Investigation of Cu$_2$ZnSnS$_4$ film by Simple Flow-Coating Technique

Nattee Khotummee$^{1, *}$, Theerawut Sumphao$^1$, Tosawat Seetawan$^2$

$^1$Optic Research Laboratory, Center of Excellent on Alternative Energy, Research and Development Institute, Sakon Nakhon Rajabhat University, Sakon Nakhon, 47000 Thailand

$^2$Program of Physics, Faculty of Science and Technology, Sakon Nakho Rajabhat University, 680 Nittayo Road, Mueang District, Sakon Nakhon Province, Saskon Nakhon, 47000 Thailand

*Corresponding Author: nuttee@snru.ac.th

Abstract. This present study aims to investigate a Cu$_2$ZnSnS$_4$ (CZTS) film obtained by simple flow-coating technique using with CZTS precursor solution synthesized by non-vacuum sol-gel process and annealing without sulfurization. The precursor solution was prepared by mixture CuCl$_2$, ZnCl$_2$, SnCl$_2$ and CH$_2$N$_2$S molar to obtain the ion of Cu, Zn, Sn and S. The CZTS film was investigated by using XRD, FE-SEM, and UV-Visible Spectroscopy, respectively. The XRD results show main peak at the angle 28.48° according with (112) plane on the kieserite phase of tetragonal structure, crystallite size average about ∼103.137 ± 0.9788 nm. The surface morphology was observing microscopic porosity structure of the particles and cross-section achieve a film thickness of approximately 32.92 ± 0.62 μm. The EDX result was revealed that whereas the composition nonuniformity from the simple flow-coating process. The optical properties show band gap energy quite close to the optimum value ~1.518 eV, good optical absorption (~10$^4$ cm$^{-1}$). These characteristics make the simple fabrication CZTS film suitable material as an absorber layer in photovoltaic.

1. Introduction

The quaternary compounds of copper zinc tin sulfide (Cu$_2$ZnSnS$_4$: CZTS) have been considered as one of the most promising to development on photovoltaic materials due to direct band gap energy of ∼1.4 – 1.6 eV [1 – 6], large absorption coefficient (>10$^4$ cm$^{-1}$) [7, 8], nontoxic and earth-abundant and environmentally benign Sn and Zn constituent [1, 9]. In the current have many techniques can employed to elaborate CZTS films such as electrochemical deposition [10, 11], thermal evaporation [12 – 14], magnetron sputtering [15, 16], SILAR [17, 18], co-evaporation [19, 20], chemical bath deposition [21, 22], electron beam evaporation [23, 24], pulsed laser deposition [25, 26],, and solution-based technique. The solution-based approach for coating CZTS film most often used, spray pyrolysis [27, 28], dip-coating [29, 30], ink-jet printing [31], spin coating [32, 33] and screen printing [34, 35]. The best efficiency of CZTS solar cell applications groups was use solution-based has been already proposed efficiency up to 12.6% [36]. The solution was prepared by the simplest sol-gel method to high high-quality CZTS. However, the flow coating method is one method for not required heating or rotating the substrate, reduce material, low-costs, and certain conditions during coating.
In this paper, we will focus on the fabrication the CZTS film deposition flow coating with precursor solution synthesis by sol–gel method on the glass substrates to study the structural, morphological, and optical properties to find the possibility of developing the light absorber layer for solar cells with low-cost method in the future.

2. Materials and Methods

2.1 Synthesis of CZTS Solution
The CZTS solution complex were synthesis by the sol-gel process prepared CZTS films were synthesis by sol-gel process using a precursor source of Cu, Zn, Sn, S such as 0.02 mol CuCl₂·H₂O (QRēC, 99.99%), 0.01 mol ZnCl₂ (QRēC, 99.99%), 0.01 mmol SnCl₂·H₂O (QRēC, 99.99%), and 0.04 mmol SC(NH₂) (HiMedia, 99.9%), mixed into C₃H₈O₂ (2-methoxyethanol: 2-metho, QRēC, 99.99%) 50 mL stirrer for 1 h at 60 °C to gives the clear homogeneous solutions and drop few drop 1 mL C₂H₇NO (mono-ethanolamine: MEA, Sigma Aldrich, 99.99%) continued stirrer for 5 min to clear yellow solution, curing the CZTS solution at room temperature for 24 h to condensation reactions. After curing, the molecules of the ionic compounds will bond together more densely, as evaporation of single aerosol droplets containing mixtures of water and ethanol makes the coating easier to adhere to the material.

2.2 Deposition CZTS film
CZTS film were coated on indium tin oxide (ITO) glass substrate (WellJoin co., ltd), size 25 × 25 × 1.1 mm³, 20 Ω sq⁻¹, thickness of conductive layer about 950 ±100 nm and maximum operating temperature must reach 600 °C. Before deposited CZTS film, the substrate was cleaned by soap solution followed sonicated clean using an ultrasonic bath (GTSONIC, VGT-1730QTD) in acetone (C₃H₆O), 2-propanol (C₃H₈O), DI water (requires about 10 min per step [37]and drying with Aragon gas. The simple flow-coating technique [38] was used for coating the CZTS solution as show in Fig. 1 with drop solution on substrate and drying sample on hotplate 10 min for 60 °C in air, repeat as 4 times.

![Fig. 1 Scheme of the flow-coating process.](image)

2.3 Annealing CZTS film
The CZTS film were annealing with commercial furnace tube at 500 °C for 60 min, ramping rate of 5 °C min⁻¹ during in argon atmosphere gas flow rate 10 mL min⁻¹ without sulfurization treatment. The temperature profile as shown in Fig. 2.
2.4 Characterization Techniques

The structural properties and confirm the formation of CZTS were characterized by X-ray Diffractometer (XRD), Shimadzu, XRD-6100 with CuKα1 radiation (λ = 1.5406 Å), operate in 2θ range of 20° – 80°, scan speed 2 °C min⁻¹, used 40 kV and 30 mA of power source. The surface morphology, cross-section and element composition were characterized by Field Emission Scanning Electron Microscope (FE-SEM), JEOL, JSM-7610F. The UV-Visible spectrophotometer Shanghai, UV-5200 was measured for study optical transmittance spectrum in the wavelength range of 400 – 1000 nm.

3. Results and Discussion

The XRD result of post-annealing CZTS shows the diffraction peaks (shown in Fig. 3) at angles 2θ = 28.48, 47.38 and 56.02°, are assigned to the (112), (220) and (312), planes of a tetragonal structure respectively. The diffraction patterns can be indexed to CZTS kesterite phase of tetragonal crystal structure followed standard peak on PDF card no.00-026-0575, confirming formation of CZTS can be achieved by flow-coating process without sulfurization. The crystallite size of sample film was calculated Scherer's equation (1);

\[ D = \frac{0.96\lambda}{\beta \cos \theta} \]  

Where \( D \) is the crystallite size, \( \theta \) is the Bragg's angle, \( \beta \) is full width at half maximum (FWHM) of (112) peak, \( \lambda \) is wavelength of x-ray source (0.15406 Å). The average crystallite size of CZTS sample film was estimated to be \( \sim 103.137 \pm 0.9788 \) nm, the crystallite size of film observations suggests that the layer CZTS film prepared by flow-coating tech that mentioned that film have formation to thick film [39]. The tetragonal lattices parameters of CZTS are \( a = b = 5.4664 \) Å, \( c = 1.1145 \) Å analysed by equation (2) [40];

\[ \frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \]

![Fig. 2 Temperature versus time for a heating rate for annealing CZTS film.](image-url)
Fig. 3 XRD patterns of CZTS sample film annealing without sulfurization.

The FE-SEM images reveal that the surface morphology of CZTS films in Fig. 4 (a), the surfaces CZTS are due to the formation of predominantly non-uniform texture, with voids or cavities, porous structure and contains large densely packed grain is caused by low viscosity of CZTS solution and ligand complex was evaporate with heating treatment at 500 °C for 60 min is causing to a lot of holes and porous film on the substrates. The thickness of CZTS film is determined to be about 32.92 ± 0.62 µm is not yet suitable for development absorber in thin-film solar cell according with suitable thickness layer 1.0 to 2.0 µm [8], could be solved by increasing times of coating film. However, the holes and porous structure of film morphology could be increasing surface area to absorption light.

Fig. 4 FE-SEM image of CZTS sample film study (a) Surface area and (b) a) Cross-sectional.
Fig. 5 The surface EDS mapping images of the CZTS film.

The EDS spectra (Fig. 5) shows the element distribution of constituent elements of the CZTS material was observed that Cu = 20.41 mol%, Zn = 26.92 mol%, Sn = 29.64 mol%, and S = 23.03 mol%, it's was investigating the homogeneity in terms of material composition on the top surface films showed the commonly optimal to grow CZTS film stoichiometry of Cu-poor (Cu/(Zn + Sn) = 0.36) and and Zn-rich (Zn/Sn = 0.91) composition (as shown in Table 1) for the global CZTS solar cell performance [41] with elemental ratio of Cu:Zn:Sn:S to 1.81 : 1.17 : 0.95, it is suggests that the distributions of Cu, Zn, Sn, and S elements which is in good agreement with the above XRD result.

| Chemical Composition (at%) | Cu  | Zn  | Sn  | S   | Cu/(Zn+Sn) | Zn/Sn | S/Metal |
|----------------------------|-----|-----|-----|-----|------------|-------|---------|
|                            | 20.41 | 26.92 | 29.64 | 23.03 | 0.36       | 0.91  | 0.30    |

Table 1 The elemental composition of CZTS films annealing at 500 °C.

Fig. 6 The EDS spectra of CZTS film.

The optical properties of CZTS sample film were investigated the transmittance (T) and absorbance spectra (A) as a function of the wavelength (λ) for simple flow-coating technique in visible light region range of 300 – 700 nm. The absorbance of CZTS was observed large absorption spectra from the visible region (Fig. 7) preferred for the solar cell absorber materials. The thickness of film from FE-SEM information can be calculated the relation of absorption coefficient (α) respect to the photon energy (hν) follow eq. (3);
\[ \alpha = 2.303 \frac{A}{d} \]  \hspace{1cm} (3)

Where \( A \) is the absorbance and \( d \) is the thickness of film. The 2.303 value is arises from the conversion factor \( \ln(10) \) [42].

The CZTS film has very high absorption coefficient in the visible light region in order of \( 10^5 \text{ cm}^{-1} \) (Fig. 8) a. The Tauc's relation was used to estimate the optical energy band gap (\( E_g \)) using the relation plot of \( (\alpha h\nu)^2 \) versus photon energy (\( \nu \)) as shown in Fig. 9. The bandgap value of CZTS film was observed to be approximately 1.518 eV, [43] and similar with the reported value in literature [1–2];

\[ \alpha h\nu = \gamma (h\nu - E_g)^2 \]  \hspace{1cm} (4)

Where \( \gamma \) is a constant, \( \alpha \) is the absorption coefficient and \( h\nu \) is the photon energy.
Fig. 8 Absorption coefficient ($\alpha$) of CZTS films.

Fig. 9 The plots ($\alpha$hv$^2$) versus hv with absorption coefficient ($\alpha$) for CZTS films.

The CZTS film coated with the simple flow-coating technique has a high absorbance property because there are many pores, it is not strong and easily broken. Therefore not suitable for making flexible films but suitable for making thin films on a solid substrate.

4. Conclusion

The CZTS films was successfully fabricated by simple flow-coating technique from precursor solution annealing in Ar atmosphere without sulfurization at 500 °C for 1 h. The X-ray diffraction result confirmed the CZTS kesterite phase tetragonal crystal structure lattices parameters of CZTS are $a = b = 5.4664$ Å, $c = 1.1145$ Å, crystallites average about $\sim 103.137 \pm 0.9788$ nm. The morphology of film was observed porous structure and film thickness about $\sim 32.92 \pm 0.62$ μm. The optical properties showed a good optical absorption coefficient ($> 10^5$ cm$^{-1}$) in the visible light region and the optical band gap energy in the range 1.518 eV.
5. Acknowledgement

The authors are thankful to the Center of Excellence on Alternative Energy (CEAE) Research and Development Institute (RDI), Sakon Nakhon Rajabhat University (SNRU) for support instrument and research place and the authors are thankful to the Prof. Dr. Tosawat Seetawan, Program of Physics, Faculty of Science and Technology of SNRU, for Research consulting for completeness.

6. References

[1] Chaudhuri, T. K., & Tiwari, D. (2012). Earth-abundant non-toxic Cu2ZnSnS4 thin films by direct liquid coating from metal–thiourea precursor solution. Solar Energy Materials and Solar Cells, 101, 46-50.

[2] Henry, J., Mohanraj, K., & Sivakumar, G. (2016). Electrical and optical properties of CZTS thin films prepared by SILAR method. Journal of Asian Ceramic Societies, 4(1), 81-84.

[3] Mohammadnejad, S., Baghban Parashkhou, A. CZTSSe solar cell efficiency improvement using a new band-gap grading model in absorber layer. Appl. Phys. A 123, 758 (2017). https://doi.org/10.1007/s00339-017-1371-x

[4] G.L. Agawane, A.S. Kamble, 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. Mater. Lett. 158(1), 58–61 (2015)

[5] Katagiri, H., Saitoh, K., Washio, T., Shinohara, H., Kurumadani, T., & Miyajima, S. (2001). Development of thin film solar cell based on Cu2ZnSnS4 thin films. Solar Energy Materials and Solar Cells, 65(1-4), 141-148.

[6] Katagiri, H. (2005). Cu2ZnSnS4 thin film solar cells. Thin Solid Films, 480, 426-432.

[7] Isah, K. U., Yabagi, J. A., Ahmadu, U., Kimpa, M. I., Kana, M. G. Z., & Obaseki, A. A. (2013). Effect of different copper precursor layer thickness on properties of Cu2ZnSnS4 (CZTS) thin films prepared by sulfurization of thermally deposited stacked metallic layers. IOSR J. Appl. Phys, 2(6), 14-19.

[8] Jiang, M., & Yan, X. (2013). Cu2ZnSnS4 thin film solar cells: present status and future prospects. Solar Cells—Research and Application Perspectives.

[9] Kumar, M. S., Madhusudanan, S. P., & Batabyal, S. K. (2018). Substitution of Zn in Earth-Abundant Cu2ZnSn (S, Se) 4 based thin film solar cells—A status review. Solar Energy Materials and Solar Cells, 185, 287-299.

[10] Zhang, X., Shi, X., Ye, W., Ma, C., & Wang, C. (2009). Electrochemical deposition of quaternary Cu 2 ZnSnS 4 thin films as potential solar cell material. Applied Physics A, 94(2), 381-386.

[11] Gür, E., Sarıtaş, S., Demir, E., Demir, K. Ç., & Coşkun, C. (2019, August). CZTS Growth for Solar Cell Application by Electrochemical Deposition: pH Effect. In 2019 IEEE Regional Symposium on Micro and Nanoelectronics (RSM) (pp. 123-125). IEEE.

[12] C. Shi, G. Shi, Z. Chen, P. Yang, M. Yao, Deposition of Cu2ZnSnS4 thin films by vacuum thermal evaporation from single quaternary compound source. Mater. Lett. 73, 89–91 (2012)

[13] Wang, K., Gunawan, O., Todorov, T., Shin, B., Chey, S. J., Bojarczuk, N. A., ... & Guha, S. (2010). Thermally evaporated Cu 2 ZnSnS 4 solar cells. Applied Physics Letters, 97(14), 143508.

[14] Khemiri, N., Chamekh, S., & Kanzari, M. (2020). Properties of thermally evaporated CZTS thin films and numerical simulation of earth abundant and non toxic CZTS:Zn (S, O) based solar cells. Solar Energy, 207, 496-502.

[15] N. Thota, M. Gurubhaskar, A.C. Kasi Reddy, G. Hema Chandra, B.R. Mehta, A. Tiwari, Y.P. VenkataSubbaiah, Growth and properties of Cu2ZnSnS4 thin films prepared by multiple metallic layer stacks as a function of sulfurization time. J. Mater. Sci. 28(16), 11702–11711 (2017)
[16] Zhuk, S., Kushwaha, A., Wong, T. K., Masudy-Panah, S., Smirnov, A., & Dalapati, G. K. (2017). Critical review on sputter-deposited Cu2ZnSnS4 (CZTS) based thin film photovoltaic technology focusing on device architecture and absorber quality on the solar cells performance. Solar Energy Materials and Solar Cells, 171, 239-252.

[17] Krishnan, A., Ali, K. R., Vishnu, G., & Kannan, P. (2019). Towards phase pure CZTS thin films by SILAR method with augmented Zn adsorption for photovoltaic applications. Materials for Renewable and Sustainable Energy, 8(3), 1-8.

[18] Banerjee, G., Das, S., & Ghosh, S. (2019). Optical Properties of Cu2ZnSnS4 (CZTS) Made By SILAR Method. Materials Today: Proceedings, 18, 494-500.

[19] Tanaka, T., Kawasaki, D., Nishio, M., Guo, Q., & Ogawa, H. (2006). Fabrication of Cu2ZnSnS4 thin films by co-evaporation. physica status solidi C, 3(8), 2844-2847.

[20] Unold, T., Just, J., & Schock, H. W. (2014). Coevaporation of CZTS Films and Solar Cells. Copper Zinc Tin Sulfide-Based Thin Film Solar Cells, 221.

[21] Govindaraj, R., & Asokan, V. (2015). Solar cells of Cu2ZnSnS4 thin films prepared by chemical bath deposition method. Indian Journal of Pure & Applied Physics (IJPAP), 52(9), 620-624.

[22] GRana, T. R., Shinde, N. M., & Kim, J. (2016). Novel chemical route for chemical bath deposition of Cu2ZnSnS4 (CZTS) thin films with stacked precursor thin films. Materials Letters, 162, 40-43.

[23] Zhang, Y., Wang, S., Wan, G., Huang, M., Ou, K., Liu, R., & Yi, L. (2019). Fabrication of 4.9% efficient Cu2ZnSnS4 solar cell using electron-beam evaporated CdS buffer layer. Thin Solid Films, 685, 145-150.

[24] Mkawi, E. M., Al-Hadeethy, Y., Shalaan, E., & Bekyarova, E. (2018). Substrate temperature effect during the deposition of (Cu/Sn/Cu/Zn) stacked precursor CZTS thin film deposited by electron-beam evaporation. Journal of Materials Science: Materials in Electronics, 29(23), 20476-20484.

[25] Aldalbahi, A., Mkawi, E. M., Ibrahim, K., & Farrukh, M. A. (2016). Effect of sulfurization time on the properties of copper zinc tin sulfide thin films grown by electrochemical deposition. Scientific reports, 6(1), 1-9.

[26] Moholkar, A. V., Shinde, S. S., Babar, A. R., Sim, K. U., Kwon, Y. B., Rajpure, K. Y., ... & Kim, J. H. (2011). Development of CZTS thin films solar cells by pulsed laser deposition: influence of pulse repetition rate. Solar Energy, 85(7), 1354-1363.

[27] Arba, Y., Rafi, M., Hartiti, B., Ridah, A., & Thevenin, P. (2011). Preparation and properties of CZTS thin film prepared by spray pyrolysis. Moroccan Journal of Condensed Matter, 13(3).

[28] Diwate, K., Mohite, K., Shinde, M., Rondiya, S., Pawbake, A., Date, A., ... & Jadkar, S. (2017). Synthesis and characterization of chemical spray pyrolysed CZTS thin films for solar cell applications. Energy Procedia, 110, 180-187.

[29] Prabeesh, P., Saritha, P., Selvam, I. P., & Potty, S. N. (2017). Fabrication of CZTS thin films by dip coating technique for solar cell applications. Materials Research Bulletin, 86, 295-301.

[30] Ziti, A., Hartiti, B., Labrim, H., Fadili, S., Batan, A., Tahri, M., ... & Thevenin, P. (2019). Characteristics of kesterite CZTS thin films deposited by dip-coating technique for solar cells applications. Journal of Materials Science: Materials in Electronics, 30(14), 13134-13143.

[31] Lin, X., Kavalakkatt, J., Brusten, N., Lux-Steiner, M. C., & Ennoufi, A. (2014). Inkjet printing of Kesterite and Chalcopyrite thin film absorbers for low cost photovoltaic application. Proceedings of the 29th European Photovoltaic Solar Energy Conference and Exhibition (pp. 1876-1879).

[32] Tchognia, J. H. N., Arba, Y., Dakhsi, K., Hartiti, B., Ndjaka, J. M., Ridah, A., & Thevenin, P. (2016). Solution-based deposition of wurtzite copper zinc tin sulfide nanocrystals as a novel absorber in thin film solar cells. Optical and Quantum Electronics, 48(4), 255.

[33] Rakhshani, A. E. (2020). Sn-rich CZTS films spin-coated from methanol-based sol-gel solution: annealing effect on microstructure and optoelectronic properties. Journal of Sol-Gel Science and Technology, 1-9.
[34] Zhou, Z., Wang, Y., Xu, D., & Zhang, Y. (2010). Fabrication of Cu2ZnSnS4 screen printed layers for solar cells. Solar Energy Materials and Solar Cells, 94(12), 2042-2045

[35] Chen, Q. M., Dou, X. M., Li, Z. Q., Cheng, S. Y., & Zhuang, S. L. (2011). Preparation of Cu2ZnSnS4 film by printing process for low-cost solar cell. In Advanced Materials Research (Vol. 335, pp. 1406-1411). Trans Tech Publications Ltd.

[36] Wang, W., Winkler, M. T., Gunawan, O., Gokmen, T., Todorov, T. K., Zhu, Y., & Mitzi, D. B. (2014). Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency. Advanced Energy Materials, 4(7), 1301465.

[37] Mattox, D. M. (1985). Substrate preparation for thin film deposition—a survey. Thin Solid Films, 124(1), 3-10

[38] Pokropivny, V., Lohmus, R., Hussainova, I., Pokropivny, A., & Vlassov, S. (2007). Introduction to nanomaterials and nanotechnology (pp. 45-100). Ukraine: Tartu University Press

[39] Chandran, M. (2019). Synthesis, characterization, and applications of diamond films. In Carbon-Based Nanofillers and Their Rubber Nanocomposites (pp. 183-224). Elsevier.

[40] Bade, B. R., Rondiya, S. R., Jadhav, Y. A., Kamble, M. M., Barma, S. V., Jathar, S. B., ... & Dzade, N. Y. (2021). Investigations of the structural, optoelectronic and band alignment properties of Cu2ZnSnS4 prepared by hot-injection method towards low-cost photovoltaic applications. Journal of Alloys and Compounds, 854, 157093.

[41] Bosson, C. J., Birch, M. T., Halliday, D. P., Knight, K. S., Gibbs, A. S., & Hatton, P. D. (2017). Cation disorder and phase transitions in the structurally complex solar cell material Cu2ZnSnS4. Journal of materials chemistry A, 5(32), 16672-16680.

[42] Zhou, M., Gong, Y., Xu, J., Fang, G., Xu, Q., & Dong, J. (2013). Colloidal CZTS nanoparticles and films: Preparation and characterization. Journal of alloys and compounds, 574, 272-277.

[43] Song, X., Ji, X., Li, M., Lin, W., Luo, X., & Zhang, H. (2014). A review on development prospect of CZTS based thin film solar cells. International Journal of Photoenergy, 2014.