

Fabrication of $\text{Cu}_2\text{ZnSnS}_4$ Films by Rapid Thermal Annealing of Cu/ZnSn/Cu Precursor Layer and Their Application to Solar Cells

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ABSTRACT: $\text{Cu}_2\text{ZnSnS}_4$ thin film have been fabricated by rapid thermal annealing of dc-sputtered metal precursor with Cu/ZnSn/Cu stack in sulfur ambient. A CZTS film with a good uniformity was formed at 560°C in 6 min. Cu_2SnS_3 and Cu_3SnS_4 secondary phases were present at 540°C and a trace amount of Cu_2SnS_3 secondary phase was present at 560°C. Single-phase large-grained CZTS film with rough surface was formed at 560°C. Solar cell with best efficiency of 4.7% ($V_{oc} = 632$ mV, $J_{sc} = 15.8$ mA/cm², FF = 47.13%) for an area of 0.44cm² was obtained for the CZTS absorber grown at 560°C for 6 min. The existence of second phase at lower-temperature annealing and rough surface at higher-temperature annealing caused the degradation of cell performance. Also poor back contact by void formation deteriorated cell performance. The fill factor was below 0.5; it should be increased by minimizing voids at the CZTS/Mo interface. Our results suggest that CZTS absorbers can be grown by rapid thermal annealing of metallic precursors in sulfur ambient for short process times ranging in minutes.

Key words: $\text{Cu}_2\text{ZnSnS}_4$, rapid thermal process, sulfurization, CZTS solar cells

1. Introduction

Recently, $\text{Cu}_2\text{ZnSnS}_4$ based solar cells has been attracting lot of attention because of its readily available elements, optimum direct band gap of 1.5 eV and high absorption coefficient over 10^4 cm⁻¹ makes a promising absorber material for low cost thin film solar cells¹. Solar cells with conversion efficiencies 10% were achieved with $\text{Cu}_2\text{ZnSnS}_4$ absorbers². Since last two decades, many groups have been reported variety of process for growth of CZTS thin films and solar cells³⁻¹⁴. At present, the most successful method for growing CZTS absorbers is sulfurization of sulfur containing or pure metallic precursors in H₂S or sulfur vapor. The precursors were grown by numerous methods such as evaporation¹⁵, electrochemical¹⁶, sputtering¹⁷, electron beam¹⁸, sol gel¹⁹. To date, highest efficiency is reported on CZTS solar cells is 6.8-7.1% grown by thermal evaporation of precursors followed by a short annealing in sulfur, in this method the precursors were deposited by molecular beam evaporation¹⁵.

Though the evaporation has certain advantages like precise control of composition, it requires above 1,450°C to evaporate

Cu. A disadvantage of evaporation process is narrow deposition temperature window due to high volatility of sulfide materials. Evaporation process is also a difficult process to scale up for large area manufacturing. Deposition of metal or alloyed targets by dc magnetron sputtering and selenization of the precursors are one of the most promising processes for production of large area CIGS absorbers²⁰. Sputtering of precursors and sulfidation for CZTS absorbers have several advantages such as deposition of metal precursors at room temperature in large area with controlled film thickness and controlled composition.

We have grown CZTS absorbers by furnace annealing of Cu/ZnSn/Cu precursors in sulfur ambient at 560°C for 30 min and achieved 4.6% efficiency in CdS/CZTS solar cells²¹. The top Cu layer on precursor acts as a protect layer for the evaporation of tin component. This work is the continuation of the work published in reference 21. Previously, our precursors were annealed in furnace for 30 min. In present work, rapid thermal annealing (RTA) was introduced and the annealing time was shortened to 6 min. We investigated phases and microstructure of CZTS film from the RTF process and applied the film for CZTS solar cells.

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Received November 25, 2013; Revised 2013 29, 2013;
Accepted December 4, 2013

2. Experimental

$\text{Cu}_2\text{ZnSnS}_4$ absorbers were grown by two-step process: precursor deposition and sulfidation. A Mo back contact with a thickness of 1 μm was deposited on soda-lime glass (SLG) substrates by dc magnetron sputtering. A precursor layer consisting of Cu/ZnSn/Cu stacks was deposited onto the Mo back contact by sequential dc magnetron sputtering of Cu and $\text{Zn}_{60}\text{Sn}_{40}$ targets. The schematic of Cu/ZnSn/Cu stacks is shown in Fig. 1(a). The base pressure of sputtering was 10^{-6} Torr, and working pressure was fixed to 2 m Torr with an Ar flow rate of 30 sccm. The sputtering powers were 80 and 20 W for and Cu and ZnSn, respectively. The deposition time was varied to achieve required final thickness of the precursors. The precursors with thicknesses approximately 630 nm were deposited and one precursor was deposited with thickness of 300 nm. The precursor layer consists of Sn, Cu_6Sn_5 , Cu_3Sn , and CuZn^{21} .

A precursor sample with dimensions of $2.5 \times 5 \text{ cm}^2$ and 500 mg sulfur were placed in a graphite box and the box was inserted into the quartz tube. The tube was evacuated to 10^{-3} Torr with a rotary pump and both ends were closed. The tube was heated with IR halogen lamps to 540 to 580°C. The sample was measured on the bottom and top of the graphite box with thermocouples. The temperature profile of the RTF process is given in Fig. 1(b). After annealing, the substrates were naturally cooled down to room temperature. The thicknesses of the films were in the range 1.2 to 1.5 μm ; these films were grown with 630 nm thick precursor layers.

Crystal phases in the CZTS thin films were identified with x-ray diffraction (XRD) and Raman spectroscopy measurements. The microstructure of sulfurized films was examined using field-emission scanning electron microscope (FESEM) and the composition of the films was analyzed with energy dispersive spectroscopy (EDS). Auger electron spectroscopy (AES) depth profile of a film was measured using a Perkin Elmer Auger

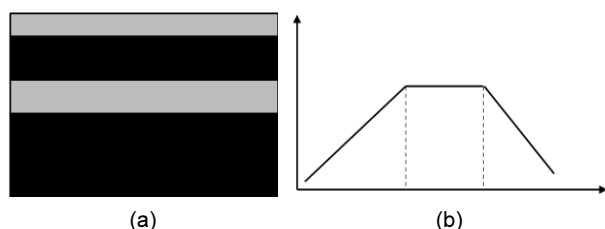


Fig. 1. (a) Schematic of precursor layer and (b) temperature profile for RTS process

electron spectrophotometer.

Solar cells with CdS buffer and intrinsic ZnO/B-doped ZnO/Al electrode were fabricated using the above absorbers. The solar cells were isolated by mechanical scribing with an area of 0.44 cm^2 . The J-V characteristics of solar cells were measured with a Mac Science solar simulator under standard test conditions (AM 1.5G spectrum, 100 mW/cm^2). External quantum efficiency (EQE) was measured with a PV measurement's QEX7 system.

3. Results and discussions

3.1 CZTS films

Fig. 2 shows the XRD pattern of metal precursor. Even though Cu/ZnSn/Cu stacks were deposited, the resultant phases in the precursors are Cu_6Sn_5 , Cu_3Sn , CuZn, Sn, and Zn^{21} . The peaks of CuZn and Zn are overlapped so that it is not easy to distinguish them. Somehow, Cu is alloyed with Sn to form Cu_6Sn_5 and Cu_3Sn phases.

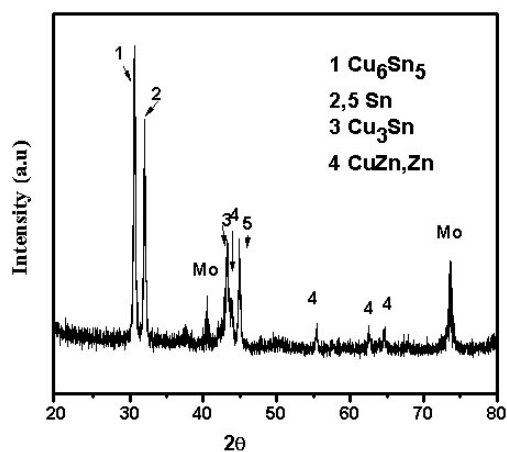


Fig. 2. XRD pattern of metal precursor layer

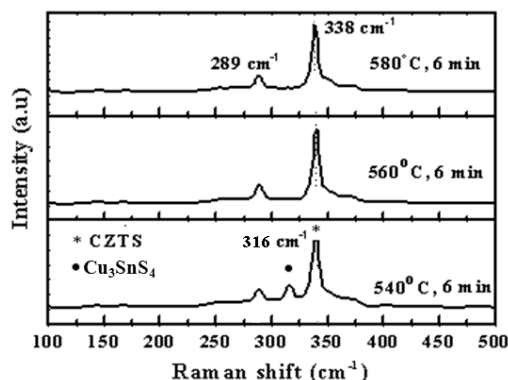


Fig. 3. Raman spectra of CZTS film prepared at 540, 560, and 580°C for 6 min, with 514 nm laser

CZTS phase starts to form above 470°C and the formation reaction is almost complete at the ramping temperature of 530°C due to the presence of binary phases²¹).

In XRS analysis, all the CZTS films annealed in the range of 540 to 580°C consisted of polycrystalline CZTS phases and no binary phases such as Cu_{2-x}S , SnS_2 and ZnS were detected. Since the (112) peak position at 28.53° of CZTS overlaps with ZnS , Cu_2SnS_3 , and Cu_2SnS_4 phases, XRD analysis cannot differentiate them. Therefore, Raman spectroscopy should be used to detect secondary phase in the CZTS films.

Fig. 3 shows the Raman spectra of the CZTS films annealed at 540, 560, and 580°C for 6 min, with excitation wavelength of 514 nm. The peaks positioned at 289 and 338 cm^{-1} correspond to the CZTS phase and it is consistent with the reported values^{2,22}). However, the film grown at 540°C showed additional peak positioned at 316 cm^{-1} ; this peak is assigned to orthorhombic Cu_3SnS_4 ²³). Therefore, it is clear, from the strong Raman peak at 316 cm^{-1} , that the film annealed at 540°C contains Cu_3SnS_4 secondary phase.

The laser penetration depth is strongly depends on the excitation wavelength of the laser used, with longer wavelengths more

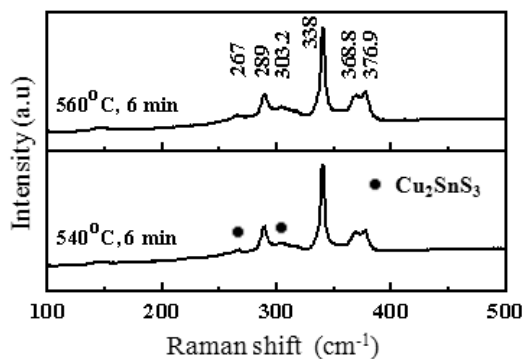


Fig. 4. Raman spectra of CZTS film prepared at 540 and 560°C for 6 min, with 785 nm laser

depth can be reached. Recently, Fernandez et al. estimated the penetration depths for various excitation wavelengths were 140, 150, 170 and 400 nm for the laser with the wavelength of 325, 488, 514, 533 and 785 nm, respectively; and identified phases present in the bulk of CZTS films²⁴). In order to identify the secondary phases clearly in the CZTS films, a laser with wavelength of 785 nm also employed for Raman analysis.

Fig. 4 shows the Raman spectra of different CZTS films using 785-nm laser. In all the spectra the main peaks of CZTS at 338-339 cm^{-1} and 289 cm^{-1} were observed and other CZTS peaks at 367-368 cm^{-1} , 375 cm^{-1} were also observed in the films. These two peaks were absent in the Raman spectra measured with 514-nm laser. The appearance of these peaks may be attributed to quasi resonant measurement conditions²⁴). The results confirm that the CZTS phase is predominant in the films. Our results agree with reported similar behavior of CZTS films at excitation wavelengths 633 and 785 nm^{2,25}).

However, all films showed a small peak at 267 cm^{-1} and a broad shoulder at 303.2 cm^{-1} may attributed to the Cu_2SnS_3 [23]. This reveals that the films may contain trace amounts of CTS phase. Apparently the amount of Cu_2SnS_3 secondary is small. The presence of Cu-rich second phase at the back contact reduces the open circuit voltage in the devices and in the films it may degrade the properties of the CZTS films^{15,26}). In our present paper, we found that the presence of the second phase at the CZTS surface reduce open circuit voltage due to shunting.

From Figs. 3 and 4, it is considered that the film synthesized by RTS process at 540°C contained Cu_2SnS_3 and Cu_3SnS_4 as secondary phases. The film synthesized at 560°C contained a trace amount of Cu_2SnS_3 and no secondary phase was found for the CTZS film at 580°C (not shown here).

Fig. 5 shows cross-sectional morphologies of CZTS films grown at 540, 560, and 580°C for 6 min. The films grown at 540

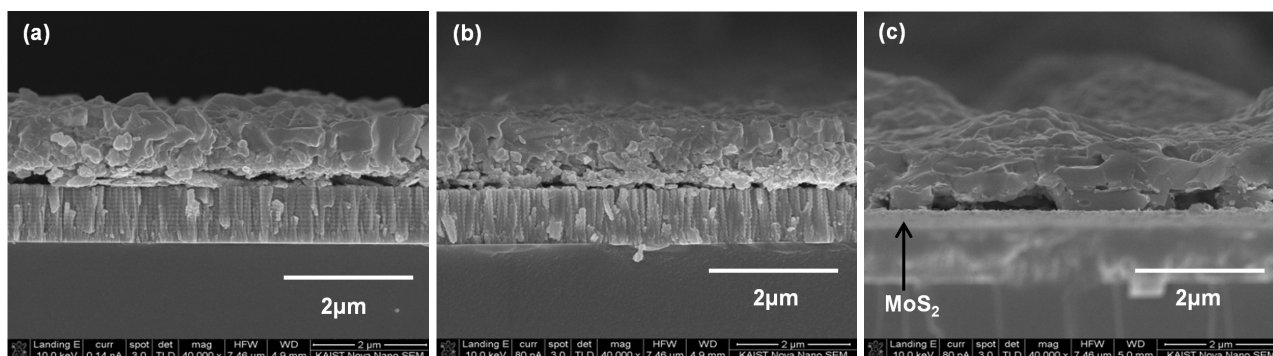


Fig. 5. FESEM cross sections of CZTS film prepared at 540 (a), 560 (b), and 580°C (c) for 6 min

and 560°C show large grains (300-600 nm) at the top and fine grains (100-200 nm) on the bottom of the films. At 580°C the film shows large grains; but a non-uniform thickness with big voids was developed and a thick MoS₂ layer between Mo and CZTS was formed. It suggests that RTS process should not be conducted above 580°C because of MoS₂ formation, which increases series resistance.

Like two step process in CIGS solar cells, large voids are developed at the interface between Mo and CZTS film in all samples. All the films have shown good adhesion to the substrate even the films consists of many voids at the CZTS/Mo interface. However, the film prepared at 580°C for 6 min was peeled off during TCO deposition, indicating that the film is not in strong adhesion with Mo substrate. So the film prepared at 580°C for 3 min was used for device fabrication.

The chemical compositions of the CZTS absorbers were determined from with EDX analysis and are given in the Table 1. The composition of the films reveals that the films are Cu poor and Zn rich. The EDX data indicate that sulfur/metal ratio in the films is greater than 50%, indicating that metallic precursors are completely sulfurized even though the process times are less than 10 min.

Table 1. EDX compositions of CZTS films prepared at 540, 560, and 580°C for 6 min

Temp. (°C)	Time (min)	Cu/ (Zn+Sn)	Zn/Sn	S/M
540	6	0.83	1.07	1.2
560	6	0.78	1.21	1.13
580	6	0.79	1.21	1.18

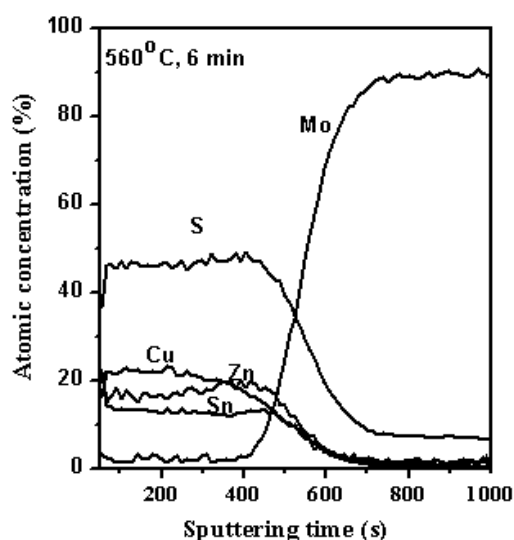


Fig. 6. AES depth profiles of Cu, Zn, Sn, and S in CZTS film grown at 560°C

Fig. 6 shows the AES depth profiles of Cu, Zn, Sn, and S in the film grown at 560°C for 6 min. The elements are distributed uniformly throughout the film thickness. The Zn concentration is slightly high near the bottom of the film. The sulfur distribution reveals that the sulfurization is completed and there is no un-reacted inter metallic compounds at the bottom of the film. The depth profile of this film confirms that CZTS films can be grown with nearly uniform distribution of elements for short annealing times.

3.2 Solar cells

Solar cells with CdS buffer and intrinsic ZnO/B-doped ZnO/Al electrode were fabricated. The difference between present work and our previous work is the use of B-doped ZnO deposited by MOCVD process instead of Al-doped ZnO deposited by sputtering process²¹. CZTS films were treated with KCN for 3 min and then a 70-nm thick CdS layer was deposited by chemical bath deposition using CdSO₄, NH₃ and thiourea (NH₂)₂SC aqueous solutions at 75°C for 12 min. After CdS deposition, intrinsic ZnO (50 nm) and B-doped ZnO (>1 μm) were deposited by metalorganic chemical vapor deposition (MOCVD) at 165°C. Finally, Al top contact was deposited by thermal evaporation using an aperture mask.

Fig. 7 shows the current-voltage characteristics of the CZTS

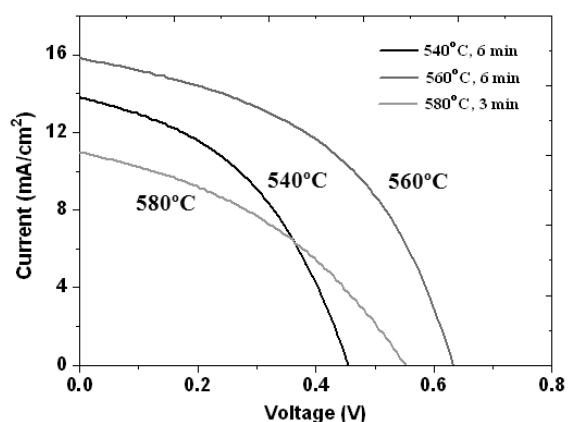


Fig. 7. Current-voltage curves of CZTS solar cells with CZTS films prepared at various temperatures

Table 2. Photovoltaic parameters of CZTS solar cells with CZTS films prepared at various temperatures

Temp. (°C)	Time (min)	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF (%)	η (%)
540	6	455	13.79	43.45	2.73
560	6	632	15.8	47.13	4.7
580	3	545	10.93	38.51	2.3

solar cells under AM1.5G, 100 mW/cm^2 illumination. The cell fabricated with CZTS absorber grown at 560°C showed 4.7% efficiency with $V_{oc} = 632 \text{ mV}$, $J_{sc} = 15.80 \text{ mA/cm}^2$, and fill factor (FF) = 47.1% for an active area of 0.44 cm^2 . The cell fabricated with CZTS absorber grown at 540°C showed 2.7% efficiency. The cell fabricated with absorber at 580°C for 6 min has peeled off during the ZnO deposition. Fortunately, a cell fabricated with CZTS absorber for 3 min at 580°C showed 2.3% efficiency. The cell parameters of the cells are summarized in the Table 2. Note that V_{oc} and J_{sc} are high for the improved cell. The shunt resistance of the all the cells was $150 \Omega\text{-cm}^2$. The series resistances of the CZTS cell with CZTS films grown at 540, 560, and 580°C were 26, 23, and $52 \Omega\text{-cm}^2$, respectively.

The best V_{oc} value here is 632 mV that is much higher compared to our previous results with furnace annealing where the efficiency = 4.6% and $V_{oc} = 545 \text{ mV}^{(21)}$. Unfortunately, the FF values here are below 50% while those with furnace annealing were above 50%⁽²¹⁾. This is likely due to high-resistivity B-doped ZnO used in these cells, instead of low-resistivity Al-doped ZnO used in the previous cells.

Fig. 8 shows the external quantum efficiency (EQE) curves of the above cells. The EQE values of the cells with CZTS absorbers prepared at 560°C showed an average value of about 60% in the visible region from 520 to 700 nm. The flat curve in the visible region indicates that the collection efficiency in the bulk region of CZTS film is good, indicating that the film quality is good. The EQE value of the cell with CZTS film prepared at 540°C for 6 min shows maximum value at 520 nm and slightly decreases in the longer wavelengths, indicating that CZTS film quality is not good enough. Whereas the EQE value of the cell with CZTS film fabricated at 580°C for 3 min showed

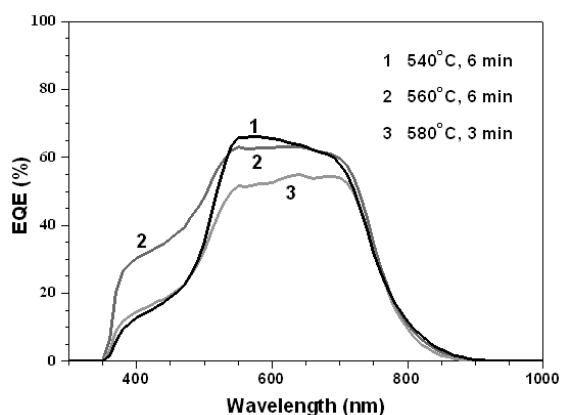


Fig. 8. EQE spectra of CZTS solar cells with CZTS film prepared at various temperatures

better collection efficiency at long wavelength, indicating the film quality is good enough. However, the absolute EQE value is lower than the cells with CZTS film prepared at 540 and 560°C ; this is probably due to the formation of highly resistive MoS_2 layer as seen in Fig. 4.

The cell with CZTS absorbed grown at 560°C shows a very high EQE value below 520 nm. The variation of collection efficiency of the cells at lower wavelengths suggests that the buffer CdS thickness is not uniform, further optimization is necessary to reduce absorption losses in the buffer/window.

In overall, the EQE values of 50-60% in the visible wavelength are considered as too low. It will be discussed at the end of this section.

The optical band gap of the CZTS absorbers can be estimated from the quantum efficiency curves using long wavelength cut offs. The estimated band gap is 1.52 eV, is in good agreement with the reported values^(2,27).

Fig. 9 shows the dark current-voltage curves of the devices. The saturation currents, J_o , of the devices fabricated with CZTS absorbers grown at 540 and 560°C are 4×10^{-5} and $8 \times 10^{-6} \text{ A/cm}^2$, respectively. The cell with smaller J_o value shows higher V_{oc} as expected. This suggests that the interface recombination at the CdS/CZTS interface should be suppressed.

In our cell, low V_{oc} , low J_{sc} , low FF, and low EQE value, were obtained. V_{oc} change could be explained with surface morphology. Poor interface between CdS and CZTS by surface roughness can cause large surface recombination, resulting in small shunt resistance and small.

One encouraging point of this paper is that the best V_{oc} value is 0.63 V which is above 600 mV. The first time we achieved with this precursor configuration. The origin of large V_{oc} could

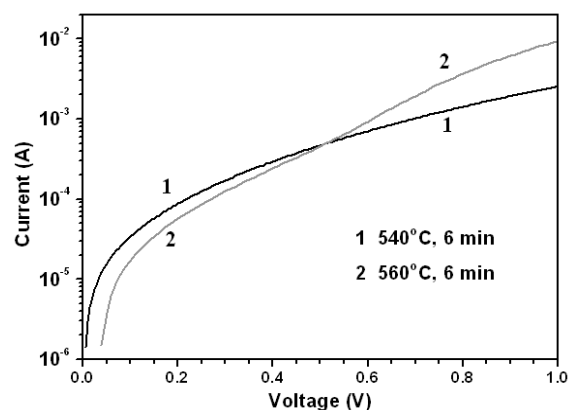


Fig. 9. Dark current-voltage curves of CZTS solar cells with CZTS films prepared at various temperatures

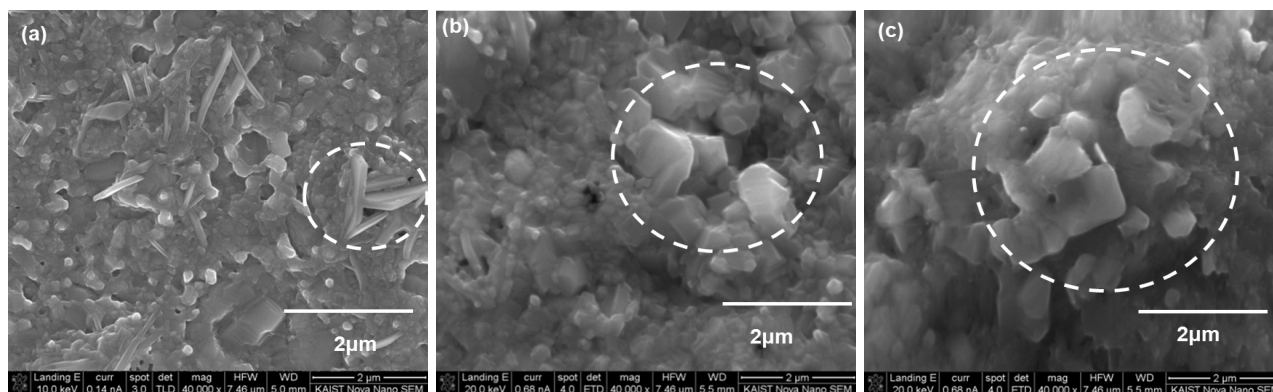


Fig. 10. SEM surface morphology of CZTS films prepared at 540 (a), 560 (b), and 580°C (c) for 6 min

be flat surface with less protrudes at the surface.

Fig. 10 shows surface micrographs of CZTS films with various preparation temperatures. From Raman analysis, the CZTS film prepared at 540°C contains second phases. Fig. 10(a) shows plate-shaped second phases at the CZTS surface, marked in dotted circle, probably Cu_2SnS_3 and Cu_3SnS_4 ; those second phases could deteriorate junction formation at the surface by shunting. The CZTS film prepared at 560°C shows large faceted grains (dotted circle in Fig. 10(b)). Due to the generation of pores with grain growth could deteriorate the surface roughness and lower V_{oc} . Somehow we were able to obtain above 600 mV with this morphology.

CZTS film prepared at 580°C for 6 min contains many large CZTS grains (dotted circle in Fig. 10(c)) and the surface was very rough (Fig. 5(c)). The film was peeled off during TCO deposition, indicating that back contact was also bad with weak connection with Mo. We were able to fabricate CZTS solar cell with CZTS film prepared at 580°C for 3 min where back contact slightly better than 6 min annealing.

The fill factor of the solar cells is lower than 50% in our devices. Factors that affect fill factor are shunt resistance and series resistance. Shunt resistance is closely related to V_{oc} where surface roughness and interface recombination play key roles. This one is discussed in the paragraphs that describe Fig. 10.

Series resistance is closely related with quality of CZTS film, back contact, and the quality of TCO layer. In our devices, large voids at the CZTS/Mo interface are clearly visible. The CZTS film fabricated at 580°C for 6 min was peeled off during device fabrication due to poor adhesion, indicating that series resistance could be large. The series resistances of the CZTS cell with CZTS films grown at 540, 560, and 580°C are 26, 23, and 52 $\Omega\cdot\text{cm}$, respectively. The result suggests that the large series

resistance is partly originated from the poor back contact. The contact problem could be partly solved by preheating metal precursor at an intermediate temperature as seen in many literatures. It is believed that our sample could get more than 8% by the recipe. But it is necessary to employ sulfide precursors or combine metal and sulfide precursors to eliminate or minimize voids at the interface.

In the present study, boron-doped ZnO deposited by MOCVD was used as a transparent conducting oxide, which is 1.4 μm thick as measured from SEM image of a solar cell and has resistivity of $10^{-3} \Omega\cdot\text{cm}$. The TCO thickness is too thick compared to typically Al-doped ZnO with 300 nm thickness. Therefore, the series resistance increased and FF was decreased. It is necessary to use high-conductivity TCO to improve FF.

Since CZTS film contains Zn which can easily occupy Cu vacancy sites and acts as donor, the doping of CZTS could be reduced by Zn doping and the hole mobility can be lowered. Our experiment in CIGS with Zn doping showed that Zn incorporation deteriorated cell performance²⁸⁾. It is necessary to reduce Zn antisites by incorporating a third element such as Na atoms into Cu sites, especially at the CZTS surface for higher efficiency CZTS solar cells.

4. Conclusions

CZTS films were grown on Mo-coated soda-lime glass substrate by rapid thermal annealing of Cu/ZnSn/Cu precursor layers in sulfur atmosphere at 540-580°C. Raman spectra revealed that Cu_4SnS_4 existed as second phase in the CZTS film prepared at 540°C for 6 min and a trace of Cu_2SnS_3 phase existed in the CZTS prepared at 540-580°C. Cross section of CZTS film showed that large grains on top and small grains on bottom of

the layer for the film prepared at 540 and 560°C, while only large grains for the film prepared at 580°C. All films have many voids at the CZTS/Mo interface and the film prepared at 580°C for 6 min was peeled off during TCO deposition due to stress, indicating that back contact is poor due to the voids.

The best cell performance was obtained from the CZTS cell prepared at 560°C for 6 min with cell efficiency of 4.7% ($V_{oc} = 632$ mV, $J_{sc} = 15.80$ mA/cm², and FF = 47.13% for the active area of 0.44 cm²). The efficiency of the cell with CZTS fabricated at lower temperature or short time was degraded due to presence of Cu-rich secondary phase which exist on the surface of the film as micro plates. The efficiency of the cell with CZTS film prepared at higher temperature also degraded even though grains were large due to rough surface morphology and worse back contact.

The efficiency could be further improved by improving the back contact with an intermediate annealing, applying Al-doped ZnO, reducing Zn content at the surface, and improving the surface roughness with optimum process. Our results suggest that rapid thermal annealing of metallic precursors in sulfur vapor is a suitable method to grow CZTS absorbers with short process times ranging in minutes for solar cell applications.

Acknowledgments

This work was supported by the Engineering Research Center Program (2008-0062289) and the Priority Research Center Program (2009-0094040) through the National Research Foundation of Korea (NRF) funded by the Korean Ministry of Education, Science, and Technology (MEST) and the Best Research Lab program (2008-N-BL-HM-E-03-0000) by the Korean Ministry of Knowledge and Economy and also supported through NRF funded by the Korean Ministry of Education, Science, and Technology (MEST: 2010-0029714).

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