

Synthesis of $\text{Cu}_2\text{ZnSnS}_4$ thin film absorbers by sulfurizing dip-coated precursors

Tuan Truong Mau and Kyoo Ho Kim*

School of Material Science and Engineering, Yeungnam University, 214-1 Daedong, Gyeongsan, Gyeongbuk 712-749, Korea

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films, a potential candidate for the absorber layers of solar cells, were successfully deposited on soda lime glass substrates by sulfurizing dip-coated precursors. This is a simple and low-cost process. In this method, the precursor films were obtained by several cycles of dipping and air-jet cutting to rinse the film and make it flat, followed by drying at 200 °C for 15 minutes. The solutions that were used in the dipping process contained copper (II) acetate monohydrate, zinc (II) acetate dehydrate, tin (II) chloride dehydrate and thiourea, dissolved in a solution of water and ethanol (30% vol). By sulfurizing the precursors in Ar + H₂S (5%) gas to prevent oxidation, a CZTS single phase can be obtained with a ratio of Cu/[Zn + Sn] = 0.89, Zn/Sn = 1.03 and S/metal = 1.01. The films had a band gap of about 1.5 eV and the absorption coefficient was higher than 10⁴ cm⁻¹. The electrical properties of the films were shown to be p-type semiconductors with a carrier concentration of 10¹⁸ cm⁻³. The films can be applied as the absorber layers in solar cells.

Key words: $\text{Cu}_2\text{ZnSnS}_4$, Solar cell, Dip-coated process, Sulfurization.

Introduction

$\text{Cu}_2\text{ZnSnS}_4$ is a promising alternative to semiconductors based on Ga or In as a solar absorber material. The CZTS absorber consists of abundant and cheap elements and in addition it shows the properties of an ideal absorber layer for photovoltaic applications, such as a direct band gap of about 1.4-1.5 eV and an optical absorption coefficient higher than 10⁴ cm⁻¹ [1, 2]. There are mainly two general approaches that have been used for the preparation of CZTS thin films: physical vapor methods and chemical deposition methods. Seol et al. prepared CZTS thin films by RF magnetron sputtering [3]. The optical absorption coefficient of the thin films was about 10⁴ cm⁻¹ in the visible region and the estimated optical band gap energy was 1.51 eV. Ito and Nakazawa deposited CZTS thin films by atomic beam sputtering [4]. Friedlmeier et al. deposited CZTS thin films by thermal evaporation [5]. Tanaka et al. fabricated CZTS thin films by co-evaporation of elemental sources on quartz glass substrates [6]. However, the preparation of CZTS absorber layers by physical vapor deposition carried out in vacuum conditions is a relatively expensive and complicated method. Thus, several groups have prepared CZTS absorber layers under non-vacuum conditions.

Tanaka and coworker [7, 8, 9, 10] prepared CZTS absorber layers by sulfurizing spin-coating precursors. The absorber layer that exhibited the highest efficiency of 1.6% was Cu poor and Zn rich (Cu/(Zn + Sn) = 0.96

and Zn/Sn = 1.17). The problem with sulfurizing spin-coating precursors was that there was a deficit of sulfur in the absorber layer even though sulfurization was carried out at a high concentration of hydro sulfur [10]. The deficit of sulfur would give rise to defects of sulfur in the crystal structure.

Nakayama et al. [11] reported that, in a spray process, when there was no ethanol in the solution several strong unidentified peaks appeared in the X-ray diffraction (XRD) pattern. However, with ethanol, the peaks of the oxide phases remained in the XRD pattern of the films after the heat treatment.

In this research, we investigate an alternative synthesis route for the preparation of a CZTS layers by multi dipping the substrates into a solution containing a metal salt and thiourea as a sulfur source. Then the dip coated precursors were annealed in an inert ambient Ar gas or Ar + H₂S (5%).

Experiment

The chemicals used for preparing the solution were: copper (II) acetate monohydrate, zinc (II) acetate dihydrate, tin (II) chloride dihydrate, and thiourea. The metal ion ratio of the base solution was not stoichiometric but rather Cu-poor and Zn-rich, i.e., Cu/(Zn + Sn) = 0.8, Zn/Sn = 1.15, which showed good efficiency [12]. We abbreviate the sample as CZTS080115. The solution of 0.667 M metal ions and 1.333 M thiourea (Table 1) was prepared by dissolving the metal salt and thiourea in a mixed solution of water and ethanol (30%), then stirring for 3 h at 45 °C. The ethanol acts as a dispersion agent and avoids several unidentified peaks appearing in the XRD pattern [11].

Soda lime glass substrates were cut to a size of 15 × 25 mm² and cleaned in an ultrasonic water bath

*Corresponding author:
Tel : +82-53-8102475
Fax: +82-53-8104628
E-mail: khokim@yu.ac.kr

Table 1. Chemical statement of base solution

Conditions	Solution containing
Cu/(Zn + Sn)	0.80
Zn/Sn	1.15
Metal ion	0.667 M
S/metal ion	2
Mixing	3 h
Name of sample	CZTS080115

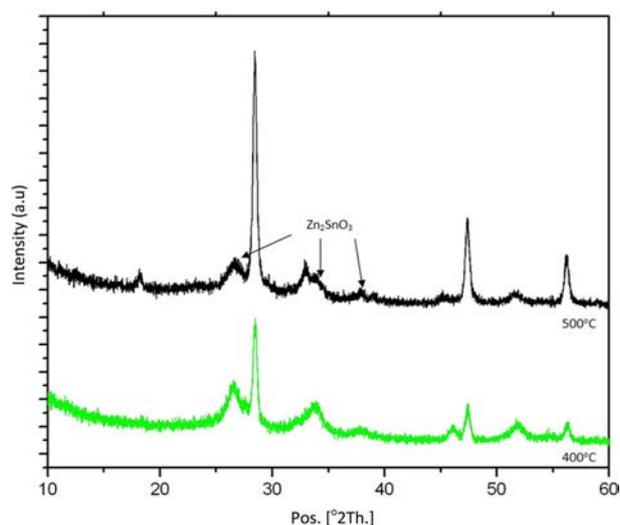
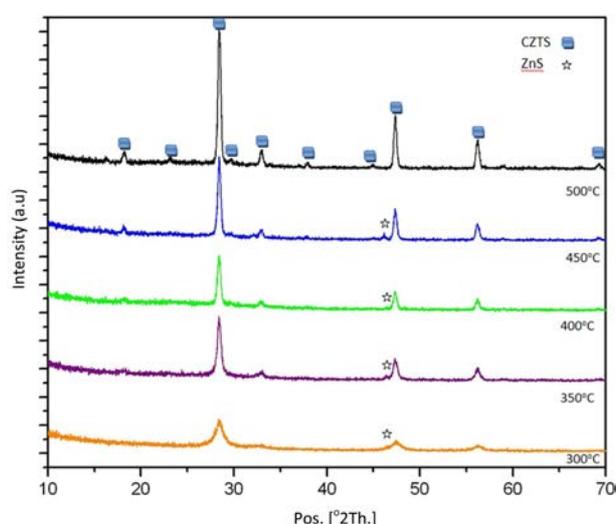
followed by ultrasonication in acetone, ethanol, de-ionized water and acetone, each for 20 minutes.

The substrates were dipped into the solution and for removing the solvents, the precursors were flattened by using a N₂ gas-jet. Then, they were dried at 200 °C for 15 minutes in air using a hot plate. The dipping and air-jet processes were repeated 10 times to obtain the desired thickness. After that, the precursors were annealed in an inert ambient Ar gas or Ar + H₂S (5%) at various temperatures for 1 hour.

The absorber layers were analyzed by using various analytical methods: X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), Hall effect measurement and ultraviolet-visible spectroscopy (UV-VIS).

Results and discussion

The precursors annealed in an inert atmosphere (Ar) at 400 and 500 °C showed the XRD patterns of not only CZTS phases but also the oxide, Zn₂SnO₃ [11] (Fig. 1). Because of the excess of thiourea, the precursor dried in an air atmosphere avoids oxidation, but decomposition of copper acetate and zinc acetate occurred when annealing at over 200 °C and thus in

**Fig. 1.** XRD patterns of CZTS080115 annealed in an Ar atmosphere at 400 and 500 °C.**Fig. 2.** XRD patterns of CZTS080115 annealed in Ar + H₂S (5%) at 300, 350, 400, 450, and 500 °C.

this case the oxide phase can be formed. Also, the electronegativity of oxygen or chlorine is higher than that of sulfur, thus the conversion of an oxide phase to a sulfide phase is difficult even at high temperature.

Fig. 2 shows the XRD patterns for the precursors that were annealed in an Ar + H₂S (5%) atmosphere. It is shown that the phase of CZTS can be obtained at over 350 °C, but to obtain a single phase of CZTS we need a high temperature of 500 °C. The effect of H₂S on the removal and conversion from the oxide phase to the sulfide phase is significant. The binary of zinc sulfide could be removed completely at 500 °C. It was reported that a high temperature treatment of CZTS could result in increased crystallinity and grain size [11]. To improve the crystallinity and grow large grains, high temperature annealing in Ar + H₂S gas of the precursor is necessary. In Fig 3, the morphology of the cross section and surface of CZTS080115 annealed in Ar + H₂S (5%) at 500 °C are shown, revealing a porous structure with many voids. The grain size is about 200 nm. During heat treatment, the decomposition of salt metals (acetate, chloride) and thiourea occurred not only in the surface but also in the bottom layer, meaning that the evaporation gives rise to many voids. Thus, an additional heat treatment is needed to avoid a porous structure.

The chemical composition of the CZTS080115 absorber layers averaged over a surface area of 15 × 15 mm² are shown in Table 2. The CZTS080115 annealed at 500 °C in Ar gas was not close to the composition of the base solution as it was zinc poor and had a much greater deficiency of sulfur. It is known that zinc and sulfur evaporate significantly much with the formation of zinc sulfide (ZnS) and other complexes [9]. The film annealed in Ar + H₂S (5%) was not stoichiometric but it was close to the chemical composition of the base solution as it was copper poor and zinc rich. The H₂S content of the gas was effective in controlling and

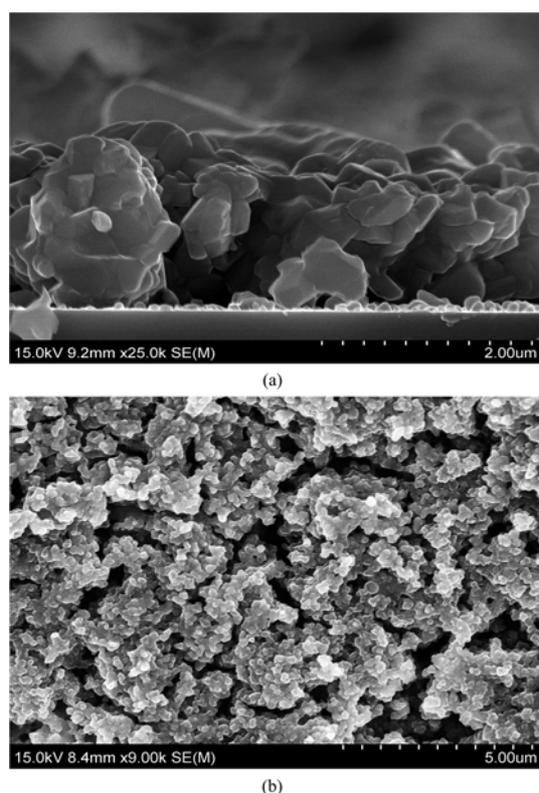


Fig. 3. Morphology of CZTS annealed in Ar + H₂S 5% at 500 °C : Cross section (a) Surface morphology

Table 2. Chemical composition ratios of CZTS 080115 annealed in different atmospheres

Ratio	CZTS080115 Ar, 500 °C	CZTS080115 Ar+H ₂ S, 500 °C
[Cu]/[Zn]+[Sn]	1.08	0.89
[Zn]/[Sn]	0.90	1.03
[S]/[Metal]	0.51	1.01

retaining a composition of metal ions in the absorber layer corresponding to the composition of the base solution. Also, by adding sulfur into the gas ambient, the deficiency of sulfur was eliminated.

The absorber layer showed low transmittance in visible light, a direct band gap of 1.48 eV and an absorption coefficient of about 10^5 cm^{-1} in visible light [Fig. 4a]. The absorber layer was a p-type semiconductor with a bulk concentration of over 10^{18} cm^{-3} . The band gap energy and absorption coefficient [Fig. 4b] are comparable to the results of several other reports [2, 3, 5, 8]. The feature of the band gap energy showed that the CZTS thin film prepared by sulfurizing the precursor deposited by the dipping method can be applied as the absorber layer of thin film solar cells.

Conclusions

CZTS absorber layers were first synthesized by sulfurizing dip-coated precursors in Ar + H₂S (5%) at

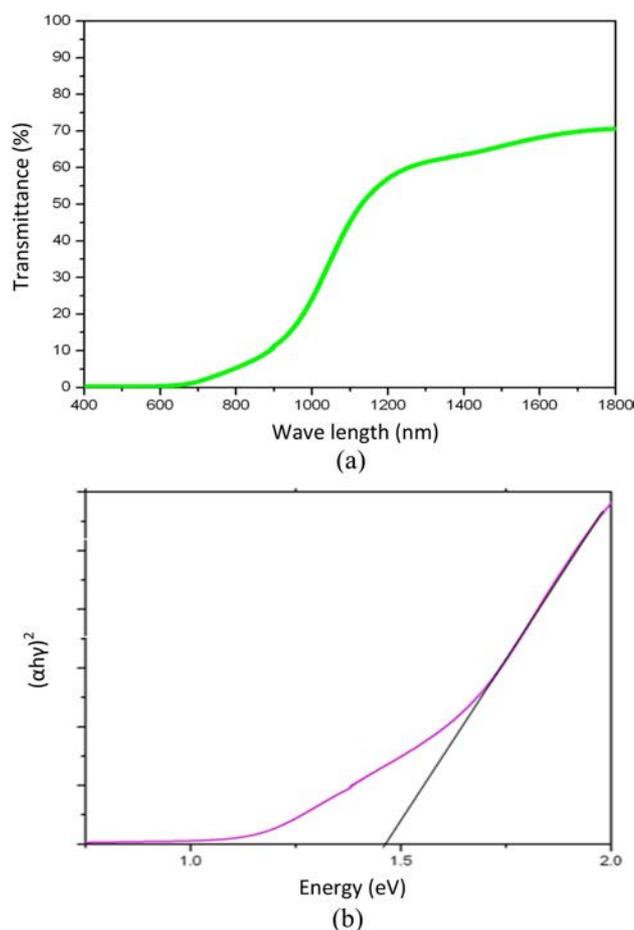


Fig. 4. Optical properties of CZTS annealed at 500 °C in Ar + H₂S (5%) : (a) Transmittance (b) Band gap energy

500 °C. The effect of 5% H₂S contained in the gas was to significantly remove the oxide phases in the absorber layer. The films showed a single phase of CZTS with a composition close to the ratio of the base solution, with $Cu/[Zn + Sn] = 0.89$, $Zn/Sn = 1.03$, and $S/metal = 1.01$. The optical properties were a band gap energy of 1.48 eV and low transmittance in visible light with an absorption coefficient of 10^5 cm^{-1} . The films were shown to be p-type semiconductors with a carrier concentration of over 10^{18} cm^{-3} . The films can be applied as absorber layers in solar cells.

Acknowledgement

This work was supported by the Center for Inorganic Photovoltaic Materials (No.2012-0001170) grant funded by the Korea government(MEST).

References

1. H. Katagiri, Thin Solid Films 480-481 (2005) 426-432.
2. H. Katagiri, K. Jimbo, W. S. Maw, K. Oishi, M. Yamazaki, H. Araki, A. Takeuchi, Thin Solid Films 517 (2009) 2455-2460.
3. J. Seol, S. Lee, J. Lee, H. Nam, K. Kim, Sol. Energy Mater.

- Sol. Cells 75 (2003) 155-162.
4. K. Ito, T. Nakazawa, *Jpn. J. Appl. Phys.* 27 (1988) 2094-2097.
 5. T..M. Friedlmeier, N. Wieser, T. Walter, H. Dittrich, H.W. Schock, *Proceedings of the 14th European Conference of Photovoltaic Science and Engineering and Exhibition, Bedford, (1997)* 1242-1251.
 6. T. Tanaka, D. Kawasaki, M. Nishio, Q. Guo, Hiroshi Ogawa, *Phys. Stat. Sol. (c)* 3 (2006) 2844-2847.
 7. N. Moritake, Y. Fukui, M. Oonuki, K. Tanaka, H. Uchiki, *Phys. Status Solidi C6* (2009) 1233-1236.
 8. K. Tanaka, N. Moritake, Y. Fukui, M. Oonuki, K. Tanaka, H. Uchiki, *Solar Energy Materials & Solar Cells* 91 (2007) 1199-1201.
 9. K. Tanaka, Y. Fukui, N. Moritake, H. Uchiki, *Solar Energy Materials & Solar Cells* 95 (2011) 838-842.
 10. K. Maeda, K. Tanaka, Y. Fukui, H. Uchiki, *Solar Energy Materials & Solar Cells* 95 (2011) 2855-2860.
 11. N. Nakayama, K. Ito, *Applied Surface Science* 92 (1996) 171-175.
 12. T. Kobayashi, K. Jimbo, K. Tsuchida, S. Shinoda, T. Oyanagi, H. Katagiri, *Jpn. J. Appl. Phys.* 44 (2005) 783-787.