Opt Quant Electron (2016) 48:134
DOI 10.1007/s11082-016-0424-2

Effect of sulfurization time on properties of Cu_2ZnSnS_4 thin films obtained by sol–gel deposited precursors

Joël Hervé Nkuissi Tchognia[1,2] · Youssef Arba[1] · Bouchaib Hartiti[1] · Abderraouf Ridah[1] · Jean-Marie Ndjaka[2] · Philippe Thevenin[3]

Received: 22 September 2015 / Accepted: 19 January 2016

Abstract As a promising and alternative solar absorber material, the Cu_2ZnSnS_4 (CZTS) has gained a broad interest over recent years due to its excellent material properties such as suitable and tunable band gap energy of 1.4–1.6 eV and absorption coefficient over 10^4 cm^{-1} (Jimbo et al. in Thin Solid Films 515(15):5997–5999, 2007; Katagiri et al. in Sol Energy Mater Sol Cells 65(1–4):141–148, 2001). In addition, all components of the CZTS are naturally abundant and non toxic. Nowadays solution based-approaches are being developed for the deposition of CZTS to overcome the problem of expensive and complicated vacuum-based methods. In this work, we report the study of properties of the novel wurtzite CZTS material prepared by sol–gel sulfurization as a function of annealing time. The effect of annealing time on structural and optical properties of the films was investigated. The X-ray diffraction analysis confirmed the formation of the wurtzite CZTS phase. The crystallinity of the films increases with an increasing sulfurization time. The values of the optical absorption coefficients for the film were found to be 10^4 cm^{-1}. The optical band-gap values were estimated to be between 1.58 and 1.79 eV depending on the sulfurization time.

Keywords Cu_2ZnSnS_4 · Solar cell · Spin coating · Annealing time · Precursor sulfurization

This article is part of the Topical Collection on Advanced Materials for photonics and electronics.

Guest Edited by Bouchta Sahraoui, Yahia Boughaleb, Kariem Arof, Anna Zawadzka.

✉ Joël Hervé Nkuissi Tchognia
hervetchognia@gmail.com

[1] Department of Physics, Faculty of Science and Technique, Hassan II University of Casablanca , Bd Yasmina, P.O. Box 146, 20650 Mohammedia, Morocco

[2] Department of Physics, Faculty of Science, University of Yaoundé I, P.O. Box 812, Yaoundé, Cameroon

[3] LMOPS Laboratory, SUPELEC, University of Lorraine, 2 rue E. Belin, 57070 Metz, France

Published online: 22 January 2016

1 Introduction

Research on thin film photovoltaic (PV) technologies such as CdTe and Cu (In, Ga) (S, $Se)_2$ (CIGS) have recently made tremendous progress academically (Jackson et al. 2011) and industrially (SOLAR FRONTIER 2011). However, the scarcity and the toxicity of raw materials will become obstacles for CdTe and CIGS to significantly snatch PV market share from dominant silicon wafer-based PV technologies. To overcome this issue, it is necessary to develop new light absorber materials that are both nontoxic and easily available. Cu_2ZnSnS_4 (CZTS) with an optimal direct band-gap of about 1.5 eV and a large absorption coefficient over 10^4 cm^{-1} (Swami et al. 2013; Katagiri et al. 2001), is one of the most promising candidates as the absorber layers in thin film solar cells. It is composed of earth abundant elements which are copper, zinc, tin and sulfur (Wadia et al. 2009; Mitzi et al. 2011). All of them are nontoxic and this allows classifying the CZTS as future replacement for CIGS in the CIGS thin film solar cells. Until now, CZTS thin film solar cells have achieved the power conversion efficiency of 12.6 % using the Cu_2ZnSn (S, $Se)_4$ kesterite absorber (Wang et al. 2014). There are a lot of reports on CZTS which utilize vacuum based techniques such as thermal evaporation, sputtering, pulse laser deposition etc. (Katagiri et al. 1997; Seol et al. 2003; Tanaka et al. 2005; Zhang et al. 2006; Moriya et al. 2007; Schubert et al. 2011). Vacuum based deposition techniques present few drawbacks like sophisticated devices and high energy consumption which raise the cost, low throughput and difficulties of deposition on large areas. Unfortunately, these drawbacks will not allow in achieving the main goal of low cost and sustainable energy conversion of thin film solar cells. Thus, it is important and necessary to develop and to use non vacuum based deposition techniques. Solution based methods offer the advantage over vacuum based techniques in terms of input capita, throughput, material utilization and large area deposition (Todorov and Mitzi 2010). Among these solution based techniques, sol–gel especially associated to spin coating has gained high attention because of simple deposition procedure and low-cost preparation to obtain high quality thin films. The sol–gel method involves many process parameters such as molar concentration of precursor, rotation speeds, annealing time, annealing temperature, stirring time and drying time, which directly or indirectly influence the quality of thin films. Hence, it is important to better understanding the relation amongst the process parameters in order to optimize the quality of thin films.

In order to use the low cost non vacuum routes to prepare CZTS thin films, in this present work, CZTS thin films were synthesized via sol gel method and deposited on ordinary glass substrates by spin coating technique. The effect of sulfurizing time on films properties has been investigated. The obtained CZTS thin films were characterized by various measurements.

2 Materials and methods

The CZTS was obtained from a sol–gel precursor which consists of copper(II) acetate monohydrate, zinc(II) acetate dihydrate and tin(II) chloride dihydrate dissolved in 2-methoxyethanol and monoethanolamine used as the solvent and the stabilizer respectively. The solution was spin coated on ordinary glass substrates and dried at 230 °C in air. The coated glasses were sulfurized by annealing at 340 °C in elemental sulfur powder at different times. The annealing time was varied from 30 min to 1 h 15 min by step of

15 min, while the annealing temperature was kept constant at 340 °C. The synthesis process of CZTS film using spin coating technique is shown on the following flowchart (Fig. 1).

The structural composition of films is determined from X-ray diffraction (XRD) patterns taken with a diffractometer (XPERT-PRO) using Ni-filtered CuKα electrode and step size of 0.067°. Optical spectra are recorded using a VIS spectrophotometer (SPECTRO VIO C5210).

3 Results and discussions

3.1 Structure analysis

X-rays diffractions (XRD) of the as-prepared films were carried out to know the crystal phase of this material. Figure 2 shows the XRD patterns of the CZTS thin films obtained at different sulfurization time. It can be seen that all films have a polycrystalline structure with peaks identified at 2θ ∼26.3°, 28.5°, 30.2°, 33.8°, 47.4° and 51.8° positions corresponding respectively to the (100), (002), (101), (102), (110) and (103) crystallographic directions of the hexagonal structure and matching well with those of the previously reported CZTS wurtzite structure (Lu et al. 2011).

Although there was no standard card for wurtzite CZTS in JCPDS databases, the crystal orientation of XRD pattern for the wurtzite CZTS can be derived from the wurtzite ZnS by replacing Zn(II) with Cu(I), Zn(II) and Sn(IV) (Lu et al. 2011). The XRD pattern of wurtzite CZTS matches in particular the combined directions of hexagonal ZnS (JCPD data n°.98-001-7525) and monoclinic Cu_2SnS_3 (JCPD data n°.98-005-8919). The broadening of the Bragg peaks is due to the small size of the nanoparticles. The films have

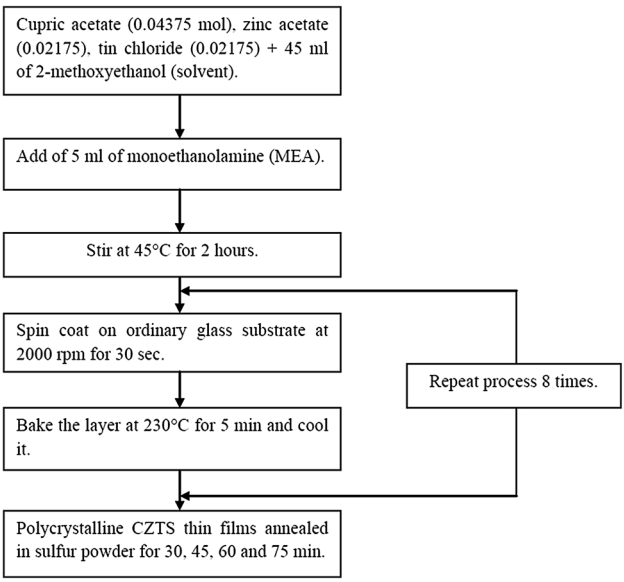

Fig. 1 Flowchart of the experimental process

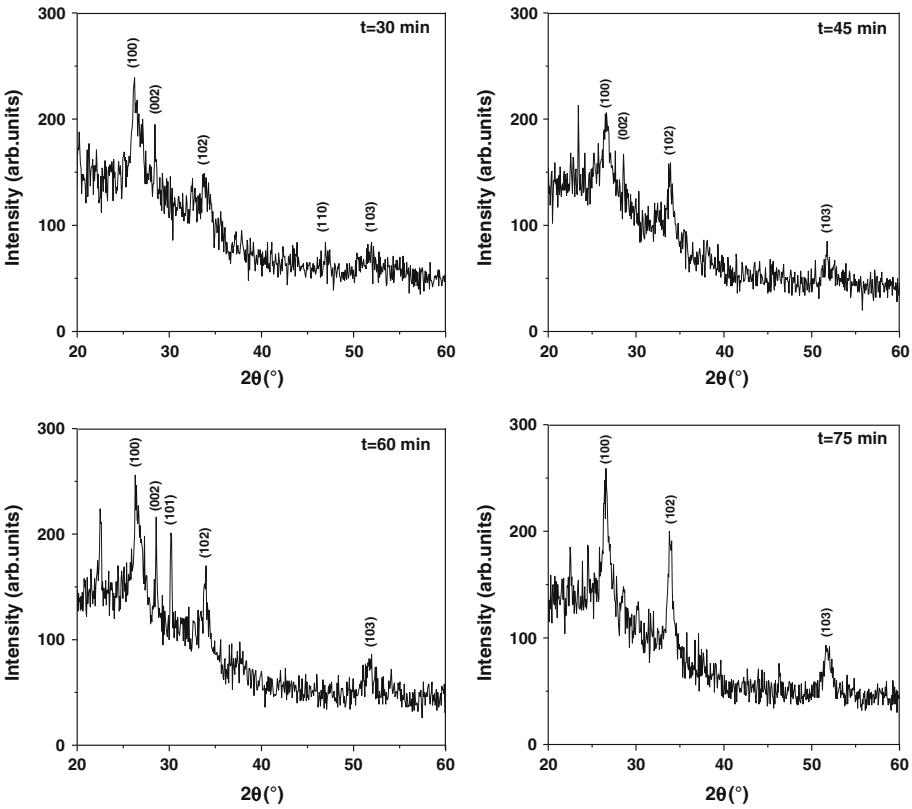

Fig. 2 XRD patterns of CZTS with different sulfurization time

random growth orientations; these random growth orientations are understandable because of the amorphous nature of glass substrates. We notice in these spectra that the intensity of peaks increases with the sulfurization time. This evolution can be interpreted by the fact that increase the annealing time allows the sulfur to well react with other components. A sufficiently long annealing time can lead to a good formation and a good growth of the final compound. With a suitable annealing temperature, the crystallization of films can be improved by increasing the annealing time to a reasonable value. It was not easy to determine the crystal phases of CZTS, ZnS and Cu_2SnS_3 only by XRD measurements; so the analysis of Raman spectra of films had been carried out to have more insight into the phase identification. Figure 3 shows the Raman spectra of as prepared films annealed in sulfur powder at 30, 45, 60 and 75 min. A single Raman intense peak located at 328.9 cm^{-1} is observed in all films and is close to the value reported for bulk CZTS (Zhou et al. 2013; Xia et al. 2014). It is noticeable that there are no additional peaks for other phases such as ZnS (351 cm^{-1}) and Cu_2SnS_3 (298 cm^{-1}) which confirms the single phase of wurtzite CZTS.

We can notice also that the intensity of Raman peak increases when the annealing time increases confirming thus the XRD results.

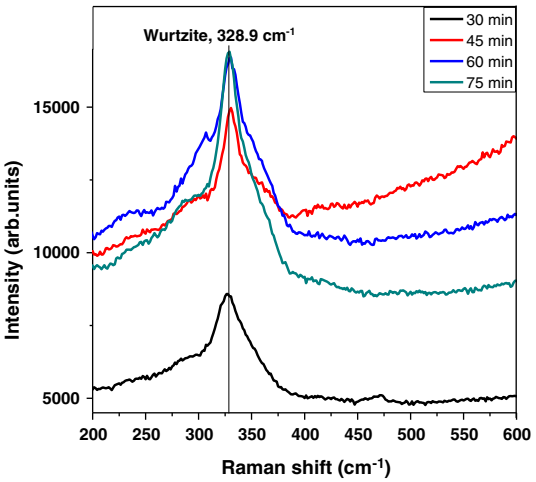

Fig. 3 Raman spectra of the resulting films obtained after 30, 45, 60 and 75 min

3.2 Optical properties

Since CZTS is a direct band gap semiconductor, the variation of absorption coefficient α with photon energy hυ for allowed transitions between parabolic bands obeys to the following Tauc's relation (Ohta et al. 1997):

$$(\alpha h\upsilon)^2 = A\left(h\upsilon - E_g\right) \quad (1)$$

where $h\upsilon$ is the energy of photon, α the absorption coefficient, A is a constant and E_g the band gap. Figure 4 shows the variation of $(\alpha h\upsilon)^2$ as a function of photon energy $(h\upsilon)$ for films annealed with different sulfurization times. According to the direct allowed inter band transition theory, the optical band gap of CZTS films can be determine by extrapolating the linear part of the curve to the zero absorption coefficient as shown on Fig. 4.

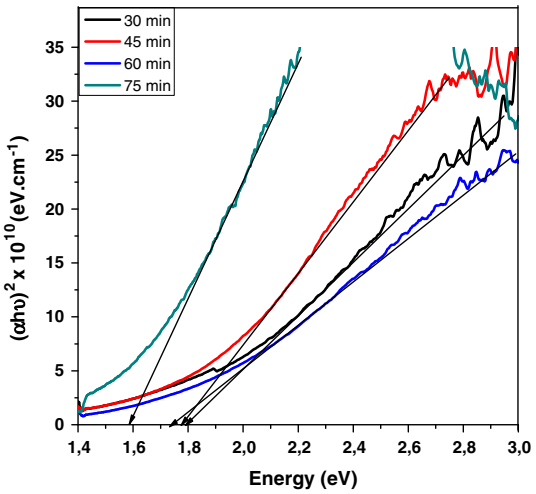

Fig. 4 Variation of $(\alpha h\upsilon)^2$ with the incident photon energy for samples prepared at different annealing times

The band gap of CZTS thin films is found to be 1.79, 1.77, 1.73 and 1.58 eV for sulfurization times of 30, 45, 60 and 75 min respectively. These values are larger than the reported value of 1.5 eV which may be owing to the quantum confinement effect of the CZTS nanoparticles at sulfurization times relatively small. It is well known that the optical band gap of nanoparticles can be tuned by controlling the size of the nanoparticles due to the quantum size effect. The estimated exciton Bohr radius for CZTS nanocrystals is find to be between 2.5 and 3.3 nm (Efros and Efros 1982). Thus the large band gap should be due to the quantum confinement of those particles with sizes smaller than 2.5 nm. It is seen that the band gap of films decreases as the sulfurization time increases. Increase the annealing time gives more possibility to the material to grow completely and to the particles to increase in size. Due to this, the band gap of nanoparticles reduces with increasing radius, and the optical absorption and emission associated with electronic transitions across the band gap shift towards lower energy. The increase in crystallite size can allow the film to be less transparent due to the increase in film thickness and this might be also a reason of the decrease in the band gap. The sample obtained after 75 min of sulfurization exhibits the best band gap of 1.58 eV comparable with those reported by others (Arba et al. 2013; Park et al. 2012) and close to the band gap of bulk CZTS based thin film solar cells.

4 Conclusion

In this study, the influence of the sulfurization time on the structural and optical properties of CZTS thin films obtained by a simple and low cost sol gel method was investigated. The XRD studies revealed a pure wurtzite structure of CZTS and that the crystallinity of films increases as the annealing time increases. The Raman analysis showed a single peak at the 328.9 cm^{-1} position without additional peak of other phases confirming the pure wurtzite phase revealed by the XRD measurements. The optical band gap is found to be decreased as annealing time increases and the best band gap energy was found for the sample annealed during 75 min.

Acknowledgments Joël Hervé Nkuissi Tchognia is grateful to the ICTP (*The Abdus Salam International Centre for Theoretical Physics*) and ANSOLE (*African Network for Solar Energy*) for financial support within the framework of the Intra-African Exchange (INEX) program.

References

Arba, Y., Rafi, M., Tchognia, H., Hartiti, B., Ridah, A., Thevenin, P.: Effect of substrate temperature on physical properties of CZTS thin films. J. Optoelectron. Adv. Mater. **15**, 1200–1203 (2013)

Efros, A.L., Efros, A.L.: Pioneering effort I. Sov. Phys. Semicond. **16**, 772–775 (1982)

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. Photovolt. **19**, 894–897 (2011)

Jimbo, K., Kimura, R., Kamimura, T., Yamada, S., Maw, W.S., Araki, H., Oishi, K., Katagiri, H.: Cu_2-$ZnSnS_4$-type thin film solar cells using abundant materials. Thin Solid Films **515**(15), 5997–5999 (2007)

Katagiri, H., Sasaguchi, N., Hando, S., Hoshino, S., Ohashi, J., Yokota, T.: Preparation and evaluation of Cu_2ZnSnS_4 thin films by sulfurization of E-B evaporated precursors. Sol. Energy Mater. Sol. Cells **49**(1–4), 407–414 (1997)

Katagiri, H., Saitoh, K., Washio, T., Shinohara, H., Kurumadani, T., Miyajima, S.: Development of thin film solar cell based on Cu_2ZnSnS_4 thin films. Sol. Energy Mater. Sol. Cells **65**(1–4), 141–148 (2001)

Lu, X.T., Zhuang, Z.B., Peng, Q., Li, Y.D.: Wurtzite Cu_2ZnSnS_4 nanocrystals: a novel quaternary semiconductor. Chem. Commun. **47**, 3141–3143 (2011)

Mitzi, D.B., Gunawan, O., Todorov, T.K., Wang, K., Guha, S.: The path towards a high-performance solution-processed kesterite solar cell. Sol. Energy Mater. Sol. Cells **95**(6), 1421–1436 (2011)

Moriya, K., Tanaka, K., Uchiki, H.: Fabrication of Cu_2ZnSnS_4 thin-film solar cell prepared by pulsed laser deposition. Jpn. J. Appl. Phys. **46**(9A), 5780–5781 (2007)

Ohta, Y., Haga, Y., Abe, Y.: Crystallographic features of ZnO single crystals. Jpn. J. Appl. Phys. **36**, L1040–L1042 (1997)

Park, H., Hwang, Y.H., Bae, B.-S.: Sol–gel processed Cu_2ZnSnS_4 thin films for a photovoltaic absorber layer without sulfurization. J. Sol-Gel. Sci. Technol. **65**, 23–27 (2012). doi:10.1007/s10971-012-2703-0

Schubert, B., Marsen, B., Cinque, S., Unold, T., Klenk, R., Schorr, S., Schock, H.: Cu_2ZnSnS_4 thin film solar cells by fast coevaporation. Prog. Photovolt. Res. Appl. **19**(1), 93–96 (2011)

Seol, J., Lee, S., Lee, J., Nam, H., Kim, K.: Electrical and optical properties of Cu_2ZnSnS_4 thin films prepared by rf magnetron sputtering process. Sol. Energy Mater. Sol. Cells **75**(1–2), 155–162 (2003)

SOLAR FRONTIER: Solar Frontier Officially Opens World's Largest. (2011)

Swami, S.K., Kumar, A., Dutta, V.: Deposition of kesterite Cu_2ZnSnS_4 (CZTS) thin films by spin coating technique for solar cell application. Energy Procedia **33**, 198–202 (2013)

Tanaka, T., Nagatomo, T., Kawasaki, D., Nishio, M., Guo, Q., Wakahara, A., Yoshida, A., Ogawa, H.: Preparation of Cu_2ZnSnS_4 thin films by hybrid sputtering. J. Phys. Chem. Solids **66**(11), 1978–1981 (2005)

Todorov, T.K., Mitzi, D.B.: Direct liquid coating of chalcopyrite light-absorbing layers for photovoltaic devices. Eur. J. Inorg. Chem. **2010**(1), 17–28 (2010)

Wadia, C., Alivisatos, A.P., Kammen, D.M.: Materials availability expands the opportunity for large-scale photovoltaics deployment. Environ. Sci. Technol. **43**(6), 2072–2077 (2009)

Wang, W., Winkler, M.T., Gunawan, O., Gokmen, T., Todorov, T.K., Zhu, Y., Mitzi, D.B.: Device characteristics of CZTSSe thin-film solar cells with 12.6 % efficiency. Adv. Energy Mater. (2014). doi:10.1002/aenm.201301465

Xia, Y., Cheng, Z., Zhang, Z., Fang, X., Liang, G.: A nontoxic and low-cost hydrothermal route for synthesis of hierarchical Cu_2ZnSnS_4 particles. Nanoscale Res. Lett. **9**(1), 208 (2014)

Zhang, J., Shao, L., Fu, Y., Xie, E.: Cu_2ZnSnS_4 thin films prepared by sulfurization of ion beam sputtered precursor and their electrical and optical properties. Rare Met. **25**(6), 315–319 (2006)

Zhou, M., Gong, Y., Xu, J., Fang, G., Xu, Q., Dong, J.: Colloidal CZTS nanoparticles and films: preparation and characterization. J. Alloy. Compd. **574**, 272–277 (2013)