

Sol–gel processed $\text{Cu}_2\text{ZnSnS}_4$ thin films for a photovoltaic absorber layer without sulfurization

Hyungjin Park · Young Hwan Hwang ·
Byeong-Soo Bae

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Abstract Sol–gel processed $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were fabricated without sulfurization for application as a photovoltaic absorber layer. The precursor solution was made from CuCl_2 , $\text{Zn}(\text{ac})_2$, SnCl_2 , thiourea, and 2-methoxyethanol and the spin-coated film was annealed at temperature above 500°C under a N_2 atmosphere. A homogeneous and compositionally uniform film with single CZTS phase was obtained. Film composition featuring larger grains, which is desirable in photovoltaic cells, was obtained with heat treatment at 540°C . The grain size was up to $1\ \mu\text{m}$ and the $\text{Cu}/(\text{Zn} + \text{Sn})$ and Zn/Sn ratios were 0.93 and 1.07, respectively and the band gap energy was 1.56 eV.

Keywords $\text{Cu}_2\text{ZnSnS}_4$ · Absorption layer · Solar cells · Sol–gel process

1 Introduction

Thin film solar cells such as $\text{CuIn}(\text{S},\text{Se})_2$ (CISSe), CdTe , and $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ (CIGSSe) have a direct band gap and correspondingly high absorption coefficient of around 10^4 – $10^5\ \text{cm}^{-1}$, thus allowing low material utilization compared with bulk silicon solar cells. As conversion efficiency as high as 20.3% has been recorded for CIGS solar cells [1], they have become a competitive substitute to bulk silicon solar cells in terms of production cost per energy produced.

Despite the advantages of high conversion efficiency and low cost, CIGS has limitations arising from scarce In reserves and increasing demand for transparent conductive oxide applications. Upon this background, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has recently attracted interest since it replaces In (group III) with inexpensive earth abundant elements, Zn (group II) and Sn (group IV). When CZTS has a kesterite crystalline structure, it exhibits a direct band gap of around 1.5 eV and an absorption coefficient over $10^{-4}\ \text{cm}^{-1}$ [2]. According to the Shockley–Queisser limit, CZTS solar cells are expected to have theoretical conversion efficiency in excess of 30% [3]. Furthermore, instead of vacuum methods such as sputtering and evaporation, non-vacuum methods can be exploited so as to lower production costs. The D. Mitzi group improved a CZTS based solar cell by replacing a part of S with Se in $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) and recorded efficiency over 9.6% [4]. However, this approach uses hydrazine, which is a highly toxic and flammable solvent, and the whole procedure should be performed in a glove box.

In this study, we have developed a non-toxic and simple process without sulfurization using the sol–gel process. Conventional aqueous sol–gel processes entail the possibility of forming M–O–M bonds in the precursor solution or during the annealing step, which can lead to the formation of involuntary phases. Spray pyrolysis using an aqueous solution, meanwhile, is a versatile and low-cost technique. However, it produces secondary phases such as binary sulfides and oxides and has a limitation in terms of heat treatment at high temperature because the film becomes S-deficient [5, 6]. Consequently, CZTS films require sulfurization to compensate the loss of volatile S and reduce oxide formation via the use of toxic hydrogen sulfide gases during the annealing process.

Ito and Nakazama [6] studied the effects of using an ethanol and water mixture as a solvent and near

H. Park · Y. H. Hwang · B.-S. Bae (✉)
Department of Materials Science and Engineering, Laboratory of
Optical Materials and Coating (LOMC), Korea Advanced
Institute of Science and Technology (KAIST), Daejeon 305-701,
Korea
e-mail: bsbae@kaist.ac.kr

stoichiometric CZTS films were obtained up to 360 °C. In addition, Jiang et al. [7] tested a nitrogen atmosphere for heat treatment instead of hydrogen sulfide gas and confirm that sulfur content reached the stoichiometry. Herein, a non-aqueous sol–gel process with heat treatment in a nitrogen atmosphere is proposed. In order to produce a colloidal suspension, 2-methoxyethanol was used as a solvent and thiourea was utilized to form M-S and/or M-S-M complexes with metal precursors [8–10]. By resolving the evaporation problem of S, heat treatment at high temperature can be applied. Accordingly, grain growth can readily occur, allowing the production of large grains and fewer grain boundaries, which deteriorate the photovoltaic property by forming recombination centers [11]. The chemical composition and the morphology of the resultant films were investigated for photovoltaic application.

2 Experimental

The CZTS precursor solution was prepared by dissolving CuCl₂ (1.6 M, 97% from Sigma Aldrich), Zn(CH₃COO)₂ (1 M, 99.99% from Sigma Aldrich), SnCl₂ (0.8 M, 98% from Sigma Aldrich), and thiourea (6.4 M, 99.0% from Sigma Aldrich) into anhydrous 2-methoxyethanol (5 mL, 99.8% from Sigma Aldrich). An excess amount of thiourea was added in order to prevent secondary phases and S loss and the composition was aimed at producing films that are slightly Cu-poor and Zn-rich. During stirring after adding thiourea at room temperature, the milky solution became a yellow and transparent solution. This solution was stable for at least several months. To prepare thin films, this solution was filtered through a 0.22 μm syringe filter and spin-coated onto a sodalime glass substrate at 2,500 rpm for 30 s followed by solvent-drying at 120 °C for 80 min on a hot plate. Finally, heat treatment was conducted in an elevator furnace under a N₂ gas flow at over 500 °C. The ramp rate was 25 °C/min, and after annealing the samples were cooled to below 100 °C in the chamber.

The coating solution was examined via a thermogravimetric analysis (TGA, TA Instrument Q50) and differential scanning calorimetry (DSC, Netzsch DSC 200F3 Maia) under a N₂ gas flow and a 5 °C/min heating rate. The bulk specimen was made by scraping the thick film from the substrate after drop-casting and drying at 120 °C for 2 h. The morphology and the structure of the films were characterized by scanning electron microscopy (Hitachi S-4000). Cross sectional images of thin films were observed with osmium to avoid electron charging of the substrates. The chemical composition was measured by an EDAX attached to SEM and Auger electron spectroscopy (Perkin-Elmer SAM4300). Thin film X-ray diffraction patterns (Rigaku D/MAX-RC) were collected by 2θ scan mode with θ_i = 2° from 20 to 60°.

Raman spectra (LabRAM HR UV/Vis/NIR) of the thin films were obtained with a 532 nm laser. Also, the optical property was measured by UV–visible-infrared spectrophotometer (Shimadzu UV3101PC).

3 Results and discussion

Figure 1 shows TGA and DSC results of the bulk precursor. It was reported that thiourea decomposes to cyanamide (H₂NCN) and ammonia from 187 to 246 °C [12]. The first weight loss below 240 °C originates from decomposition of thiourea and residual solvent and the second transition is related to zinc acetate, which decomposes at 237 °C. Above 350 °C, the weight loss corresponds to evaporation of excess S and binary sulfide combined with zinc or tin [13]. The DSC data show endothermic and exothermic reactions corresponding to decomposition and crystallization. Endothermic peaks below 240 °C indicate decomposition of thiourea. As thiourea decomposes and starts to form various types of sulfides, exothermic peaks arise and appear until 300 °C. From DSC data, in order to fabricate crystalline CZTS, heat treatment over 300 °C is required, which is consistent with an earlier report that the CZTS phase requires temperature as high as 300 °C to be synthesized [14].

Figure 2 shows SEM images of sol–gel deposited CZTS thin film surfaces and cross sections after application of different heat treatment conditions. The films uniformly covered the substrate and their thickness was around 0.6 μm with a single coating process. Figure 2a, b show the morphology of samples heat-treated at 500 °C for 1 and 3 h, respectively. Grain growth observed in the film

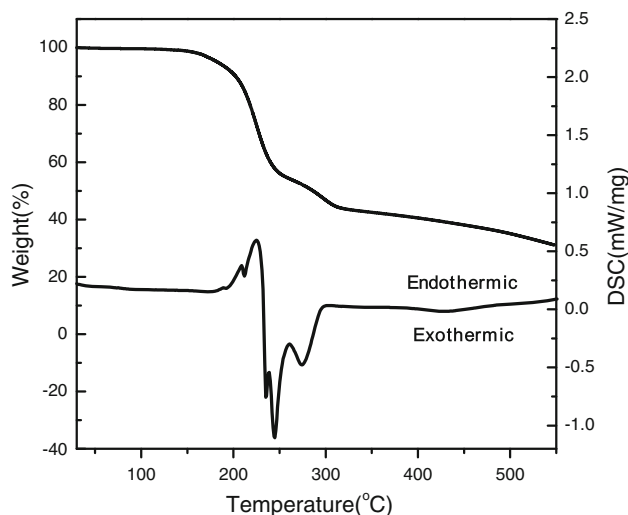


Fig. 1 TGA (*top*) and DSC (*bottom*) of CZTS precursor solution. The heat treatment temperature should be over 300 °C at which decomposition and crystallization are completed

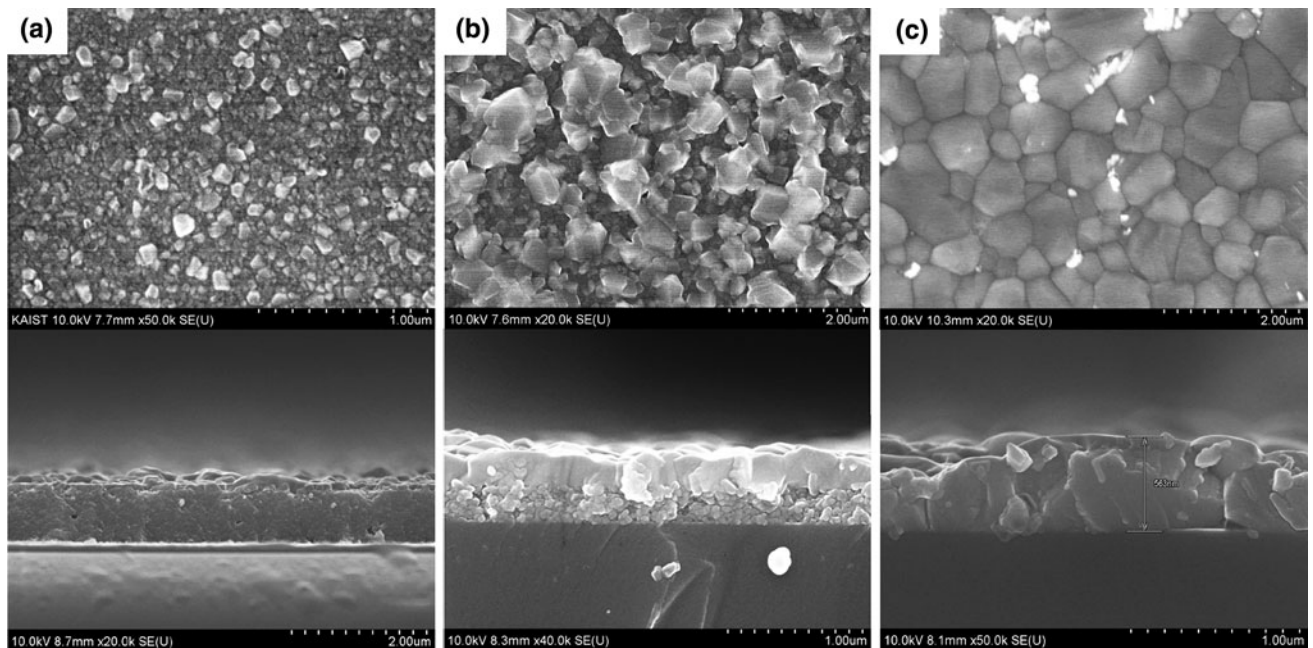


Fig. 2 Surface and cross section images of CZTS films heat-treated at **a** 500 °C for 1 h, **b** 500 °C for 3 h, **c** 540 °C 1 h

Table 1 Elemental composition of the sol–gel processed CZTS films

| Heat treatment | Chemical composition (at %) | | | | Ratio of composition | |
|----------------|-----------------------------|-------|-------|-------|----------------------|-------|
| | Cu | Zn | Sn | S | Cu/(Zn + Sn) | Zn/Sn |
| 500 °C 1 h | 23.2 | 14.14 | 12.35 | 50.31 | 0.88 | 1.14 |
| 500 °C 3 h | 23.91 | 14.32 | 12.64 | 49.09 | 0.89 | 1.13 |
| 540 °C 1 h | 23.36 | 13.01 | 12.21 | 51.42 | 0.93 | 1.07 |

Sulfur content is near stoichiometry and Cu-poor and Zn-rich compositions are achieved

heat-treated at 500 °C for 1 h is limited and the sizes of the grains are less than 100 nm. Even though the annealing time was increased to 3 h, the grains grew only at the surface and those inside the film remained small. Heat treatment at 500 °C seems to be incapable of inducing large grain growth for the sol–gel CZTS thin films. In the case of heat treatment at 540 °C (Fig. 2c), grain growth was observed throughout the film. Grain size up to 1 μm was achieved and grains expanded across the film thickness. In terms of the performance of a polycrystalline solar cell, a decrease in the amount of grain boundaries by large grains diminishes recombination, which increases the effective diffusion length of the minority carriers and thereby causes high short circuit photocurrent [15]. For photovoltaic application, the film annealed at 540 °C is more appropriate than the other films judging from the grain size.

The elemental compositions of the films corresponding to heat treatment conditions are shown in Table 1. Without sulfurization, the films fabricated over 500 °C have sulfur

content near stoichiometry. As the heat treatment time increases, sulfur is evaporated and accounts for slightly less than half of the elemental composition. In previous reports, sulfurization was found to be necessary in order to achieve stoichiometric sulfur content in the film [16]. However, the present data indicate that sulfurization can be simply replaced by designing an appropriate precursor solution. The ratios of metal elements in Cu/(Zn + Sn) and Zn/Sn were around 0.9 and 1.1, showing that Cu-poor and Zn-rich compositions are sustained up to 540 °C. S. Chen et al. reported that a Cu-poor condition leads to the formation of Cu vacancies, which generate shallow acceptors in CZTS, whereas a Zn-rich condition suppresses the Cu substations at Zn sites, which increases deep acceptors. The present study indicates that Cu-poor and Zn-rich CZTS films have higher p-type conductivity and result in high efficiency solar cells [11].

The X-ray diffraction data obtained from the film annealed at 540 °C for 1 h are shown in Fig. 3a. According to JCPDS 26-0575, the XRD peaks at 28.5°, 33.0°, 47.4°,

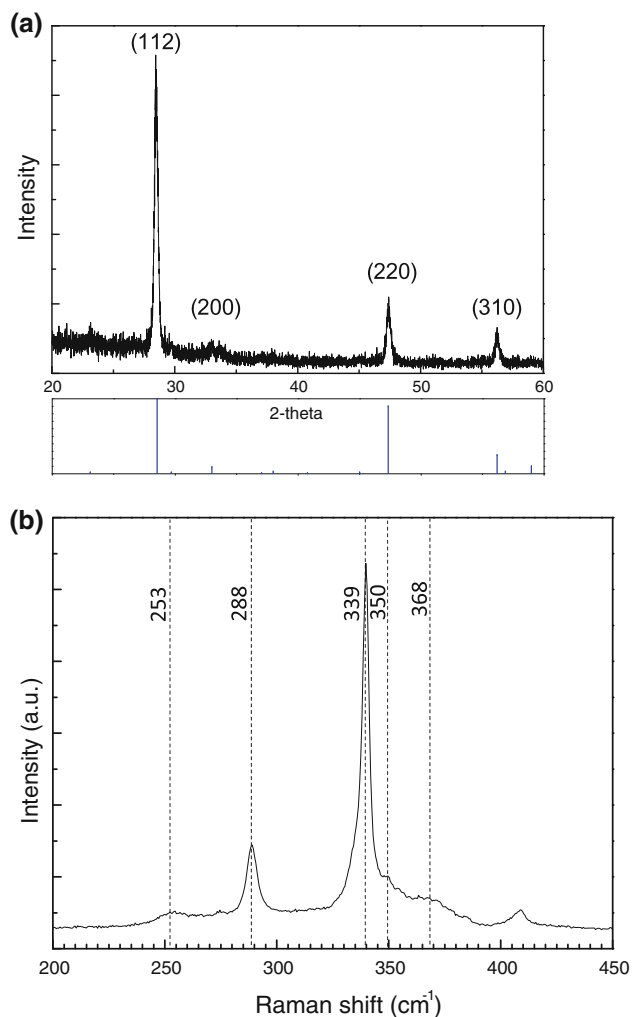


Fig. 3 **a** X-ray diffraction and **b** Raman spectrum of the film annealed at 540 °C for 1 h in a N₂ atmosphere. A single phase CZTS film without secondary phases was confirmed

and 56.3° denotes single phase kesterite CZTS. There were no notable peaks related to secondary phases from XRD, but binary or ternary sulfides such as ZnS, Cu_{2-x}S, and Cu₂SnS₃ have similar diffraction patterns with CZTS owing to their similar zinc blend-type structures [17]. Raman spectroscopy was further carried out to distinguish the CZTS phase of the kesterite structure from other sulfides. Figure 3b presents a Raman spectrum indicating the existence of CZTS solely with characteristic peaks of the kesterite structure at 253, 288, 339, 350 cm, and 368 cm⁻¹ [5, 17, 18]. ZnS and other sulfides did not appear in either the XRD or Raman spectroscopy results.

The AES depth profile of the film heat-treated at 540 °C for 1 h is shown in Fig. 4. The composition of the film is uniform before the e-beam collides with the substrate and the signal of the AES electrons is scattered. Given that the dimension of the grains is larger than the thickness, Cu, Zn, and Sn are interdiffused and the grains have attained a

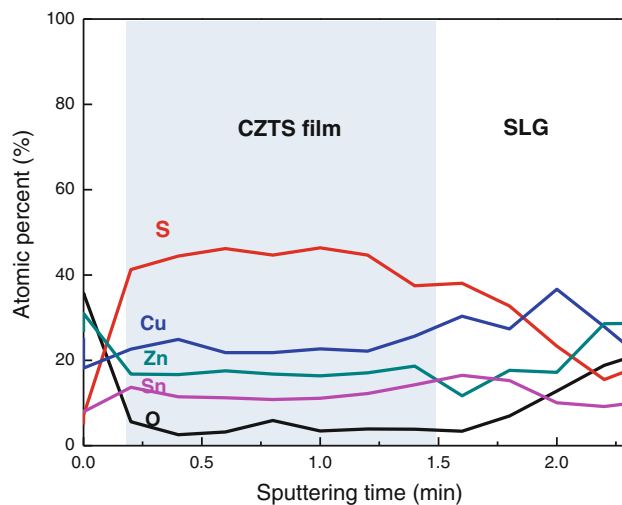


Fig. 4 AES depth profile of the film annealed at 540 °C for 1 h in a N₂ atmosphere. The film demonstrates compositional uniformity with a Zn-rich composition

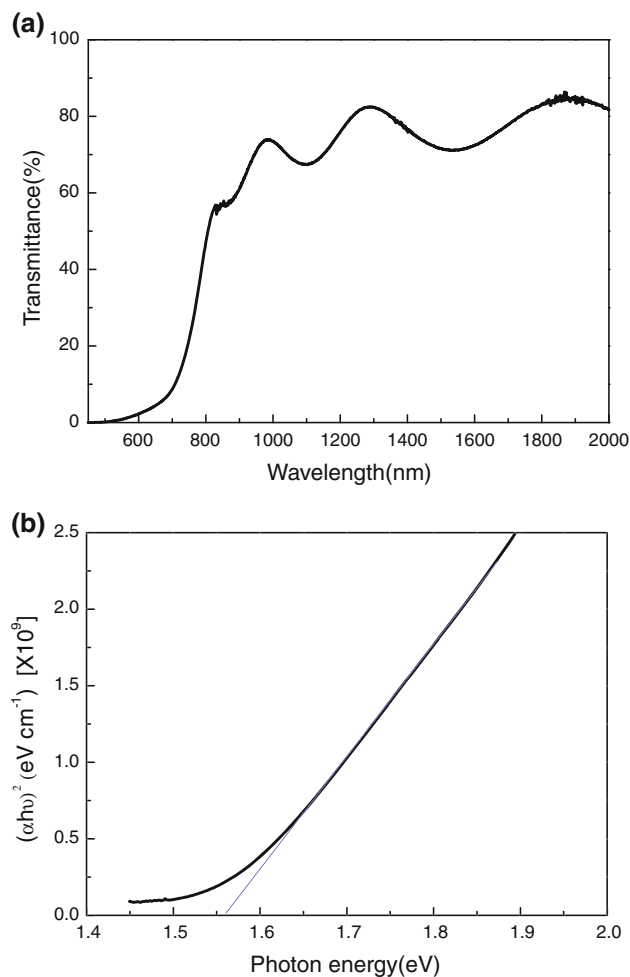


Fig. 5 **a** Transmittance and **b** $(\alpha h\nu)^2$ as a function of photon energy of the CZTS film annealed at 540 °C. The estimated band gap energy is 1.56 eV

homogeneous composition. In addition, a Zn-rich stoichiometry is confirmed throughout the depth of the film, which is beneficial for CZTS solar cells [11].

The transmittance of the CZTS film annealed at 540 °C is shown in Fig. 5a. The oscillations at wavelength over 800 nm arise from interference and reflectance. The absorption coefficient calculated from transmittance data is larger than 10^4 cm^{-1} in the visible range. The optical band gap was estimated from the $(\alpha h\nu)^2$ versus $h\nu$ graph by extrapolating the linear part of the curve as depicted at Fig. 5b. The band gap energy of 1.56 eV is slightly greater than the reported data [16]. Tanaka et al. [19] found that the band gap energy of CZTS film shifts to the higher value as the chemical composition of Cu/(Zn + Sn) decreases. Since Cu/(Zn + Sn) of the synthesized CZTS film was 0.93, Cu-poor, the band gap energy marked higher than stoichiometric CZTS.

4 Conclusion

The CZTS thin films for the absorber layer of solar cells are fabricated by a simple sol–gel process without a sulfurization process. CuCl_2 , $\text{Zn}(\text{ac})_2$, SnCl_2 , and thiourea were used as precursors and 2-methoxyethanol was used as a solvent for preparing CZTS thin films. After spin-coating, the precursor film was dried and heat treated in a N_2 atmosphere. The CZTS film annealed at 540 °C exhibited a kesterite CZTS polycrystalline phase with large grains on a SLG substrate. Cu-poor and Zn-rich CZTS films were synthesized and had a sufficient amount of S inside the film. Most of the fabrication procedure of this method is conducted under an ambient atmosphere and chemical homogeneity is guaranteed. The non-aqueous sol–gel process described here provides the formation of an earth-

abundant material for use in solar cells via a facile and non-toxic approach without sulfurization.

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