

$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ -type thin film solar cells using printing and high-pressure sintering process

Feng Gao, Tsuyoshi Maeda, and Takahiro Wada

Department of Materials Chemistry, Ryukoku University
Seta, Otsu, 520-2194, Japan

Phone: +81-77-543-7468 E-mail: t11d501@mail.ryukoku.ac.jp

1. Introduction

A $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ (CIGS) solar cell was achieved with a conversion efficiency of 20.3% [1]. An increasing number of companies moved to commercialize CIGS PV modules. Therefore, substituting abundant elements for indium and gallium in CIGS has become an important issue because they are expensive rare metals. $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is anticipated to be an indium-free absorber material [2]. Katagiri *et al.* reported a CZTS solar cell with 6.7% efficiency fabricated by a combination of precursor layer sputtering and post-sulfurization [3]. An IBM group fabricated $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) solar cell with an efficiency of 11.1% by the hybrid coating process [4].

We studied the fabrication of CIGS films by a non-vacuum particulate-based deposition process. In such processes, solid particles are dispersed in a solvent to form an ink that can be coated onto a substrate [5]. We fabricated CIGS films by a combination of mechanochemical and screen printing/sintering processes [6, 7]. CIGS powder suitable for screen printing was prepared using a mechanochemical process (MCP) [8, 9]. First, we fabricated a CIGS solar cell with 2.8% efficiency [6]. Then we fabricated CIGS films by a mechanochemical process, wet bead-milling of CIGS powder, and screen printing and sintering processes, and obtained a CIGS solar cell with 3.1% efficiency [7]. Recently, we fabricated high-density CIGS films by a printing and high-pressure sintering (PHS) process and obtained a CIGS solar cell with 3.2% efficiency [10].

Recently, we prepared Cu deficient $\text{Cu}_{2(1-x)}\text{ZnSnSe}_4$ and characterized their crystal structures by XRD and XAFS [11]. Then, we characterized their optical properties. The band gaps of the $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$ solid solutions were determined from diffuse reflectance spectra of the powders and transmittance spectra of the films. The band gap (E_g) of the CZTSSe solid solution linearly increases from 1.05 eV for CZTSe ($x=0.0$) to 1.51 eV for CZTS ($x=1.0$) [12].

In this study, we fabricated CZTSSe films by PHS process [10] and CZTSSe solar cells with the device structure of $\text{Ag}/\text{ITO}/\text{i-ZnO}/\text{CdS}/\text{CZTSSe}/\text{Mo}/\text{soda-lime glass}$. Devices were completed using a chemical bath deposited CdS buffer and RF sputtered ZnO and indium tin oxide (ITO) window layers. Ag collection grid was deposited on top of the device by RF-sputtering using a shadow mask. The CZTSSe solar cell showed an efficiency of 1.7%, with V_{oc} of 267 mV, J_{sc} of 13.0 mA/cm^2 and FF of 0.479.

2. Experimental Procedures

2.1 Fabrication of CZTSSe powder

Elemental powders such as Cu, Zn, Sn, S, and Se were weighed to give a molar ratio of $\text{Cu}_{1.9}\text{Zn}_{1.25}\text{Sn}(\text{S}_{0.4}\text{Se}_{0.6})_{4.5}$. The milling was conducted in a planetary ball mill (Fritsch premium line P-7) under a rotational speed of 800 rpm and a milling period of 20 min. The CZTSSe powder was synthesized from elemental powders by planetary ball milling and post-heating at 550°C for 5 h in an N_2 gas atmosphere.

2.2 Fabrication of CZTSSe films

Particulate precursor ink was prepared by mixing the obtained CZTSSe powder with an organic solvent such as ethylene glycol monophenyl ether by planetary ball milling (Fritsch premium line P-7) under a rotational speed of 750 rpm and a milling period of 5 h. The precursor CZTSSe layer was deposited on a soda-lime glass substrate by a screen-printing technique. The organic solvent was removed from the screen-printed CZTSSe films by heating at about 110°C in an N_2 gas atmosphere. The porous precursor layer was sintered into a dense polycrystalline film at 100°C for 30 min by high-pressure sintering. The pressure was as high as 6 MPa. The schematic of high-pressure sintering equipment is shown in Fig. 1 [10]. The obtained dense CZTSSe film was post-annealed at 550°C for 10 min under an N_2 and $\text{N}_2 + 3\% \text{ H}_2$ gas atmosphere. The annealing process was present with Se, S and Sn powders in the quartz box.

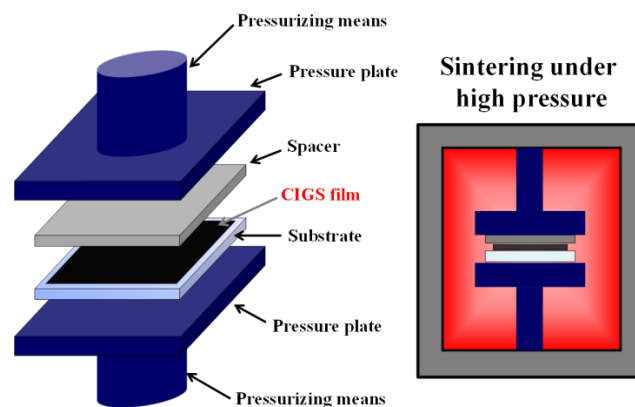


Figure 1 Schematic high-pressure sintering equipment [10].

2.3 Fabrication of CZTSSe solar cells

CZTSSe solar cells with our standard Ag/ITO/i-ZnO/CdS/CZTSSe/Mo/soda-lime glass structure solar cell with an area of about 0.34 cm^2 were fabricated. A CdS buffer layer (100 nm) was formed by a conventional chemical bath deposition (CBD). The i-ZnO (100 nm), ITO (200 nm) layers and Ag grid (100 nm) were deposited by RF-sputtering. The performance of the solar cells was evaluated under standard AM1.5 illumination.

3. Results and Discussion

Figures 2 (a) and (b) show the surface SEM micrographs of the CZTSSe films deposited on Mo coated soda-lime glass substrate. Figures 2 (a) shows the surface of hot-pressed the CZTSSe film without annealing. Figure 2 (b) shows the surface of the CZTSSe film hot-pressed and post-annealed under N_2 gas atmosphere. The CZTSSe surfaces of hot-pressed and post-annealed CZTSSe film are without large pores. The size of the grains is less than $1 \mu\text{m}$, which is smaller than CIS films [6]. In the case of CIS, the grains grew by adding CuSe as a sintering additive.

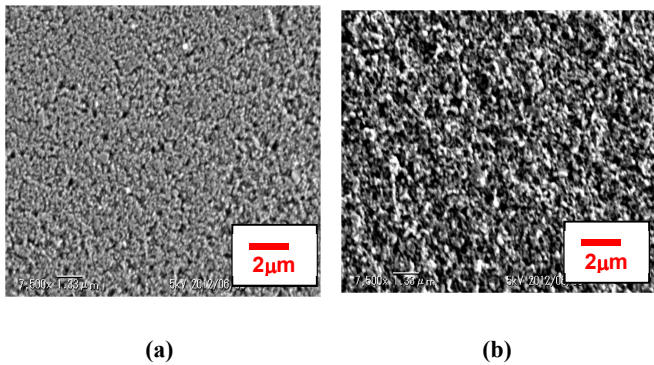


Figure 2 Surface SEM micrographs of hot-pressed (a) and hot-pressed and post-annealed (in N_2) CZTSSe film (b).

Figure 3 shows the I - V characteristics of the CZTSSe solar cell with the CZTSSe film post-annealed at 550°C under an N_2 and $\text{N}_2 + 3\% \text{H}_2$ gas. The efficiency of the CZTSSe film post-annealed in N_2 atmosphere is low. The CZTSSe solar cell post-annealed in $\text{N}_2 + 3\% \text{H}_2$ gas atmosphere showed the higher efficiency of 1.7% owing to a high fill factor of 0.48. Figure 4 shows the quantum efficiencies of the solar cell with the CZTSSe film post-annealed at 550°C under N_2 and $\text{N}_2 + 3\% \text{H}_2$. The quantum efficiency at about $550\text{nm} \sim 1100\text{nm}$ of the cells annealed in $\text{N}_2 + 3\% \text{H}_2$ gas was higher than that annealed in N_2 gas. This is because the impurities or defects in the CZTSSe film were reduced by the annealing in $\text{N}_2 + 3\% \text{H}_2$ gas atmosphere.

Acknowledgements

This work was supported by a grant based on the Advanced Low Carbon Technology Research and Development (ALCA) programs from Japan Science and Technology Agency (JST) under the Ministry of Education, Culture, Sports, Science and Technology in Japan.

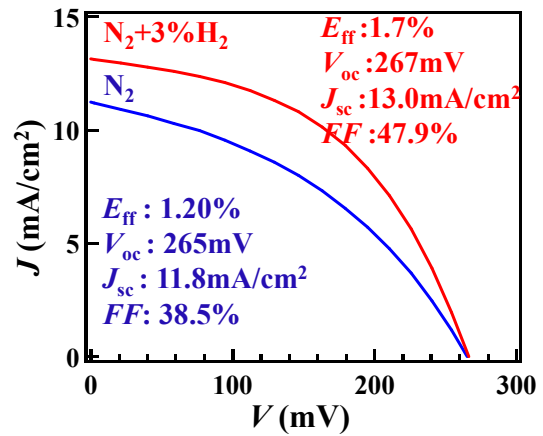


Figure 3 I - V characteristics of CZTSSe solar cells with the CZTSSe films post-annealed at 550°C under N_2 and $\text{N}_2 + 3\% \text{H}_2$ gas.

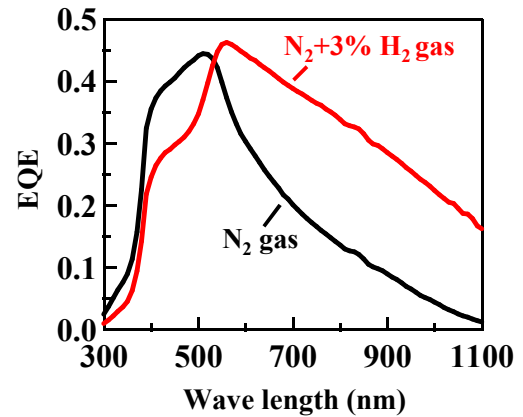


Figure 4 Quantum efficiency of solar cell shown in Fig. 3.

References

- [1] P. Jackson *et al.*, Menner, Prog. Photovolt. Res. Appl. **19**, 894 (2011).
- [2] T. M. Friedlmeier *et al.*, Proceedings of the 14th European Photovoltaic Specialists Conference, Barcelona, p. 1242 (1997).
- [3] H. Katagiri *et al.*, Applied Physics Express **1**, 041201 (2008).
- [4] T. K. Todorov *et al.*, Adv. Energy Mater. **3**, 34 (2013).
- [5] C. Eberspacher *et al.*, Thin Solid Films **387**, 18 (2001).
- [6] T. Wada *et al.*, Phys. Stat. Sol. (a) **203**, 2593 (2006).
- [7] J. Kubo *et al.*, Thin-Film Compound Semiconductor Photovoltaics-2009, (Mater. Res. Soc. Symp. Proc. Vol. **1165**), 1165-M05-13.
- [8] T. Wada *et al.*, Thin Solid Films **431-432**, 11 (2003).
- [9] T. Wada *et al.*, J. Phys. Chem. Solids **66**, 1987 (2005).
- [10] T. Wada *et al.*, Proc. 25th European Photovoltaic Solar Energy Conference and Exhibition/5th WCPEC (Valencia), p. 3465 (2010).
- [11] F. Gao *et al.*, Jpn. J. Appl. Phys. **51**, 10NC28 (2012).
- [12] F. Gao *et al.*, Jpn. J. Appl. Phys. **51**, 10NC29 (2012).