Effect of thiourea on structure, morphology and optical properties of spray deposited CZTS thin films for solar cell applications

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ABSTRACT

Cu$_2$ZnSnS$_4$ (CZTS) films of different Thiorea (SC (NH$_2$)$_2$) molarity were deposited by using simple chemical spray technique at substrate temperature 275°C. Analytical reagent Grade Copper chloride (CuCl$_2$), Zinc chloride (ZnCl$_2$), Tin chloride (SnCl$_4$·5H$_2$O) were used as Cu$^{+}$, Zn$^{+}$, and Sn$^{+}$ ion sources respectively and thiourea (SC(NH$_2$)$_2$) (0.02, 0.04 0.06 0.08, and 0.1 M) was used as a S$^-$ ion source. A set of five CZTS films was deposited using five different molarity of thiourea. The structure, Morphology, Elemental analysis and optical properties of these films were studied using X-ray diffratometer (XRD), Scanning Electron Microscopy (SEM) Energy Dispersive X-ray Analysis (EDX) and UV-Visible spectroscopy techniques respectively. The XRD spectra showed that all films are polycrystalline tetragonal structure with preferential orientation along (112) plane. The calculated crystallite size was increased with increase in thiourea concentration. Variations of optical band gap with thiourea molarity have been investigated using Tauc plots. SEM micrographs exhibits CZTS spherical granules regularly arranged with some void spaces. Purity of deposited films was investigated using EDX analysis. All the CZTS films exhibits higher absorption coefficient ($\alpha > 10^4$ cm$^{-1}$) and band gap in the reported range (1.2-1.53 eV) can be used as an absorber layer in solar cells.

Keywords:
CZTS thin films
Energy band gap
Kastertite structure
Optical properties
Spray pyrolysis

1. INTRODUCTION

Solar energy is one of the green and clean energy which is found to be an alternative and promising source of energy, to fulfill the present and future global energy demand. Solar cell devices or photovoltaic cells have been used for harvesting and converting the solar energy into usable form. Silicon-based solar cells are widely used solar cells, but it needs a very thick absorber layer. Thin film solar cells based on copper indium gallium sulfur (CIGS) [Cu$_2$ (InGa) S$_4$] and copper indium gallium selenide CIGSe [Cu$_2$ (InGa) Se$_4$] and and cadmium telluride (CdTe) systems are well established systems of conversion efficiency up to 22 % [1-3]. Latest report show 11.1% and 12.6 % conversion efficiency of CZTSe based solar cells [4]. However Indium and gallium elements are toxic, less abundance, and expensive which limits the large scale production.
of device applications [5] and element Se is too toxic and expensive with CZTSe, whereas cadmium (Cd) is toxic to environment [6]. Therefore researchers are much interested in copper Zinc tin sulfur Cu2ZnSnS4 (CZTS) eco-friendly thin film based solar cells. CZTS is quaternary p-type promising semiconductor has direct optical band gap about 1.2-1.5 eV, absorption coefficient \( \geq 10^4 \text{ Cm}^{-1} \) and of 9.6 % conversion efficiency is very similar to CIGS type thin film solar cells [7-10]. The elements used in fabrication of CZTS material are non-toxic, higher abundance and cheap in cost and ecofriendly. CZTS is therefore a suitable candidate to replace the CIGS as an absorber layer thin film solar cell devices.

Several techniques have been employed in the preparation of CZTS thin films, such as R F sputtering [11], Sol-Gel sulfurization method [12], pulsed laser deposition [13] chemical vapor deposition [14], electrodeposition [15], SILAR method [16, 17] etc.

All of mentioned deposition techniques required sulfurization of deposited sample for stoichiometric CZTS phase formation. In this article we explore simple low cost chemical spray pyrolysis (CSP) technique [18] using locally available perfume atomizer. Present CSP technique is simple, inexpensive, non vaccume and suitable for large area deposition with low chemical wastage. The novelty of this present technique is to achive the stoichiometry of CZTS phase formation without sulfurization process. In CSP method stoichiometry of CZTS is very sensitive to the concentrations of precursors in the spraying solutions. There are several reports on fabrication of CZTS thin films using CSP method [19-21]; however single report of Biplav Daual et al. was reported on studies related to sulphur concentration on properties of CZTS and showed that the optical band gap was increased with increase in thiourea concentration [22]. Up to now, a record efficiency of 9.6 % has been achieved but still improvements are essential to achive high efficiency for industrial application. Therefore in present paper we study influence of sulphur (S) concentration on structural, morphology, and optical properties of CZTS thin films prepared by present chemical spray pyrolysis (CSP) method using locally available perfume atomizer.

2. MATERIAL AND METHOD

Cu2ZnSnS4 (CZTS) thin films were deposited on simple soda lime glass substrates. Before deposition, the substrates were cleaned ultrasonically using acetone, ethanol and distilled water and dried by hair drier. To achive good quality CZTS thin film medium of precursor preparation plays vital role. Different aqueous and nonaqueous medium have been used for precursor preparation however Ethanol was found good in case of CZTS thin films using present CSP method. The precursor solution was obtained by mixing solutions of (0.04) M Copper chloride (CuCl2), (0.02) M Zinc chloride (ZnCl2), (0.02) M Stannic chloride (SnCl3 5 (H2O)) and (0.02, 0.04, 0.06, 0.08, and 0.1 M) thiourea (SC(NH2)2). The pure ethanol medium is used for all three cationic solutions and thiourea solution is prepared by using 50% ethanol to avoid the formation of tin hydroxyl Sn(OH)2 ions so that free Sn+ ions are sufficiently available for CZTS phase formation. The experiment shows that turbidity of mixture was depend on molarity of thiourea (or cation to anion ratio). The cation to anion ratio was displayed in Table 1.

The above prepared solutions were stirrer for one and half hour. Three cationic solutions were mixed together one by one with stirring continue and then thiourea was added slowly such that turbid mixture becomes clear homogenous precursor. This precursor was sprayed on substrate maintained at desire temperature on hot plate by locally available perfume atomizer. The temperature of hot plate is controlled by digital temperature controller. The distance of spraying nozzle form substrate was adjusted such that the whole surface of substrate was exposed. The spray rate 5 ml per second and substrate temperature 275 °C were kept fixed to study the effect of thiourea on characterizations of CZTS thin films [23]. After deposition the samples were annealed in mufel furnace at 275 °C. The annealed samples were characterized using XRD, SEM, and UV-Visible spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Physical characterizatiopn

The thickness (\( t \)) of the deposited CZTS films is calculated by using weight and difference method [10], given by relation (1).

\[
t = \frac{m}{\rho A}
\]
Where \( m \) (gm) is the deposited mass, \( \rho \) (gm/cm\(^3\)) is density of deposited material and \( A \) (cm\(^2\)) is the area of deposited film. The film thickness was shown in Table 1. Film thickness was increased with increase in thiourea concentration. Thickness of the CZTS films was in the range of 266-289 \( \mu \)m. The maximum thickness 289 \( \mu \)m of CZTS film for 0.08 M thiourea was to be obtained however beyond 0.08 M concentration thickness of film sample (CZTS5) was to be decreased.

| Film Sample | Cationic Molarity | Sulfur ion Molarity | Cation/Anion Ratio | Film Thickness (\( \mu \)m) |
|-------------|------------------|---------------------|-------------------|--------------------------|
| CZTS1       | 0.08             | 0.02                | 0.04              | 266                      |
| CZTS2       | 0.08             | 0.04                | 0.02              | 268                      |
| CZTS3       | 0.08             | 0.06                | 1.33              | 271                      |
| CZTS4       | 0.08             | 0.08                | 1.0               | 289                      |
| CZTS5       | 0.08             | 0.1                 | 0.8               | 269                      |

3.2. Structure of CZTS thin films

XRD spectra were recorded in the range 20° - 80° and presented in Figure 1. XRD patterns for all films show Bragg’s reflections at (20\~28.35°, 32.06°, 47.23° and 56.98°) which are assigned to (112), (200), (220) and (312) lattice planes respectively. These values are in good agreement with the standard JCPDS card number (26-0575) which represents the polycrystalline tetragonal Kieserite crystal Structure of CZTS material. The obtained XRD patterns are in good agreement with the pattern reported by Deokate R. J. et al. which confirm the purity of the CZTS films. They have been reported the pure and good quality CZTS thin films exhibited the crystal structure with absence of the impurity peaks and secondary phases confirmed by Raman analysis [24]. The Figure 1 showed that intensity of (112), (220) and (312) peaks gradually increased with increase in thiourea molarity, however for CZTS5 sample height of (112), (220) and (312) peaks was decreased as compared to CZTS4 sample. This concluded that crystallinity of CZTS films were depending on sulfur ion concentration. The full width at half maximum (FWHM) of (112) preferential orientation was decreased with increase in thiourea molarity. The crystallite size was calculated from following Suscherrer’s relation (2) using FWHM (\( \beta \)) corresponding to (112) orientation [25].

![Figure 1. XRD spectra of CZTS thin films](image-url)
\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  

Where, \( \lambda \) is wavelength of X-ray (0.1504 nm), \( \beta \) full width at half maximum and \( \theta \) is Brag’s angle (degree). The FWHM and crystallite size were displayed in Table 2. The crystallite size was increased with increase in thiourea molarity or sulfur ion concentration. However the intensity of (112) peak, FWHM and crystallite size show odd behavior as thiourea molarity was increased above 0.08 M. Thus the optimum value of thiourea molarity or sulfur ion concentration plays important role to maintain the stoichiometry of CZTS films. It is reported that when the thiourea concentration (sulfur ion content) of the composition increases, the mobility of the atoms located on the surface increases, so these atoms can rearrange their positions to occupy more stable sites. This process controls the favorite growth orientation of the CZTS crystal structures similar have been reported by Nabeel A. Bakr et al. [26].

| Film Sample | 2θ (degree) | d (degree) | FWHM β (radians) | Millar Indices (hkl) | D (nm) |
|-------------|-------------|------------|-------------------|----------------------|--------|
| CZTS1       | 28.352      | 3.108      | 3.610             | (112)                | 24     |
| CZTS2       | 28.3757     | 3.139      | 2.569             | (112)                | 33.5   |
| CZTS3       | 28.4148     | 3.0723     | 2.302             | (112)                | 37     |
| CZTS4       | 28.5992     | 3.114      | 2.304             | (112)                | 37.15  |
| CZTS5       | 28.6314     | 3.139      | 4.592             | (112)                | 20.47  |

3.3. Surface morphology of CZTS3 film

Scanning Electron micrograph (SEM) of Sample CZTS3 was presented in Figure 2. Sample is scanned at 5000 magnification. SEM image showed that whole surface is uniformly coated over which spherical granules of CZTS material schematically arranged with some void spaces. The average grain size 1.244 μm is obtained by using linear intercept method. The average grain size is larger than crystallite size obtained from XRD data. The increase of grain size is due to agglomeration of CZTS nano crystals.

![SEM micrograph of CZTS thin films](image)

Figure 2. SEM micrograph of CZTS thin films

3.4. Elemental analysis of CTZS3 sample

Elemental analysis of CZTS sample was carried out using Energy-Dispersive X-ray Analysis (EDX). The Figure 3 shows the EDAX spectra. The Figure 3 showed that all the peak corresponding to Cu, Zn, Sn, and S elements. Therefore prepared sample composed of Copper, Zinc and Tin and Sulfur elements. The initial and final atomic % was shown in Table 3. Initial and final atomic % confirms the Cu₂ZnSnS₄ phase formation. Initial and final atomic percent shows that the prepared CZTS film was stiochiomertric.
3.5. Optical absorption and band gap of CZTS thin films

Optical absorption spectra of CZTS films were recorded in spectral range of (350–999) nm by using Systronics (2201) double beam UV–visible spectrophotometer. The variation of optical absorption with wavelength (nm) was shown in Figure 4. It was noticed that the optical absorption for all CZTS films decreased exponentially as wavelength increased in the range 350–800 nm, and then increases slowly at higher wavelengths. The absorption was observed decreased with increase in thiourea concentration up to 0.08 M and above it shows abrupt increase. The absorption curves of sample CZTS1 and CZTS5 show similar nature. All the films show higher absorption coefficient \( \alpha > 10^4 \) cm\(^{-1} \) in the visible and near infrared region of electromagnetic spectrum which favors increase of probability of direct transition. Similar results have been predicted in other reports \([24, 27]\). The deposited CZTS films exhibits higher absorption coefficient \( (\alpha > 10^4) \) cm\(^{-1} \) may be used in solar cell device applications. The optical band gap is obtained by using Tauc (3) \([28]\).

\[
\alpha h\nu = A(h\nu - E_g)^n
\]  
(3)

where \( (E_g) \) the optical energy gap of the film, \((A)\) is a constant, \((h\nu)\) is the incident photon energy and \(n\) is a numeric value equal to \((1/2)\) for allowed direct transition. The optical band gap was estimated by using Tauc’s plots was as shown in Figure 5 for CZTS thin films, where a graph of \((\alpha h\nu)^2\) versus \((h\nu)\) is plotted and the extrapolating linear portion of the curve gives the value of the direct optical band gap of the deposited CZTS films \([20]\). The band gaps of CZTS1, CZTS2, CZTS3, CZTS4 and CZTS5 obtained respectively were 1.2, 1.52, 1.50, 1.275 and 1.53 eV. It is clear that the optical band gap of all CZTS films lies in the range 1.2 to 1.53 eV similar findings have been reported in the earlier literature \([29]\).
4. CONCLUSION

CZTS thin films were deposited simple soda lime glass substrates by chemical spray pyrolysis technique using locally available perfume atomizer. The XRD results showed that the prepared films are polycrystalline having tetragonal Kieserite crystal structure. The overall results and discussion concluded that optimum value of thiourea molarity plays important role in CZTS phase formation. However CZTS4 sample of 0.8M thiourea molarity exhibits good crystallity, maximum grain size 37.5nm and 1.275 eV band gap. Hence it is concluded that CZTS4 is to be optimized sample with present reagent combination, represent a good candidate as an absorber layer in solar cells.
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REFERENCES

[1] P. Jackson, D. Wuerz, D. Hariskos, E. Lotter, W. Witte, M. Powa1la, “Effects of Heavy Alkali Elements in Cu(In, Ga)Se2 Solar Cells with Efficiencies up to 22.6%,” Physica Status Solidi (RRL)-Rapid Research Letters, vol. 10, 583-586, 2016, doi:10.1002/pssr.201601992.

[2] T. K Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, & D. B. Mitzi, “Beyond 11% efficiency: characteristics of state-of-the-art Cu2ZnSn(S,Se)4 solar cells,” Advanced Energy Material, vol. 1(3), pp. 34-38, 2013, https://doi.org/10.1002/aenm.201200348.

[3] M. Green, K. Emery, Y. Hishikawa, W. Warta, E. Dunlop, D. Levi, A. Ho-Baillie, “Solar cell efficiency tables (version 49),” Prog. Photovolt: Res. Appl., vol. 25(1), pp. 3-13, 2016, DOI: 10.1002/pip.2855.

[4] W. Wang, M. T Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu, & D. B. Mitzi, “Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency,” Advanced energy materials, vol. 4(7), pp. 301465, 2013, https://doi.org/10.1002/aenm.201301465.

[5] H. Katagiri, “Cu2ZnSnS4 thin film solar cell,” Thin Solid Film, vol. 480(481), pp. 426-32, 2005, DOI: 10.1016/j.tsf.2004.11.024.

[6] G. Larramona, S. Bourdain, A. Jacob, C. Chone, T. Muto, Y. Cuccaro, B. Delatouche, C. Moisan, D. Perez, G. Dennler, “8.6% Efficient CZTSSe solar cells sprayed from water-ethanol CZTS colloidal solutions”, J. Phys. Chem. Lett., vol. 5, pp. 3763–3767, 2014.

[7] A. Paraye, A. Shukla, R. Manivannan and S. Noel Victoria, “Single-Step Electrodeposition of CZTS Thin Film for Solar Cell Application: Effect of Annealing Time,” V. Sivasubramanian and S. Subramanian (eds.), Global Challenges in Energy and Environment, Lecture Notes on Multidisciplinary Industrial Engineering, © Springer Nature Singapore Pte Ltd. 2020, https://doi.org/10.1007/978-981-13-9213-9_1.

[8] H. Katagiri, N. Ishigaki, T. Ishida & K. Saito, “Characterization of Cu2ZnSnS4 Thin Films Prepared by Vapor Phase Sulfurization,” Jpn. J. Applied Physics, vol. 40 (2A), pp. 500–504, 2001, doi.org/10.1143/JJAP.40.500.

[9] X. Zhang, X. Shi, W. Ye, C. Ma & C. Wang, “Electrochemical deposition of quaternary Cu2ZnSnS4 thin films as potential solar cell material,” Materials Science and Processing, vol. 4, pp. 381-386, 2009, doi 10.1007/s00339-008-4815-5.

[10] Aron Walsh, Shiyou Chen, X. G. Gong and Su-Huai Wei, “Crystal structure and defect reactions in the kesterite solar cell absorber Cu2ZnSnS4 (CZTS): Theoretical insights,” American Institute of Physics. Conf. Proceeding., vol. 1399, pp. 63-64, 2011, doi.org/10.1063/1.3666258.

[11] J. Seol, S. Lee, J. Lee, H. Nam & K. Kim, “Electrical and optical properties of Cu2ZnSnS4 thin films prepared by rf magnetron sputtering process,” Solar. Energy Material and Solar Cells, vol. 75, pp. 155–162, 2003, doi: 10.1016/S0927-0256(02)00127-7.

[12] Tanaka K., Moritake N. & Uchiki H., “Preparation of Cu2ZnSnS4 thin films by sulfurizing sol-gel deposited precursors,” Solar Energy Material and Solar Cells, vol. 91, pp. 1999–1201 2007, doi:10.1016/j.solmat.2007.04.012.

[13] K. Sekiguchi, K. Tanaka, Moriya & H. Uchiki, “Epitaxial growth of Cu2ZnSnS4 thin films by pulsed Laser deposition,” Physica Status Solidi C, vol. 3(8), pp. 2618–2621, 2006, doi:10.1002/pssc.200606903.

[14] T. Washio, T. Shinji, S. Tajima, T. Fukano, T. Motohiro, K. Jimbo, H. Katagiri, “6% Efficiency Cu2ZnSnS4-based thin film solar cellsusing oxide precursors by open atmosphere type CVD,” J. Mater. Chem., vol. 22, pp. 4021–4024, 2012.

[15] Tulshi Shiyani, Dhyey Raval, Malkeshkumar Patel, Indrajit Mukhopadhyay, Abhijit Ray, “Effect of initial bath condition and post-annealing on co-electrodeposition of Cu2ZnSnS4,” Materials Chemistry and Physic, vol. 171, pp. 63-72, 2016, http://dx.doi.org/10.1016/j.matchemphys.2015.11.001.

[16] J. Henry, K. Mohanraj and G. Shivkumar, “Electrical and optical Properties of CZTS thin films Prepared by SILAR Method,” Journal of Asian Ceramic Series, vol. 4, pp. 81-84 2016, https://doi.org/10.1016/j.jascer.2015.12.003.

[17] Mani P., Manikandan K., Janaki Ramya A., Iruthaya seelan A., Syed Zahirullah S., Shaahul hameed M. & Joseph Prince J., “Influence of Molar Concentrations on Optical Properties of Copper Su-phide Thin Films by SILAR Method,” International Journal of ChemTech Research, vol. 6(7), pp. 3573-3578, 2014.

[18] Ramesh B Mahewar, Limbaj S Ravangave, “Structure, morphology and optical parameters of spray deposited CZTS thin films for solar cell applications,” Indian Journal of Science and Technology, vol. 13(21), pp. 2149-2156, 2020, https://doi.org/10.17485/ijst/v13i21.642.

[19] Kishore Kumar, Y. B. Suress G. Babu, P. Uday Bhaskar, & V. Sundara Raj, “Preparation and characterization of spray-deposited Cu2ZnSnS4 thin films,” Solar Energy Materials and Solar Cells, vol. 93(8), pp. 1230–1237, 2009, doi:10.1016/j.solmat.2009.01.011.

[20] N. M. Shinde, R. J. Deokate, & C. D. Lokhande, “Properties of spray deposited Cu2ZnSnS4 (CZTS) thin films,” Journal of Analytical and Applied Pyrolysis, vol. 100, pp.12-16, 2013, doi:10.1016/j.jaap.2012.10.018.

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[21] M. I. Fathima, A. M. S. Arulanandham, & K. S. J. Wilson, “Effect of ZnS nanowire ARC on CZTS/CdS thin film solar cell by Nebulizer Spray Pyrolysis Technique,” Materials Research Express, vol. 7(1), pp. 015510, 2020 doi:10.1088/2053-1591/ab6399.

[22] Biplav Dahal, Leela Pradhan Joshi, Satyendra N. Pandey and Shankar Prasad Shrestha, “Effect of Thiourea Concentration on Structural, Optical and Electrical Properties of Cu2ZnSnS4 Thin Films Prepared by using Spray Pyrolysis”, Asian Journal of Chemical Sciences, vol. 2(4), pp. 1-8, 2017, DOI: 10.9734/AJOC/2017/34313.

[23] Ramesh B. Mahewar and Limbraj S. Ravangave, “Effect of Copper Concentration on Structure Morphology and Optical band gap of Spray Deposited CZTS Thin Films,” International Journal of Research in informative science Application and Techniques, vol. 4(5), pp. 204516-204525, 2020.

[24] R. J. Deokate, R. S. Kate, S. C. Bulakhe, “Physical and optical properties of sprayed Cu2ZnSnS4 (CZTS) thin film:effect of Cu concentration.” Journal of Materials Science: Materials in Electronics, vol. 30, pp. 3530–3538, 2019, https://doi.org/10.1007/s10854-018-00630-0.

[25] Cullity B., Stock S., Elements of X-ray Diffraction, 3rd Ed, Princeton Hall, 2001.

[26] Nabeel A Bakr, T. K. Ziad, M. A. Shahlaa, “Influence of Thiourea Concentration on Some Physical Properties of Chemically Sprayed Cu2ZnSnS4 Thin Films,” International Journal of Materials Science and Applications, vol. 5(6), pp. 261-270, 2016.

[27] M. A.Olgar,”Influence of Sulfurization on the Properties of Cu2ZnSnS4 (CZTS) thin films prepared by a two-stage process,” Omer Halisdemir University Journal of Engineering Sciences, vol. 8(3), pp.1064-1072, 2019, doi: 10.28948/ngumuh.598096.

[28] J. Tauc, Amorphous and Liquid Semiconductors, Plenum, London, 1974.

[29] Nabeel A. Bakr, Sabah A. Salman, Sabreen A. Hameed, “Deposition and Characterization of Cu2ZnSnS4 Thin Films for Solar Cell Applications,” International Journal of Applied Engineering Research, vol. 13(6), pp. 3379-3388, 2018.

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