

Properties of kesterite $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films prepared by sol-gel method using two types of solution

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$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were synthesized by the sol-gel method using two kinds of mixture solvents with post annealing at 550 °C. Solutions were prepared by dissolving copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), zinc (II) chloride (ZnCl_2), tin (II) chloride (SnCl_2) and thiourea ($\text{SC}(\text{NH}_2)_2$) into mixed solvents of 2-methoxy-ethanol and mono-ethanolamine (2-metho/MEA) and methanol and de-ionized water (methanol/DIW). CZTS films attained from both solutions are oriented to the (112) plane, indicating kesterite structure. Compared to methanol/DIW solvent, reduced void defects and better surface roughness are observed using 2-metho/MEA solvent, attributable to different vaporization tendency of constituents in the solutions. Raman and energy dispersive spectroscopy indicates that secondary phases such as Cu_2SnS_3 and SnS_2 are present as a result of Zn-poor and Sn-rich components in the film, but 2-metho/MEA solvent produces less secondary phases and compositional ratio is closer to ideal value. Optical energy band gap and resistivity of CZTS thin film with 2-metho/MEA solvent are 1.27 eV and $2.7 \times 10^{-1} \Omega \cdot \text{cm}$, respectively, which are suitable for an absorber layer in thin film solar cell. These results suggest that material properties of the sol-gel processed CZTS thin film are strongly affected by types of solvent in the solution.

Key words: CZTS, Sol-gel, Sulfurization, Thin film solar cell.

Introduction

Renewable energies have been extensively investigated as alternatives to fossil-based energy. Among them, solar cell has received a great attention and bulk silicon (single- or multi-crystalline) has been a mainstream material in the commercial market so far. However, for the complete grid parity, it is still necessary to reduce fabrication cost further as well as increase cell efficiency. Compared to bulk material as a light absorber layer, adoption of thin film semiconductor materials could be a better solution due to low material consumption even though thin film solar cells have not beaten the light to power conversion efficiency of bulk Si based solar cell yet because light absorption becomes weak with decreasing film thickness. Therefore, thin film materials with higher absorption coefficient have been strongly explored like amorphous thin Si film, chalcogenide-based materials and cadmium-telluride. Especially, chalcopyrite $\text{Cu}(\text{In}, \text{Ga})(\text{Se}, \text{S})_2$ (= CIGS) compound solar cell has been aggressively investigated because this p-type semiconductor has desirable properties as an absorber layer: high absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$) in the visible region, a direct energy band gap (1.4 ~

1.5 eV) and long-term stability. Even though ~20% cell efficiency has been reported with CIGS cell, In and Ga in constituent elements are not suitable for the cost-effective and environmental-friendly approach because they are highly demanding materials for other applications such as light emitting diodes and displays, expensive, rare-earth (only sub-0.01% on the earth crust) and highly toxic in nature. Therefore, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) as an alternative absorber layer has been suggested since material properties are similar to CIGS and the earth-abundant constituent materials such as Zn and Sn are cheap, non-toxic and readily available in nature [1-2]. Absorption coefficient and energy band gap (E_g) of CZTS material is greater than $\sim 10^4 \text{ cm}^{-1}$ and 1.0 ~ 1.5 eV, respectively. CZTS solar cell showed about 10% of the highest cell efficiency in the recent report [3].

Two approaches to attain CZTS film have been proposed - vacuum process and non-vacuum process -. The vacuum-based process includes sputtering or evaporation methods and has some advantages with higher crystallinity and larger grain size [4-5]. Multiple metal stacks deposition [6], metal/sulfide stack deposition combined with e-beam evaporation [7], vapor phase sulfurization after co-sputtering [8], and reactive sputtering with H_2S gas annealing [9] have been reported. H. Katagiri et al. reported CZTS thin film on Mo coated soda lime glass (SLG) by radio frequency- sputtering process from ZnS, SnS and Cu targets using an inline type vacuum

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apparatus, showing 6.7% cell efficiency [10]. For non-vacuum method, it has some advantages such as lower cost and faster process than vacuum process. Also, it is compatible with the process for large area applications. Non-vacuum process involves spin coating [11-12], spray pyrolysis [13], electro-deposition [14] and chemical bath deposition [15]. Especially, spin coating method is the easiest one to evaluate non-vacuum processed CZTS film. However, one of the critical issues in spin coating method is to find an appropriate combination between precursor and solvent because relevant precursor should be dissolved into a certain solvent. For example, K. Tanaka et al. reported spin-coated CZTS films showing 1.01% cell efficiency, where precursor was prepared by copper (II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), zinc (II) acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and tin (II) chloride dihydrate as a precursor while 2-methoxyethanol (2-metho) and mono-ethanolamine (MEA) were used as a solvent and a stabilizer, respectively [11]. Spin-coated CZTS films demonstrated by Min Yen Yeh et al were about properties of synthesized CZTS thin films using chloride forms (CuCl_2 , ZnCl_2 and SnCl_2) and thiourea ($\text{SC}(\text{NH}_2)_2$) as for a precursor while ethanol and deionized water (DIW) were used as a solvent [12]. As reported, types of precursor and solvent significantly affect material properties of spin-coated CZTS thin films. However, there are few systematic and comparative studies on the effects on different types of solvents and precursors.

In this study, we studied spin-coated CZTS thin films by changing solvents. Precursor was fixed with all chloride forms such as copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), zinc (II) chloride (ZnCl_2), and tin (II) chloride (SnCl_2) with thiourea ($\text{SC}(\text{NH}_2)_2$). Thiourea was added to supply sulfur content into the precursor. Even though mixed solutions from both ethanol/DIW with acetate/chloride precursor and 2-metho/MEA with all chloride form precursor were demonstrated as aforementioned, different solvents using ① 2-methoxyethanol and mono-ethanolamine and ② methanol and deionized water with all chloride-based precursor have not been studied yet. Therefore, we did comparative studies on spin-coated CZTS thin films prepared using two kinds of mixed solution from different solvents - “2-metho/MEA” and “methanol/DIW”- with chloride precursor and investigated how solvent affects material's properties of spin-coated CZTS thin films.

Experimental details

Mixed solution of chloride precursor with 2-metho/MEA solvent – precursor was prepared by copper (II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), zinc (II) chloride (ZnCl_2), tin (II) chloride (SnCl_2) with thiourea ($\text{SC}(\text{NH}_2)_2$). This precursor was dissolved in 2-methoxyethanol (2-metho) and monoethanolamine (MEA) for 30 minutes at

Table 1. Detail information about quantities of two types of precursor solutions based spin-coated of CZTS layers.

Precursor	Quantity	Unit
Copper (II) chloride dehydrate, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	7.4586	g
Zinc (II) chloride, ZnCl_2	2.9819	g
Tin (II) Chloride, SnCl_2	4.1479	g
Thiourea, $\text{SC}(\text{NH}_2)_2$	13.3212	g
Solvent		
Methanol	35	ml
DIW	15	ml
2-Methoxyethanol (2-metho)	50	ml
Monoethanolamine (MEA)	5	ml

the ultrasonic bath. MEA was used for a stabilizer.

Mixed solution of chloride precursor with methanol/DIW solvent – same precursor was used. However, precursor was dissolved into methanol and deionized water (3 : 7, volume ratio) for 30 minutes at the ultrasonic bath. Concentration of both mixed solutions was kept to 1.75 M. Detail quantities of precursor and solvents are summarized in table 1

Spin coated layer using mixed solutions – thin films were synthesized by spin coating methods. A mixed solution was spin-coated with two steps after cleaning on SLG as a substrate with size of $2.5 \text{ cm} \times 2.5 \text{ cm}$. The first coating was with 300 rpm for 1 second, followed by second coating with 3000 rpm for 30 seconds to attain uniform thin film layer. After spin coating, post-baking was carried out at 300°C during 20 minutes to stabilize as-spun film and eliminate unwanted residues in the film layer. For attaining a thick enough thickness, we repeated spin coating 5 and 3 times for “methanol/DIW” and “2-metho/MEA” cases, respectively.

Sulfurization of spin-coated layers – spin-coated samples were annealed in the pressure-controllable furnace with $\text{N}_2 + \text{H}_2\text{S}$ (5 wt %) gas ambient - sulfurization - to supply additional sulfur into CZTS film. After pumping down to 1.0×10^{-2} torr and flowing the Ar gas to remove the initial oxygen, a mixture gas of $\text{N}_2 + \text{H}_2\text{S}$ (5 wt %) was introduced into the furnace once temperature reached to 550°C . Annealing time and ramping rate were 1 hour and $5^\circ\text{C}/\text{min}$, respectively.

Material characterization – Material properties of spin-coated CZTS films were characterized with x-ray diffractometer (XRD, Rigaku-denki D/MAX-2500) for crystal structure and phase state, raman spectroscopy for phase state, surface profiler (α -step) for thickness, scanning electron microscopy (SEM, JSM-6340F) for thickness and morphology, UV-visible spectrometer (UV-vis, UV-3600 SHIMADZU) for optical band gap, energy dispersive spectroscopy (EDS, JSM-6340F) for chemical compositions and Hall measurement for resistivity.

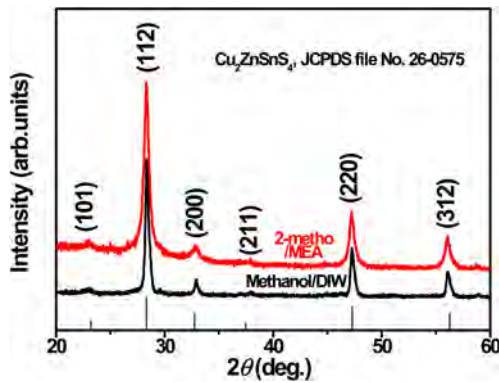


Fig. 1. XRD diffraction patterns of CZTS layers prepared by different solvents.

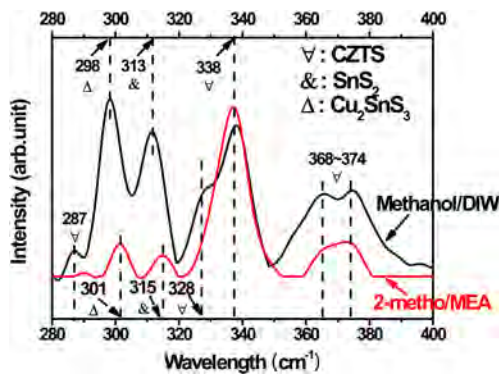


Fig. 2. Raman spectroscopy analysis of CZTS layers with methanol/DIW and 2-metho/MEA solvents.

Results and Discussion

Figure 1 shows XRD analysis of CZTS films synthesized using different solvents. Regardless of solutions, all films show good crystallinity with (112), (220), (312), (200), (101), and (211) peaks. The preferred orientation is observed with (112) plane at 28.3° , indicating kesterite CZTS phase according to JCPDS file No. 26-0575. Considering peak ratio of $(112)_{\text{methanol/DIW}}$ to $(112)_{\text{2-metho/MEA}}$ is 0.80, the synthesized layer using 2-metho/MEA has more CZTS intensity than film using methanol/DIW, attributing to different volatility between two solutions. Compared to solvent with methanol/DIW, solvent composed of 2-metho/MEA has a higher boiling point and a lower volatility (i.e., lower vapor pressure). Boiling temperatures of methanol, DIW, 2-metho, and MEA are 65, 100, 125, and 170°C , respectively. Also, vapor pressure for methanol, DIW, 2-metho, and MEA are 97.68, 17.54, 6.17, and 0.2 mmHg at 20°C , respectively. Sol-gel processed thin films experience the solvent vaporization, precursor decomposition and the crystallization upon subsequent thermal treatment. These sequential events affect the density and orientation of the sol-gel processed thin film [16]. Grain size is obtained using Debye-Scherrer equation as below [17].

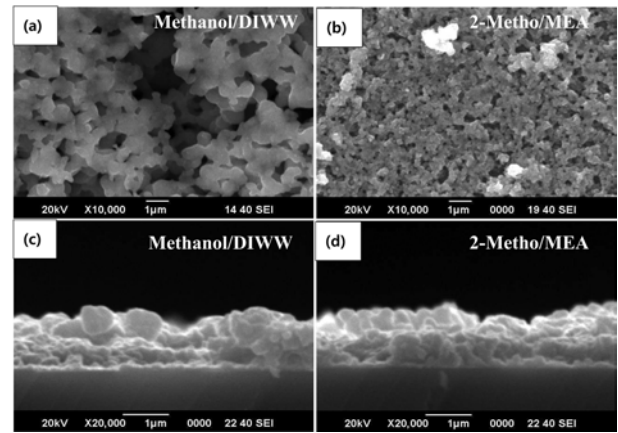


Fig. 3. SEM top-view and cross-sectional images of CZTS layers by (a)-(b) and (c)-(d), respectively. “Methanol/DIW” solvent is with (a) and (c). “2-metho/MEA” solvent is (b) and (c).

$$d = \frac{0.9\lambda}{\beta \cos \theta_B} \quad (1)$$

where d is a calculated grain size of the film, λ is a wavelength of x-ray radiation ($\lambda = 1.54 \text{ \AA}$ of $\text{CuK}\alpha$ radiation). β is full width at half-maximum (FWHM), θ_B is a peak position of diffracted x-ray beam. Mean grain size are 24.5 nm and 16.6 nm for methanol/DIW and 2-metho/MEA samples, respectively.

Three types of crystal structure have been reported for CZTS such as kesterite, stannite, and wurtz-stannite types. In order to investigate phase states in detail, raman spectroscopy analysis was performed because CZTS and secondary phases like Cu_2SnS_3 (CTS) and ZnS phases cannot be distinguished in XRD analysis [18]. Figure 2 shows Raman spectra of synthesized layers from 280 cm^{-1} to 400 cm^{-1} ranges. CZTS, Cu_2SnS_3 and SnS_2 phases of synthesized layer are detected. For both samples, peaks shown at 338 and $368 \sim 374 \text{ cm}^{-1}$ correspond to kesterite CZTS as reported [19-21]. The synthesized film using methanol/DIW has other kesterite CZTS peaks at 287 cm^{-1} and 328 cm^{-1} , which are agreement with the previous reports [22-23]. However, we also observed other peak points associated with secondary phases. Peaks at 298 cm^{-1} and 301 cm^{-1} correspond to SnS_2 phase for methanol/DIW and 2-metho/MEA cases, respectively. Peaks at 313 cm^{-1} and 315 cm^{-1} represent Cu_2SnS_3 for methanol/DIW [19] and 2-metho/MEA [21], respectively. Spin-coated CZTS film using methanol/DIW solvent shows higher intensity at secondary peaks while film with 2-metho/MEA solvent has higher intensities of CZTS phase, suggesting improved quality of CZTS film attained with 2-metho/MEA solvent.

Figure 3 shows top-view SEM and cross-sectional images of CZTS films using different solvents. Figure 3 (a) and (b) show top-view images of CZTS layers using methanol/DIW and 2-metho/MEA, respectively. Compared to CZTS layer with 2-metho/MEA, thin film using methanol/DIW solvent has more voids, higher

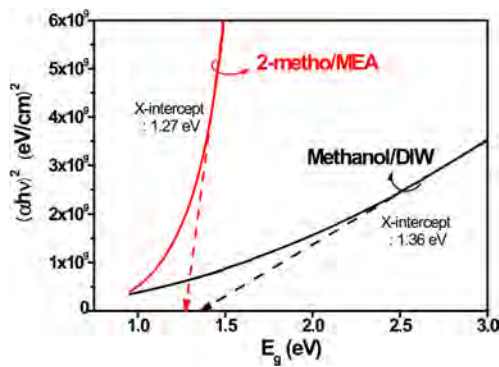


Fig. 4. Optical energy band gap of CZTS layers.

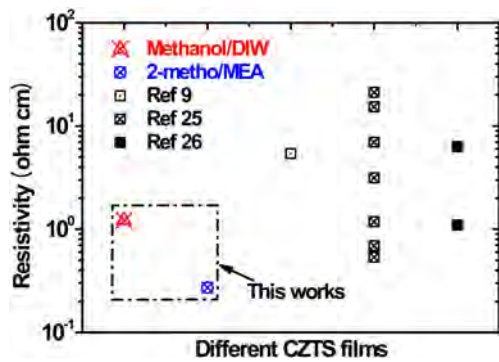


Fig. 5. Resistivity of synthesized CZTS layers.

roughness, and bigger grain size. Each grain size is nearly same. It is speculated that the amount of residual porosities in the layer is dependent of vaporization behavior of solvents during post-baking step aforementioned. The solvent with lower boiling leads to more porous surface. Figure 3 (c) and (d) show cross-sectional images of synthesized layers using methanol/DIW and 2-metho/MEA, respectively. Spin-coated CZTS films after sulfurization have 1.10 and 0.95 μm thickness for 2-metho/MEA and methanol/DIW samples, respectively.

Optical energy band gap (E_g) of synthesized films was calculated and plotted in figure 4. E_g was attained from UV-vis analysis based on the following equation.

$$(\alpha h\nu)^2 = h\nu \quad (2)$$

where α is the light absorption coefficient, h is the Planck constant and ν is the frequency. Extrapolation method in conjunction with the above equation produces E_g [24]. The E_g of synthesized layer using methanol/DIW and 2-metho/MEA are 1.36 and 1.27 eV, respectively,

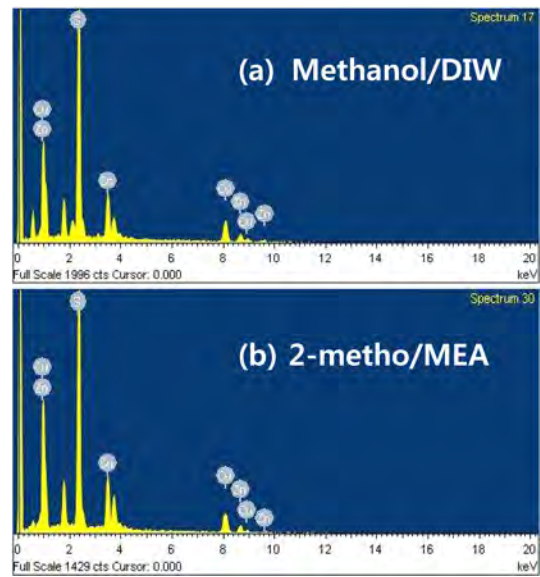


Fig. 6. EDX data for synthesized CZTS layers prepared by two different solvents.

which are acceptable as an absorber layer application.

Figure 5 compares resistivity of spin-coated CZTS layers using methanol/DIW and 2-metho/MEA solvent. 2-metho/MEA-based CZTS film shows better resistivity than the other sample. Specifically, CZTS thin film with methanol/DIW solvent has $12.2 \times 10^{-1} \Omega \cdot \text{cm}$ while 2-metho/MEA case shows $2.7 \times 10^{-1} \Omega \cdot \text{cm}$, which is related with the amount of porosity in the thin film aforementioned. These values are comparable or lower than the reported data [9, 25-26].

Compositional analysis of spin-coated CZTS films using different solvents are summarized in the table 2 and EDX spectrums are shown in figure 6. Ideal stoichiometric composition of CZTS film is 25% Cu, 12.5% Zn, 12.5% Sn, and 50% S. Both solvents cause Zn-poor and Sn-rich composition. However, synthesized layer using 2-metho/MEA is close to ideal ratio. This behavior is strongly associated with peak intensities of secondary phase in Raman spectra aforementioned. Considering relative peak intensity comparison between main CZTS phase and secondary phases, methanol/DIW case shows higher secondary phase peak intensity than that of CZTS peaks in Raman spectra, corresponding to Zn-poor phases such as Cu_2SnS_3 or SnS_2 . This composition results suggest that 2-metho/MEA solution is an appropriate solvent for the chloride precursor rather than methanol/DIW case.

Table 2. EDS composition data of CZTS thin films synthesized using different solvents.

Precursor	Cu	Zn	Sn	S	Total	Cu/(Zn+Sn)	Zn/Sn	S/metals
Methanol/DIW	25.63	10.39	14.21	49.77	100	1.04	0.73	0.99
2-metho/MEA	24.55	11.28	12.87	51.30	100	1.02	0.88	1.05

Conclusions

We synthesized CZTS thin film layers as an absorption layer of solar cells by sol-gel method using two different types of solvent such as methanol/DIW and 2-metho/MEA as well as copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), zinc (II) chloride (ZnCl_2), tin (II) chloride (SnCl_2) and thiourea ($\text{SC}(\text{NH}_2)_2$) for precursor. Regardless of solvents, spin-coated CZTS films are oriented to (112), indicating kesterite structure. Compared to 2-metho/MEA solvent, CZTS layer with methanol/DIW solvent has more void defects and higher roughness since this solvent has a lower boiling temperature, leading to faster vaporization. Different solvent vaporization and thermal decomposition of precursor solutes significantly affect material properties. An appropriate E_g from both solvents is attained with 1.3 ~ 1.4 eV while resistivity using 2-metho/MEA solvent is a one order of magnitude lower than that of methanol/DIW. Zn-poor and Sn-rich states from both solvents cause additional secondary phases such as Cu_2SnS_3 and SnS_2 , affecting material properties, but film with 2-method/MEA solution has less secondary phases, closer to ideal composition ratio. Considering effects of solvents and precursor solute on the material properties, appropriate solvent, precursor and post heat treatments should be taken into consideration for the spin-coated CZTS thin film.

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