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Characterization of the CZTS (Cu_2ZnSnS_4) thin film for solar cell absorber layer synthesized from the nitrate-based sol-gel precursor solution

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ABSTRACT

Manufacture of eco-friendly CZTS (Cu_2ZnSnS_4) thin film absorption layer of pure keserite structure for solar cell is far-reaching. We have manufactured the CZTS thin films by sol-gel dip-coating means from the nitrate-based chemicals. After hardening at 550°C in vacuum condition, we characterize the films by UV–vis spectroscopy, X-ray diffraction (XRD), Scanning Electron Microscope (SEM), and energy dispersive X-ray spectroscopy (EDS) methods. The CZTS films provided high optical absorption coefficient ($2.92 \times 10^4 cm^{-1}$) and average band gap energy (1.58 eV). X-ray diffraction analysis proved the kesterite structure of films. The surface morphology analysis proved the deposition of crammed, condensed and granulated CZTS films. The thin films have intermittent disposal of agglomerated particles with clear-cut edges. The energy dispersive X-ray spectroscopy analysis conferred stoichiometric ratio as Cu: Zn: Sn: S= 2.1: 1.3: 1: 5.2.

Keywords: Thin film, Sol-gel, Absorption layer, Solar cell, Cu_2ZnSnS_4, XRD, SEM, EDS.

1. Introduction

The research of thin film photovoltaic technology underwent constant evolution over the past decades and the industry of solar cells have been flourishing as a result of low manufacturing cost, usage of eco-friendly materials and scalable design. Scientist mainly concentrated on cost reduction and scalability factors for making photovoltaic technology to challenge the fossil fuels[1]. The modern polycrystalline thin film photovoltaic cells–gallium arsenide (GaAs), cadmium telluride (CdTe), copper indium selenide (CIS) and copper indium gallium selenide (CIGS) – have matured economically. Even with power conversion efficiencies (PCE) between 11 to 20%, the CdTe and CIGS are not favoured for ultimate terawatt-scale fabrication because of rarity and price of Te, In, and Ga[1-5]. Besides, Cd, Se and As are very noxious elements – hazardous for animals and human beings. Thus, manufacturing of thin film solar cells using the earth rich as well as harmless elements is centrally important and CZTS (Cu_2ZnSnS_4) is turning out as the 'next generation' solar absorber. CZTS has alike configuration to CIGS, but consist of harmless and earth abundant (Cu: 50 ppm, Zn: 75 ppm, Sn: 2.2 ppm, S: 260 ppm)[6] elements. CZTS has additional benefits too – best direct band gap energy (1.4 ~ 1.6 eV), great absorption coefficient ($>10^4$ cm^{-1}) and hypothetical high energy transformation efficiency (~ 32.2%)[3, 7-9].

Scientists have deposited CZTS thin films by several means–pulsed laser deposition[10], thermal evaporation[11], chemical vapour deposition[12] and sputtering deposition[13]. But, rigorous processing is still mandatory during deposition for high efficiency thin films – which eventually increase the price. So, to reduce the price many scientists have proposed deposition of CZTS thin films in non-vacuum conditions[14,15] and a hydrazine-based non-vacuum circumstance provided with the greatest outputs (PCE - 12.6%[16,17]). Nonetheless, the PCE of CZTS is still below 21% (η of CIGS[18]). In addition to this, hydrazine is awfully hazardous and unsteady chemical compound – a compulsory care for storage[19]. Therefore, we need a robust, easily scalable, and eco-friendly solution-based fabrication method for the CZTS thin films, which will possess the ideal optical and structural characteristics; and eventually provide high power conversion efficiency.

Several other factors also affect the output of CZTS thin-film photovoltaic cells: low open circuit voltage (VOC)[20], low minority carrier lifetime (several nanoseconds)[21] and difficulty in the formation of a perfect CZTS state from Cu, Zn, Sn, and S.

The constituent particles – Cu, Sn and Zn – of CZTS thin films create secondary phases during the fabrication[22] – the Cu-, Sn-, and Zn-abundant composition creates a Cu_2S, SnS and ZnS auxiliary states, respectively[23,24] and any of these secondary phases deteriorates the performance. The exact structure of CZTS thin-film photovoltaic cells is yet not clear, though widely accepted as a kesterite-structured. The compound CZTS material is exposed to deformity and altering of precursor state affects the phase creation of kesterites, which ultimately determine the output of photovoltaic cells[26,27].

We have previously fabricated and characterized the CZTS thin film using acetate-based and chloride-based chemicals[28,29]. In this research, we have studied – optical and structural properties – the CZTS thin films absorption layer manufactured by sol-gel dip-coating method using nitrate based chemicals. Here, the precursor solution was prepared by using nitrate-based chemicals – as the source of Copper and Zinc. We have used hydrate form of tin chloride and thiourea – as the source of tin and sulphur. We have also applied 2-methoxyethanol and mono-ethanolamine (MEA) being solvent and stabilizer respectively. MEA enables the growth of durable CZTS sol-gel precursor.

2. Experimental Procedures

First, the substrate was wiped carefully with a tissue paper soaked with methanol and deionized water respectively. After that, the glass slide was submerged in methanol for few minutes and followed by an ultrasonic bath for 10 minutes. Similarly, the glass slide was submerged in acetone and DI water respectively for few minutes followed by an ultrasonic bath for 10 minutes in both cases.

The precursor solution was made of Copper (II) Nitrate Trihydrate (1.8M), Zinc Nitrate (1.2M), Tin (II) Chloride Dihydrate (1.2M), Thiourea (9M), 2-methoxyethanol, and Monoethanolamine[30]. Thiourea was used as the source of sulfur. The solutes were dissolved in 2-methoxyethanol. The 2-methoxyethanol acted as a solvent and few drops of mono-ethanolamine being a mediator for the precursor solution. The solution was stirred by a magnetic stirrer for homogenous and continuous mixing of the chemicals – stirred until the solution temperature reached to 70^0C. Then, the solutions were further stirred for another 30 minutes at a constant temperature of 70^0C.

The CZTS thin films were produced from the nitrate-based sol-gel precursor solution on glass substrates. Each glass substrate was dipped for 3 minutes into the sol-gel precursor. The glass slides were dipped into and picked up at three different dipping speeds. Depending on the speed, the samples were labelled as sample 1, 2 and 3 respectively. The deposited glass slides were put into an oven for drying after raising the starting temperature of the oven to 150 °C. Then the temperature was raised to 250 °C and all the slides were put in the oven for 30 minutes to clear away the solvent and constituent elements from the CZTS thin films. The dried CZTS thin films were sulfurized in an annealing chamber at 550 °C, and then cooled down to the ambient condition.

The thickness *"d"* of the films was measured by using a stylus profiler (BRUKER Dektak XT^{TM}, Germany). The optical characteristics i.e. transmittance, reflectance, and absorbance were measured using the UH4150, Hitachi, UV-vis spectrophotometer (Japan). The measured wavelength range was from 300 to 700 nm. The X-ray diffraction method was applied to study the structural characteristics of the CZTS films. The diffraction pattern was recorded using the GBC (Australia) system. The Cu-Kα emission was employed to get the possible fundamental diffraction peaks from the sample. The SEM EVO 18, Zeiss (Germany) high-performance scanning electron microscope was employed to study the surface morphology and uniformity of the deposited CZTS thin films.

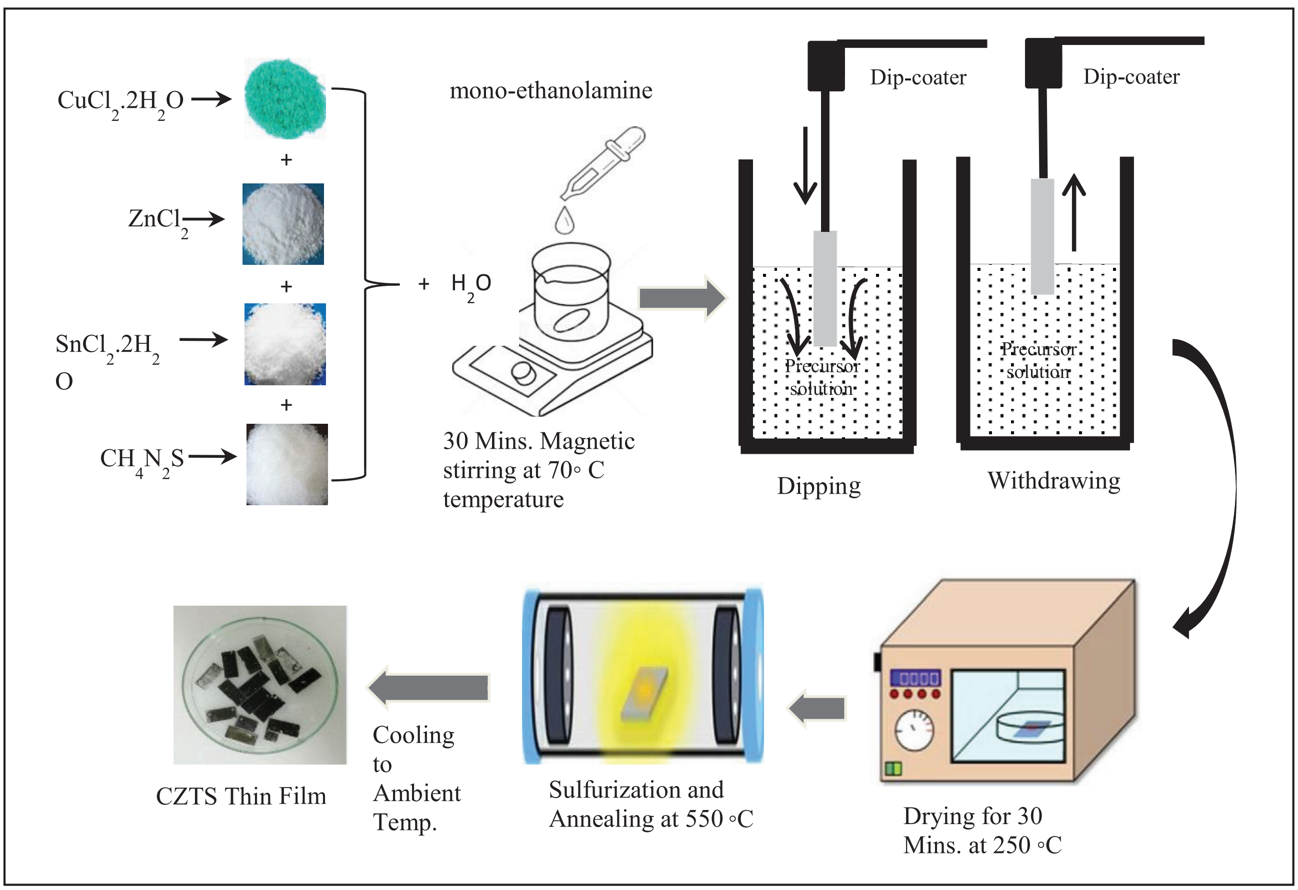


Fig. 1. Synthesis process of CZTS thin films is laid-out in the diagram: preparation of precursor solution, deposition of CZTS films on glass substrate through dip coating method, drying and annealing. The deposited CZTS thin films are finally presented in a petri dish in the diagram.

3. Results and Discussion

Thickness

Thickness is an important criterion for the CZTS absorption layer. The CZTS thin film's behaviour changes with thickness, because surface characteristics are sensitive to thickness. We observed the change of film-thickness of the CZTS films with dip-coating speed. The film thickness did not vary significantly with dipping speeds – average thickness of the CZTS film obtained as 1.97 µm. Usual absorption coefficients for the CZTS thin films has a range: 10^4-10^5 cm^{-1} and a bulky absorber adequately take in the solar spectrum and cut down recombination – increase the minority carrier lifetimes – at the back contact[31-34]. Todorov et al. suggested that absorber thickness greater than 2.5 μm would increase the efficiency of the CZTS thin film[35]. We have shown the picture of homogeneous and solid CZTS thin films at 50, 75 and 100 ms^{-1} dipping speed onto the clean glass substrate in Fig. 1. The big glass substrate area – 10 cm^2 – indicates the practicability of sol-gel technique for big size CZTS film development.

Optical Studies

We have measured the optical characteristics of CZTS thin films at different wavelengths made from the nitrate based precursor solution and deposited on glass substrates. We obtained above 95% absorbance and below 4.5% and 1.15% transmittance and reflectance for all the samples in the visible light spectrum. Figure 2 shows the change of optical characteristics with wavelengths for sample 1, 2 and 3.

Table 1: Optical characteristics of all the samples

CZTSs	Absorbance / %	Transmittance / %	Reflectance / %
Sample 1	98.63	0.27	1.15
Sample 2	95.25	4.5	0.25
Sample 3	99.40	0.5	0.10

We have summarised the absorbance, transmittance and reflectance values in Table 1. The higher percentage of absorbance values and extremely lower percentages of transmittance and reflectance values validated the hypothesis of using CZTS materials as the solar cell absorber layer.

From the experimentally obtained absorbance data, we calculated the absorption coefficient values, *"α"* of the CZTS thin films for all the samples using the Beer-Lambert law[3] –

$$a = 2.303\,\frac{A}{d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where, 'A' and 'd' represent the absorbance and thickness of the film. Absorbance, 'A' is related to the incident, *'I_0'* and transmitted light intensity, *'I'* by the the expresiion $A = \log_{10}\left(\frac{I_0}{I}\right)$. Our obtained *"α"* values for all the samples were closer to the standard absorption coefficient value – 10^4 cm^{-1}. The averaged *"α"* value for all the samples of the CZTS thin films was 2.92x 10^4 cm^{-1}. The *"α"* value > 10^4 cm^{-1} of the nitrate based CZTS thin films agreed with other published research works[1].

Later, we used th absorption coefficient data to determine the band gap energy *"E_g"* values[1]. The absorption coefficient values *"α"* depend on the photon energy, *"hv"* values and are linked by the equation –

$$a = \frac{Ao(hv - Eg)^n}{hv} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where *'A_o'* is a constant associated with effective masses, 'n' represents bands and depending on materials[7] – direct or indirect band gap – 'n' can have value either 0.5 or 2. CZTS being a direct band gap material, we have assumed *'n'* = 0.5. After simplification, we get

$$(\alpha h\nu)^2 = A_o^{\,2}(h\nu - E_g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

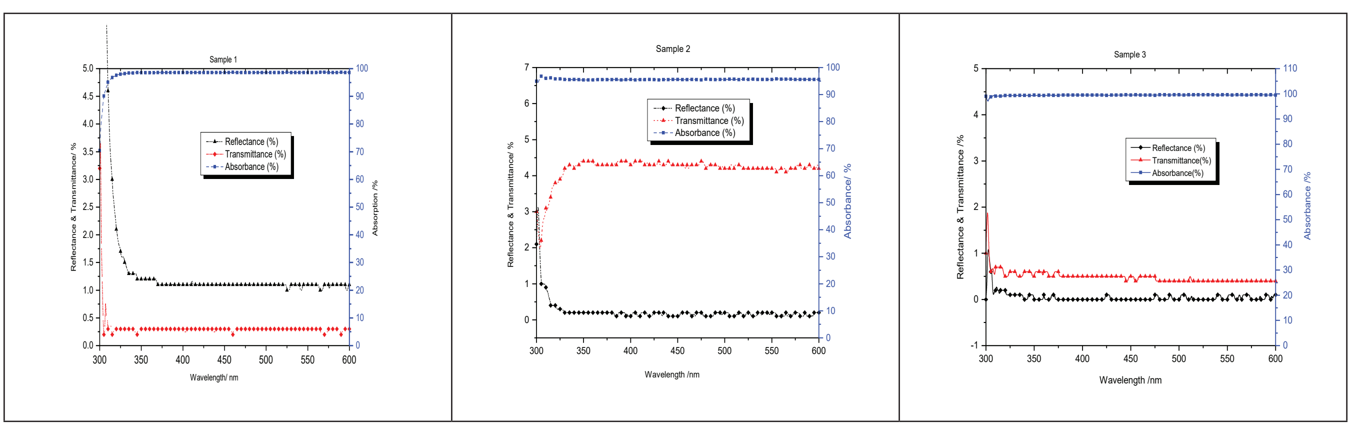


Fig. 2. Shows the change of absorbance, transmittance and reflectance of the CZTS films with the wavelengths.

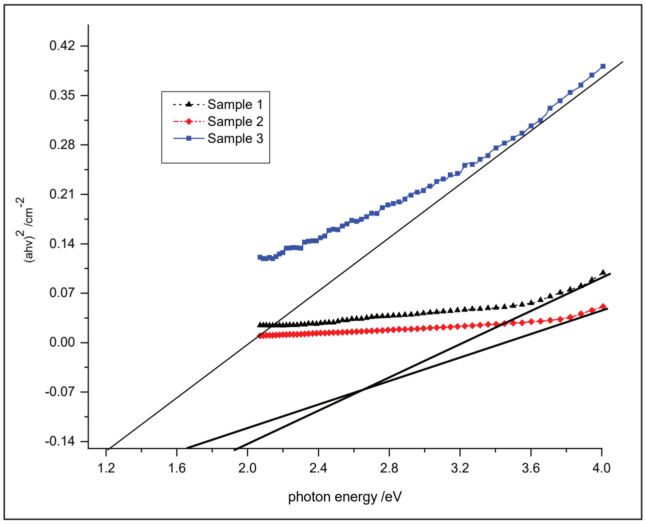


Fig. 3. Tauc plot of the CZTS thin films prepared from the chloride chemical-based precursor solution

We have estimated the band gap energy from the Tauc plot – $(\alpha h\nu)^2$ values vs photon energies (hν). The band gap energy for sample 1, 2 and 3 was obtained as 1.86, 1.67 and 1.22 eV respectively. The average value was 1.58 eV for the three samples. Our band gap energy value agreed with many authors [2, 3, 7, 22, 35-41] and close to the optimum value (1.5 eV)[42] required for a solar cell.

Structural Studies

For structural studies we have taken only sample 3 (dip coating speed, 50ms^{-1}) – which has absorbance (99.4%) and bang gap (1.22 eV). Fig. 4 presents the XRD patterns of the sulfurized CZTS thin films. The sulfurization process improved the crystallinity of the films – without sulfurization no diffraction peaks were found. The primary diffraction peaks were visible at angles $2\theta = 28.73^o, 31.93^o, 33.14^o, 47.58^o$ and 56.44^o sequentially along the planes *(112)*, *(103), (200), (220)* and *(312)*. The XRD spectra proved the polycrystalline-kesterite-tetragonal crystal structure[36] [JCPDS card no. 26–0575] of the CZTS film. We computed the lattice parameters from the XRD spectral data by using the equation –

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (5)$$

Where h, k, and l represent the Miller indices. *"a"* and *"c"* represent the lattice parameters, which are constant for the specific thin film. *"d"* is the spacing expressed as –

$$d = \frac{\lambda}{2 \sin \theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

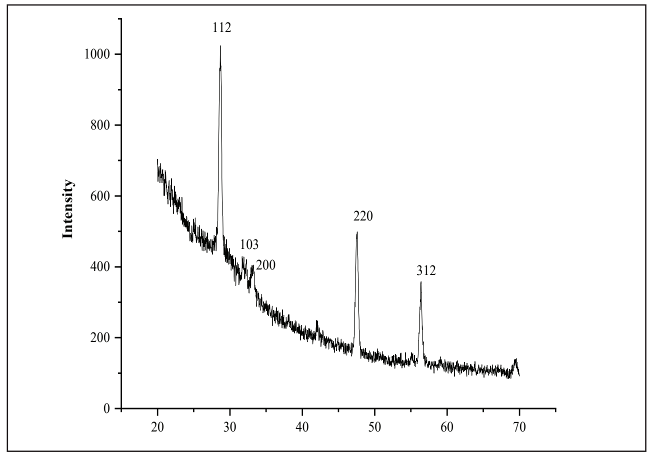


Fig. 4. The XRD patterns of the sulfurized CZTS thin films prepared from the chloride chemical based precursor.

So, first, the value of d was computed by using λ (= 0.15406 nm) and θ (taken from the XRD Spectra), then six different equations were formed from the Miller indices *h, k,* and *l* values – *(112), (103), (220)* and *(312)* – and d. The solution of these six equations gave lattice parameter, *'a' & 'c'*. The obtained average values of the lattice parameters – *"a"* = 0.5431 nm and *"c"* = 1.064235 nm were very close to the standard values – *"a_o= 0.5435 nm"* and *"c_o = 1.0843 nm"* of the CZTS crystal[6, 9] respectively. Next, we determined the particle size by applying the Debye and Scherrer formula[43] –

$$D = \frac{0.94\,\lambda}{\beta\, Cos(\theta)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where *'D'* represents the mean particle size and *'β'* represents the FWHM of the peak of *(hkl)* plane.

The mean grain dimension of the CZTS thin films was 12.10 nm.

The estimated lattice parameters and mean particle size are tabulated in Table 1

Table 2: Lattice parameters and crystal size of the deposited CZTS thin films

d /nm	hkl	2θ / °	'a' /nm	Average 'a' /nm	'c'/nm	Average 'c' /nm	Standard 'a' /nm	Standard 'c_o'/nm	β / °	D /nm	Average D /nm
0.311	112	28.73	0.54	0.5403	1.0721	1.047747	0.5435	1.0843	0.64756	13.226	12.10
0.280	103	31.93	0.5403		0.98223				1.8	4.795	
0.270	200	33.14	0.54						3.25045	2.663	
0.191	220	47.58	0.5403						0.48942	18.528	
0.163	312	56.44	0.5403		1.08891				0.44181	21.313	

Surface morphology and compositional studies

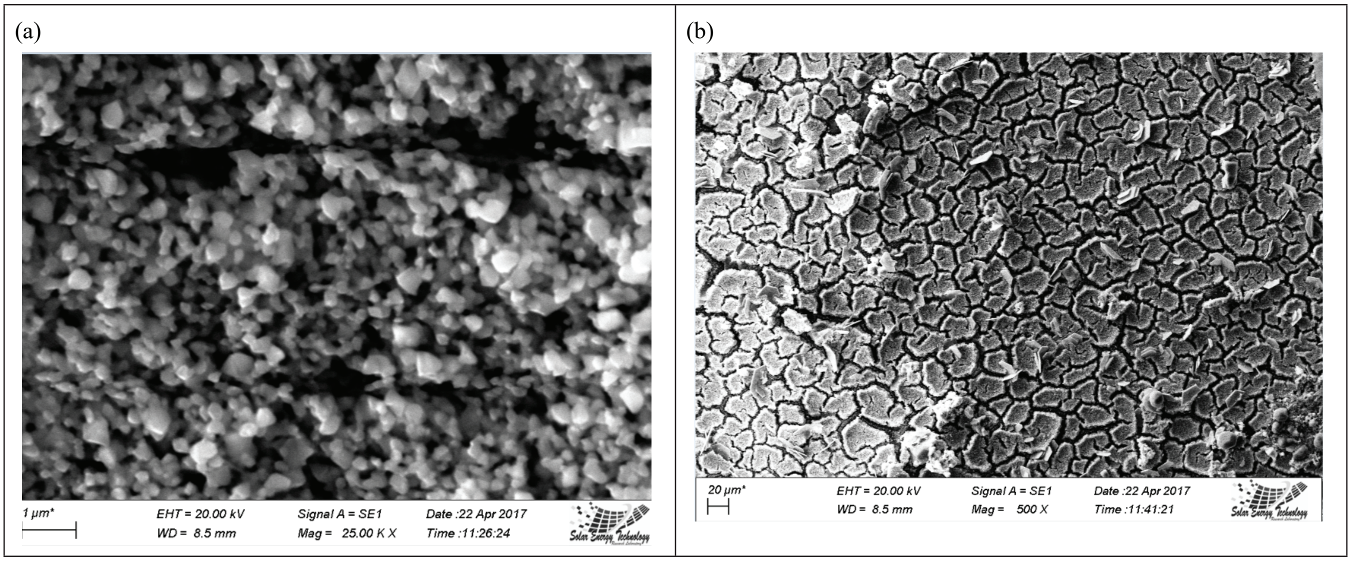
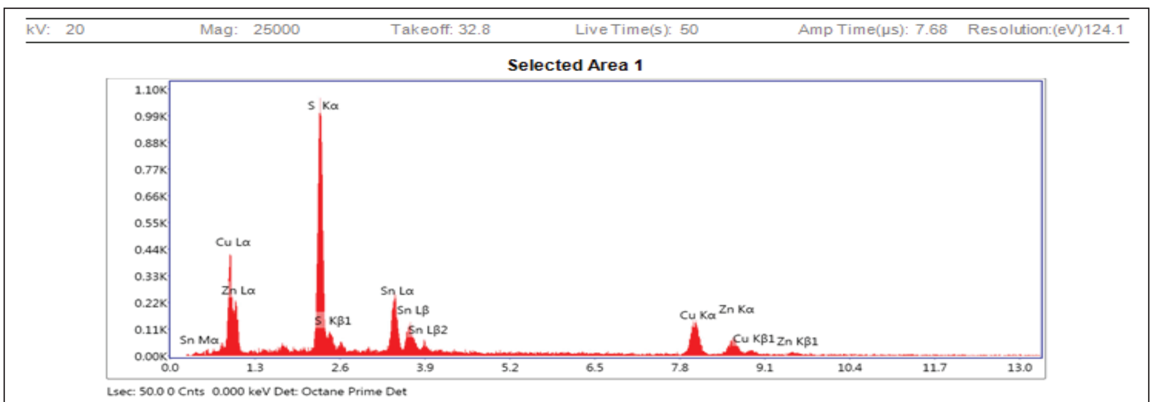


Fig. 5. The surface morphology of the CZTS thin film [(a) 25000X (b) 500X].

We analysed the surface structure of nitrate based CZTS thin films by a scanning electron microscope and also did the elemental analysis by EDX technique. For this, we chose the sample 3 for having maximum absorbance and optimum band gap among all the samples. The **Fig. 5** (a & b) exhibits the scanning electron microscopy picture of the CZTS films at 2500- and 500-times magnification. The scanning electron microscope displayed compact and dense arrangement of particles in the films (Fig. 5 (a & b)). The picture also approved the irregular disposal of big agglomerated particles with distinct edges and as per Zao et al.[44] and Ford et al.[45] minimize the recombination rate of electrons and results in higher open circuit. The scanning electron microscope images also confirmed the consistency and surface smoothness of the film (Fig. 5 a & b). The findings of this research also conformed to the findings of other researchers. Caballero et al.[46] found an identical kind of homogeneous, polycrystalline and compact CZTS thin films. Riha et al.[47] contrived a jam-packed nanocrystals that has steady distribution of particle everywhere on the surface with no fractures. Pawar et al.[42] formed equivalent crystal of CZTS by the electro-deposition process in presence of complexing agent. Wangperawong et al.[48] reported identical densely filled design for Cu_2ZnSnS_4 by an aqueous bath procedure.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
S K	31.9	52.6	174.9	5.4	0.2539	1.1502	0.9233	0.6847	1.0115
SnL	23.2	10.3	47.5	8.7	0.1884	0.8478	1.1289	0.9353	1.0261
CuK	27.6	23.0	40.5	6.4	0.2809	0.9698	1.0054	0.9744	1.0759
ZnK	17.3	14.0	21.0	9.9	0.1760	0.9696	1.0092	0.9782	1.0694

Fig. 6. EDS image and content scrutiny of the CZTS thin films

From the compositional analysis of the annealed CZTS thin film, we got the atomic weight percentage ratio of the CZTS film as – Cu: Zn: Sn: S= 2.1**:** 1.3**:** 1**:** 5.2, which was approximate to the correct stoichiometric ratio – Cu: Zn: Sn: S =2**:** 1**:** 1**:** 4. The copper, zinc, and sulphur rich CZTS thin films deposited from the nitrate-based chemicals were in unison with the ascertainment of other scientist[3, 18, 22, 24-27,49-51] and authenticated the rightness of our nitrate chemical based CZTS films for high potential photovoltaic cells. However, Gua et al.[49] reported that surplus copper in can create binary and / or ternary phases of copper chalcogenide in the film, which depreciate the solar cell attainment. High constituents of sulphur probably affected the band gap energy deviation of the nitrate chemical based CZTS thin films from the standard value ~1.5 eV to 1.58 eV.

4. Conclusions

In this paper, we have reported the characteristics of the CZTS thin film solar cell absorber layer deposited by sol-gel dip-coating method. The optical and morphological studies help us explain the carrier-induction and transportation process in the absorber layer. We got strong optical absorption (2.92×10^4 cm^{-1}) and average band gap energy – 1.58 eV for the nitrate chemical based CZTS absorber layer. Through morphological study, we proved the kesterite crystal structure of the CZTS thin film. The particle deposition in the films was compact and dense in nature. Large agglomerated particles distributed non-uniformly with well-defined boundaries throughout the film – which might reduce the recombination rate of the photo generated electrons. Our research suggests a relatively straightforward, achievable and economical method for producing CZTS films. As a whole, the manufacturing process is innovative and versatile to malleable materials.

References

1. D. Ginley, M. A. Green, and R. Collins, Solar Energy Conversion Toward 1 Terawatt. *MRS Bulletin,* **33(4)**, 355-364, 2008.

2. J. J. Scragg, P. J. Dale, L. M. Peter *et al.* New routes to sustainable photovoltaics: evaluation of Cu_2ZnSnS_4 as an alternative absorber material. *physica status solidi (b),* **245(9)**, 1772-1778, 2008.

3. K. Jimbo, R. Kimura, T. Kamimura *et al.* Cu_2ZnSnS_4-type thin film solar cells using abundant materials. *Thin Solid Films,* **515(15)**, 5997-5999, 2007.

4. J. Britt, and C. Ferekides, Thin-film CdS/CdTe solar cell with 15.8% efficiency. *Applied Physics Letters,* **62(22)**, 2851-2852, 1993.

5. S. A. Khalate, R. S. Kate, and R.J. Deokate, A review on energy economics and the recent research and development in energy and the Cu_2ZnSnS_4 (CZTS) solar cells: A focus towards efficiency. *Solar Energy,* **169 (2018)**, 616–633, 2018.

6. M. Green, K. Emery, Y. Hishikawa *et al. Solar cell efficiency tables* ***(version 48)***, 2016.

7. B. L. Guo, Y. H. Chen, X. J. Liu *et al.* Optical and electrical properties study of sol-gel derived Cu_2ZnSnS_4 thin films for solar cells. *AIP Advances,* **4(9)**, 097115, 2014.

8. H. Katagiri, K. Saitoh, T. Washio *et al.* Development of thin film solar cell based on Cu_2ZnSnS_4 thin films. *Solar Energy Materials and Solar Cells,* **65(1)**, 141-148, 2001.

9. Q. Guo, H. W. Hillhouse, and R. Agrawal, Synthesis of Cu_2ZnSnS_4 nanocrystal ink and its use for solar cells. *J Am Chem Soc,* **131(33)**, 11672-3, 2009.

10. J. He, L. Sun, N. Ding *et al.,* Single-step preparation and characterization of $Cu_2ZnSn(S_xSe_{1-x})_4$ thin films deposited by pulsed laser deposition method. *Journal of Alloys and Compounds,* **529(Supplement C)**, 34-37, 2012.

11. C. Shi, G. Shi, Z. Chen *et al.,* Deposition of Cu_2ZnSnS_4 thin films by vacuum thermal evaporation from single quaternary compound source. *Materials Letters,* **73(Supplement C)**, 89-91, 2012.

12. T. Washio, T. Shinji, S. Tajima *et al.,* 6% Efficiency Cu_2ZnSnS_4-based thin film solar cells using oxide precursors by open atmosphere type CVD. *Journal of Materials Chemistry,* **22(9)**, 4021-4024, 2012.

13. M. Banavoth, S. Dias, and S. B. Krupanidhi, Near-infrared photoactive Cu_2ZnSnS_4 thin films by co-sputtering. *AIP Advances,* **3(8)**, 082132, 2013.

14. K. Tanaka, Y. Fukui, N. Moritake *et al.,* Chemical composition dependence of morphological and optical properties of Cu_2ZnSnS_4 thin films deposited by sol–gel sulfurization and Cu_2ZnSnS_4 thin film solar cell efficiency. *Solar Energy Materials and Solar Cells,* **95(3)**, 838-842, 2011.

15. Z. Yan, A. Wei, Y. Zhao *et al.,* Growth of Cu_2ZnSnS_4 thin films on transparent conducting glass substrates by the solvothermal method. *Materials Letters,* **111(Supplement C)**, 120-122, 2013.

16. T. K. Todorov, J. Tang, S. Bag *et al.* Beyond 11% Efficiency: Characteristics of State-of-the-Art $Cu_2ZnSn(S,Se)_4$ Solar Cells. *Advanced Energy Materials,* **3(1)**, 34-38, *2013*.

17. W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu, and D. B. Mitzi, Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency. *Advanced Energy Materials* **4(7)**, 201301465, 2013.

18. P. Jackson, D. Hariskos, R. Wuerz *et al.,* Cover Picture: Properties of Cu(In,Ga)Se_2 solar cells with new record efficiencies up to 21.7%. *Phys. Status Solidi* ***RRL 1/2015***.

19. G. Y. Kim, D.-H. Son, T. T. T. Nguyen *et al.,* Enhancement of photo-conversion efficiency in $Cu_2ZnSn(S,Se)_4$ thin-film solar cells by control of ZnS precursor-layer thickness. *Progress in Photovoltaics: Research and Applications.* **24(3)**, 292-306, 2016.

20. D. B. Mitzi, T. K. Todorov, K. Wang and S. Guha, The path towards a high-performance solution processed kesterite solar cell. *Solar Energy Materials and Solar Cell,* **95**, 1421–1436, 2011.

21. B. Shin, O. Gunawan, Y. Zhu *et al.,* Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant Cu_2ZnSnS_4 absorber. *Progress in Photovoltaics: Research and Applications,* **21(1)**, 72-76, 2013.

22. A. Walsh, S. Chen, S.-H. Wei *et al.,* Kesterite Thin-Film Solar Cells: Advances in Materials Modelling of Cu_2ZnSnS_4. *Advanced Energy Materials,* **2(4)**, 400-409, 2012.

23. A. Polizzotti, I. L. Repins, R. Noufi *et al.,* The state and future prospects of kesterite photovoltaics. *Energy & Environmental Science,* **6(11)**, 3171-3182, 2013.

24. S. Chen, A. Walsh, J.-H. Yang *et al.,* Compositional dependence of structural and electronic properties of Cu(2) ZnSn(S,Se)(4) alloys for thin film solar cells. *Physical Review B,* **83(12)**, 125201, 2011.

25. K. Hironori, J. Kazuo, Y. Satoru *et al.,* Enhanced Conversion Efficiencies of Cu_2ZnSnS_4 -Based Thin Film Solar Cells by Using Preferential Etching Technique. *Applied Physics Express,* **1(4)**, 041201, 2008.

26. W. C. Hsu, I. Repins, C. Beall *et al.* Growth mechanisms of co-evaporated kesterite: a comparison of Cu-rich and Zn-rich composition paths. *Progress in Photovoltaics: Research and Applications,* **22(1)**, 35-43, 2014.

27. A. Fairbrother, E. Garcia-Hemme, V. Izquierdo-Roca *et al.,* Development of a selective chemical etch to improve the conversion efficiency of Zn-rich Cu_2ZnSnS_4 solar cells. *J Am Chem Soc,* **134(19)**, 8018-21, 2012.

28. M. Rahman, N. Islam, R. Matin & M. Bashar. Fabrication and characterization of the CZTS thin film absorption layer using easy and low cost sol-gel dip-coating technique. DUJASE, **6(1),** 58-65, 2021.

29. M. Rahman, M. Bashar, & N. Islam. Optical and structural study of the CZTS (Cu2ZnSnS4) thin film for solar cell derived from the chloride-based sol-gel precursor solution. *Dhaka University Journal of Science*, ***70*(1),** 1–7, 2022.

30. C. Platzer-Björkman, J. Scragg, H. Flammersberger *et al,*. Influence of precursor sulfur content on film formation and compositional changes in Cu_2ZnSnS_4 films and solar cells. *Solar Energy Materials and Solar Cells,* **98(Supplement C)**, 110-117, 2012.

31. Z. Guan, W. Luo, and Z. Zou, Formation mechanism of ZnS impurities and their effect on photoelectrochemical properties on a Cu_2ZnSnS_4 photocathode. *CrystEngComm,* **14**, 2929-2936, 2014.

32. M. Jiang, Y. Li, R. Dhakal *et al.,* Cu_2ZnSnS_4polycrystalline thin films with large densely packed grains prepared by sol-gel method. *J. of Photonics for Energy,* **1(1)**, 1-6, 2011.

33. I. Kentaro, and N. Tatsuo, Electrical and Optical Properties of Stannite-Type Quaternary Semiconductor Thin Films. *Japanese Journal of Applied Physics,* **27(11R)**, 2094.

34. J. S. Seol, S.-Y. Lee, J.-C. Lee *et al.,* Electrical and optical properties of Cu_2ZnSnS_4 thin films prepared by rf magnetron sputtering process. *Solar Energy Materials and Solar Cells,* **75(1)**, 155-162, 2003.

35. T. K. Todorov, K. B. Reuter, and D. B. Mitzi, High-efficiency solar cell with Earth-abundant liquid-processed absorber. *Adv Materials,* **22(20)**, E156- E159, 2010.

36. K. Tanaka, M. Oonuki, N. Moritake *et al.,* Cu_2ZnSnS_4 thin film solar cells prepared by non-vacuum processing. *Solar Energy Materials and Solar Cells,* **93(5)**, 583- 587, 2009.

37. A. Fischereder, T. Rath, W. Haas *et al.,* Investigation of Cu_2ZnSnS_4 formation from metal salts and thioacetamide. *Chemistry of Materials,* **22(11)**, 3399- 3406, 2010.

38. S. M. Pawar, B. S. Pawar, A. V. Moholkar *et al.,* Single step electrosynthesis of Cu_2ZnSnS_4 (CZTS) thin films for solar cell application. *Electrochimica Acta,* **55(12)**, 4057-4061, 2010.

39. H. M. Pathan and C. D. Lokhande, Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method. *Bulletin of Materials Science,* **27 (2)**, 85-111, 2004.

40. J. A. Thornton, The microstructure of sputter-deposited coatings. *Journal of Vacuum Science & Technology.* **4(6)**, 3059-3065, 1986.

41. K. Tanaka, N. Moritake, and H. Uchiki, Preparation of Cu_2ZnSnS_4 thin films by sulfurizing sol-gel deposited precursors. *Solar Energy Materials and Solar Cells,* **91(13)**, 1199-1201, 2007.

42. B. S. Pawar, S. M. Pawar, S. W. Shin *et al.,* Effect of complexing agent on the properties of electrochemically deposited Cu_2ZnSnS_4 (CZTS) thin films. *Applied Surface Science,* **257(5)**, 1786-1791, 2010.

43. B.D. Cullity, S.R. Stock, Elements of X-ray Diffraction, Prentice-Hall, Pearson, 2001

44. Y. Zhao, H. Pan, Y. Lou *et al.,* Plasmonic $Cu_{(2-x)}S$ nanocrystals: optical and structural properties of copper-deficient copper(I) sulfides. *J Am Chem Soc,***131(12)**, 4253-61, *2009.*

45. G. M. Ford, Q. Guo, R. Agrawal *et al.,* Earth Abundant Element $Cu_2Zn(Sn_{1-x}Ge_x)S_4$ Nanocrystals for Tunable Band Gap Solar Cells: 6.8% Efficient Device Fabrication. *Chemistry of Materials,* **23(10)**, 2626-2629, *2011.*

46. R. Caballero, C. Maffiotte, and C. Guillén, Preparation and characterization of $CuIn_{1-x}GaxSe_2$ thin films obtained by sequential evaporations and different selenization processes. *Thin Solid Films,***474(1)**, 70-76, 2005.

47. S.C. Riha, S. J. Fredrick, J. B. Sambur *et al.,* Photoelectrochemical characterization of nanocrystalline thin-film Cu_2ZnSnS_4photocathodes. *ACS Appl Mater Interfaces,* **3(1)**, 58-66, 2011.

48. A. Wangperawong, J. S. King, S. M. Herron *et al.,* Aqueous bath process for deposition of Cu2ZnSnS4 photovoltaic absorbers. *Thin Solid Films,* **519(8)**, 2488-2492, 2011.

49. Q. Guo, G. M. Ford, W.-C. Yang *et al.,* Fabrication of 7.2% Efficient CZTSSe Solar Cells Using CZTS Nanocrystals. *Journal of the American Chemical Society,* **132(49)**, 17384-17386, 2010.

50. S. A. Nazligul, M. Wang and L. K. Choy, Recent Development in Earth-Abundant Kesterite Materials and Their Applications. *Sustainability,* **5138(12)**, 1-19, *2020.*

51. O. A. M. Abdelraouf and N. K. Allam, Plasmonic scattering nanostructures for efficient light trapping in flat CZTS solar cells. *Proc. of SPIE,* **10227 (12)**, 1-9, 2017.