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Characteristics of Cu_2ZnSnS_4 thin film prepared by calcination and sulfurizing of metal (Cu, Zn, Sn)-ethanolamine precursor complexed from metal (Cu, Zn, Sn)-hydrate

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Abstract

Cu_2ZnSnS_4 (CZTS) thin film was synthesized from Cu-Zn-Sn precursor which was prepared from (Cu,Zn,Sn)-ethanolamine complex compound solution using drop coating technique. Ethanolamine used as solvent and complexant simultaneously. The CZT precursor showed Cu_xZn_y and Cu_xSn_y binary compound films without Zn_xSn_y binary or metal oxide compound after drying process. The CZTS thin film was successfully formed as copper poor and zinc rich with chemical composition ratio after being sulfurization at 550 °C for 120 minutes under Ar + H_2S (5%) atmosphere Cu/(Zn+Sn) = 0.83, Zn/Sn = 1.76, and S/metal = 1.08) without presence of C, O, and Cl in the thin film as impurities. Optical properties of CZTS thin film were direct band gap of 1.52 eV with absorption coefficient more than 10^5 cm^{-1} and electrical properties were exhibited by p-type semiconductor with mobility and resistivity of 7.64 cm^2/Vs, 3.78 Ωcm respectively.

Keyword: CZTS, ethanolamine, complex compounds, chemical synthesis.

1. Introduction

Almost every non-vacuum process in making CZTS absorber layer uses precipitation principle between metal salts (copper, zinc and tin) with thiourea or thioacetamide as sulfur source for starting solution [1,2] or using other starting materials containing sulfur, such as dithiocarbonates [3] or dithiocarbamate [4]. Among them, only electrochemical deposition which is not through the metal sulfide precipitation pathway. However, this technique still uses special apparatus such as computer-controlled potentiostat for deposited CZT precursor [5].

Usually, water, methanol and alcohol derived (i.e. ethylene glycol, 2-methoxyethanol) are used as solvent in colloidal based deposition [1,6,7]. On the other hand Zn^{2+} with OH^- molecules in water or alcohol will easily form $Zn(OH)_2$ particles as precipitation due to the very low solubility product constant (K_{sp}) of $Zn(OH)_2$, that is about 3 x 10^{-17}. The $Zn(OH)_2$ particle is difficult to attached onto the substrate and difficult to get its homogeneous composition. To prevent this problem, we changed the medium from colloidal into real solution based that used ethanolamine as solvent and complexant simultaneously, since ethanolamine could solve copper, zinc, and tin salts and could form some stable complex compound among them. Through this novel deposition technique, deposition process will be easier and more homogenous without any precipitation.

In this paper, we reported a novel, facile, doesnt requiring special equipment (i.e. computer-controlled potentiostat, Teflon-lined stainless steel autoclave [5,8]), low cost, and non-toxic process to synthesize the CZTS absorber layer which is prepared from metals (copper, zinc, and tin) ethanolamine complex compound as CZT precursor, and continued with the sulfurization process for crystallization. The CZTS structure, morphology, composition, optical properties and electrical properties that prepared with this new technique were also reported in this paper.

2. Experimental Detail

Complex compound metal-ethanolamine was consist of Cu 0.0176 M, Zn 0.0120 M, and Sn 0.0100 M which prepared from copper (II) acetate monohydrate (1.0981 g), zinc acetate dehydrate (0.8780 g), and tin (II) chloride dihydrate (0.5557 g). Cu, Zn, and Sn salts were dissolved in 20 mL ethanolamine respectively using ultrasonic apparatus, mix all of the solutions and added ethanol 50% until volume of solution was 100 mL. The CZT precursor solution has dark blue solution appearance. The CZT precursor solution was deposited on 1.25 cm x 1.25 cm soda lime glass (SLG) with 0.05 mL of CZT precursor solution using drop coating technique and then drying in the air at 200°C for 10 minutes until black shinny color and finally CZTS thin film obtained was sulfurized by sulfurization in tubular furnace at 550°C for 120 minutes under Ar + H_2S (5%) atmosphere. After the heat treatment, the sample was cooled to room temperature under natural condition.

The morphology and composition of the deposited film was characterized using Hitachi S4800 scanning electron microscope (SEM). The chemical composition of the thin films was analyzed by energy dispersive spectrometry (EDS) HORIBA. The phase of crystallographic information was obtained from the X-ray diffraction (XRD) patterns using PANalitycal XRD apparatus from 2θ = 10° - 65°. The spectra absorption was recorded in the wavelength range 300 - 2000 nm using Varian Carry 5000 UV-Vis-NIR Spectrophotometer. The spectra from organic phase information was obtained from Fourier transform infra-red (FTIR) Perkin Elmer C86199. Electrical properties were determined from Hall-Effect using HMS-3000 Ecopia Apparatus at 0.1 µA.

3. Result and discussion

The composition of CZT precursor solution was made for copper poor and zinc rich (Cu/(Zn+Sn) = 0.80 and Zn/Sn = 1.20), since this composition has good efficiency [9]. In this experiment, we used ethanolamine as complexant and solvent simultaneously, however, since ethanolamine has high surface tension (81.61 dyne/cm) which makes ethanolamine difficult to evaporate. In order to reduce the ethanolamine surface tension we added ethanol 50% into (Cu,Zn,Sn)-ethanolamine complex compound solution until 100 mL. In this condition, zinc with hydroxide in water or ethanol cannot form $Zn(OH)_2$ particle anymore due to the formation of complex compound between zinc, ethanolamine and other metals in the solution [10,11,12], therefore, zinc atom cannot make a bond with hydroxide from water or ethanol. That is why after adding some ethanol 50%, the solution remains clear without any precipitation.

However, since this method through complex reaction pathway, it can be many probability of reaction, in this report we proposed a reaction pathway for this complex reaction. Generally the formation reaction for complex compound between copper, zinc, and tin with ethanolamine is described by the following reaction:

$$Cu^{2+} + Zn^{2+} + Sn^{2+} + x\ ETA \rightarrow [(Cu,Zn,Sn)(ETA)_x]^y$$

Since the ethanolamine is an organic compound which has amine molecule, it can be decomposed into carbon dioxide, water vapor, and ammonia if getting heat treatment over 170ºC (ethanolamine boiling point), even after being formed metals-ethanolamine complex compound, it still can be decomposed under 200oC [13], therefore, in drying process the CZT precursor released some gases such as carbon dioxide, water vapor, and ammonia. In other hand, since among copper with zinc and tin there is a metal bonding which is stronger than covalent bonding between metal with oxide or amine in ethanolamine, therefore, when heating treatment process, the Cu_xZn_y and Cu_xSn_y binary compound was formed and deposited onto substrate. General reaction for this process described by the following reaction:

$$[(Cu,Zn,Sn)(ETA)_x]^y \rightarrow CuZn + CuSn + a\,CO_2 + b\,H_2O + c\,NH_3 + d\,Cl$$

In sulfurization, Cu_xZn_y and $CuxSn_y$ which were made from drying process react with sulfur in the atmosphere and made CZTS compound. The formation reaction is described by following reaction:

$$CuZn + CuSn + 4S \rightarrow Cu_2ZnSnS_4$$

The XRD pattern which was obtained from CZT precursor before and after sulfurization was proved through assumption shown in Fig. 1. The XRD pattern of (a) CZT precursor exhibits only two peaks at 2θ: 43.33º and 50.41º, these peaks belong to intermetallic binary Cu_xZn_y and Cu_xSn_y compounds such as Cu_5Zn_8 (ICDD: 00-025-1228) and Cu_5Sn_6 (ICDD: 00-045-1488) without any evidence for Zn_xSn_y compound or even metal oxide from metal-ethanolamine residue, it means the CZT precursor was made as intermetallic binary Cu_xZn_y and Cu_xSn_y compounds (Cu_5Zn_8 and Cu_5Sn_6).

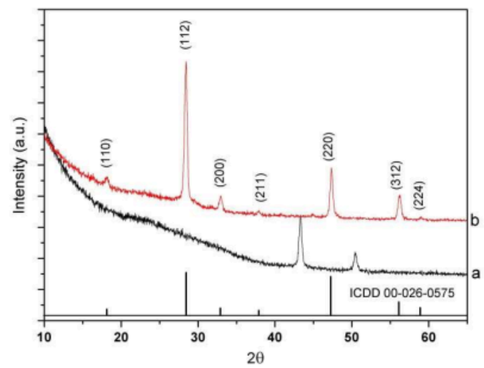

Fig. 1. XRD patterns of CZT precursor (a) before and (b) after sulfurization under Ar + H_2S (5%) at 550ºC for 120 min.

Compared with the after sulfurization process, there are seven peaks at 2θ: 18.22º, 28.45º, 32.95º, 37.93º, 47.35º, 56.26º, and 58.84º which can be indexed to (110), (112), (200), (211), (220), (312), and (224) these peaks belong to CZTS peaks (ICDD: 00-026-0575). It means the CZTS was formed in single phase.

Fig. 2. shows the representatives scanning electron microscopy (SEM), image of microsurfaces CZT precursor before (a) and after sulfurization process (b) also cross-section CZT precursor before (c) and after sulfurization process (d). Fig. 2a is microsurface for CZT precursor with small granular surface compared with Fig. 2b which becomes larger and more compact due to reaction during sulfurization as explained in sulfurization reaction, the sulfur in high temperature will react with each element due to enough energy to react with each element. However, during sulfurization few amounts of copper, zinc, and tin evaporated [14,3], it is concluded that the CZTS becomes thinner from the CZT precursor. As being seen at Fig. 2d, the CZTS has a thickness approximately 800 nm, packed, no porous, and homogenous formed.

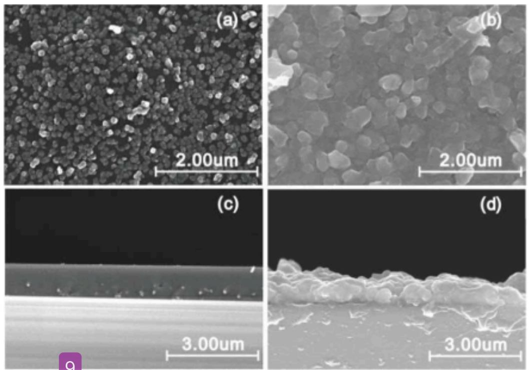

Fig. 2. SEM images of (a) CZT precursor before sulfurization, (b) CZTS, (c) CZT precursor cross-section before sulfurization, and (d) CZT cross-section after sulfurization.

The chemical composition of thin film was analyzed by energy dispersive X-ray spectroscopy (EDX) in the SEM apparatus and the results are shown in Fig. 3. Before sulfurization, the CZT precursor still has some organic impurities such as C, O, and Cl from anions (acetate and chloride) and ethanolamine as ligand. However, after sulfurization all impurities was removed due to high temperature and H_2S effect during sulfurization. Fig. 3. shows CZTS with Cu, Zn, Sn, and S peaks without organic impurities such as C, Cl, and O peaks.

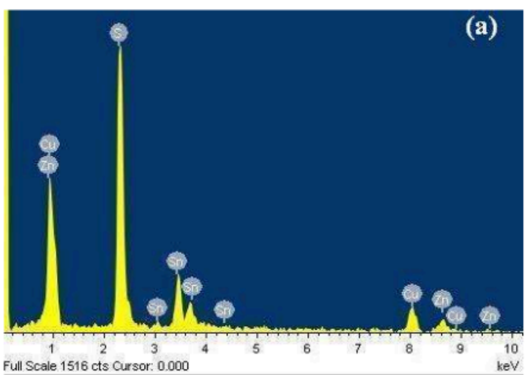

Fig. 3. EDX spectrums of CZTS after sulfurization under Ar + H_2S (5%) at 550°C for 120 min.

The impurities in the CZT precursor thin film such as C, O, and Cl could not identified by XRD due to those materials are in the organic form. However, the organic impurities could detected by fourier transform infra red (FTIR) either in (Cu,Zn,Sn)-ethanolamine solution or CZT precursor after drying. The (Cu,Zn,Sn)-ethanolamine solution provide a specific of FTIR spectrum for (Cu,Zn,Sn)-ethanolamine complex compound, after drying the transmittance of CZT precursor was shifted little bit to higher wavenumber and lower intensity than (Cu,Zn,Sn)-ethanolamine complex compound in almost every part, this phenomena due to there was coordination bonding between metal as main atom and ethanolamine as ligand, especially at oxygen and nitrogen atom. Moreover, due to some organic compounds was decomposed, particularly for hydro-carbon organic compound. This phenomena is indicated at wavenumber below 2000 1/cm. Fig. 4 shows FTIR spectrum for CZT precursor before and after drying.

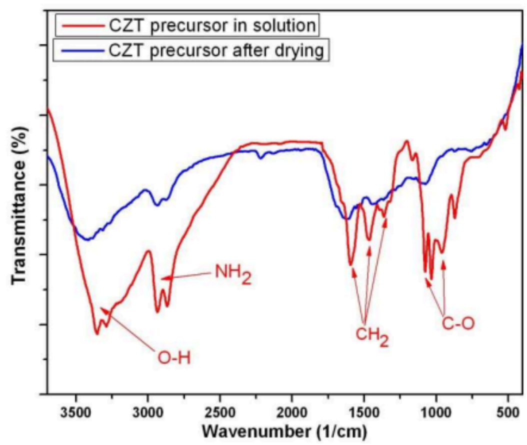

Fig. 4. FTIR spectrum for CZT precursor before and after drying.

Table 1 shows the composition of CZT precursor as solution, after drying and after sulfurization, the CZTS films was obtained from sulfurization at 550°C for 120 minutes under Ar + H_2S (5%) atmosphere.

Table 1. Chemical composition of CZT precursor in solution, after drying, and after sulfurization at 550°C for 120 minutes

Sample	Elements	Atomic Percent (%)	Zn/Sn	Cu/(Zn+Sn)	S/metal
CZT Solution	S	-			
	Cu	44.31	1.20	0.8	-
	Zn	30.15			
	Sn	25.54			
CZT After Drying	S	-			
	Cu	43.98	1.25	0.78	-
	Zn	31.10			
	Sn	24.92			
CZT After Sulfurization	S	51.81			
	Cu	21.80			
		45.25*			
	Zn	16.83	1.76	0.83	1.08
		34.93*			
	Sn	9.55			
		19.82*			

*Calculated by excluding sulfur atom

Chemical composition ratio between starting material as CZT solution and after drying as CZT precursor was just slightly different. It means in the thin film leaving only the metals whereas the organic compound was evaporated.

After sulfurization, the chemical composition was effected by temperature. Tin composition was decreased with increasing temperature due to tin was easily to evaporate compared copper and zinc as its form. As consequences, Zn/Sn ratio was increased significantly and by calculation for each element excluding sulfur, tin composition was decreased meanwhile copper and zinc composition as if increased compared drying step.

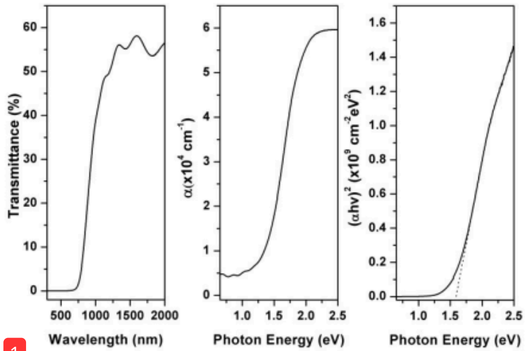

Fig 5. Optical properties of CZTS annealed at 550oC for 120 minutes under Ar + H_2S (5%) (a) Transmittance, (b) absorption coefficient, and (c) direct optical band gap

The optical properties of the CZTS films (i.e., transmittance and optical band gap) were measured by spectrophotometer apparatus and the result are shown in Fig. 5. The CZTS films have low transmittance in visible light (under 800 nm) and transmit more than 50% in the infrared light range (1200 nm to 2000 nm). The CZTS thin film has a direct band gap of 1.52 eV (Fig. 4c) and absorption coefficient more than 10^5 cm^{-1} in visible light (Fig. 5b).

The band gap energy and absorption coefficient was compared by several reports [1,5,7]. The CZTS thin film that was prepared from sulfurized (Cu,Zn,Sn)-ethanolamine complex compound can be applied as absorber layer in the thin film solar cells.

Table 2. Electrical properties of CZTS after sulfurization at 550°C for 120 minutes

Semiconductor type	Mobility (cm^2/Vs)	Resistivity (Ωcm)
p-type	7.64	3.78

Table 2. shows the electrical properties of CZTS thin film. The electrical properties were measured at room temperature using Hall-Effect apparatus and compared the result with another report.

Mobility for CZTS ranges in 6-30 cm^2/Vs and for resistivity ranges 0.1 - 5.7 Ωcm [15,16,17]. Both mobility and resistivity that we had been synthesized are still in range of mobility and resistivity of CZTS absorber layer for thin film solar cell application.

4. Conclusions

In this experiment, ethanolamine used as solvent and complexant simultaneously, since ethanolamine could solve copper, zinc, and tin salts and could form some stable complex compound among them. The CZTS thin film was synthesized by sulfurization of Cu-Zn-Sn precursor that was prepared from (Cu,Zn,Sn)-ethanolamine complex compound at 550°C for 120 minutes under Ar + H_2S (5%) atmosphere with single phase of CZTS as final result. The CZTS was formed from Cu_xZn_y and Cu_xSn_y (Cu_5Zn_8 and Cu_5Sn_6) binary compound as CZT precursor with final chemical compositions, copper poor and zinc rich with ratio Cu/(Zn+Sn) = 0.83, Zn/Sn =1.76, and S/metal = 1.08 without presence of C, O, and Cl in the thin film as impurities from anions (acetate and chloride) and ethanolamine as ligand. For optical properties there is direct band gap energy of 1.52 eV and low transmittance in visible light with an absorption coefficient 10^5 cm^{-1}. The electrical properties of this thin films are shown to be p-type semiconductor, mobility and resistivity of 7.64 cm^2/Vs, 3.78 Ωcm respectively. The CZTS thin film prepared using this method can be applied as absorber layer in thin film solar cells.

5. Acknowledgements

This study was supported by the Basic Science Research Program (2013R1A1A2013408) and Center for Inorganic Photovoltaic Materials (No.2012-0001170) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning

6. References

[1] Yuxiu Sun, Kai Zong, Huijuan Zheng, Hao Wang, Jingbing Liu, Hui Yan, Mankang Zhu, Materials Letter 92 (2013) 195-197.

[2] Seung Wook Shin, Jun Hee Han, Chan Yeok Park, Sae-Rok Kim, Yeon Chan Park, G.L. Agawane, A.V. Moholkar, Jae Ho Yun, Chae Hwan Jeong, Jeong Yong Lee, Jin Hyeok Kim. Journal of Alloy and Compound 541 (2012) 192-197.

[3] A. Fischereder, Alexander Schenk, Thomas Rath, Wernfried Haas, Sebastian Delbos, Corentin Gougaud, Negar Naghavi, Angelika Pateter, Robert Saf, Dorith Schenk, Michael Edler, Kathrin Bohnemann, Angelika Reichmann, Boril Chernev, Ferdinand Hofer, Gregor Trimmel, Chem. Mater. 22 (2010) 3399-3406.

[4] Michael Edler, Thomas Rath, Alexander Schenk, Achim Fischereder, Wernfried Haas, Matthias Edler, Boril Chernev, Birgit Kunert, Ferdinand Hofer, Roland Resel, Gregor Trimmel, Materials Chemistry and Physics 136 (2012) 582-588.

[5] K.V. Gurav, S.M. Pawar, Seung Wook Shin, M.P. Suryawanshi, G.L. Agawane, Applied Surface 283 (2013) 74-80.

[6] K.S. Swami, Anuj Kumar, Viresh Dutta, Energy Procedia 33 (2013) 198-202.

[7] T.K. Chaudhuri and Devendra Tiwari, Solar Energy Material & Solar Cells 101 (2012) 46-50.

[8] Yan-Li Zhou, Wen-Hui Zhou, Yan-Fang Du, Mei Li, Si-Xin Wu, Materials Letter 65 (2011) 1535-1537.

[9] T. Kobayashi, K. Jimbo, K. Tsuchida, S. Shinoda, T. Oyanagi, H. Katagiri, Jpn. J. Appl. Phys. 44 (2005) 783-787.

[10] A. Bhaw-Luximon, A. Jhurry D, S. Motala-Timol, Y. Lochee, Macromol. Symp. 231 (2006) 60–68.

[11] Jin Choo Woo, Agus Ismail, Se Jin Park, Woong Kim, Sungho Yoon Byoung Koun Min, Appl. Mater. Interfaces 5 (2013) 4162-4165.

[12] Nadia Z. Shaban, Alaa E. Ali, Mamdouh S. Masoud, Journal of Inorganic Biochemistry 95 (2003) 141–148.

[13] S.C. Rustagi and G.N. Rao. Journal of Inorganic and Nuclear Chemistry 36 (1974) 1161-1163.

[14] Muhammad I. Amal and Kyoo Ho Kim, Thin Solid Films 534 (2013) 144-148.

[15] Chen-He Ruan, Chung-Cheng Huang, Yow-Jon Lin, Guan-Ru He, Hsing-Cheng Chang, Ya-Hui Chen, Thin Solid Films 550 (2014) 525–529.
[16] S.W. Shin, S.M. Pawar, C. Y. Park , J.H. Yun , J.H. Moon, J.H. Kim, J.Y. Lee, Solar Energy Materials & Solar Cells 95 (2011) 3202-3206.
[17] Tooru Tanaka, Takeshi Nagatomo, Daisuke Kawasaki, Mitsuhiro Nishio, Qixin Guo, Akihiro Wakahara, Akira Yoshida, Hiroshi Ogawa, Journal of Physics and Chemistry of Solids 66 (2005) 1978–1981.

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