VNU Journal of Science: Mathematics – Physics, Vol. 34, No. 3 (2018) 55-60

VNU Journal of Science: Mathematics - Physics

Journal homepage: https://js.vnu.edu.vn/MaP

Effect of Temperature on Cu_2ZnSnS_4 Nanomaterial Synthesized by Hydrothermal Approach

Pham Thi Hong[1], Nguyen Viet Tuyen[1,*], Tran Thi Ha[2], Ho Khac Hieu[3]

[1]*Faculty of Physics, VNU University of science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam*

[2]*Faculty of Basis Sciences, Hanoi University of Mining and Geology, Duc Thang, Tu Liem, Hanoi, Vietnam*

[3]*Institute of Research and Development, Duy Tan University, 03 Quang Trung, Hai Chau, Da Nang, Vietnam*

Received 26 July 2018
Revised 10 September 2018; Accepted 11 September 2018

Abstract: Cu_2ZnSnS_4 (CZTS) is a p-type semiconductor with high absorption coefficient and direct bandgap from 1 to 1.5 eV, which is ideal for making absorber layer for solar cell. However, it is difficult to get single phase of CZTS due to the competitive formation of binary and ternary secondary phases. In this paper, we prepared CZTS nanoparticles by hydrothermal method and investigate the influence of hydrothermal temperature on the product. Raman scattering, X-ray diffraction, scanning electron microcopy, energy dispersive X-ray spectroscopy and diffusion reflective measurement were applied to characterize the products. The products are high quality nanocrystals of kesterite phase with uniform size which is applicable for solar absorber layer fabrication.

Keywords: Cu_2ZnSnS_4, hydrothermal, kesterite, Raman.

1. Introduction

CZTS material is a p-type semiconductor and with direct band gap of around 1.5 eV which is an ideal value for absorber layer [1, 2]. Besides, CZTS material composes of four elements: copper, zinc, tin and sulfur, which are all non-toxic elements and available abundantly in the earth's crust, so CZTS can help to reduce cost of solar cells in the market. Solar cells based on CZTS light absorber layer is a promising candidate with the hope of replacing CdTe, CIS, CIGS in the near future [3].

There are various methods for manufacturing CZTS material, which can be categorized into physical (vacuum) methods and chemical (non-vacuum) methods... In fact, most available methods for synthesis of CZTS require two or more steps, where sulfurization process of the as-prepared materials

*Corresponding author. Tel.: 84-977128393.
Email: nguyenviettuyen@hus.edu.vn

https//doi.org/ 10.25073/2588-1124/vnumap.4280

in sulfur rich media such as S or H_2S… is applied to enhance quality of the CZTS layer [4-6]. The drawback of annealing process is long time and especially harm to environment. So single-step method is preferred for fabrication of CZTS. In phase diagram of ternary system Cu_2S, ZnS, and SnS_2, CZTS exists only in very small area, implying that binary and ternary secondary phases such as Cu_2S, ZnS, Cu_2SnS_3, Cu_3SnS_4… are much easier to form than CZTS [7, 8]. Hence, study to control the formation of secondary phases and residues is very important. In this report, we fabricate CZTS nanoparticles by hydrothermal method, which is cost effective, environment friendly, and easily to upscale for mass production.

2. Experiment

CZTS nanopowder was fabricated by hydrothermal method because this method is simple and no further annealing process is required. Starting materials were 0.2M Copper (II) nitrate $Cu(NO_3)_2$, 0.1 M Zinc nitrate $Zn(NO_3)_2$, 0.1M Tin (II) chloride $SnCl_4$, 0.4 M Thiourea

$C_2H_5(NO_2)$. Equal volumes of metal salts were mixed well by magnetic stirrer followed by adding dropwise of thiourea of equal molar. The solution was continuously stirred for two more hours and then transferred to a Teflon container for hydrothermal reaction. The obtained products were cleaned with distilled water and ethanol by centrifugation at 5000 rpm for at least 5 cycles. The products were then dried at 65°C during 3h to obtain final products in form of black powder. Three samples were prepared by hydrothermal at different temperatures 120, 180 and 240 ^oC while hydrothermal time was kept constant in 24h.

The crystal structure characterization was studied using X-ray diffractometer (XRD) SIEMES D5005, Bruker, Germany. Raman spectrum measurement was collected using LabRam HR800 Raman spectroscopy from Horiba Jobin Yvon. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were performed on Nova nano SEM 450 FEI to study the surface morphology and elemental composition of the product. Diffuse reflectance spectra of the samples were measured with Cary 5000 spectrometer from Varian – USA.

3. Results and discussion

XRD patterns of the samples are shown in Fig. 1. Prominent diffraction peaks, which could be observed at 28.4°, 33.9°, 47.4° and 56.3°, match well with the JCPS card No. 26-0575 of kesterite CZTS. Besides the peaks due to reflection from (112), (200), (220) and (312) planes of CZTS kesterite, weaker peaks corresponding to CuS appear in the patterns of samples prepared at 120 and 180^{o}C. It is well known that copper sulfide is a detrimental secondary phase of CZTS, which increases the shunt current, and lower substantially the efficiency of CZTS solar cells. One key problem in dealing with CZTS solar cell is to suppress the formation of secondary phases, especially secondary phases of high conductivity like copper tin sulfur or copper sulfur [9].

The XRD patterns likely show that hydrothermal reaction at 240^{o}C helps to convert the precursors to CZTS of single phase, which is hopefully applicable for solar cell fabrication.

Higher hydrothermal temperature also better the crystal quality of the CZTS nanoparticles as demonstrated by the smaller full width at half maximum of the diffraction peak. However, it also should be noted that, many secondary phases of CZTS share the same diffraction peaks with the main phase due to similar scattering cross section area. In order to confirm the purity of the nanoproduct prepared at 240 ^{o}C, it is necessary to cross check phase purity by Raman measurement.

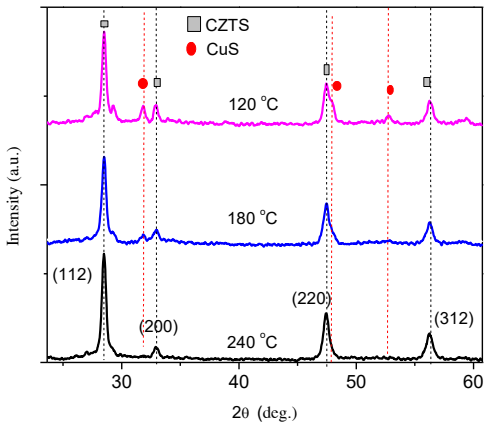

Fig. 1. XRD pattern of CZTS synthesized at 120℃, 180℃ and 240℃ in 24h.

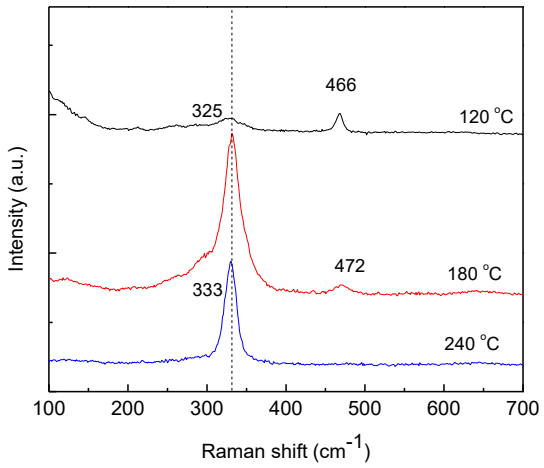

Fig. 2. Raman spectra of samples prepared at 120, 180 and 240 °C in 24 h.

Fig. 2 shows Raman spectra of the samples prepared at different temperatures. Unlike XRD pattern, Raman spectra of CZTS is resolved clearly from those of binary and ternary secondary phase such as: $Cu_{1-x}S$, Cu_2SnS_3…[10]

Raman spectra of samples prepared at 120°C in 6h, shown in Fig. 2, are composed of a strong peak located at around 466 cm^{-1} which can be assigned to $Cu_{2-x}S$. A weaker and broader peak at 325 cm^{-1} could be convolutions of different phases such as: Cu_2SnS_3, Cu_3SnS_4, CZTS… At higher hydrothermal temperature, a strong A_1 peak at 330 cm^{-1} of CZTS could be observed clearly in addition to a small peak of $Cu_{2-x}S$. The results demonstrate that at 180 °C, most of the precursors were converted into CZTS of kesterite structure. However the sample still contains of $Cu_{2-x}S$ and not excluded some other secondary phases at low concentration because the A1 peak characterized by CZTS is still quite broad. The purity of the sample prepared 240 °C is demonstrated by the sharp A1 peak of CZTS at 333 cm^{-1}. No other peaks of secondary phases could be found in the spectra.

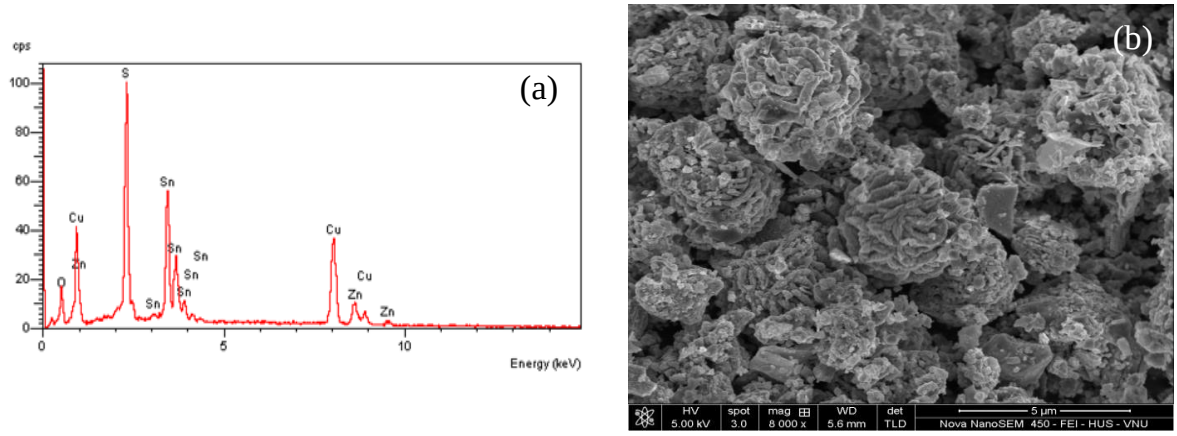

Fig. 3. EDS spectrum of CZTS nanopowder (a) and SEM image of CZTS nanoparticles (b) prepared at 240 ^{o}C in 24h.

Energy dispersive spectroscopy, shown in Fig. 3a, was applied to verify the purity as well as the stoichiometry of the CZTS nanoproduct prepared at 240 ^{o}C. The quantitative measurement shows that percentage of Cu:Zn:Sn:S element was closed to stoichiometry ratio 2:1:1:4. No clear trace of carbon was detected in the sample. It is important to get a pure CZTS product without carbon residue because carbon is reported to increase the series resistance of solar cell and results in detachment of CZTS absorber layer from substrates [11- 13]. The results show that the as-prepared CZTS powder met the criteria for making absorber layer for solar cell.

SEM image of the sample prepared at 240 ^{o}C in 24h (Fig. 3b) shows that particle size is relatively uniform, which aggregates together to form large cluster with average size of about 500 nm. The uniformity of the nanoparticles demonstrates the potential for making ink to fabricate absorber layer thin films.

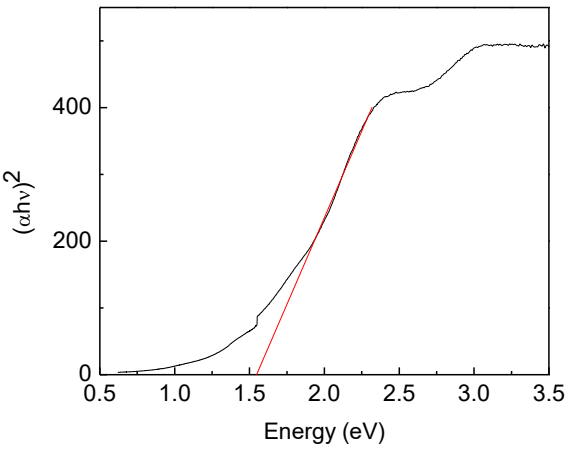

Fig 4. Absorption spectrometry of CZTS at 240℃ in 24h.

Fig. 4 shows the plot of $(\alpha h\nu)^2$ *vs.* $h\nu$ of CZTS nanoparticles prepared at 240 ^oC. The band gap of the nanoproduct was estimated by extrapolating the linear part of the plot to the horizontal axis. The result shows that the band gap of CZTS is 1.52 eV, which is consistent with bandgap reported for CZTS prepared by solution methods. This value is also closed to the optimum required bandgap for solar absorber [14- 16].

4. Conclusion

In this study, we have investigated the effect of temperature on CZTS nanoparticles prepared by hydrothermal method. It was found that temperature of 240 ^oC is required for the formation of single phase CZTS nanoparticles of uniform size and shape. The optical bandgap of 1.52 eV was estimated from diffusion reflective measurement. Together with the low cost of precursors, the processing route reported in this paper is very potential for fabricating CZTS ink towards commercial solar cell product.

Acknowledgements

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2017.351.

References

[1] C. Malerba, F. Biccari, C.L.A. Ricardo, M. Valentini, R. Chierchia, M. Müller, A. Santoni, E. Esposito, P. Mangiapane, P. Scardi, A. Mittiga, CZTS stoichiometry effects on the band gap energy, J.Alloy.Compd582 (2014), 528-534.

[2] N. Ali, R. Ahmed, B.-U.-Haq, and A. Shaari, Advances in CZTS thin films and nanostructured, Opto-Electronics Review (2015), 137-142.

[3] S. Zhuka, A. Kushwahaa, T.K.S. Wongb, S.M.-Panaha, A. Smirnovd, G.K. Dalapatia, Critical review on sputter-deposited Cu_2ZnSnS_4 (CZTS) based thin film photovoltaic technology focusing on device architecture and absorber quality on the solar cells performance, Sol. Energy Mater. Sol. Cells 171 (2017), 239-252.

[4] J. Zhong, Z. Xia, M. Luo, J. Zhao, J. Chen, L. Wang, X. Liu, D.-J. Xue, Y.-B. Cheng, H. Song, and J. Tang, Sulfurization induced surface constitution and its correlation to the performance of solution-processed $Cu_2ZnSn(S,Se)_4$ solar cells, Sci Rep (2014), 6288(1)-6288(9).

[5] C.-L. Wang, C.-C. Wang, B. Reeja-Jayan and A. Manthiram, Low-cost, $Mo(S,Se)_2$-free superstrate-type solar cells fabricated with tunable band gap $Cu_2ZnSn(S_{1-x}Se_x)_4$nanocrystal-based inks and the effect of sulfurization, RSC Advances (2013), 19946-19951.

[6] M.P.Suryawanshi, U.V.Ghorpade, U.P.Suryawanshi, M. He, J. Kim, M.G. Gang, P.S.Patil, A.V.Moholkar, J.H. Yun, and J.H. Kim, Aqueous-Solution-Processed$Cu_2ZnSn(S,Se)_4$Thin-Film Solar Cells via an Improved Successive Ion-Layer-Adsorption-Reaction Sequence, ACS Omega 2 (2017), 9211-9220.

[7] I.D. Olekseyuk, I.V. Dudchak, L.V.Piskach, Phase equilibria in the Cu_2S-ZnS-SnS_2 system, J.Alloy.Compd 368 (2003),135-143.

[8] S. Das, R.M. Krishna, S. Ma, K.C. Mandal, Single phase polycrystalline Cu_2ZnSnS_4 grown by vertical gradient freeze technique, J.Cryst. Growth 381 (2013), 148-152.

[9] S. Siebentritt, S. Schorr, Kesterites-a challenging material for solar cells, Prog.Photovoltaics Res. Appl.20 (2012), 512-519.

[10] P.A. Fernandes, P.M.P. Salomé, A.F. da Cunha, Study of polycrystalline $Cu_2ZnSnSe_4$ films by Raman scattering, J.Alloy.Compd 509 (2011), 7600-7606.

[11] G.M. Ilari, C.M. Fella, C.Ziegler, A.R. Uhl, Y.E. Romanyukand, A.N. Tiwari, $Cu_2ZnSnSe_4$ solar cell absorbers spin-coated from amine-containing ether solutions, Sol. Energy Mater. Sol. Cells 104 (2012), 125-130.

[12] E.J. Lee, S.J. Park, J.W. Cho, J.H. Gwak, M.K. Oh and B.K. Min, Nearly carbon-free printable CIGS thin films for solar cell applications, Sol. Energy Mater. Sol. Cells 95 (2011), 2928-2932.

[13] S.J. Ahn, C.W. Kim, J.H. Yun, J.H. Gwak, S.H. Jeong,B.H. Ryu and K.H. Yoon, $CuInSe_2$ (CIS) Thin film solar cells by direct coating and selenization of solution precursors, J. Phys. Chem. C 114 (2010) 8108–8113.

[14] W.C. Liu, B.L. Guo, X.S. Wu, F.M. Zhang, C.L. Mak and K.H. Wong, Facile hydrothermal synthesis of hydrotropic Cu_2ZnSnS_4nanocrystal quantum dots: band gap engineering and phonon confinement effect, J. Mater. Chem A1 (2013), 3182-3186.

[15] K. Woo, Y. Kim and J. Moon, A non-toxic, solution-prcessed, earth abundant absorbing layer for thin-film solar cells, Energy Environ. Sci. 5 (2012), 5340-5345.

[16] S. Chen, J.-H.Yang, X.G. Gong, A. Walsh, amd S.-H.Wei, Intrinsic point defect and complexes in the quaternary kesterite semiconductor Cu_2ZnSnS_4, Phys. Rev. B 82 (2010), 245204-245204.