CZTS layers for solar cells by an electrodeposition-annealing route

Md Ibrahim Khalil, Roberto Bernasconi, Luca Magagnin [*]

Dip. Chimica, Materiali e Ing. Chimica Giulio Natta, Politecnico di Milano, Via Mancinelli 7, 20131 Milano, Italy

Article history:
Received 8 April 2014
Received in revised form 3 September 2014
Accepted 3 September 2014
Available online 6 September 2014

1. Introduction

In recent times abundant, inexpensive and environmentally friendly materials have got lot of attention from researcher for thin film solar cells. Cu_2ZnSnS_4 (CZTS) is a promising absorber material for thin film which has all those qualities unlike its predecessors CdTe and Cu(In,Ga)Se_2(CIGS), current commercial material for thin film photovoltaic devices. CZTS has direct band gap energy of 1.4–1.5 eV and large absorption coefficient over $10^4\,cm^{-1}$[1] as well as theoretical conversion efficiency of 32%, which makes it suitable for next generation thin film solar cells. Several methods have been used to prepare this thin film namely sputtering [2–4], photochemical deposition [5], the sol-gel method [6], screen-printing [7], physical vapour deposition [8–10], a solution-processed approach [11–13], and electrodeposition [14–19]. The highest conversion efficiency of CZTS achieved till date is 12.6% by Wang et al. using hydrazine-based solution process [13]. Through electrodeposition, the highest efficient CZTS solar cell was demonstrated by Ahmed et al. with 7.3% conversion efficiency [19]. Point to be noted, Wang et al. achieved the highest efficiency when they added sulfur (S) and selenium (Se) in the precursor using hydrazine based solutions. Electrodeposition is a potentially suitable preparation method to obtain low-cost precursor films because it is inexpensive, non-vacuum, uses an environment-friendly process, produces large deposition areas by low temperature growth. Usually electrodeposition base processes can be divided into two categories. One is a two-steps process where metal precursors need sulfurization after electrodeposition of Cu-Zn-Sn. The other one is a single-step electrodeposition where Cu,Zn,Sn and S are directly deposited from electrolyte to form CZTS compound. However, it is very difficult to deposit homogeneous and good crystalline films from single-step electrodeposition as the reduction potential gap of the metal ions is considerably large. For this reasons, up to present, very few reports have been published on this process [16,20]. Therefore, electrodeposition of metal precursor followed by sulfurization has been preferred. Two-steps process could be accomplished in two approaches either by sulfurization of sequential electrodeposited precursors or sulfurization of co-electrodeposited Cu-Zn-Sn precursors. In case of sequential electrodeposition of Cu-Zn-Sn, there are some issues like (i) poor adhesion of Sn to the Mo surface [21] (ii) morphology of Sn precursors are quite porous compared to other elemental precursors (iii) volatility of Sn during sulfurization if Sn is deposited at the upper surface (iv) non-homogeneous nucleation of Zn which leads to poor morphology of CZTS with many secondary phases after sulfurization [22]. On the other side, proper complexing agents and optimized parameters are the main issues to deposit Cu-Zn-Sn simultaneously from single electrolyte. Most of the published works on co-electrodeposition of Cu-Zn-Sn has been done using trisodium citrate as a complexing agent. Araki et al. fabricated CZTS from co-electrodeposited Cu-Zn-Sn precursor with 3.16% power conversion efficiency [14]. Gougaud et al. demonstrated recently the effect

---

[*] Corresponding author. Tel.: +39 0223993124; fax: +39 0223993180.
E-mail address: luca.magagnin@polimi.it (L. Magagnin).

of two complexing agents (sodium citrate and tartaric acid) on co-electrodeposition of Cu-Zn-Sn with 5.8% conversion efficiency of CZTS [23]. Scragg et al. demonstrated the fabrication of CZTS from stacked metallic layer with 3.2% conversion efficiency [22]. Lin et al. recently showed the optimized parameters (temperature, time) to preheat the metallic stacked precursor of Cu-Zn-Sn before sulfurization with conversion efficiency of 5.6% [24]. Ennaoui et al. reported the fabrication of CZTS from co-electrodeposited metallic precursor with 3.4% conversion efficiency [15]. This group used pyrophosphate along with some other complexing agents to deposit Cu-Zn-Sn simultaneously from single solution. Later precursor was sulfurized by annealing using a gas mixture of Ar with 5% H_2S at 550 °C for 2 hours. This is the only report as far as our concern where pyrophosphate along with some other complexing agents was used, even if co-electrodeposition of Cu-Zn-Sn from pyrophosphate electrolyte was developed long time ago [25].

Our research introduces a novel electrodeposition route for the simultaneous deposition of Cu-Zn-Sn alloy from single electrolyte. Here we used only pyrophosphate as a complexing agent for the co-electrodeposition of Cu-Zn-Sn. Afterwards precursors are annealed in elemental sulfur environment to get stoichiometric CZTS film instead of H_2S atmosphere to avoid toxic environment.

2. Experimental

Electrodeposition was carried out galvanostatically in a conventional electrochemical cell assembly. Mo foil substrate (200 μm thick from Goodfellows) with an exposed area of 2 cm × 1 cm was used as a working electrode, a graphite electrode as an inert counter electrode. Before deposition, Mo substrates were cleaned in acetone, dipped in 32% HCl for 10 minutes, distilled water and finally dried under N_2 atmosphere. The electrolytic bath contained 0.016 M $CuSO_4{\cdot}5H_2O$, 0.072 M $ZnSO_4{\cdot}7H_2O$, 0.037 M $Na_2SnO_3{\cdot}3H_2O$, 0.60 M $K_4P_2O_7$. All the chemicals were purchased from SIGMA ALDRICH and used as received. The pH of the solution bath was adjusted to 11 by using 20% H_2SO_4 and 30% KOH to stabilize the electrolyte. Electrodeposition was carried out at 5.5 mA/cm^2 for 6 minutes in ambient temperature with a moderate stirring for the desired composition; the highest cathodic current efficiency CE achieved on Mo was 84%. Current efficiency was calculated on the basis of Faraday's law from the metal contents of deposits, as determined by EDS analysis, as follows:

$$CE(\%) = 100\frac{I_{Cu} + I_{Zn} + I_{Sn}}{I_{tot}} = 100\frac{\left(\frac{2m_{Cu}}{A_{Cu}} + \frac{2m_{Zn}}{A_{Zn}} + \frac{4m_{Sn}}{A_{Sn}}\right)}{I_{tot}} \times \frac{F}{t}$$

where I_{Cu}, I_{Zn} and I_{Sn} are partial currents for copper, zinc and tin, I_{tot} is total current; m_{Cu}, m_{Zn} and m_{Sn} are weights of copper, zinc and tin deposited; A_{Cu}, A_{Zn} and A_{Sn} are the atomic weights of metals; F is the Faraday constant and t is the deposition time.

No precipitate, e.g. tin(IV) oxides, appeared from the electrolyte after two months storage at room temperature. After electroplating, the Cu-Zn-Sn precursors were annealed at 550 °C temperatures for 15 minutes or 2 hours with different ramping rates (20 °C/minute or 2 °C/minute) with 30 mg elemental sulfur environment and presence of a very small flow of N_2. The electrochemical characterization of the plating solution was performed using a Solartron analytical Modulab. Graphite was used as counter and glassy carbon (selected as inert material for preliminary electrolyte formulation and electrochemical characterization) as standard working electrode, while SCE was used as reference. The crystallographic phase of as deposited Cu-Zn-Sn precursors and annealed thin films was analyzed with the help of X-ray diffractometer (XRD, Philips X-pert MPD with CuKα = 1.5406 Å). Surface morphology and composition of the films were studied by using Scanning Electron Microscopy (Model Zeiss EVO 50) equipped with an energy dispersive X-ray analyzer (EDS) Oxford instrument (Model 7060). Raman spectroscopy was obtained at room temperature in air by a Labram HR800 W Horiba Jobin Yvon microscope spectrometer. The 514.5 nm line of an Ar$^+$ laser was used as the excitation source with the intensity of 10 mW. Glow discharge optical emission spectroscopy (GDOES) was also carried out using Spectrum Analytic GMBH (Model GDA 750 analyzer)

3. Results and Discussion

The reduction potential of the Cu, Zn and Sn cations could be expressed in the following equations [26]:

$$Cu^{2+} + 2e^- \rightarrow Cu; E = 0.093V + \frac{RT}{2F}\ln[Cu^{2+}](vs.SCE)$$

$$Zn^{2+} + 2e^- \rightarrow Zn; E = -1.007V + \frac{RT}{2F}\ln[Zn^{2+}](vs.SCE)$$

$$Sn^{4+} + 2e^- \rightarrow Sn^{2+}; E = -0.096V - \frac{RT}{2F}\ln\left[\frac{Sn^{2+}}{Sn^{4+}}\right](vs.SCE)$$

$$Sn^{2+} + 2e^- \rightarrow Sn; E = -0.384V + \frac{RT}{2F}\ln[Sn^{2+}](vs.SCE)$$

As the gap among the reduction potential of copper, zinc and tin is considerably large, it is difficult to co-electrodeposit them from single electrolyte. Above equations make it clear that Zn has considerably more negative potential than Cu and Sn. In order to reduce the potential gap among the three elements, most of the researchers used trisodium citrate as a complexing agent. In our studies we have used potassium pyrophosphate as complexing agent. Pyrophosphate is known to complex copper in an efficient way over a wide pH range, giving $[CuH_q(P_2O_7)_2]^{(6-q)-}$species [27]. Also Zn is chelated by pyrophosphate, giving similar complexes over a good pH range [28]. According to the speciation diagrams, Sn is not complexed at the pH selected, i.e. 11, and is present in the solution as free stannate ions $Sn(OH)_6{}^{2-}$ [29]. This was one of the reasons for selecting pH 11, together with the difficulty in achieving the desired chemical composition at values lower than 10.5. It was found that pyrophosphate has narrowed down the potential gap more with respect to the trisodium citrate. This is visible (from Fig. 1) considering the relative positions of the detected reduction peaks: -0.3 V for the $Cu^{2+} \rightarrow Cu^0$, -0.5 V in case of the $Sn^{2+} \rightarrow Sn^0$ reaction and -1 V for $Zn^{2+} \rightarrow Zn^0$. The $Sn^{4+} \rightarrow Sn^{2+}$ reaction is not clearly visible in the graph, as it is probably either superimposed with the reduction peak of Cu or not present (a behavior common for some electrolytes containing Sn(IV) [30]). Fig. 1 shows the CV performed on the electrolyte at a scan rate of 2 mV/s in a potential range from -2 to 2 V vs. SCE. Pyrophosphate has a great effect in lowering the reduction potential of Cu, while for the other two metals the complexation is less efficient. For comparison it is possible to cite the reduction potentials obtained in a citrate electrolyte: 0.2 V for Cu, -0.6 V for Sn and -1.1 V in the case of Zn [31]. The corresponding oxidation potentials were also observed in the anodic part of the curve. It is well known that Cu-poor and Zn-rich Cu-Zn-Sn precursor is favorable for good CZTS thin films [32]. Our results have also matched up well with the literature. The atomic metal composition of Cu-Zn-Sn precursor was Cu: 39.90% Zn: 34.47% and Sn: 25.63%; Cu/(Zn + Sn) ≈ 0.66, Zn/Sn ≈ 1.34 by EDS measurement in our experiment.

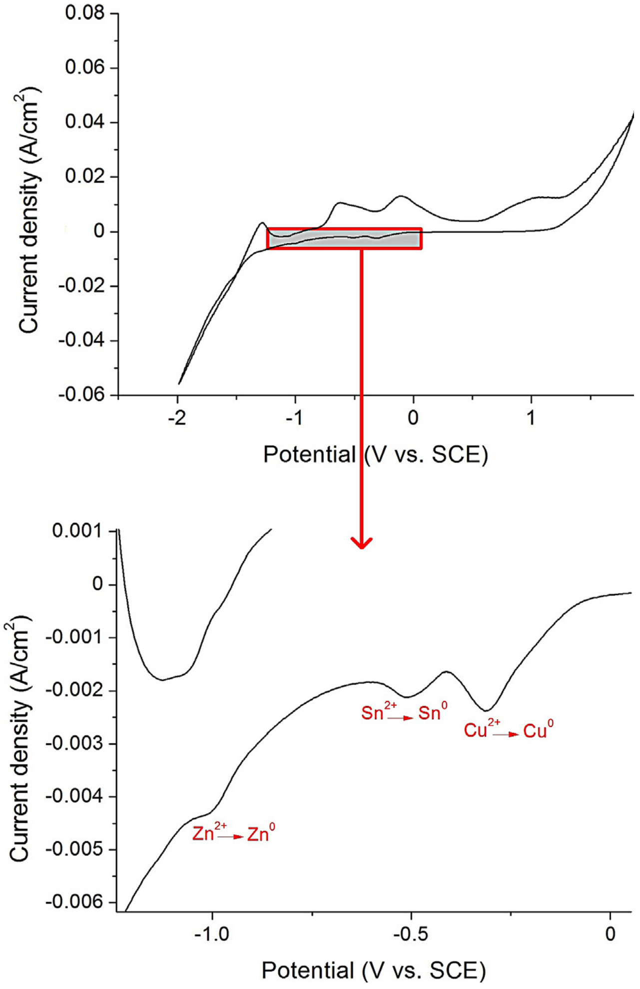

Fig. 1. Cyclic voltammetry curve in ternary (Cu-Zn-Sn) electrolyte.

Fig. 2 and Fig. 3 show the XRD spectra of as deposited Cu-Zn-Sn precursor and sulfurized thin films after annealing at 550 °C for 2 hours with ramping rate 20 °C/minute and 2 °C/minute. XRD pattern of as deposited Cu-Zn-Sn precursor was composed of pure Sn (JCPDS card 86–2265) and Cu_5Zn_8 (JCPDS card 25–1228) which is not in agreement with some data of the literature [30,33]. Our new electrolyte might be the reason behind it as they deposited from acidic electrolyte. Formations of Cu-Zn and Cu-Sn phases on as deposited precursor have also been reported earlier [18,34]. As expected, there has been no formation of a Zn-Sn phase during the deposition of Cu-Zn-Sn precursor, as these two metals do not form any intermetallic compound. XRD pattern of sulfurized film exhibited mostly the peaks related to kesterite structure of CZTS. In case of 20 °C/minute ramping rate, all the XRD patterns of sulfurized samples correspond to the kesterite structure of CZTS (JCPDS card 26–0575). On the other hand, in case of 2 °C/minute ramping rate, kesterite structure of CZTS has been formed along with some other secondary phases. Dominant peak (112) of the XRD pattern of these polycrystalline films lies at diffraction angle (2 Theta) 28.53° which was commonly observed by others [16,35–37]. It was reported earlier that low ramping rates used to increase the grain size of the film [15]. The main issue that was found in our case is the formation of secondary phases at low ramping rate, which can be connected to the use of pure sulfur atmosphere instead of H_2S plus long duration of the process during sulfurization. The presence of MoS_2 (JCPDS 06-0097) was observed as well. More work will be necessary on this aspect of the sulfurization process. Fig. 4 shows the as deposited Cu-Zn-Sn precursor (a) on Mo substrate which transformed into polycrystalline thin film (b) after annealing at 550 °C for 2 hours with ramping rate 20 °C/minute. The thickness of as deposited precursors was near about 750 nm on 200 µm thick Mo substrate. Earlier work [19] suggests that during sulfurization the conversion of CuZnSn metal into the Cu_2ZnSnS_4 thin film causes three times volume expansion with respect to the original thickness of the CuZnSn layer. After sulfurization, we detected a thickness of 2.4 µm for the CZTS film. In Fig. 4 (b) some very thin layers of adsorbed material on some grains of CZTS are visible. These are probably connected to some secondary phases of CuSnS and SnS as those zones showed a deviation from stoichiometric ratio of CZTS by SEM (EDS) analysis; this is also confirmed by preliminary micro-Raman evaluations. The atomic composition of sulfurized films was Cu: 20.59% Zn: 15.59% Sn: 11.44% S: 52.59% by EDS measurement which is near to the stoichiometric ratio of CZTS. Sample annealed at 550 °C for 2 hours with 2 °C/minute ramping rate, reported in Fig. 4(c) showed a lot of secondary phases after sulfurization with non-stoichiometric ratio of CZTS. Annealing at 550 °C for 15 minutes with 20 °C/minute ramping rate showed a nearly stoichiometric ratio for CZTS (Cu: 29.03% Zn: 10.67%

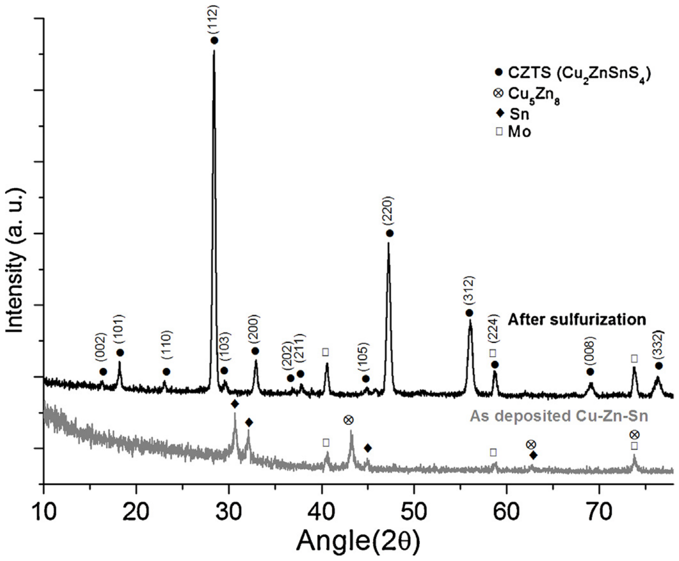

Fig. 2. XRD pattern of as deposited precursor and sulfurized films with 20 °C/minute ramping rate.

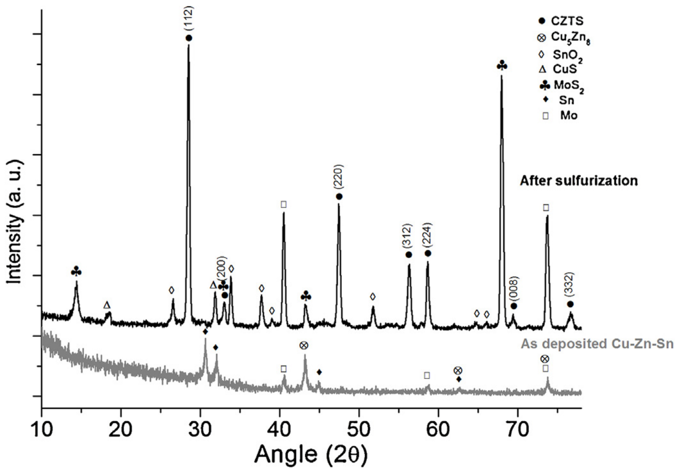

Fig. 3. XRD pattern of as deposited precursor and sulfurized film with 2 °C/minute ramping rate.

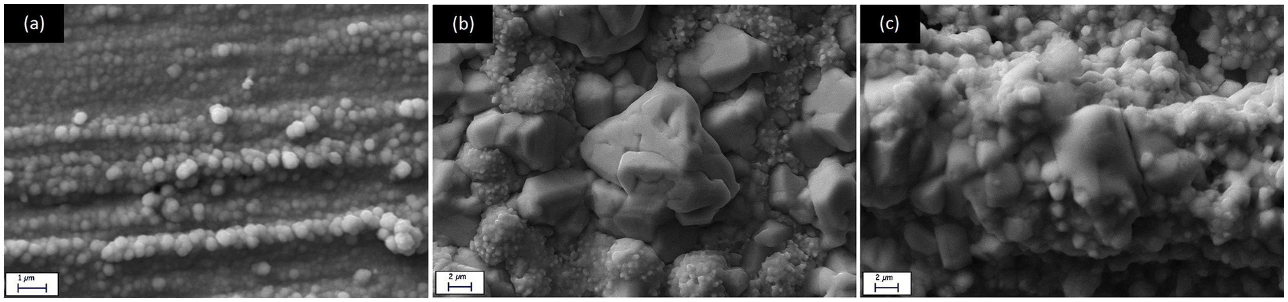

Fig. 4. SEM images of (a) as deposited precursor, (b) sulfurized film (annealed at 550 °C for 2 hours with ramping rate 20 °C/minute), and (c) sulfurized film (annealed at 550 °C for 2 hours with 2 °C/minute ramping rates).

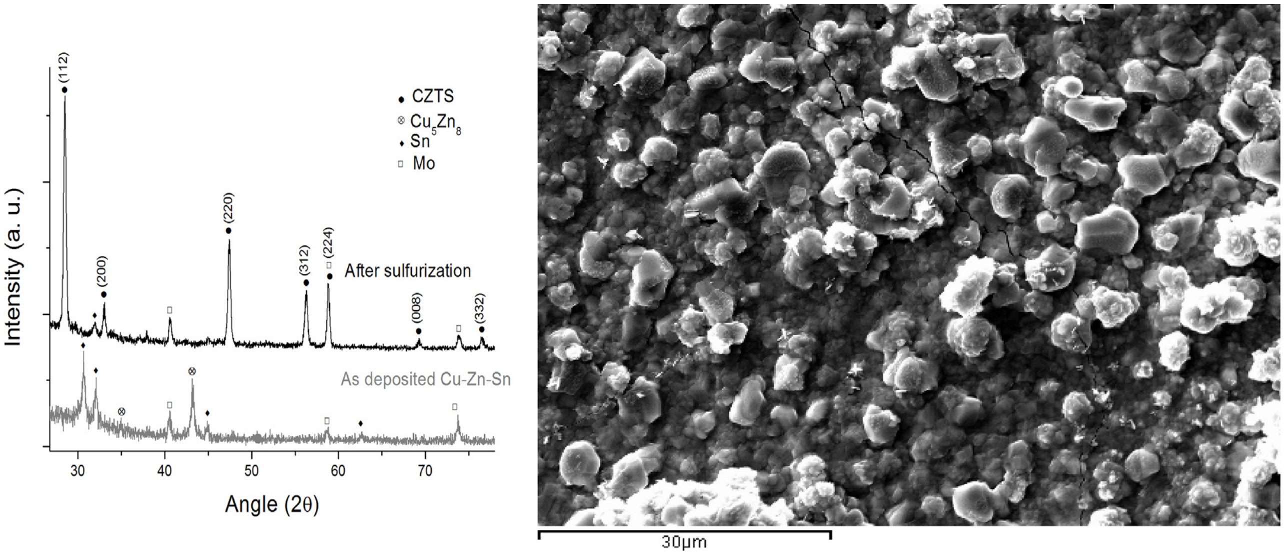

Fig. 5. XRD result and SEM image of the sample annealed at 550 °C for 15 minute with 20 °C/minutes ramping rate.

Sn: 10.78% S: 49.03%), lack of secondary phases, but the quality of the film (grain size) is lower with respect to the 2 hours annealed sample (Fig. 5). Fig. 6 shows Raman spectrum of the sample annealed at 550 °C for 2 hours with 20 °C/minute ramping rate with major peaks at 237 cm^{-1}, 288 cm^{-1}, 338 cm^{-1}, 374 cm^{-1} which are in good agreement with the result of previous studies [10,38–41]: specifically with commonly acknowledged peak at 338 cm^{-1} [44]. No peak was observed corresponding to ZnS (271 cm^{-1}, 352 cm^{-1}) and Cu_2SnS_3 (305 cm^{-1}, 350 cm^{-1}) indicating the presence of good quality single phase CZTS [41–43]. ZnS and Cu_2SnS_3 are the main secondary phases which used to be present along with CZTS after sulfurization. Though up to 18 phases of the ternary Cu-Sn-S system have been described [45], secondary phases peaks were not detected indicating a good quality of the electrodeposited films. Sample was further characterized by glow

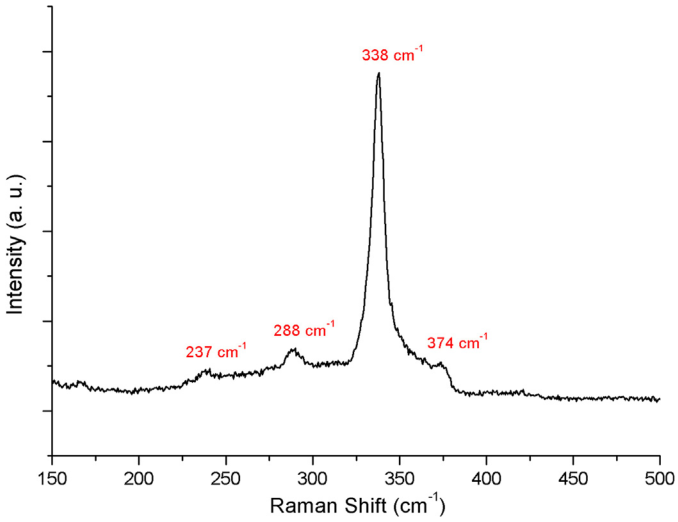

Fig. 6. Raman spectrum of sulfurized sample (annealed at 550 °C for 2 hours with 20 °C/minute ramping rate).

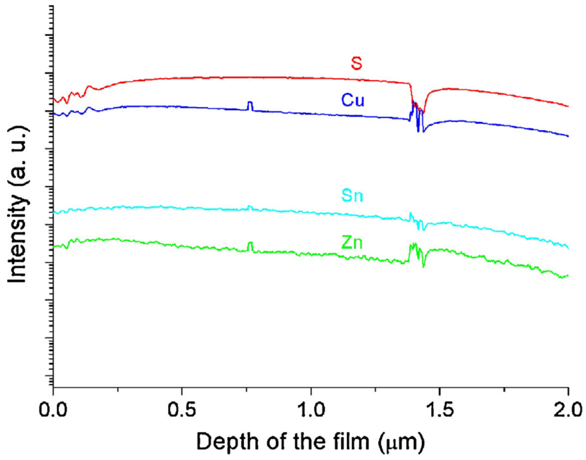

Fig. 7. GDOES results on sulfurized sample (annealed at 550 °C for 2 hours with 20 °C/minute ramping rate).

discharge optical emission spectroscopy to see how the composition of CZTS changes along the film thickness as EDS analysis only shows the average composition of the film. From Fig. 7, it is evident that the composition of CZTS does not change along the thickness of the film. The characterization of the deposit/substrate interface with possible formation of a MoS_2 layer is still under investigation.

4. Conclusions

CZTS thin films were successfully prepared on Mo substrate using co-electrodeposition of Cu-Zn-Sn in a novel electrolyte. Different characterization results have well matched up with the literature. It was found that duration of annealing at high temperature increases the grain size of the film. On the other hand it was also found that a low ramping rate does not increase the grain size of the film rather it creates secondary phases in the film. It was found that as deposited precursor and sulfurized film are quite rough, thus an attempt to reduce the roughness, e.g. using pulse plating, will be subject of future developments. At the same time by optimizing the sulfurization parameters, roughness of the film after sulfurization could be decreased. This work demonstrates a novel procedure to fabricate stoichiometric CZTS thin films from co-elctrodeposited metallic precursors and sulfurization, with homogeneous distribution of the elements along the cross section of the films.

References

[1] K. Ito, T. Nakazawa, Electrical and optical properties of stannite-type quaternary semiconductor thin films, The Japanese J. Appl. Phys. 27 (1988) 2094–2097.

[2] R.B.V. Chalapathy, G.S. Jung, B.T. Ahn, Fabrication of Cu_2ZnSnS_4 films by sulfurization of Cu/ZnSn/Cu precursor layers in sulfur atmosphere for solar cells, Sol. Energy Mater. Sol. Cells 95 (2011) 3216–3221.

[3] T. Tanaka, T. Nagatomo, D. Kawasaki, et al., Preparation of Cu_2ZnSnS_4 thin films by hybrid sputtering, J. Phys. Chem. Solids 66 (2005) 1978–1981.

[4] J.S. Seol, S.Y. Lee, J.C. Lee, H.D. Nam, K.H. Kim, Electrical and optical properties of Cu_2ZnSnS_4 thin films prepared by rf-magnetron sputtering process, Sol. Energy Mater. Sol. Cells 75 (2003) 155–162.

[5] K. Moriya, K. Tanaka, H. Uchiki, Characterization of Cu_2ZnSnS_4thin films prepared by photo-chemical deposition, Jpn. J. Appl. Phys. 44 (2005) 715–717.

[6] K. Tanaka, Y. Fukui, N. Moritake, H. Uchiki, 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, Sol. Energy Mater. Sol. Cells 95 (2011) 838–842.

[7] Z.H. Zhou, Y. Wang, D. Xu, Y. Zhang, Fabrication of Cu_2ZnSnS_4 screen printed layers for solar cells, Sol. Energy Mater. Sol. Cells 94 (2010) 2042–2045.

[8] H. Katagiri, N. Sasaguchi, S. Hando, S. Hoshino, J. Ohashi, T. Yokota, Preparation and evaluation of Cu_2ZnSnS_4 thin films by sulfurization of EB evaporated precursors, Sol. Energy Mater. Sol. Cells 49 (1997) 407–414.

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

[10] K. Wang, O. Gunawan, T. Todorov, B. Shin, S.J. Vhey, N.A. Bojarczuk, Structural and elemental characterization of high efficiency Cu_2ZnSnS_4 solar cells, Appl. Phys. Lett. 98 (2011) 051912.

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

[12] T.K. Todorov, K.B. Reuter, D.B. Mitzi, High-Efficiency Solar Cell with Earth-Abundant Liquid-Processed Absorber, Adv. Mater. 22 (2010) 156–159.

[13] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency, Adv. Energy Mater. 4 (2014) 1301465.

[14] H. Araki, Y. Kubo, K. Jimbo, et al., Preparation of Cu_2ZnSnS_4 thin films by sulfurization of co-electroplated Cu-Zn-Sn precursors, Phys. Status Solidi C 61 (2009) 1266–1268.

[15] A. Ennaoui, M. Lux-Steiner, D. Abou-Ras, et al., Cu_2ZnSnS_4 thin film solar cells from electroplated precursors: Novel low-cost perspective, Thin Solid Films 517 (2009) 2511–2514.

[16] 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 (2010) 4057–4061.

[17] C.P. Chan, H. Lam, C. Surya, Preparation of Cu_2ZnSnS_4 films by electrodeposition using ionic liquids, Sol. Energy Mater. Sol. Cells 94 (2010) 207–211.

[18] R. Schurr, A. Holzing, S. Jost, et al., The crystallisation of Cu_2ZnSnS_4 thin film solar cell absorbers from co-electroplated Cu–Zn–Sn precursors, Thin Solid Films 517 (2009) 2465–2468.

[19] S. Ahmed, K.B. Reuter, O. Gunawan, L. Gao, L.T. Romankiw, H. Deligianni, A high efficiency electrodeposited Cu_2ZnSnS_4 solar cell, Adv. Energy Mater. 2 (2012) 253–259.

[20] Y. Cui, S. Zou, J. Jiang, S. Yuan, J. Chu, Synthesis and characterization of co-electroplated Cu_2ZnSnS_4 thin films as potential photovoltaic material, Sol. Energy Mater. Sol. Cells 95 (2011) 2136–2140.

[21] J. Iljina, O. Volobujeva, T. Raadik, N. Revathi, J. Raudoja, M. Loorits, R. Traksmaa, E. Mellikov, Selenisation of sequentially electrodeposited Cu-Sn and Sn precursor layers, Thin Solid films 535 (2013) 14–17.

[22] J.J. Scragg, D.M. Berg, P.J. Dale, A 3.2% efficient kesterite device from electrodeposited stacked elemental layers, J. Electronal. Chem. 646 (2010) 52–59.

[23] C. Gougaud, D. Rai, S. Delbos, E. Chassaing, D. Lincot, Electrochemical studies of one-step electrodeposition of Cu-Sn-Zn Layers from aqueous electrolytes for photovoltaic applications, J. Electrochem. Soc. 160 (2013) D485–D494.

[24] Y. Lin, S. Ikeda, W. Septina, Y. Kawasaki, T. Harada, M. Matsumura, Mechanistic aspects of preheating effects of electrodeposited metallic precursors on structural and photovoltaic properties of Cu_2ZnSnS_4 thin films, Sol. Energy Mater. Sol. Cells 120 (2014) 218–225.

[25] G.N. Guseva, T.A. Vagramyan, Electrodeposition of Cu-Zn-Sn from pyrophosphate electrolyte, Protection of Metals 21 (1985) 381.

[26] Petrucci, Harwood, Herring, Madura, General Chemistry: Principles and Modern Applications, 9th ed., Pearson Education, Upper Saddle River, New Jersey, 2007.

[27] C. Heitner-Wirguin, J. Kendy, An ion exchange study of copper pyrophosphate complexes in solution, Journal of Inorganic and Nuclear Chemistry 22 (1961) 253–257.

[28] OAM Jr., S.A. Wiest, Determination of Stability Constants for Zinc-Pyrophosphate Complexes, Anal. Biochem. 77 (1977) 73–78.

[29] J.R. Duffield, D.R. Williams, Speciation studies of the solubility and aqueous solution chemistry of Tin(II)- and Tin(IV)- pyrophosphate complexes, Polyhedron 10 (1991) 377–387.

[30] U. Unal, G. Somer, Simultaneous determination of trace Sn(II) and Sn(IV) using differential pulse polarography and application, Turk J Chem 35 (2011) 73–85.

[31] K.V. Gurav, S.M. Pawar, S.W. Shin, M.P. Suryawanshi, G.L. Agawane, P.S. Patil, J.H. Moon, J.H. Yun, J.H. Kim, Electrosynthesis of CZTS films by sulfurization of CZT precursor: Effect of soft annealing treatment, Appl. Surf. Sci 283 (2013) 74–80.

[32] J. Li, M. Wei, W. Li, G. Jiang, C. Zhu, The $Cu_2ZnSnSe_4$ thin films solar cells synthesized by electrodeposition route, Appl. Surf. Sci. 258 (2012) 6261–6265.

[33] X. He, H. Shen, W. Wang, J. Pi, Y. Haob, X. Shi, Synthesis of Cu_2ZnSnS_4 films from co-electrodeposited Cu–Zn–Sn precursors and their microstructural and optical properties, Appl. Surf. Sci 282 (2013) 765–769.

[34] Z. Chen, L. Han, L. Wan, C. Zhang, H. Niu, J. Xu, $Cu_2ZnSnSe_4$ thin films prepared by selenization of co-electroplated Cu–Zn–Sn precursors, Appl. Surf. Sci. 257 (2011) 8490–8492.

[35] A. Wangperawong, J.S. King, S.M. Herron, B.P. Tran, K. Pangan-Okimoto, S.F. Bent, Aqueous bath process for deposition of Cu_2ZnSnS_4 photovoltaic absorbers, Thin Solid Films 519 (2011) 2488–2492.

[36] X. Zhang, X. Shi, W. Ye, C. Ma, C. Wang, Electrochemical deposition of quaternary Cu_2ZnSnS_4 thin films as potential solar cell material, Appl. Phys. A 94 (2009) 381–386.

[37] Y. Zhou, W. Zhou, Y. Du, M. Li, S. Wu, Sphere-like kesterite Cu_2ZnSnS_4 nanoparticles synthesized by a facile solvothermal method, Mater, Lett. 65 (2011) 1535–1537.

[38] X. Fontané, L. Calvo-Barrio, V. Izquierdo-Roca, E. Saucedo, A. Pérez-Rodriguez, J.R. Morante, D.M. Berg, P.J. Dale, S. Siebentritt, In-depth resolved Raman scattering analysis for the identification of secondary phases-characterization of Cu_2ZnSnS_4 layers for solar cell applications, Appl. Phys. Lett. 98 (2011) 1819051–1819053.

[39] H. Yoo, J. Kim, Growth of Cu_2ZnSnS_4 thin films using sulfurization of stacked metallic films, Thin Solid Films 518 (2010) 6567–6572.

[40] R.B.V. Chalapathy, C. Lee, B.T. Ahn, Cu_2ZnSnS_4 (CZTS) Thin Films Grown by Sulfurization of Different Precursor Layers in Sulfur Atmosphere, Proceedings 37th IEEE PVSC 2011, Seattle, USA, 2014.

[41] P.A. Feranades, P.M.P. Salome, A.F. Da Cunha, Study of polycrystalline Cu_2ZnSnS_4 films by Raman scattering, J.Alloys Compd. 509 (2011) 7600–7606.

[42] E.M. Mkawi, K. Ibrahim, M.K. Ali, A.S. Mohamed, Dependence of copper concentration on the properties of Cu_2ZnSnS_4 thin film prepared by electrochemical method, Int. J. Electrochem. Sci. 8 (2013) 359–368.

[43] J. Wang, S. Li, J. Cai, B. Shen, Y. Ren, G. Qin, Cu_2ZnSnS_4 thin films: facile and cost-effective preparation by RF-magnetron sputtering and texture control, J.Alloys Compd. 552 (2013) 418–422.

[44] X. Wang, Z. Sun, C. Shao, D.M. Boye, J. Zhao, A facile and general approach to polynary semiconductor nanocrystals via a modified two-phase method, Nanotechnology 22 (2011) 245605.

[45] F.D. Benedetto, I. Bencista, et al., Electrodeposition of ternary $Cu_xSn_yS_z$ thin films for photovoltaic applications, Prog. Photovolt. Res, Appl. 22 (2014) 97–106.