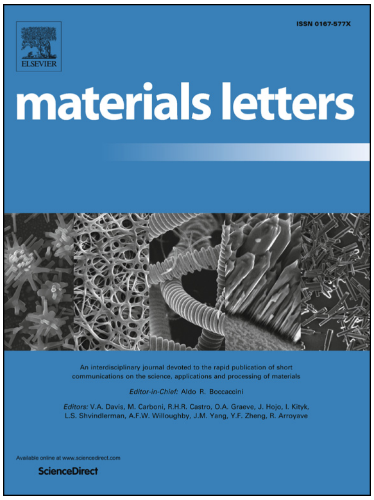


Cu_2ZnSnS_4 thin films by sulfurization in melted sulfur

S.A. Bashkirov, U.S. Hekkel, M.S. Tivanov, A.M. Saad

PII: S0167-577X(18)30391-4
DOI: https://doi.org/10.1016/j.matlet.2018.03.035
Reference: MLBLUE 23996

To appear in: *Materials Letters*

Received Date: 11 January 2018
Revised Date: 2 March 2018
Accepted Date: 4 March 2018

Please cite this article as: S.A. Bashkirov, U.S. Hekkel, M.S. Tivanov, A.M. Saad, Cu_2ZnSnS_4 thin films by sulfurization in melted sulfur, *Materials Letters* (2018), doi: https://doi.org/10.1016/j.matlet.2018.03.035

Cu_2ZnSnS_4 thin films by sulfurization in melted sulfur

S.A. Bashkirov[1*], U.S. Hekkel[1], M.S. Tivanov[2], A.M. Saad[3]

[1]Scientific-Practical Materials Research Centre of NAS of Belarus, Minsk, 220072, Belarus

[2] Belarusian State University, Nezavisimosti av. 4, 220030 Minsk, Belarus

[3] Al-Balqa Applied University, PO Box 4545, Amman 11953, Jordan

*Corresponding author's e-mail: sp-box@yandex.ru

Abstract

Cu_2ZnSnS_4 (CZTS) thin films were synthesized by sulfurization of subsequently electrochemically deposited Cu/Sn/Zn metal precursors on Mo foil substrates in melted sulfur on air at the temperature of 440 °C close to the sulfur boiling point for 1 hour. The films contain only CZTS phase with lattice parameters $a = 5.422 \pm 0.002$ Å and $c = 10.811 \pm 0.006$ Å and components at. % ratio: Cu/(Sn+Zn) = 1.05, Zn/Sn = 1.22, (Cu+Sn+Zn)/S = 0.93. The film surface is densely packed without cracks or pinholes. The obtained results show the practical ability to obtain CZTS thin films by a novel technically simple and low-cost liquid-based process.

Keywords: Cu_2ZnSnS_4; CZTS; thin films; electrochemical deposition; sulfurization; liquid-based process.

1. INTRODUCTION

Recent years Cu_2ZnSnS_4 (CZTS) thin films attract increasing attention as a promising material for the light absorbing layers of third generation solar cells. CZTS is believed to substitute currently implemented $Cu(In,Ga)Se_2$ (CIGS) materials that contain rare metals (In, Ga) limiting their wide use [1-3]. The CZTS possess *p*-type conductivity, a high absorption coefficient of about 10^4 cm^{-1} in the visible spectral region, the band gap of 1.5 eV being close to the optimum value for photovoltaic conversion of sunlight (1.35 eV) and, unlike CIGS, it contains only low-cost earth abundant components. The current photovoltaic conversion efficiency record for the CZTS-based solar cells is 11 % [4] and for the CZTSSe-based cells it is 12.6 % [5].

The convenient way to obtain CZTS thin films is sulfurization of Cu-Sn-Zn metallic precursors. The precursors can be deposited by various vacuum and non-vacuum methods, simultaneously or subsequently [6]. Electrochemical subsequent deposition of the metal layers appears to be the most suitable method for precursor deposition due to its technical simplicity, low cost and ability to control the precursor composition precisely by controlling the deposition time and current density for each metal layer. The efficiency record for CZTS-based solar cells obtained from electrochemically deposited precursors is 8% [7].

The most commonly used process for metal precursors sulfurization is thermal treatment in sulfur vapor or sulfur-containing chemically passive gas (Ar, N_2 etc.). However, this approach raises a number of problems, such as the formation of volatile binary phases (SnS) that are blown out of the film destroying stoichiometry, as well as technical complication caused by using the gaseous media. On contrary, sulfurization via the annealing in melted sulfur may solve the problems mentioned above. It does not require special equipment for working with gas media and can proceed on air. Moreover, the liquid media may inhibit the tin loss caused by evaporation of SnS. Despite the obvious advantages of the liquid phase sulfurization to form CZTS thin films, this process has not been presented in the current literature yet. In this paper, we report on the first results showing the practical ability to obtain single phase CZTS thin films by sulfurization of the electrochemically deposited metal precursors in melted sulfur on air.

2. EXPERIMENTAL DETAILS

Flexible 0.05 mm thick molybdenum foil substrates were mechanically polished, cleaned with ethanol, rinsed with deionized water. The metal precursors were deposited in the subsequence of layers as Cu/Sn/Zn by electrochemical deposition in the two-electrode cell in galvanostatic mode. The plates of high purity (99.999%) copper, tin, and zinc were used as anodes for the respective metal layers deposition. The regimes of electrochemical deposition (current density and time) were applied in order to obtain total Cu/Sn/Zn thickness of 1 μm that is expected to result in approximately 2 μm CZTS film. The electrolytes were prepared basing on the sulfates solutions of the respective metals. Each metal layer was polished with industrial polishing past (K2 Ultra cut, Poland) and cleaned with acetone to improve the surface quality. The metal ratio was primarily controlled by weighing samples on analytical scales after each layer deposition. Between the electrodeposition steps and before the sulfurization, the samples were kept in ethanol in order to avoid metal oxidation on air.

The sulfurization was conducted in melted sulfur on air near the boiling point. Sulfur was placed into open quartz tube and heated to the melting point (113 °C). The precursors were put into the sulfur after the complete melting. Then the sulfur was heated to the temperature of 440 °C close to the boiling point with the heating rate of 30 °C / min and kept at this temperature for 1 hour. After that, the samples were replaced form sulfur liquid and naturally cooled.

The phase composition of the materials was studied using x-ray diffractometer Ultima IV (Rigaku) with the $CuK_{\alpha 1}$ radiation (λ = 1.5406 Å). To confirm the phase analysis of the materials, room-temperature Raman measurements using Nanofinder HE (LOTIS TII) confocal Raman spectrometer proceeded with a spectral resolution better than 3 cm^{-1}. The Raman spectra were excited with a solid laser emitting at a wavelength of 532 nm with an optical power of 0.2, 0.6, 1.6, and 2 mW. The diameter of the laser beam at the sample surface was 0.6–0.7 μm. The surface morphology of CZTS films was studied by scanning electron microscopy (SEM) using LEO-1455VP Electron Microscope (Carl Zeiss) with Ronteg Spectrometer to determine the chemical composition of the films by energy dispersive X-ray microanalysis (EDX).

3. RESULTS AND DISCUSSION

Typical XRD pattern of the CZTS thin films obtained by sulfurization in melted sulfur is presented in Fig. 1.

According to the results, the obtained films are single-phase and show reflexes only from the CZTS film (tetragonal, space group I-42m) and the substrate material Mo (cubic, space group Im-3m). The reflexes intensity distribution corresponds to the polycrystalline nature of the films without pronounced preferred orientation. The lattice parameters for CZTS phase are $a = 5.422 \pm 0.002$ Å and $c = 10.811 \pm 0.006$ Å, slightly lower than the bulk material data ($a = 5.4353$ Å and $c = 10.8464$ Å in [8]).

As sphalerite ZnS (cubic, space group F-43m) has reflexes overlapping with CZTS and, thus, may not be seen in XRD patterns, Raman scattering measurements were carried out to confirm the phase composition. Typical Raman spectrum of the CZTS film is presented in Fig. 2.

Raman spectrum shows peaks at 289 cm^{-1}, 338 cm^{-1} and 351 cm^{-1} assigned by many authors as the characteristic peaks for CZTS [8-11]. The spectrum does not contain any peaks form side phases and, thus, confirms the XRD data proving single-phase composition of the films. It should be noted that in some cases ZnS Raman peaks may overlap with the CZTS peaks. However, the intensity distribution shows that ZnS is not presented in the film composition or its amount is negligible to be identified by Raman measurements.

According to the EDX measurements, the at. % ratio of the CZTS components is Cu/(Sn+Zn) = 1.05, Zn/Sn = 1.22 and (Cu+Sn+Zn)/S = 0.93 indicating the partial substitution of Sn by Zn. It was shown in a number of works (summarized in [12]) that Zn enrichment up to

Zn/Sn = 1.25 does not lead to the formation of any secondary phases. Moreover, the solar cells based on Zn-rich films with the Zn/Sn ratio of 1.2-1.25 demonstrates enhanced efficiency comparing to the films with stoichiometric composition [12]. Generally, binary sulfide phase can influence substantially on optical properties of CZTS [13]. Thus, the further optimization of the CZTS formation process will be related to the correction of the chemical composition in order to avoid the presence of undesirable secondary phases.

Typical SEM image of the CZTS film surface is presented in Fig. 3. The film surface is relatively smooth and densely packed without cracks or pinholes. We observed small areas of inhomogeneity with the highly developed surface (light regions on SEM image, Fig. 3) which composition, according to EDX, can be identified as CuS. However, the amount of these inhomogeneities is so small that they are not detected by phase analysis.

4. CONCLUSIONS

The results showed that sulfurization of subsequently deposited Cu/Sn/Zn metal precursors on Mo foil substrate in liquid sulfur on air near the boiling point leads to the formation of the CZTS thin films confirmed by XRD and Raman measurements. The CZTS crystallized in tetragonal structure with lattice parameters a = 5.422 ± 0.002 Å and c = 10.811 ± 0.006 Å. The films show component at. % ratio Cu/(Sn+Zn) = 1.05, Zn/Sn = 1.22, (Cu+Zn+Sn)/S = 0.93. According to SEM, the films are densely packed without cracks or pinholes.

The further research will focus on optimization of the process parameters (temperature, time, precursor thickness) in order to produce high-efficient solar cells basing on low cost and technically simple liquid-processing methods.

ACKNOWLEDGEMENTS

Funding: This study was supported by the Belarusian Republican Foundation for Fundamental Research (F17RM-089) and by the Belarusian State Programme for Research «Physical material science, new materials and technologies» (MATTECH 1.06).

REFERENCES

[1] K. Ramasamy, M.A. Malik, P. O'Brien, Routes to copper zinc tin sulfide Cu_2ZnSnS_4 a potential material for solar cells, Chem. Commun. 48 (2012) 5703-5714.

[2] Ch. Platzer-Björkman, Kesterite compound semiconductors for thin film solar cells, Current Opinion in Green and Sustainable Chemistry 4 (2017) 84-90.

[3] H. Katagiri, K. Jimbo, Fabrication of earth-abundant CZTS thin film solar cells, 23rd International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD) (2016) 54-55.

[4] K. Sun, C. Yan, F. Liu, J. Huang, F. Zhou, J.A. Stride, M. Green, X. Hao, Over 9% efficient kesterite Cu_2ZnSnS_4 solar cell fabricated by using $Zn_{1-x}Cd_xS$ Buffer Layer, Adv. Energy Mater. 6 (2016) 1600049.

[5] 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) 1301465-1301465.

[6] J. Shulin, Y. Changhui, Cu_2ZnSnS_4 as a new solar cell material: the history and the future, Reviews in Advanced Sciences and Engineering 1 (2012) 42-58.

[7] F. Jiang, S. Ikeda, T. Harada, M. Matsumura, Pure sulfide Cu_2ZnSnS_4, thin film solar cells fabricated by preheating an electrodeposited metallic stack, Adv. Energy Mater. 4 (2014) 1301381

[8] A. Lafond, L. Choubrac, C. Guillot-Deudon, P. Fertey, M. Evain, S. Jobic, X-ray resonant single-crystal diffraction technique, a powerful tool to investigate the kesterite structure of the photovoltaic Cu_2ZnSnS_4 compound, Acta. Crystallogr. B Struct. Sci. Cryst. Eng. Mater. 70 (2014) 390-394.

[9] M. Altosaar, J. Raudoja, K. Timmo, M. Danilson, M. Grossberg, J. Krustok, E. Mellikov, $Cu_2Zn_{1-x}Cd_xSn(Se_{1-y}S_y)_4$ solid solutions as absorber materials for solar cells, Phys. Stat. Sol. 1 (2008) 167–170.

[10] P.A. Fernandes, P.M.P. Salome, A.F. Gunha, Growth and Raman scattering characterization of Cu_2ZnSnS_4 thin films, Thin Solid Films 517 (2008) 2519–2523.

[11] 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, Energy Mater. Sol. Cells 95 (2011) 3216–3221.

[12] Chen, S., Walsh, A., Gong, X.-G. and Wei, S.-H. (2013), Classification of Lattice Defects in the Kesterite Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ Earth-Abundant Solar Cell Absorbers. Adv. Mater., 25: 1522–1539.

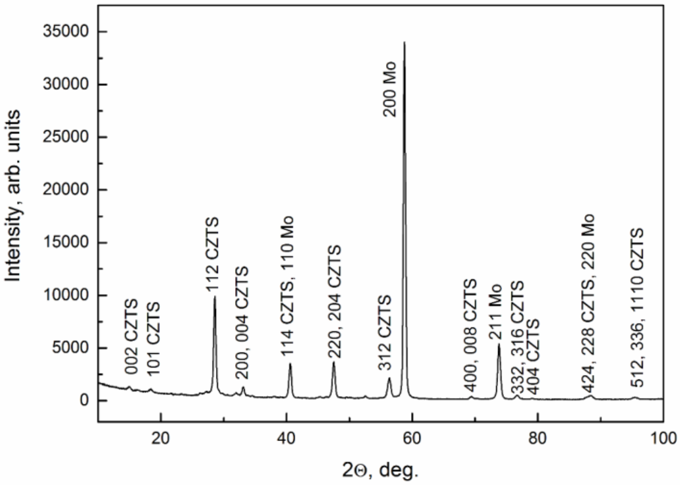
[13] D. Mamedov, M. Klopov, S. Zh. Karazhanov, Influence of Cu_2S, SnS and $Cu_2ZnSnSe_4$ on optical properties of Cu_2ZnSnS_4, Mater. Lett. 202 (2017) 70-72.

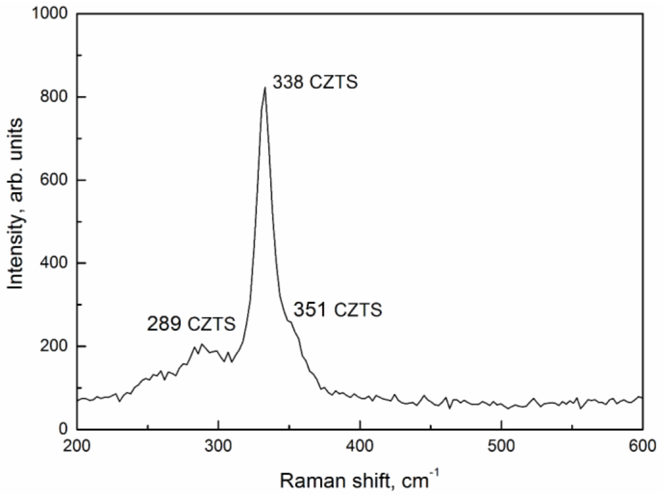
Figure captions

Figure 1. XRD pattern for the CZTS thin film on Mo foil substrate.

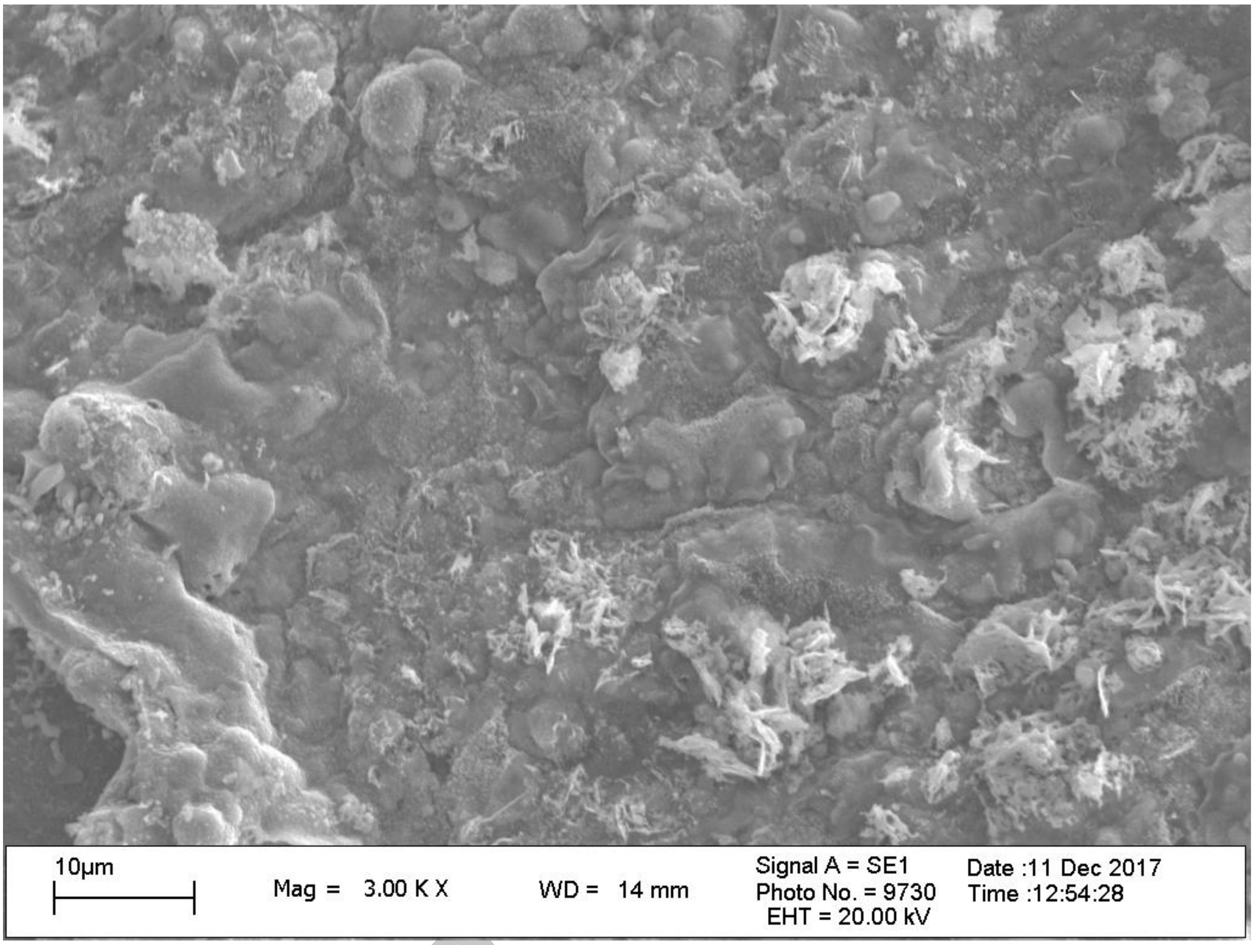
Figure 2. Raman spectrum for the CZTS thin film

Figure 3. SEM surface image of the CZTS thin films.


Intensity, arb. units
35000
30000
25000
20000
15000
10000
5000
0
20
40
60
80
100
2Θ, deg.
002 CZTS
101 CZTS
112 CZTS
200, 004 CZTS
114 CZTS, 110 Mo
220, 204 CZTS
312 CZTS
200 Mo
400, 008 CZTS
211 Mo
332, 316 CZTS
404 CZTS
424, 228 CZTS, 220 Mo
512, 336, 1110 CZTS



338 CZTS
351 CZTS
289 CZTS
Intensity, arb. units
Raman shift, cm^{-1}
0
200
400
600
800
1000
200
300
400
500
600


10µm
Mag = 3.00 K X
WD = 14 mm
Signal A = SE1
Photo No. = 9730
EHT = 20.00 kV
Date :11 Dec 2017
Time :12:54:28

Highlights

1. We obtained Cu_2ZnSnS_4 thin films by sulfurization of Cu/Sn/Zn precursors in melted sulfur.

2. Flexible Mo foil with a thickness of 0.05 mm was used as the substrate.

3. The films phase composition is confirmed by X-Ray diffraction and Raman scattering.