Opt Quant Electron (2016) 48:255
DOI 10.1007/s11082-016-0535-9

Solution-based deposition of wurtzite copper zinc tin sulfide nanocrystals as a novel absorber in thin film solar cells

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

Received: 10 September 2015 / Accepted: 21 March 2016

Abstract Cu_2ZnSnS_4 (CZTS) is considered to be one of the most promising absorber materials capable of driving the development of low cost and high performance photovoltaic. Its direct and tunable band gap of 1.4–1.6 eV, high absorption coefficient over 10^4 cm^{-1}, earth abundant and non-toxic constituents give it a number of advantages and rise it above other thin film absorber materials like polycrystalline cadmium telluride, copper indium diselenide and its combinations with gallium and/or sulfur ($Cu(In,Ga)(S,Se)_2$). In this present study, wurtzite CZTS nanocrystals have been prepared by a sol–gel route associated to spin coating. The CZTS samples have been characterized structurally by X-ray diffraction (XRD) and Raman spectroscopy, morphologically by scanning electron microscope (SEM) and optically by a vis spectrophotometer. XRD result and Raman analysis revealed a wurtzite structure. SEM studies showed a condensed surface composed of agglomerated nanocrystals and optical absorption showed a band gap of 1.55 eV suitable for photovoltaic applications.

Keywords Cu_2ZnSnS_4 · Wurtzite · Sol–gel method · Spin coating · Photovoltaic absorber

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] MAC and PM Laboratory, Faculty of Science and Technique, Hassan II University of Casablanca , P.O. Box 146, Bd Yasmina, 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: 26 March 2016

1 Introduction

Thin films chalcogen materials such as $CuInS_2$ (CIS), $CuInGa(S,Se)_2$ (CIGS) and CdTe are currently produced at large scale and have already reached the commercialization stage. However, the scarcity of indium, gallium and tellurium in the earth crust will limit the future development of CIGS- and CdTe-based solar cells. In addition, the price of indium will increase in the near future because of the extensive use of indium in display technologies and opto-electronic devices. The toxicity of cadmium to health and environment would be another problem to the development of CdTe-based solar cell. To solve these issues, it is necessary to search and to develop new type absorber materials that are both non toxic and abundant. Cu_2ZnSnS_4 (CZTS) and its alloy with selenium have recently gained a broad interest thanks to their remarkable properties, namely large absorption coefficient ($>10^4 cm^{-1}$) and ideal band gap energy between 1.4 and 1.6 eV for photovoltaic devices (Kahraman et al. 2013). CZTS comparing to other quaternary semiconductors above-mentioned has the advantages of earth-abundant and non toxic elements which make it one of the promising candidates for cost-effective as well as environmentally benign devices. The conversion efficiency of CZTS-based solar cells has been improved recently from 6.7 % in 2008 to 9.7 % in 2010 and 11.1 % in 2012 indicating the promise of this new thin film PV materials system (Todorov et al. 2010, 2013a; Katagiri et al. 2008). The current record efficiency of CZTS-based thin film is 12.6 % and was reported by Wang et al. (2014). Since 2010, the efficiency is improved by partly selenizing the CZTS thin film in order to have a broader spectral photoresponse (Todorov et al. 2013b). In this new record, Wang et al. have used hydrazine pure-solution approach targeting a Cu-poor and Zn-rich condition (Todorov et al. 2013c). Many researchers have addressed on various kinds of CZTS nanocrystals and CZTS nanocrystals with different crystalline structure and shape had been synthesized. The first synthesis of kesterite CZTS nanocrystals were reported by Hillhouse et al. (2009). Lu and coworkers were the first to synthesize the wurtzite phase of CZTS nanocrystals using hot-injection method (Lu et al. 2011). Li et al. (2012a) reported that wurtzite CZTS nanocrystals showed higher carrier concentration than kesterite CZTS nanocrystals. Following this report, many research groups have focused on the synthesis of wurtzite CZTS nanocrystals. Recently, many processing protocols have been investigated for depositing wurtzite CZTS nanocrystals including noninjection (Regulacio et al. 2012), hot-injection (Lu et al. 2011), hydrothermal (Wang et al. 2011), one-pot (Kang et al. 2013).

The sol–gel method is based on poly-condensation and hydrolysis reactions. Oxyhydrate precursors can be usually deposited by the sol–gel method and oxides are obtained by annealing in air (Tanaka et al. 2007). The method is very simple but however sulfides cannot be deposited by this method. Kavanagh and Cameron reported that zinc sulfide thin films were produced from films of zinc oxide obtained by annealing in air oxyhydrate precursors. The zinc oxide films became zinc sulfide by an annealing in a hydrogen sulfide-containing atmosphere (Kavanagh and Cameron 2001). Tanaka and coworkers have used this idea to prepare the CZTS thin films with a kesterite phase by sulfurizing oxyhydrate precursors directly in an $N_2 + H_2S$ (5 %) atmosphere without the oxide conversion process (Tanaka et al. 2007).

In this paper, we are presenting the synthesis of CZTS nanocrystals with wurtzite phase by sulfurizing oxyhydrate precursors in sulfur powder atmosphere which were deposited by the sol–gel method. This revealed to be very simple and useful method for preparing CZTS thin films.

2 Experimental

The CZTS was obtained from a sol–gel precursor solution which consists of copper (II) acetate monohydrate, zinc (II) acetate dihydrate and tin (II) chloride dihydrate dissolved in 2-methoxyethanol as solvent and monoethanolamine (MEA) as stabilizer. Copper (II) acetate, Zn (II) acetate and tin (II) chloride of 0.044, 0.022 and 0.022 mol respectively were dissolved in 45 ml of 2-methoxyethanol and 5 ml of MEA was added to the solution as stabilizer. After adding the metals salts, a dark brown solution was obtained which has been stirred during 2 h at 60 °C. The final solution was spinning coated on ordinary glass substrates at 2500 rpm and dried at 230 °C in air. The coating and drying processes were repeated 10 times to obtain a suitable thickness of the film. The coated glass was sulfurized by annealing at 340 °C in elemental sulfur powder containing atmosphere during 60 min. The prepared film was analyzed with an X-ray diffractometer (XRD), a Raman spectroscope and a scanning electron microscope (SEM) to carry out the crystal structure and morphology of the as-deposited CZTS nanocrystals. The optical properties were recorded by the measurements of the absorbance using a Vis spectrophotometer.

3 Results and discussion

In our sol–gel method, $Cu(CH_3COO)_2 \cdot H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$ and $SnCl_2 \cdot 2H_2O$ were used as the starting materials with the stoichiometry (2:1:1). The tin (II) chloride dehydrate is a strong reducing agent (Guo et al. 2014). The Cu^{2+} and Sn^{2+} ions are changed into Cu^{+} and Sn^{4+} through oxidation–reduction reaction, as shown in Eq. (1) below (Guo et al. 2014) (Fig. 1).

$$2Cu^{2+} + Sn^{2+} \rightarrow 2Cu^{+} + Sn^{4+} \tag{1}$$

Figure 2 shows the surface morphology of the CZTS thin film.

After spin-coating the precursor on ordinary glass substrates, the free sulfur ions were released from the elemental sulfur powder during the annealing of the metal complex.

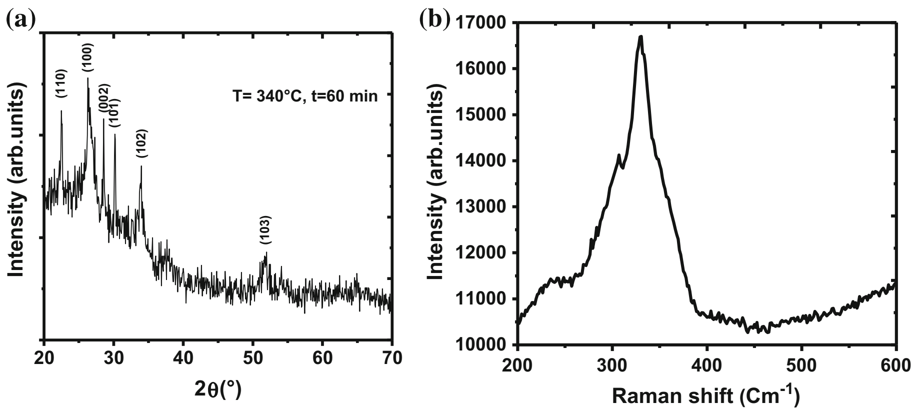

Fig. 1 **a** XRD pattern of as-synthesized wurtzite CZTS nanocrystals. **b** Raman spectrum of wurtzite CZTS nanocrystals

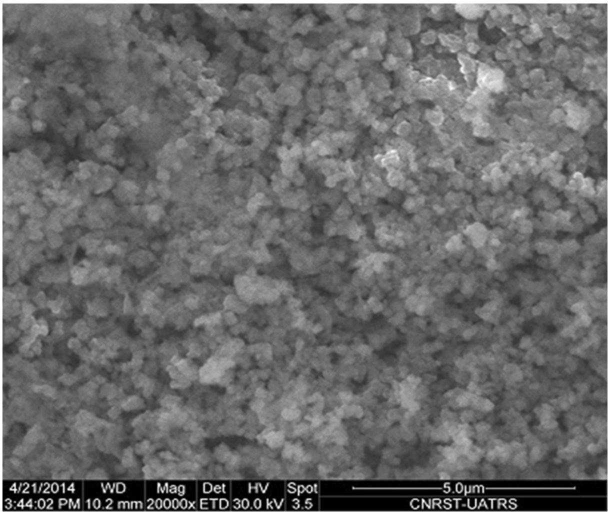

Fig. 2 Surface SEM image of the CZTS thin film

Finally, the free sulfur ions react with Cu, Zn and Sn metal complex ions to form CZTS nuclei as seen in Eq. (2).

$$2Cu^{+} + Zn^{2+} + Sn^{4+} + 4S^{2-} \rightarrow Cu_2ZnSnS_4 \tag{2}$$

X-ray diffraction of the resulting deposited film was carried out to know the crystal phase of the nanocrystals. Figure 1 shows the XRD pattern of the as-prepared CZTS nanocrystals synthesized at 340 °C during 60 min. The observed XRD pattern showed (100), (002), (101), (102) and (103) peaks at 26.33°, 28.46°, 30.14°, 33.86° and 51.59° respectively and matching well with those of the previously reported CZTS wurtzite structure (Lu et al. 2011). This structure can be obtained by substituting zinc with copper and tin atoms in the wurtzite ZnS (Lu et al. 2011).

In particular, the XRD pattern of the wurtzite CZTS matches the combined reflections from hexagonal ZnS and monoclinic Cu_2SnS_3 (Singh et al. 2012). The Raman spectroscopy showed a single peak at 330.49 cm^{-1} which is close to the value reported for bulk CZTS (Fernandes et al. 2009). The noted broadening of the Raman peak is due to the phonon confinement within the nanocrystals (Bersani et al. 1998). The average crystallite size of the CZTS film was estimated using Scherrer's formula (Knuyt et al. 1996).

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{3}$$

where D is the average crystallite size, λ is the wavelength of the X-ray radiation ($\lambda = 0.154$nm), θ is the Bragg's diffraction angle of the related peak and β is the angular width of the peak at FWHM. The estimated average crystallite size of the sample is 30.12 nm. A thickness of 1518 nm was obtained from profilometer measurements.

From Fig. 2, we can see a homogeneous surface of the film formed from aggregation of nanocrystals. The grains size is less large although they are densely packed. The small size of the grains can be due to the low annealing temperature because it is well known that higher temperature treatment above 500 °C of CZTS films showed increased crystallinity

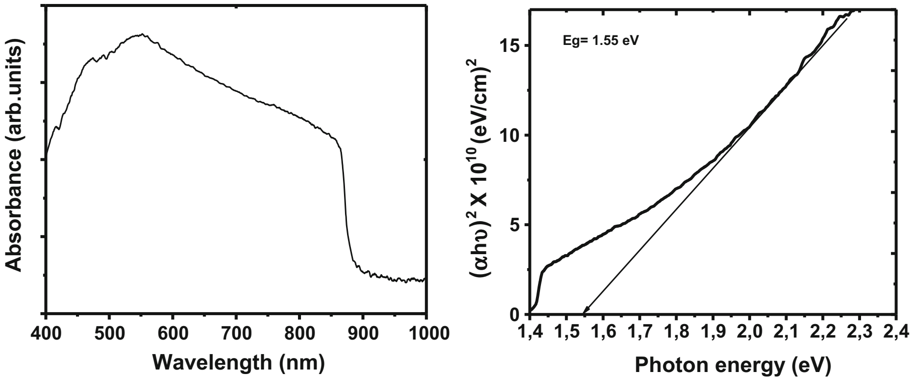

Fig. 3 Vis absorption spectrum of the film and the optical gap energy estimated from the absorption spectrum

and grain size (Seol et al. 2003; Tanaka et al. 2006). To improve the cristallinity and grain size in our film, higher annealing temperature in sulfur powder of the precursors is required.

Figure 3 shows the absorption spectrum of the CZTS thin film annealed at 350 °C. The sample exhibits broad absorption in the visible range. The dependence of the absorption coefficient upon the photon energy for near edge optical absorption in semiconductors takes the form of the following Tauc's formula (Ghobadi 2013):

$$(\alpha h\upsilon) = B(h\upsilon - Eg)^m \tag{4}$$

where Eg is the optical band gap, B is a constant, $h\upsilon$ the incident photon energy, α the absorption coefficient and $m = \frac{1}{2}, \frac{3}{2}, 2$ *and* 3 for direct allowed, indirect allowed, direct forbidden, indirect forbidden transitions respectively (Ghobadi 2013). Since CZTS is a direct allowed transition semiconductor, the optical band gap was determined by taking $m = \frac{1}{2}$, $(\alpha h\upsilon)^2$ was plotted versus $h\upsilon$ using data obtained from the optical absorbance spectra. A typical plot is shown in Fig. 3. The band gap of the CZTS film was estimated by taking the value of $h\upsilon$ for $(\alpha h\upsilon)^2 = 0$ that means by extrapolating the linear part of the curve as shown in Fig. 3. The band gap was estimated from the plot to be 1.55 eV. This value is consistent with the reported values of 1.4–1.6 eV for CZTS (Kahraman et al. 2013; Zhao et al. 2014; Li et al. 2012b), and is near the optimum value for photovoltaic solar conversion in a single-band-gap device. This feature shows that the wurtzite-CZTS thin film prepared by sulfurizing deposited precursors in a sulfur powder by the sol–gel method can be suitable for thin film solar cells.

4 Conclusion

CZTS thin film with a wurtzite phase was prepared by annealing in sulfur powder the precursors deposited by sol–gel spin coating method. XRD, Raman and SEM results showed that wurtzite CZTS was formed on the substrate. The energy band gap of the film was found to be 1.55 eV which lies in the optimal range of bulk CZTS band gap and can be applied as an absorber layer in thin films solar cells.

Acknowledgments Joël. H. 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 in the framework of the Intra-African Exchange (INEX) program.

References

Bersani, D., Lottici, P.P., Ding, X.: Phonon confinement effects in the Raman scattering by TiO_2 nanocrystals. Appl. Phys. Lett. **72**, 73–75 (1998)

Fernandes, P.A., Salome, P.M.P., da Cunha, A.F.: Growth and Raman scattering characterization of Cu 2 ZnSnS 4 thin films. Thin Solid Films **517**, 2519–2523 (2009)

Ghobadi, N.: Band gap determination using absorption spectrum fitting procedure. Int. Nano Lett. **3**(2), 1–4 (2013)

Guo, Q.J., Hillhouse, H.W., Agrawal, R.: Synthesis of Cu2ZnSnS4 nanocrystal ink and its use for solar cells. J. Am. Chem. Soc. **31**, 11672–11673 (2009)

Guo, B.L., Chen, Y.H., Liu, X.J., Li, A.D.: Optical and electrical properties study of sol–gel derived Cu_2ZnSnS_4 thin films for solar cells. AIP Adv. **4**(097115), 1–10 (2014)

Kahraman, S., Çetinkaya, S., Podlogar, M., Bernik, S., Çetinkara, H.A., Güder, H.S.: Effects of the sulfurization temperature on sol gel-processed Cu 2 ZnSnS 4 thin films. Ceram. Int. **39**, 9285–9292 (2013)

Kang, C.-C., Chen, H.-F., Yu, T.-C., Lin, T.-C.: Aqueous synthesis of wurtzite Cu 2 ZnSnS 4 nanocrystals. Mater. Lett. **96**, 24–26 (2013)

Katagiri, H., Jimbo, K., Yamada, S., Kamimura, T., Maw, W.S., Fukano, T., Ito, T., Motohiro, T.: Enhanced conversion efficiencies of Cu2ZnSnS4-based thin film solar cells by using preferential etching technique. Appl. Phys. Express **1**, 041201 (2008)

Kavanagh, Y., Cameron, D.C.: Zinc sulfide thin films produced by sulfidation of sol–gel deposited zinc oxide. Thin Solid Films **398**, 24–28 (2001)

Knuyt, G., Quaeyhaegens, C., Haen, J.D., Stals, L.M.: A model for thin film texture evolution driven by surface energy effects. Phys. Status Solidi B **195**, 179–193 (1996)

Li, M., Zhou, W.-H., Guo, J., Zhou, Y.-L., Hou, Z.-L., Jiao, J., Zhou, Z.-J., Du, Z.-L., Wu, S.-X.: Synthesis of pure metastable wurtzite CZTS nanocrystals by facile one-pot method. J. Phys. Chem. **C116**, 26507–26516 (2012a)

Li, C., Ha, E., Wong, W.-L., Li, C., Ho, K.-P., Wong, K.-Y.: A facile arrested precipitation method for synthesis of pure wurtzite Cu 2 ZnSnS 4 nanocrystals using thiourea as a sulfur source. Mater. Res. Bull. **47**, 3201–3205 (2012b)

Lu, X.T., Zhuang, Z.B., Peng, Q., Li, Y.D.: Wurtzite Cu2ZnSnS4 nanocrystals: a novel quaternary semiconductor. Chem. Commun. **47**, 3141–3143 (2011)

Regulacio, M.D., Ye, C., Lim, S.H., Bosman, M., Ye, E., Chen, S.: Colloidal nanocrystals of Wurtzite-type Cu2ZnSnS4: facile noninjection synthesis and formation mechanism. Chem. Eur. J. **18**, 3127–3131 (2012)

Seol, J., Lee, S., Lee, J., Nam, H., Kim, K.: Electrical and optical properties of Cu 2 ZnSnS 4 thin films prepared by rf magnetron sputtering process. Sol. Energy Mater. Sol. Cells **75**, 155–162 (2003)

Singh, A., Geaney, H., Laffir, F., Ryan, K.M.: Colloidal synthesis of wurtzite Cu2ZnSnS4 nanorods and their perpendicular assembly. J. Am. Chem. Soc. **134**, 2910–2913 (2012)

Tanaka, T., Kawasaki, D., Nishio, M., Guo, Q., Ogawa, H.: Fabrication of Cu2ZnSnS4 thin films by co-evaporation. Phys. Stat. Sol. (c) **3**, 2844–2847 (2006)

Tanaka, K., Moritake, N., Uchiki, H.: Preparation of Cu2ZnSnS4 thin films by sulfurizing sol–gel deposited precursors. Sol. Energy Mater. Sol. Cells **91**, 1199–1201 (2007)

Todorov, T.K., Reuter, K.B., Mitzi, D.B.: High-efficiency solar cell with earth-abundant liquid-processed absorber. Adv. Mater. **22**, E156-E159 (2010)

Todorov, T.K., Sugimoto, H., Gunawan, O., Gokmen, T., Mitzi, D.B.: In: Proceedings of the 39 th IEEE Photovoltaic Specialists Conference, Tampa, FL, USA, June, (2013)

Todorov, T.K., Tang, J., Bag, S., Gunawan, O., Gokmen, T., Zhu, Y., Mitzi, D.B.: Beyond 11 % efficiency: characteristics of state-of-the-art Cu2ZnSn (S, Se) 4 solar cells. Adv. Energy Mater. **3**, 34–38 (2013a)

Todorov, T.K., Gunawan, O., Gokmen, T., Mitzi, D.B.: Solution-processed Cu (In, Ga)(S, Se) 2 absorber yielding a 15.2 % efficient solar cell. Prog. Photovolt. Res. Appl. **21**, 82–87 (2013b)

Wang, C., Cheng, C., Cao, Y., Fang, W., Zhao, L., Xu, X.: Synthesis of Cu2ZnSnS4 nanocrystallines by a hydrothermal route. Jpn. J. Appl. Phys. **50**, 065003 (2011)

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. **4**, 1301465 (2014)

Zhao, Y., Qiao, Q., Zhou, W.-H., Cheng, X.-Y., Kou, D.-X., Zhou, Z.-J., Wu, S.-X.: Wurtzite Cu 2 ZnSnS 4 nanospindles with enhanced optical and electrical properties. Chem. Phys. Lett. **592**, 144–148 (2014)