



1st International Conference on Energy and Power, ICEP2016, 14-16 December 2016, RMIT University, Melbourne, Australia

Synthesis and characterization of chemical spray pyrolysed CZTS thin films for solar cell applications

Kiran Diwate^a, Kakasaheb Mohite^b, Manish Shinde^c, Sachin Rondiya^a, Amit Pawbake^a, Abhijit Date^d, Habib Pathan^e, Sandesh Jadkar^{e,*}

^aSchool of Energy Studies, Savitribai Phule Pune University, Pune 411 007, India

^bDepartment of Physics, C.T.Bora College, Shirur, Shirur, Pune, Pin 412210, India

^cCentre for Materials for Electronics Technology (C-MET), Pashan Road, Pune, 411008, India

^dSchool of Engineering, RMIT University, Melbourne 3000, Australia

^eDepartment of Physics, Savitribai Phule Pune University, Pune 411 007, India

Abstract

In present work, thin films of CZTS have been prepared by chemical spray pyrolysis (CSP) by spraying precursor solution directly onto the soda lime glass (SLG) substrates by varying sulphur molar concentration. Copper chloride [CuCl₂·2H₂O], zinc chloride [ZnCl₂·2H₂O], tin chloride [SnCl₄·5H₂O] and thiourea [(NH₂)₂CS] were used as precursor materials to deposit CZTS thin films by using home-built chemical spray pyrolysis system. Influence of sulphur variation on structural, optical, morphology and electrical properties of CZTS films have been investigated by using variety techniques such as low angle x-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FE-SEM), UV-Visible spectroscopy, four probe method, etc. The formation of CZTS has been confirmed by low angle XRD and Raman spectroscopy. The structural analysis reveals formation of kesterite tetragonal phase with preferential orientation along (112) direction. The band gap values of CZTS thin films have been calculated and found in the range 2 - 2.25 eV over the entire range of sulphur variation studied. The change in band gap may be due to quantum confinement effects at nanoscale. The morphological studies show formation of islands of nanoscale particulate clusters which constitute the films in most of the samples. The films exhibit higher resistivity values (in KΩ) which may be due to presence of the strain in the films.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of the 1st International Conference on Energy and Power.

* Corresponding author. Tel.: +91 02 25695201; fax: +91 02 25695201.
E-mail address: sandesh@physics.unipune.ac.in

Keywords: CZTS; Field emission scanning electron microscopy; Chemical spray pyrolysis; Thin films

1. Introduction

Thin films solar cells based on copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) absorbers have been proven to be an alternative to Si based solar cells technology owing to their lower processing cost. Among them, thin-film CIGS solar cells have demonstrated a record efficiency of more than 20 % owing to their gleaming photovoltaic properties and great efforts have been devoted to the research of CIGS thin film solar cells in recent years due to these achievements [1]. However, the wide range commercial applications, CIGS solar cells has received the set back by the shortage of In and Ga leading to their expensiveness. On the other hand, CdTe solar cells technology has also not lagged behind in terms of solar cells performance. They have exhibited efficiencies to the tune of 14 % to 17 % regularly [2-4]. However, CdTe based solar cell technology suffers from the use of potentially hazardous substance in both absorber layer (CdTe) and window material (CdS), thus posing the problems of safe disposal of non-function, outdated CdTe solar cells.

Recently, considerable work has been done on the quaternary compound semiconductor, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) to make it a good absorber layer for thin film solar cells [5, 6] and thermoelectric power generators [7]. CZTS has excellent physical properties, such as the direct band gap (~ 1.5 eV), high optical absorption coefficient ($> 10^4$ cm^{-1}), low thermal conductivity etc. It is derived from the CIGS structure by the isoelectronic substitution of two In (or one In and one Ga) atoms by one Zn and one Sn atom. As a consequence, CZTS has some similar properties as CIGS. The availability of Cu, Zn, Sn and S in the earth's crust are ~ 50 , 75, 2.2 and 260 ppm respectively and the availability of In is only ~ 0.049 ppm [8], so that all the constituents of CZTS are abundant in the earth's crust. Intrinsic point defects in CZTS make its conductivity p-type. Crystal structure of CZTS can allow some deviation from stoichiometry [9] making its deposition process easier. Moreover, grain boundaries in CZTS thin films are favorable to enhance the minority carrier collection [10]. Theoretical calculations have shown that conversion efficiency as high as 32.2 % [11] is possible for CZTS thin film solar cells with a CZTS layer of few micrometers. *Wadia et al.* [12] calculated the minimum cost of raw materials for the existing PV technologies and the emerging PV technologies and found that the cost of raw material for CZTS PV technology is much lower than that of the existing thin film PV technologies. Various methods have been applied for CZTS thin film fabrication which includes solution methods [13-15], sol-gel [16, 17], electroplating [18-20], co-evaporation [21], pulsed laser deposition [22, 23], evaporation [21, 24] etc. These techniques have several problems such as high energy consumption, not suitable for large-area fabrication, and require high temperature anneal and/or sulfurization processes. Chemical spray pyrolysis (CSP) is an important preparation method for CZTS thin films because of its simplicity, moderate temperature processing and ability to prepare highly crystalline, large area thin films. 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; however studies of influence of change in sulphur concentration on CZTS properties are few. With this motivation an attempt has been made to synthesize CZTS thin films by CSP method. In present paper we report influence of sulphur (S) concentration on structural, optical, morphology and electrical properties of CZTS thin films prepared by chemical spray pyrolysis method.

2. Experimental

In present work, copper chloride (CuCl_2), zinc chloride (ZnCl_2), tin chloride (SnCl_4) and thiourea [$(\text{NH}_2)_2\text{CS}$] were used as precursor materials to deposit CZTS films by using home-built chemical spray pyrolysis unit onto soda lime glass (SLG) and fluorine doped tin oxide (FTO) substrates. All the chemicals used were of analytical grade as obtained from Sigma Aldrich (99.99 % purity) and were used as received. The molar concentration of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were kept constant at 0.04 M, 0.02 M and 0.02 M respectively whereas the concentration of $(\text{NH}_2)_2\text{CS}$ was varied from 0.12 M to 0.18 M. The substrate temperature was kept constant at 325 $^\circ\text{C}$ using in-built thermocouple and temperature controller. The air flow rate and nozzle-to-substrate distance were kept fixed at 22 LPM and 26 cm, respectively. The deposition was carried out for desired period of time and samples were allowed to cool to room temperature and then taken out for the characterization.

Thickness of films was determined by profilometer (KLA Tencor, P-16+). X-ray diffraction patterns were obtained by X-ray diffractometer (Bruker D8 Advance, Germany) using $\text{CuK}\alpha$ line ($\lambda = 1.54056 \text{ \AA}$) at a grazing angle of 1° . The average crystallite size was estimated using the classical Scherrer's formula [25]. The surface morphology of the films was investigated using field emission scanning electron microscopy (FE-SEM) (Hitachi, S-4800, Japan). The optical band gap of CZTS films was deduced from transmittance and reflectance spectra of the films deposited on soda-lime glass and were measured using a JASCO, V-670 UV-Visible spectrophotometer in the range 250-1100 nm. Raman spectra were recorded with Raman spectroscopy (Jobin Yvon Horibra LABRAM-HR) in the range 200-1200 cm^{-1} . The excitation source was 632.8 nm line of He-Ne laser. Four probe measurements were done to find out electrical properties of the films using Jandel Model RM3 instrument. The type of conductivity and carrier's mobility of CZTS films were determined by Hall Effect measurement using Ecopia HMS 3000 unit at 0.54 Tesla.

3. Results and discussion

3.1. Variation in film thickness

The results corresponding to thickness measurements of CZTS films prepared at different S molar concentration is shown in Table 1. Table reveals that as S molar concentration increases from 0.12 M to 0.16 M, film thickness decreases from 505 nm to 392 nm. However, further increase in S molar concentration to 0.18 M thickness of CZTS film increases to 439 nm. These results suggests that the growth of CZTS films takes place via different complex nucleation and growth processes simultaneously occurring on substrate at various S concentrations.

3.2. X-ray diffraction analysis

To identify the crystallinity and presence of material phase in the films deposited by CSP at different S concentrations, low angle x-ray diffraction (XRD) studies were carried out. Fig. 1.(a) shows low angle XRD pattern of CZTS films deposited at different S molar concentrations. It is evident from figure that the XRD pattern show three peaks at $2\theta \sim 27.4^\circ$, 46.4° and 55.0° corresponding to (112), (220) and (312) crystal orientations of CZTS kesterite tetragonal phase [JCPDS data card # 26-0575], respectively indicating that these films are polycrystalline. The dominant peak is (112), indicating that the crystallites in the film have preferential orientation in (112) direction.

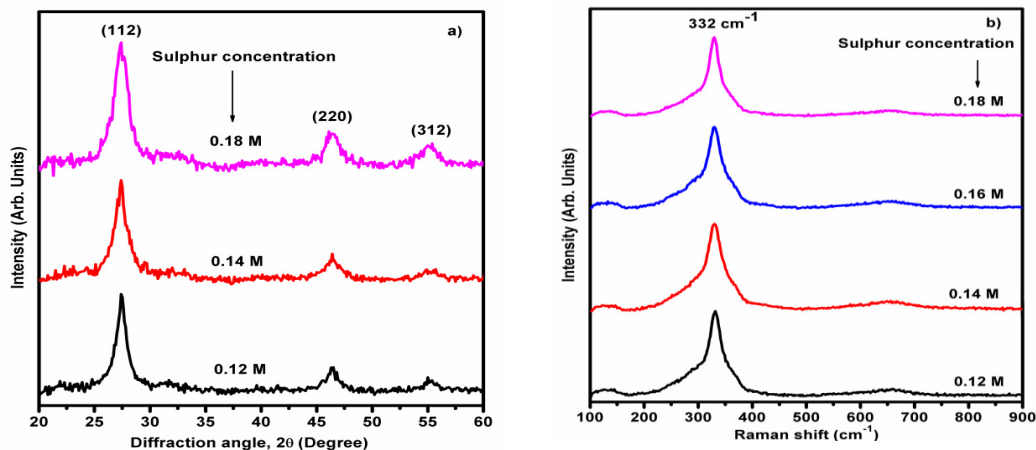


Fig. 1. (a) XRD patterns; (b) Raman spectra of $\text{Cu}_2\text{ZnSnS}_4$ thin films grown by chemical spray pyrolysis deposition.

The average crystallite size calculated from Scherrer's formula is listed in Table 1. The average crystallite size decreases with increase in S molar concentration.

Table 1. Variation of Grain size (XRD) and thickness of CZTS films deposited by CSP method

Sulphur Concentration	Grain-size (XRD), nm	Thickness (μm)
0.12 M	8.93	0.505
0.14 M	7.44	0.413
0.16 M	6.03	0.392
0.18 M	5.53	0.439

3.3. Raman spectroscopy analysis

Raman techniques have recently been used by a number of researchers to investigate the phase purity of CZTS. Fig. 1.(b) shows the Raman spectra of the CZTS thin films prepared by varying S molar concentration. A single Raman intense peak located at $\sim 332 \text{ cm}^{-1}$ is observed in all films and is close to the value reported for bulk CZTS [26, 27].

It is interesting to note that no additional peaks due to the phases such as SnS (characteristic modes at 160 cm^{-1} , 190 cm^{-1} , 220 cm^{-1}), SnS_2 (characteristic mode at 315 cm^{-1}), Cu_{2-x}S , Sn_2S_3 , ZnS (characteristic modes 475 cm^{-1} , 304 cm^{-1} and 356 cm^{-1}) and Cu_3SnS_4 (characteristic modes at 318 cm^{-1} , 348 cm^{-1} , and 295 cm^{-1}) corresponding to have been observed [28-31]. These results suggest the formation of the single phase CZTS by chemical spray pyrolysis method. Similar results have been reported by *Zhai et al.* [32] for CZTS film grown on flexible steel substrates by solvothermal method and *Tchognia et al.* [33] by sol-gel method.

3.4. UV-Visible Spectroscopy Analysis

Fig. 2.(a) shows the transmittance spectra of CZTS thin films grown at different sulphur concentrations. As seen very low transmission have been observed ($< 15\%$) in the visible region for all films. Transmittance of $\sim 50\%$ to 55% has been observed in the IR region for the CZTS films prepared at sulphur concentration 0.12 M and 0.14 M.

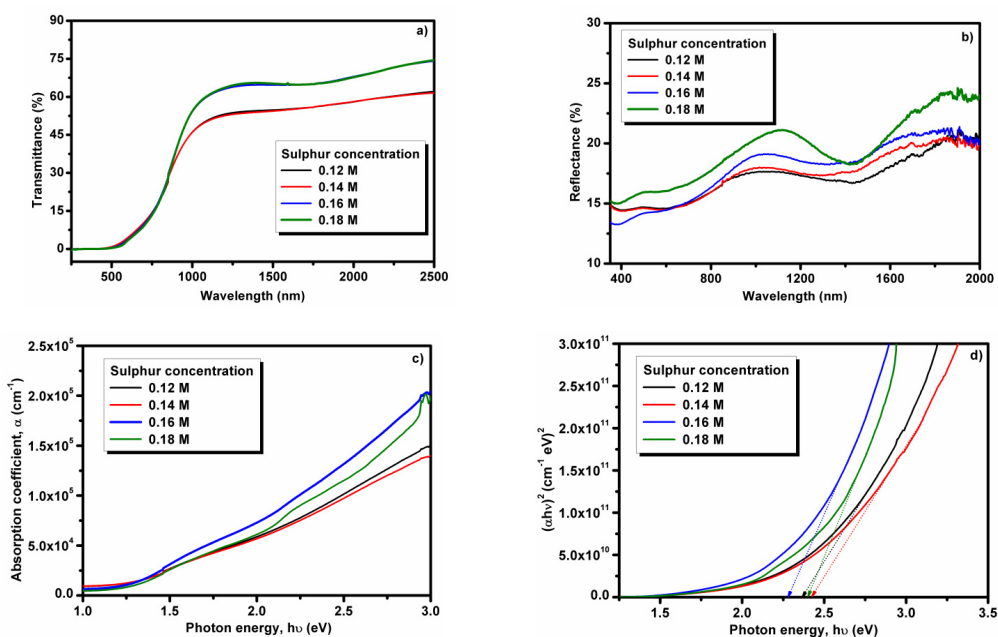


Fig. 2. (a) Transmittance; (b) Reflectance spectra; (c) Absorption coefficient; (d) Tauc plot of CZTS thin films at sulphur concentrations.

However, CZTS film prepared at higher molar concentration (0.18 M), the transmittance value reached up to 75%. The reflectance spectra of CZTS thin films grown at different sulphur concentrations display that the optical reflectance of these films varies over the range 16-18% in the visible range and 19-24% in the IR region, with highest reflectance observed for film grown at 0.18 M sulphur concentrations as shown in Fig. 2.(b) The ripples in reflectance

spectra in CZTS films can attribute to optical interference effects [34].

Fig. 2.(c) shows the plot of absorption coefficient (α) versus the photon energy for CZTS thin films deposited by varying sulphur concentration. It can be seen that all the films have relatively high absorption coefficients between 10^4 cm^{-1} and 10^5 cm^{-1} in the visible and the near-IR spectral range. It is also noted that the absorption coefficient increases for thin films deposited with increasing sulphur concentrations, especially at 0.16 M and 0.18 M.

Tauc plots of CZTS thin films which have been deposited by varying sulphur concentration have been shown in Fig. 2.(d) The band gap values increases with increase in sulphur concentration and was found in the range 2 eV to 2.25 eV. The increase in band gap may be due to increase in average crystallite size with increase in sulphur concentration as revealed from low angle XRD analysis (Table 1). The observed band gap values are higher than the reported experimental as well as theoretical value of CZTS thin films (1.45 eV to 1.6 eV) [35-38]. The higher band gap values may be due to the quantum confinement effects arising due to nanoscale nature of the particles constituting the films.

3.5. Field emission scanning electron microscopy (FE-SEM) analysis

Fig. 3. shows the Field emission scanning electron microscopy (FE-SEM) images of CZTS thin films prepared at different sulphur concentrations. The FESEM images show formation of nanoscale particulate clusters which constitute the films. In case of CZTS film prepared at 0.14 M sulphur concentration (Fig. 3.(a)) exhibited more surface roughness as compared to the films prepared at higher molar concentration. The sizes of the islands vary in the range of 30-150 nm. At sulphur concentration 0.16 M (Fig. 3.(b)), the smooth film of smaller nanoparticles was observed, however, bigger islands regions having bigger nanoparticles were also found out at few locations. The islandic regions have bigger particle size of 40-80 nm.

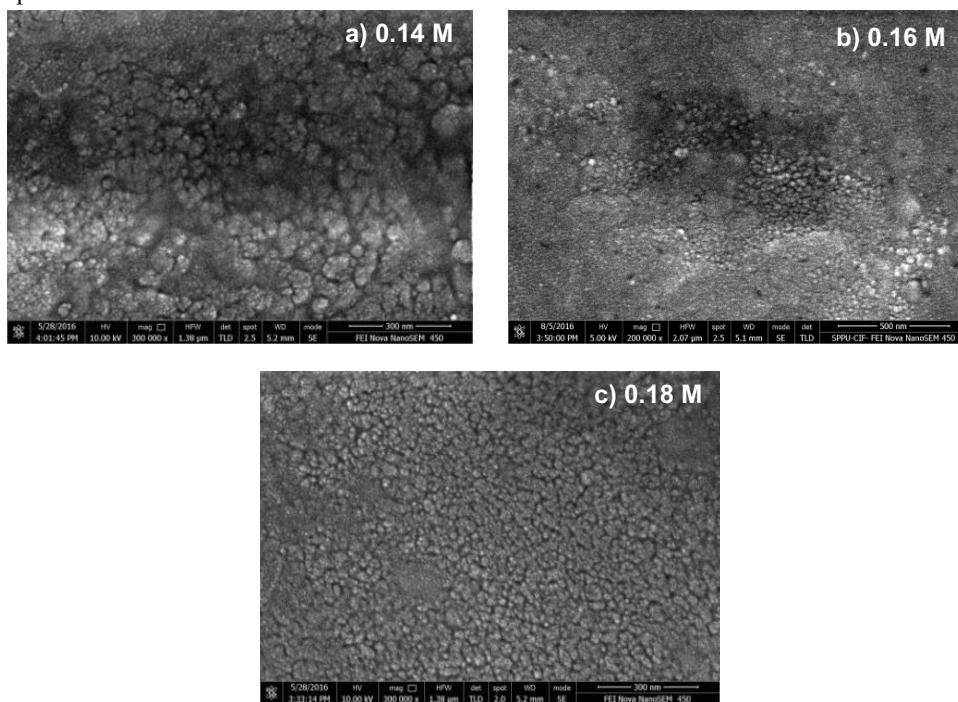


Fig. 3. FE-SEM images of CZTS films prepared at (a) 0.14 M; (b) 0.16 M; (c) 0.18 M sulphur concentration.

At higher sulphur concentration, the film becomes smoother with less surface roughness as displayed in Fig. 3.(c) The size of these islandic clusters is $\sim 30\text{-}40 \text{ nm}$. The particle size in all the cases is found to be less than 10 nm . Elemental composition and $\text{Cu}/(\text{Zn}+\text{Sn})$, S/Metal and Zn/Sn ratios of CZTS thin films prepared at different sulphur concentration are presented in Table 2. All the films are inherently sulphur and tin rich. With increase in thiourea

concentration in the spraying solution, it is seen that the sulphur concentration in the films has increased for 52 % to 54 %. However, tin, copper and zinc concentration in the films decreases with increase in thiourea concentration in the spraying solution.

Table 2. Elemental compositions of CZTS thin films prepared at different sulphur concentration.

Sulphur concentration	Atomic %				Composition ratio		
	Cu	Zn	Sn	S	Cu/(Zn + Sn)	Zn/Sn	S/Metal
Ideal	25.00	12.50	12.50	50.00	1.0000	1.00	1.0000
0.12 M	21.39	11.25	15.21	52.15	0.8084	0.7396	1.0899
0.14 M	21.01	10.41	15.19	53.39	0.8207	0.6853	1.1455
0.16 M	21.19	10.63	14.76	53.42	0.8346	0.7202	1.1468
0.18 M	21.05	10.50	14.41	54.04	0.8450	0.7287	1.1758

3.6. Electrical properties

The electrical properties of the CZTS thin films have been measured using four probe method and the results are summarized in Table 3 which exhibit higher resistivity which may be due to the strain present in the films

Table 3: Electrical properties of CZTS films deposited at different sulphur concentration

S-molar concentration (M)	0.12	0.14	0.16	0.18
Four Probe Method				
Sheet resistance (K Ω)	60.85	74.25	218.72	269.11
Resistivity (Ω.cm)	3.07×10^{-2}	3.07×10^{-2}	8.57×10^{-2}	1.18×10^{-1}
Hall Probe Method				
Mobility (cm ² /Vs)	1.61	6.29	8.90×10^{-1}	1.93
Sheet-conc. (/cm ²)	6.12×10^{13}	5.23×10^{13}	1.60×10^{14}	6.59×10^{14}
Resistivity (Ω.cm)	3.19	7.83	1.72×10^{-1}	2.16×10^{-1}

From Hall data acquisitions all as-prepared CZTS films displayed p-type behaviour, matching well with other reports [39]. The observed p-type conduction in CZTS may be due to free majority carriers (holes) from acceptor levels of metal vacancies Cu, Zn and Sn as shown in Table 3. The hole mobility for the films prepared at 0.12M, 0.14M, 0.16M and 0.18M molar concentration are found to be 1.61, 6.30, 8.90×10^{-1} and 1.93 cm²/Vs, respectively. These values are in accordance with the reported value of 2.21 cm²/Vs by [26] Rajeshmon et al. [39]. The Hall measurement data showed that the films have sheet concentration of 6.12×10^{13} , 5.27×10^{13} , 1.60×10^{14} and 6.59×10^{14} / cm² for films prepared at 0.12M, 0.14M, 0.16M and 0.18M molar concentrations respectively. The sheet resistance are 60.85, 74.25, 218.72 and 269.11 KΩ for the films prepared at 0.12M, 0.14M, 0.16M and 0.18M molar concentrations respectively. The change in the sheet resistance may be due to the change in sheet concentration as well as mobility of charge carriers.

4. Conclusion

Thin films of CZTS have been prepared by chemical spray pyrolysis varying sulphur concentration in the precursor solution. Influence of sulphur variation on structural, optical, morphology and electrical properties of CZTS films have been investigated by using variety techniques such as low angle x-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FE-SEM), UV-Visible spectroscopy, four probe method, etc. The

formation of CZTS has been confirmed by low angle XRD and Raman spectroscopy. The XRD analysis reveals formation of kesterite tetragonal phase with preferential orientation along (112) direction. The morphological studies show formation of islands of nanoscale particulate clusters which constitute the films in most of the films. The FE-SEM images shows that films deposited at higher sulphur concentrations are smoother than that of deposited at lower concentration. The band gap values of CZTS thin films were found higher and in the range 2.0-2.25 eV over the entire range of sulphur concentration studied. The films exhibit higher resistivity values (in $K\Omega$) which may be due to presence of the strain in the films. The Hall measurement results confirmed that all the films are p-type. The optical and electrical properties together imply that these films can be used for the fabrication of numerous opto-electrical devices like solar radiation absorbers, solar cells, photocatalysts etc.

Acknowledgements

Authors are thankful to Department of Science and Technology (DST) and Ministry of New and Renewable Energy (MNRE), Government of India, New Delhi for the financial support. One of the authors SRJ is thankful to University Grants Commission, New Delhi for special financial support under UPE program. Mr. Sachin Rondiya gratefully acknowledges the financial support from Dr. Babasaheb Ambedkar Research and Training Institute (BARTI), Pune, for the award of Junior Research Fellowship.

References

- [1] Jackson P, Hariskos D, Lotter E, Paetel S, Wuerz R, Menner R, Wischmann W, Powalla M. New world record efficiency for Cu (In, Ga) Se₂ thin film solar cells beyond 20 %. *Prog Photovoltaics* 2011;19:894-897.
- [2] Razykov TM, Ferekides CS, Morel D, Stefanakos E, Ullal HS, Upadhyaya HM. Solar photovoltaic electricity: Current status and future prospects. *Sol Energy* 2011;85:1580-1608.
- [3] Rios-Flores A, Arés O, Camacho JM, Rejon V, Peña JL. Procedure to obtain higher than 14 % efficient thin film CdS/CdTe solar cells activated with HCF₂Cl gas. *Sol Energy* 2012;86:780-785.
- [4] Bosio A, Romeo N, Mazzamuto S, Canevari V. Polycrystalline CdTe thin films for photovoltaic applications. *Progr Cryst Growth Characterization of Mater* 2006;52:247-279.
- [5] Wahab LA, El-Den MB, Farrag AA, Fayek SA, Marzouk KH. Electrical and optical properties of chalcopyrite compounds. *J Phys Chem Solids* 2009;70:604-608.
- [6] Zhang J, Shao L, Fu Y, Xie E. Cu₂ZnSnS₄ thin films prepared by sulfurization of ion beam sputtered precursor and their electrical and optical properties. *Rare metals* 2006;25:315-319.
- [7] Liu M, Huang F, Chen L, Chen I. A wide-band-gap p-type thermoelectric material based on quaternary chalcogenides of Cu₂ZnSnQ₄, Q=S,Se. *Appl Phys Lett* 2009;94:202103 - 3.
- [8] Hossain MI. Prospects of CZTS solar cells from the perspective of material properties, fabrication methods and current research challenges. *Chalcogen Lett* 2012;9:231-242.
- [9] Choubrac L, Lafond A, Guillot-Deudon C, Moëlo Y, Jobic S. Structure flexibility of the Cu₂ZnSnS₄ absorber in low-cost photovoltaic cells: from the stoichiometric to the copper-poor compounds. *Inorg Chem* 2012;51:3346-3348.
- [10] Li JB, Chawla V, Clemens BM. Investigating the role of grain boundaries in CZTS and CZTSSe thin film solar cells with scanning probe microscopy. *Adv Mater* 2012;24:720-723.
- [11] Shockley W, Queisser HJ. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *Jpn J Appl Phys* 1961;32:510-519.
- [12] Wadia C, Alivisatos AP, Kammen D. Materials availability expands the opportunity for large-scale photovoltaics deployment. *Environ Sci Technol* 2009;43:2072-2077.
- [13] Zaberca O, Gillorin A, Durand B, Chane-Ching JY. A general route to the synthesis of surfactant-free, solventdispersible ternary and quaternary chalcogenide nanocrystals. *J Mater Chem* 2011;21:6483-6486.
- [14] Shinde NM, Lokhande CD, Kim JH, Moon JH. Lowcost and large area novel chemical synthesis of Cu₂ZnSnS₄ (CZTS) thin films. *J Photochem Photobio A* 2012;235:14-20.
- [15] Rath T, Haas W, Pein A. Synthesis and characterization of copper zinc tin chalcogenide nanoparticles: influence of reactants on the chemical composition. *Sol Energy Mater Sol Cells* 2012;101:87-94.
- [16] Tanaka K, Moritake N, Uchiki H. Preparation of Cu₂ZnSnS₄ thin films by sulfurizing sol-gel deposited precursors. *Sol Energy Mater Sol Cells* 2007;91:1199-1201.
- [17] Yeh MY, Lee CC, Wu DS. Influences of synthesizing temperatures on the properties of Cu₂ZnSnS₄ prepared by sol-gel spin-coated deposition. *J Sol-Gel Sci Technol* 2009;52:65-68.
- [18] Chan CP, Lam H, Surya C. Preparation of Cu₂ZnSnS₄ films by electrodeposition using ionic liquids. *Sol Energy Mater Sol Cells* 2010;94:207-211.
- [19] Jeon M, Tanaka Y, Shimizu T, Shingubara S. Formation and characterization of single-step electrodeposited Cu₂ZnSnS₄ thin films: effect of complexing agent volume. *Energy Procedia* 2011;10:255-260.

- [20] Pawar SM, Pawar BS, Moholkar AV. Single step electrosynthesis of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films for solar cell application. *Electrochim Acta* 2010;55:4057–4061.
- [21] Tanaka T, Kawasaki D, Nishio M, Guo Q, Ogawa H. Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ thin films by co-evaporation. *Phys Status Solidi C* 2006;3:2844–2847.
- [22] Pawar SM, Moholkar AV, Kim IK. Effect of laser incident energy on the structural, morphological and optical properties of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films. *Current Appl Phys* 2010;10:565–569.
- [23] Sun L, He J, Kong H, Yue FY, Yang PX, Chu JH. Structure, composition and optical properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films deposited by Pulsed Laser Deposition method. *Sol Energy Mater Sol Cells* 2011;95:2907–2913.
- [24] Repins I, Beall C, Vora N. Co-evaporated $\text{Cu}_2\text{ZnSnSe}_4$ films and devices. *Sol Energy Mater Sol Cells* 2012;101:154–159.
- [25] Cullity B, Stock S. *Elements of X-ray Diffraction*, 3rd Ed. Princeton Hall; 2001.
- [26] Zhou M, Gong Y, Xu J, Fang G, Xu Q, Dong J. Colloidal CZTS nanoparticles and films: preparation and characterization. *J. Alloy. Compd.* 2013;574:272–277.
- [27] Xia Y, Cheng Z, Zhang Z, Fang X, Liang G. A nontoxic and low-cost hydrothermal route for synthesis of hierarchical $\text{Cu}_2\text{ZnSnS}_4$ particles. *Nanoscale Res Lett* 2014;9:208–214.
- [28] Zhou YL, Zhou WH, Lei M, Du YF and Wu SX. Hierarchical $\text{Cu}_2\text{ZnSnS}_4$ Particles for a Low-Cost Solar Cell: Morphology Control and Growth Mechanism. *J Phys Chem C* 2011;115:19632–19639.
- [29] Parkin IP, Price LS, Hibbert TG, Molloy KC. The first single source deposition of tin sulphide coatings on glass: aerosol-assisted chemical vapour deposition using $[\text{Sn}(\text{SCH}_2\text{CH}_2\text{S})_2]$. *J Mater Chem* 2001;11:1486–1490.
- [30] Munce CG, Parker GK, Holt SA, Hope GA. A Raman spectroelectrochemical investigation of chemical bath deposited Cu_xS thin films and their modification. *Colloids Surf A* 2007;295:152–158.
- [31] Serrano J, Cantarero A, Cardona M, Garro N, Lauck R, Tallman RE, Ritter, Weinstein BA. Raman scattering in β -ZnS. *Phys Rev B* 2004;69:014301–11.
- [32] Zhai X, Jia H, Zhang Y, Lei Y, Wei J, Gao Y, Chu J, He W, Yin J, Zheng Z. In situ fabrication of $\text{Cu}_2\text{ZnSnS}_4$ nanoflake thin films on both rigid and flexible substrates. *Cryst Eng Comm* 2014;16:6244–6249.
- [33] Herve J, Tchognia N, Arba Y, Hartiti B, Ridah A, Ndjaka J, Thevenin P. Effect of sulfurization time on properties of $\text{Cu}_2\text{ZnSnS}_4$ thin films obtained by sol–gel deposited precursors. *Opt Quant Electron* (2016);48:134–7.
- [34] Rabeh MB, Touatti R, Kanzari M. Substrate Temperature Effects on Structural Optical and Electrical Properties of Vacuum Evaporated $\text{Cu}_2\text{ZnSnS}_4$ Thin Films. *Int J Engg Pract Res (IJEPR)* 2013;2:71–76.
- [35] Ito K, Nakazawa T. Electrical and Optical Properties of Stannite-Type Quaternary Semiconductor Thin Films. *Jpn J Appl Phys* 1988;27:2094–2097.
- [36] Katagiri H, Sasaguchi N, Hando S, Hoshino S, Ohashi J, Yokota T. Preparation films by and evaluation of $\text{Cu}_2\text{ZnSnS}_4$ thin sulfurization of E-B evaporated precursors. *Sol Energy Mater Sol Cells* 1997;49:407–414.
- [37] Paier J, Asahi R, Nagoya A, Kresse G. $\text{Cu}_2\text{ZnSnS}_4$ as a potential photovoltaic material: A hybrid Hartree-Fock density functional theory study. *Phys Rev B* 2009;79:115126–8.
- [38] Chen S, Gong XG, Walsh A, Wei SH. Crystal and electronic band structure of $\text{Cu}_2\text{ZnSnX}_4$ X=S and Se... photovoltaic absorbers: First-principles insights. *Appl Phys Lett* 2009;94:041903–3.
- [39] Rajeshmon VG, Kartha CS, Vijayakumar KP, Sanjeeviraja C, Abe T, Kashiwaba Y. Role of precursor solution in controlling the opto-electronic properties of spray pyrolysed $\text{Cu}_2\text{ZnSnS}_4$ thin films. *Sol Energy* 2011;85:249–255.