thin films.

Results and Discussion

The present research has revealed the optimum conditions for the present deposition situation which are listed in Table-1.

Table 2- the optimum conditions for the present CTS deposition process

A mixture solution of Cu:Sn:S		NSD (cm)	Platform speed (mm/sec)	Substrate temperature
Concentration ratio	pH			
1:1:5	≈1.5	30	7	310 ±5 °C

According to the above table , structural properties of CTS thin film were investigated by the XRD technique. XRD pattern of CTS thin films that were deposited at the present optimal condition are displayed in Figure-1.

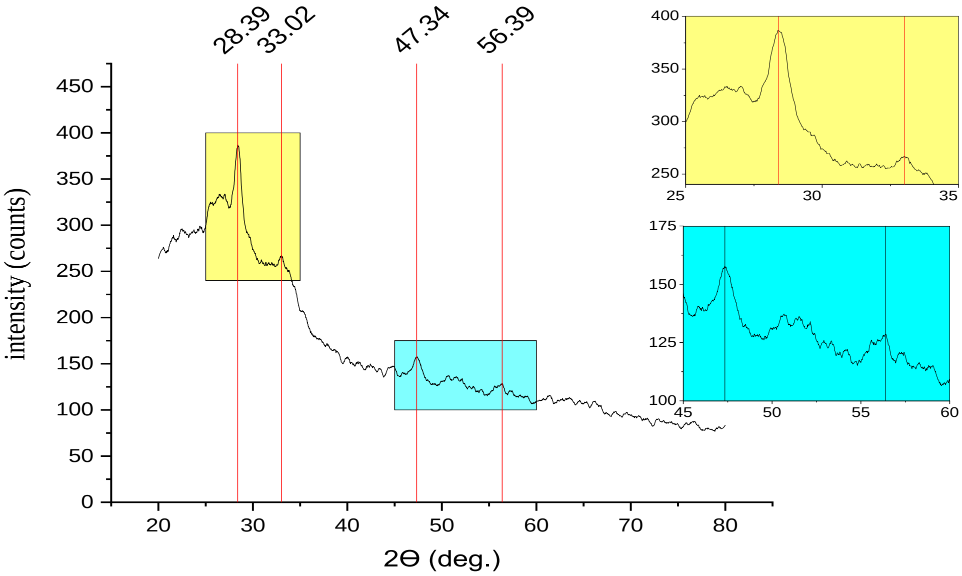

Figure 1-XRD patterns of CTS thin films deposited

The CTS sample has a monoclinic polycrystalline structure of copper tin sulfide. The XRD peaks appeared at diffraction angles of 2θ = 28.39°, 33.02°, 47.34°, and 56.39° for the planes $(\bar{2}\,\bar{1}\,1)$, $(\bar{2}\,0\,6)$, $(\bar{2}\,0\,10)$, and $(\bar{3}\,\bar{2}\,10)$, respectively. These patterns corresponds to the ICDD card (27-0198) of XRD reference data [13].

According to the XRD study, the ternary CTS was certified. There is a good agreement with an accuracy of about 99.5% in matching the recorded and typical values of diffraction angles. Thereinafter, by Debye-Scherer's formula [14], the crystallite size of the selected sample was found to be around 80 nm.

For chemical bonding investigations, Figure- 2 showed the FTIR spectrum of Cu_2SnS_3 thin film.

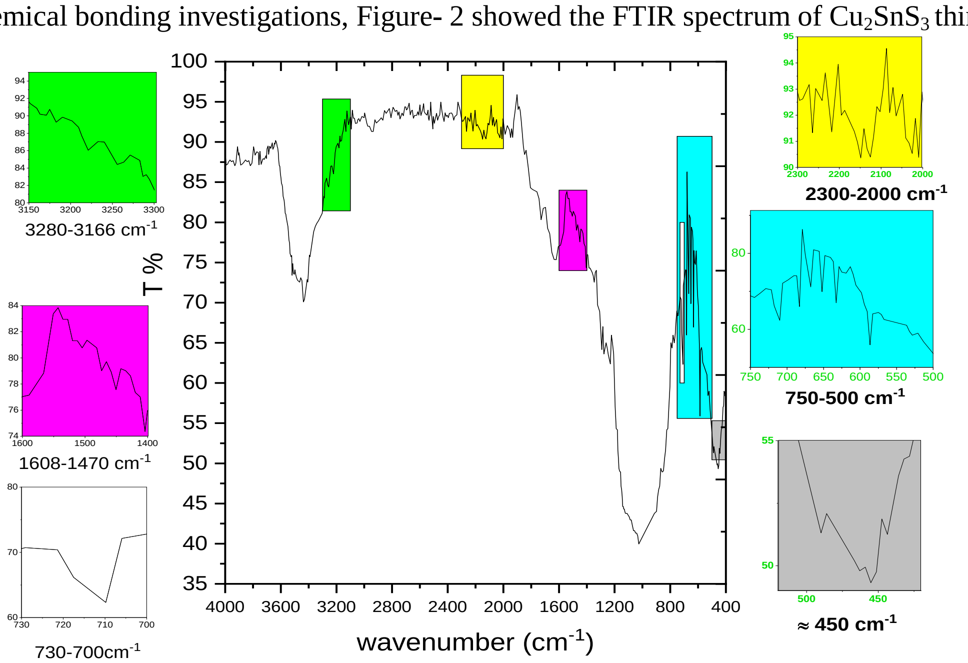

Figure 2-FTIR Spectroscopy of CT thin film

The band around 450 cm^{-1} is assigned to Cu-O vibrations bond in copper oxides such as CuO and Cu_2O. Whilst, the vibrations energies in the range 750-500 cm^{-1} were accorded to Cu-S, Sn-S, and S-oxides bonds. In the range of 2300-2000 cm^{-1}, there is a weak bond that is assigned to C≡S and nitrile bond C≡N. In addition, other bonds such as N-H, O-H, and C-H were vibrated in region 3500-3350

cm^{-1} [15]. The band at 774 cm^{-1} represents the symmetric stretching of C=S vibrational band in thiourea. The peaks noticed in the range 720-680 cm^{-1} and 850-800 cm^{-1} correspond to the presence of ligands such as –S–C≡N and –N=C=S in the compound Cu_2SnS_3 [16].

The peak at 730 cm^{-1} in the thiourea spectrum is assigned to C=S stretching shifts to 700 cm^{-1} in the Cu-Sn-thiourea complex spectrum. The frequencies 1470 cm^{-1} and 1608 cm^{-1} in the spectrum of thiourea were noticed to shift to higher values of 1490 cm^{-1} and 1620 cm^{-1}, respectively. Thus the N-H stretching frequencies 3166 cm^{-1} (symmetric) and 3280 cm^{-1} (asymmetric) in thiourea spectrum shift to higher values of 3185 $cm^{-1}$and 3300 cm^{-1} in Cu-Sn-thiourea complex spectrum [7]

The chemical elements of CTS were examined by EDX. As illustrated in Figure- 3, EDX displayed Cu-Sn-S individually in the selective sample. Where, Si was definitely referred to the glass substrate, while, oxygen gives an indication of metal oxides such (Sn, and Cu oxides) that are externally formed during the thermal chemical reaction.

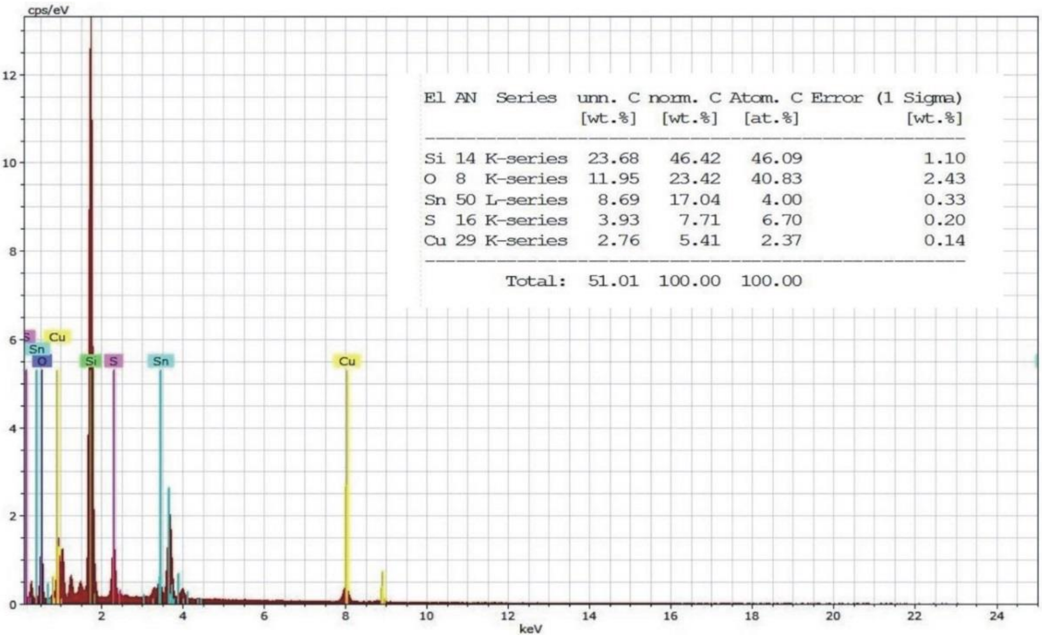

Figure 3-EDX of the prepared CTS sample

The surface morphology of the CTS films was examined using scanning electron microscope SEM. Figure-4 shows the SEM images of the CTS thin films of different zoom scale.

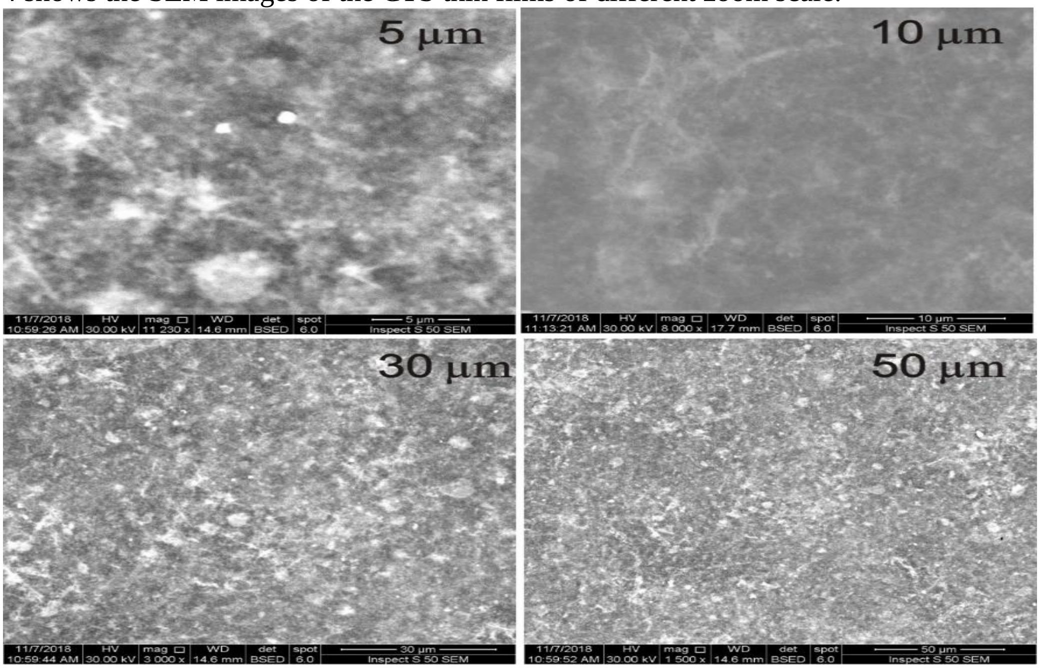

Figure 4-SEM of CTS thin film on a different zooming scale

Conclusion

Platform speed has an immediate effect on the thin film formation. The ternary CTS films are in good adhesion to glass substrates. The crystal structure was monoclinic. Different chemical vibrating bonds of elements Cu-, Sn-, and S- were revealed. Thin films have a fine roughness of surface morphology.

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