

Structural and Optical Properties of $\text{Cu}_2\text{ZnSnS}_4$ Films Prepared by Sol-Gel method

*Abdulhameed Saeed

Sattar Jabbar Kasim

Department of physics, College of Science, Basrah University, Basrah, Iraq.

*Corresponding Author E-mail: abdulhameedsaeed916@gmail.com

ARTICLE INFO.:

Article history:

Received: 7 DEC, 2017

Accepted: 13 SEP, 2018

Available Online: 22 LUN, 2019

Keywords:

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS)
thin film
Sol-Gel
kesterite

ABSTRACT:

Chest x-ray medical images are widely used for diagnostic purposes for $\text{Cu}_2\text{ZnSnS}_4$ thin films are prepared by sol gel and spin coating methods. In this study, some physical properties such as structural and optical properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films are investigated. Prepared thin films are annealed at 400°C for 1 h under N_2 atmosphere. XRD pattern for the peaks 28.31° , 47.26° , and 56.12° which have indexed plans (112), (220) and (312) confirmed that all $\text{Cu}_2\text{ZnSnS}_4$ thin films prepared have kesterite structure. The results of XRD patterns and UV-Visible spectra demonstrated kesterite phase and a great optical absorption coefficient more than 10^5 cm^{-1} in visible region. The estimation of the band gap which equal $E_g \approx 1.5 \text{ eV}$ by dependent at the optical characteristics.

DIO.: <http://dx.doi.org/10.31257/2018/JKP/2019/110107>

الخصائص التركيبية والبصرية لأغشية $\text{Cu}_2\text{ZnSnS}_4$ المحضرة بواسطة طريقة

ستار جبار قاسم

عبد الحميد سعيد عبد الحميد

جامعة البصرة كلية العلوم قسم الفيزياء

الكلمات المفتاحية:

الخلاصة:

تم تحضير أغشية $\text{Cu}_2\text{ZnSnS}_4$ الرقيقة بواسطة طريقة (محلل - هلام). في هذا البحث، أجريت دراسة بعض من الخصائص البصرية والتركيبية لأغشية $\text{Cu}_2\text{ZnSnS}_4$ الرقيقة المحضرة بواسطة طريقة (محلل - هلام). أجري التلدين على الزجاج المطلي عند 400°C درجة مئوية في النروجين. كشفت حيود الأشعة السينية ان القيم 28.31° ، 47.26° و 56.12° والتي لها المستويات (112) و (220) و (312) لجميع أغشية $\text{Cu}_2\text{ZnSnS}_4$ الرقيقة أظهرت بنية kesterite. كذلك أظهرت نتائج أنماط حيود الأشعة السينية وأطياف الأشعة المرئية UV-Visible في المستوي kieserite ومعامل امتصاص بصري كبيرة أكثر من 10^5 cm^{-1} في المنطقة المرئية. تم حساب قيمة فجوة الطاقة ووجدت انها $E_g \approx 1.5 \text{ eV}$ بالاعتماد على دراسة الخصائص البصرية.

1. INTRODUCTION

Kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has created a significant enthusiasm as a potential absorber material conveying a promising substitute to $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ (CIGSe) for thin film solar cells due to the non-toxicity and plenitude of its constituents [1,2]. CZTS thin films have near ideal band gap $E_g \approx 1.5$ eV for the photoelectric energy change and are recognized by an extensive absorption coefficient ($>10^5 \text{cm}^{-1}$) [3]. The components elements of CZTS thin film, for example, Cu, Zn, Sn, S are abundant, minimized effort, and non-toxic, accordingly employing of CZTS thin film will bring about both huge cost savings and in addition environmental benefits [4]. Industrial methods for CZTS solar cells including vacuum and non-vacuum deposition, for example, evaporation [5], sputtering [6,7,8], and pulsed laser deposition [9] have been used. The non-vacuum methods open possibilities for the low-cost fabrication process. CZTS films, set by the spin coating of a sol-gel solution are described by the most elevated strength and technologically reproducible electro-physical and optical properties. Thin film solar cells with a CZTS absorber, prepared by the sol-gel method, achieve the photoelectric transformation efficiency of 8% [10]. In 2013, the evaporated CZTS thin film solar cells have exhibit 8.4% conversion efficiency [11] and more recently a most elevated transformation efficiency of 9.2% was reached [12]. The objective of this commitment is the make of high quality CZTS films by spin coating. This technique should bring about the advancement of a basic and slight effort manufacture process of CZTS films.

2. EXPERIMENTAL SECTION

CZTS thin films solution were prepared by used $\text{Cu}(\text{Ac})_2$ as a source of Cu^{+2} with purity of 98% mixed with 0.25M $\text{Zn}(\text{Ac})_2$ also as the main source of zinc ions together with 0.25M SnCl_2 99.9%, 2M $(\text{NH}_2)_2\text{CS}$ 99% used to supply

sulphur particle, Weigh materials using a sensitive balance type Mettler. A E-160 with high sensitivity up to 10^{-4} gm. Different compounds were mixed, $\text{Cu}(\text{Ac})_2$, hydrated SnCl_2 and in addition $(\text{NH}_2)_2\text{CS}$ to mixture were dissolved in 50 ml 2-methoxyethanol and set in a magnetic stirrer, 5 ml from diethanolamine used with little of same solvent, stirred about 10 min, the mixture was added drop by drop using syringe. The action was continue up to one hour at RT. and in addition $(\text{NH}_2)_2\text{CS}$ to mixture were dissolved in 50 ml 2-methoxyethanol and set in a magnetic stirrer, 5 ml from diethanolamine used with little of same solvent, stirred about 10 min, the mixture was added drop by drop using syringe. The action was continue up to one hour at RT. After fast solubility the $\text{Cu}_2\text{ZnSnS}_4$ was show up and kept in volumetric flask for 24h period. The mixing ratio was 8:1:1:2 for Cu/Zn/Sn/S compound 10 min period time was in magnetic stirrer before precipitate the solution after using filter paper, the acidity was measured using pH meter and found it 8. The solution was covered in glass plate after cleaner by water and acetone. The prepared sol-gel was spin coated at 3000 rpm during 40 s. The first thermal treatment of the deposition layers was done at $\approx 220^\circ\text{C}$ in air. The samples are then placed in a convection oven at 400°C in 1h with nitrogen. Thermal processing has reduced the crystalline defects caused by the preparation and the defects of the interface by giving the atoms of the material sufficient energy to rearrange itself. CZTS films with this thickness can be obtained by the successive spin coating of 3–6 layers of a sol-gel depending upon its consist.

2.2 Characterization

The CZTS thin films have been considered using X-Ray Diffraction (XRD) (X' Pert Pro MPD) with $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{\AA}$). The general morphology of the items was portrayed by Field Emission Scanning Electron Microscopy (FESEM, Zeiss Supra 55VP, Germany). The optical properties of the CZTS

thin films were estimated using an UV/VIS/NIR spectrophotometer (Shmadzu) in the range 300-1100 nm at room temperature.

3. RESULTS AND DISCUSSIONS

3.1 STRUCTURAL PROPERTIES

Fig. 1(a) show the XRD patterns of the spin coating method $\text{Cu}_2\text{ZnSnS}_4$ thin films comprise of a single phase and have the kesterite structure. the better XRD peaks showed up at $2\theta = 28.38^\circ, 47.3^\circ$, and 56.03° can be credited to the diffraction of (112), (220), and (312) planes of kesterite stage CZTS thin films, respectively

(JCPDS no. 26-0575). Fig. 1(b) When the process is performed at 400°C with N_2 for the CZTS membrane. The results of X-ray diffraction show that there is an increase in height and intensity (FWHM). This means that thermal treatment has reduced the crystalline defects caused by the preparation and the defects of the interface by giving the material atoms sufficient energy to rearrange itself., The XRD patterns showed $2\theta = 28.31^\circ, 32.77^\circ, 47.26^\circ$, and 56.12° equivalent to the planes (112), (200), (220), (312).

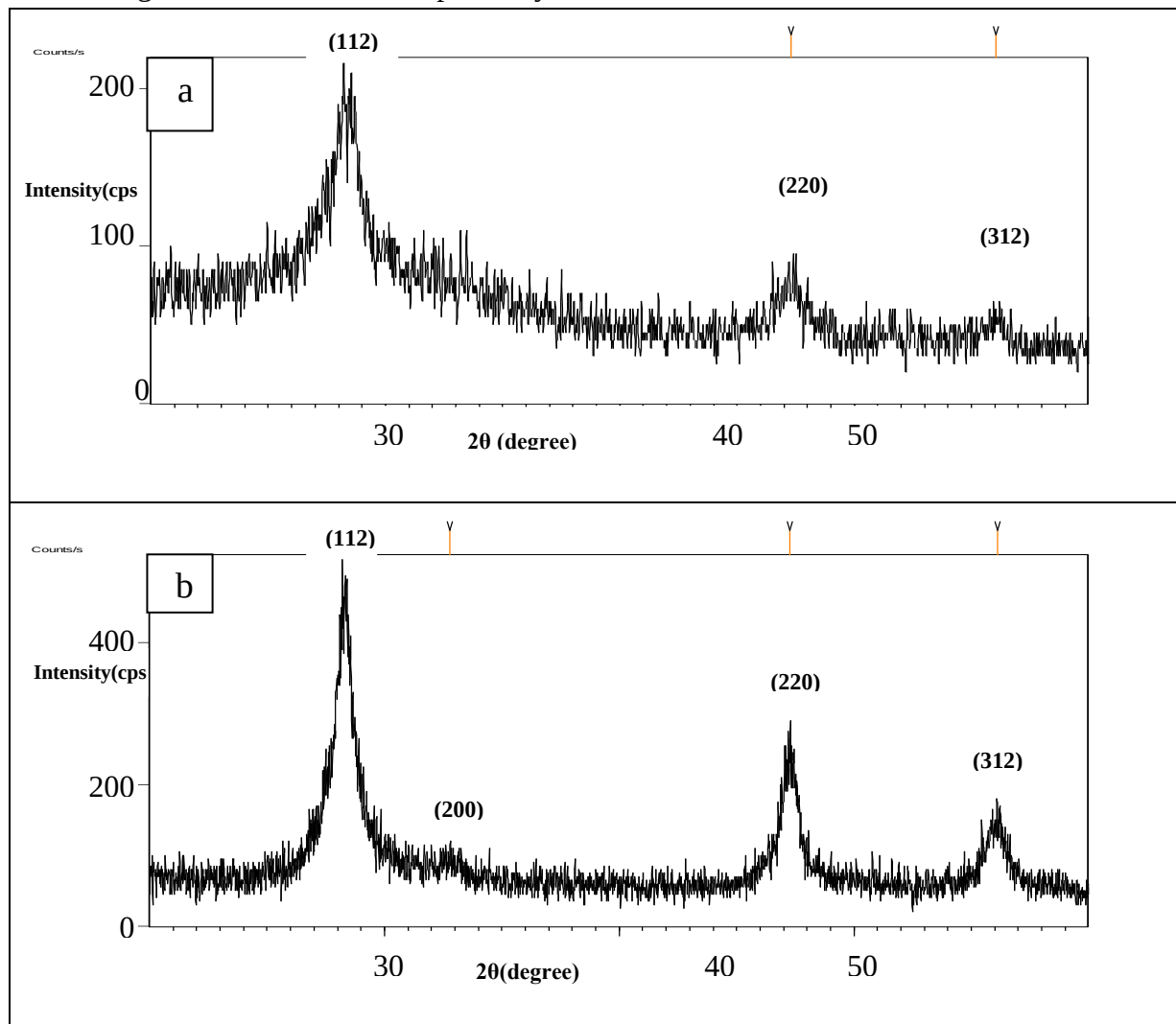


Figure 1: XRD pattern of CZTS (a) Before annealing (b) at annealing 400°C

3.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FE-SEM) ANALYSIS

Figure (2) shows a FESEM picture of the prepared item by responding to copper, zinc, tin

and sulphur precursors in 2-methoxyethanol dissolvable for 1h. The surface picture of the CZTS thin films was appeared in the figure(2). The surface properties of the membrane of the composite CZTS shows the emergence of (nanosheet), and the results indicates that the thickness of the sheet is about 10 nm. Which

provides a large surface area to help absorb more electrons and this advantage can be used as an application for photovoltaic cells

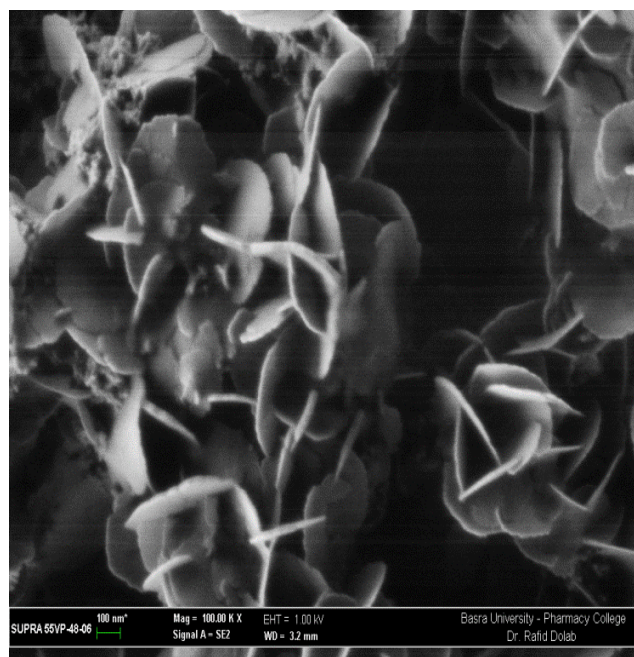


Figure 2: FESEM image of the CZTS nanosheet.

3.3 UV-VISIBLE SPECTROSCOPY ANALYSIS

Fig(3a) shows the UV-Vis absorption spectroscopy of the CZTS thin films, CZTS is an immediate band gap semiconductor, it was measured in the range of wavelengths (400-1100) nm. In the present investigation, the band gap was achieved by plotting the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) (Where α = absorbance, h = Planck's steady, and ν = frequency), Figure (3b) shows the change in the absorbance spectrum as a function of the wavelength of the CZTS membrane, after attaching at 400 °C for one hour with N_2 . The results showed that the film had a optical gap value of 1.5 eV, being reliable with the announced estimations of CZTS in writing (1.45 – 1.5 eV) [13-14].

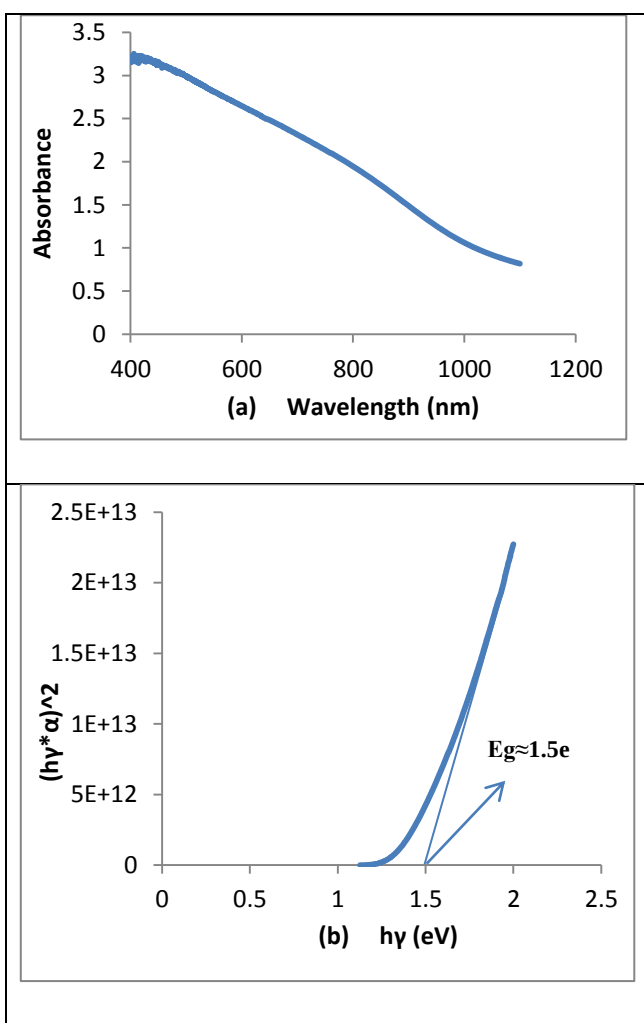


Figure 3a: UV-vis absorption of the CZTS film (b)the energy gap of CZTS at 400°C in N_2 .

4. CONCLUSION

Cu_2ZnSnS_4 Nanosheet with kesterite structure can be prepared by Sol-Gel method which synthesized at room temperature using solution method by taking copper, zinc, Tin chloride and Thiourea at molar concentration ratio (Cu: Zn: Sn: S). XRD, FESEM characterizations confirm the structure, composition and morphology of as-obtained nanosheet. XRD characterization resembled with JCPDS number (26-0575) confirmed the kesterite phase of CZTS (Cu_2ZnSnS_4). annealing temperature has important positive effect on removal of secondary phases and achieved single phase kesterite CZTS at annealing temperature 400°C for 1h in N_2 atmosphere. the diffraction peaks (112),(312) and (220) related to tetragonal structure of Cu_2ZnSnS_4 . Sheet thickness is about 10 nm. and

a high absorption coefficient as 10^4 cm^{-1} completed by this synthesis technique. The optical energy band-gap of the prepared nanosheet CZTS sample is about 1.5 eV, which is very close to the optimum value for a solar-cell. These results show that CZTS films could be easily prepared by this technology for the solar cell application. The simple preparation and low cost nature of Sol-Gel method make it quite charming.

5. REFERENCES

- [1] B. Shin, O. Gunawan, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant $\text{Cu}_2\text{ZnSnS}_4$ absorber, *Prog. Photovolt.: Res. Appl.* 21 (2013) 72–76.
- [2] C. Yan, J. Chen, F. Liu, N. Song, H. Cui, B.K. Ng, J.A. Stride, X. Hao, Kesterite $\text{Cu}_2\text{ZnSnS}_4$ solar cell from sputtered $\text{Zn}/(\text{Cu Sn})$ metal stack precursors, *J. Alloy. Compd.* 610 (2014) 486–491.
- [3] Y. Zhao, C. Burda, Development of plasmonic semiconductor nanomaterials with copper chalcogenides for a future with sustainable energy materials, *Energy Environ. Sci.* 5 (2012) 5564–5576.
- [4] G.L. Agawane, A.S. Kamble, S.A. Vanalakar, S.W. Shin, M.G. Gang, J.H. Yun, J. Gwak, A.V. Moholkar, J.H. Kim, Fabrication of 3.01% power conversion efficient high-quality CZTS thin film solar cells by a green and simple sol–gel technique. (2015) *Materials Letters* 158:58–61
- [5] Y. S. Lee, T. Gershon, O. Gunawan, T. K. Todorov, T. Gokmen, Y. Virgus, and S. Guha, $\text{Cu}_2\text{ZnSnSe}_4$ thin-film solar cells by thermal coevaporation with 11.6% efficiency and improved minority carrier diffusion length, *Advanced Energy Materials* 2015; 5: 1401372.
- [6] H. Katagiri, K. Jimbo, S. Yamada, T. Kamimura, W.S. Maw, T. Fukano, T. Ito, T. Motohiro, Enhanced conversion efficiencies of $\text{Cu}_2\text{ZnSnS}_4$ -based thin film solar cells by using preferential etching technique, *Applied Physics Express* 2008; 1: 41201.
- [7] H. Sugimoto, C. Liao, H. Hiroi, N. Sakai, and T. Kato, Lifetime improvement for high efficiency $\text{Cu}_2\text{ZnSnS}_4$ submodules, *Proc. PVSC* 2013;39
- [8] S. Tajima, M. Umehara, M. Hasegawa, T. Mise and T. Itoh, $\text{Cu}_2\text{ZnSnS}_4$ photovoltaic cell with improved efficiency fabricated by high-temperature annealing after CdS buffer-layer deposition, *Prog. Photovolt: Res. Appl.* 2017; 25:14–22
- [9] A.V. Moholkar, S.S. Shinde, A.R. Babar, Kyu-Ung Sim, Hyun Kee Lee, K.Y. Rajpure, P.S. Patil, C.H. Bhosale, J.H. Kim, Synthesis and characterization of $\text{Cu}_2\text{ZnSnS}_4$ thin films grown by PLD: Solar cells, *Journal of Alloys and Compounds* 2011; 509: 7439-7446
- [10] Hao Xin, John K. Katahara, Ian L. Braly, Hugh W. Hillhouse. 8% Efficient $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Solar Cells from Redox Equilibrated Simple Precursors in DMSO, *Adv. Energy Mater.* (2014) 1301823.
- [11] B. Shin, O. Gunawan, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant $\text{Cu}_2\text{ZnSnS}_4$ absorber. *Prog. Photovolt. Res. Appl.* 21, 72 (2013)
- [12] H. Hiroi, N. Sakai, T. Kato, H. Sugimoto, High voltage $\text{Cu}_2\text{ZnSnS}_4$ submodules by hybrid buffer layer, in *Proceedings of the IEEE 39th*

Photovoltaic Specialists Conference (PVSC), (2013), p. 0863

- [13] K. Ito and T.Nakazawa, Electrical and Optical Properties of Stannite-Type Quaternary Semiconductor Thin Films, Japanese Journal of Applied Physics, Volume 27, Part 1, Number 11 November 1988,27,2094.
- [14] H.Katagiri, Cu₂ZnSnS₄ thin film solar cells, Thin Solid Films Volumes 480–481, 1 June 2005, Pages 426-432.