

Enhanced Conversion Efficiencies of $\text{Cu}_2\text{ZnSnS}_4$ -Based Thin Film Solar Cells by Using Preferential Etching Technique

Hironori Katagiri, Kazuo Jimbo, Satoru Yamada, Tsuyoshi Kamimura, Win Shwe Maw, Tatsuo Fukano^{1*}, Tadashi Ito¹, and Tomoyoshi Motohiro¹

Department of Electrical and Electronic Systems Engineering, Nagaoka National College of Technology, 888 Nishikatahai, Nagaoka, Niigata 940-8532, Japan

¹Materials Department, Toyota Central Research and Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan

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$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin film solar cells have been fabricated by co-sputtering technique using three targets of Cu, SnS, and ZnS. CZTS-based thin film solar cells over 6.7% efficiency were obtained for the first time by soaking the CZTS layer on the Mo coated soda-lime glass substrate in deionized water (DIW) after forming the CZTS layer. It was found that DIW-soaking had the effect of preferential etching, which eliminated selectively metal oxide particles in the CZTS layer, by electron probe X-ray micro analysis.

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Recently, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a promising material for absorber layers of thin film solar cells, since (1) CZTS thin films have the suitable optical band-gap energy of 1.4–1.5 eV and large optical absorption coefficient of $\sim 10^4 \text{ cm}^{-1}$,^{1–6)} (2) all constituents of CZTS films are abundant in the crust of the earth and non-toxic. In the previous paper, we fabricated CZTS-based thin film solar cell with 5.74% in conversion efficiency (η) using an inline-type vacuum apparatus.⁷⁾ The CZTS absorber layer was formed on the Mo coated soda-lime glass (SLG) substrate, and then the CdS buffer layer was deposited by chemical bath deposition (CBD) method. The Al-doped ZnO (ZnO:Al) window layer was formed on the buffer layer by sputter-deposition. However, $\eta = 5.74\%$ is still low compared to conversion efficiencies exceeding 18% of Cu(In,Ga)Se_2 -based thin film solar cells in spite of the more suitable optical properties of CZTS.^{8,9)} In the present work, we fabricate the CZTS-based solar cells with efficiencies exceeding 6% by innovating a new way to etch the absorber layer.

Mo electrode layers with 1 μm thickness were formed on SLG substrates by sputter-deposition. The CZTS precursors with $\sim 1.3 \mu\text{m}$ thickness were deposited by RF magnetron co-sputtering technique using three targets of Cu, SnS, and ZnS. The pressure of Ar sputtering-gas was 0.5 Pa. The RF-powers to the 4-in. Cu, SnS, and ZnS targets were 80, 100, and 155 W, respectively. The CZTS absorber layers were formed by sulfurizing the CZTS precursors. The sulfurization was carried out by heating the CZTS precursors to 580 °C and keeping them for 3 h in 20 vol % H_2S balanced with N_2 . Thicknesses of CZTS absorber layers were $\sim 2.2 \mu\text{m}$. Figure 1 shows the scanning electron microscope (SEM) image of the cross-sectional view of the CZTS absorber layer on the Mo electrode layer. Despite of the dense structure of the CZTS precursor, many voids were formed in the CZTS layer by sulfurization. The components of the CZTS absorber layers were estimated using inductively coupled plasma–atomic emission spectroscopy (ICP–AES). The atomic ratios of Cu/(Zn + Sn), Zn/Sn, and S/(Cu + Zn + Sn) of them were estimated ~ 0.85 , ~ 1.25 , and ~ 1.10 , respectively. The CZTS absorber layer on the Mo coated SLG substrate (SLG/Mo/CZTS) was soaked in

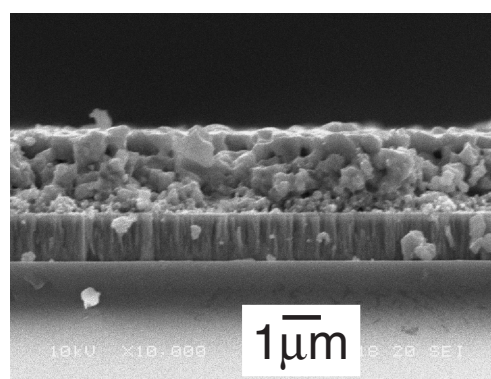


Fig. 1. SEM image of the cross-sectional view of the CZTS absorber layer on the Mo electrode layer. Many voids in the CZTS absorber layer were confirmed.

deionized water (DIW) for 10 min after forming of the CZTS absorber layer. And then a CdS buffer layer was chemically grown on the CZTS absorber layer by CBD method. The solution for CBD was prepared by mixing 400 ml of 0.42 mol $\text{CH}_4\text{N}_2\text{S}$ aqueous solution, 50 ml of 0.04 mol CdI_2 aqueous solution and 110 ml of 28% ammonium hydroxide solution. The CBD was carried out by soaking the SLG/Mo/CZTS in the mixture for 20 min, which was heated by hot-water bath of 70 °C. Then it was dried at 200 °C. The thickness of the CdS buffer layer was about 70 nm. A ZnO:Al window layer of 12 Ω/sq in sheet resistance and an Al interdigital electrode formed by sputtering and vacuum evaporation techniques, respectively. No anti-reflection layer was formed on the ZnO:Al window layer.

The current density–voltage (J – V) characteristics of the CZTS-based solar cell through DIW-soaking process were measured using a solar simulator under air mass (AM) 1.5 and 100 mW/cm^2 illumination after light soaking for 5 min. Figure 2 shows the J – V characteristic of the best performance CZTS-based solar cell presenting $\eta = 6.77\%$ with open-circuit voltage (V_{oc}) = 610 mV, short-circuit current density (J_{sc}) = 17.9 mA/cm^2 , filling factor (FF) = 0.62, series resistance (R_s) = 4.25 Ω , and shunt resistance (R_{sh}) = 370 Ω . The active area of this device was 0.15 cm^2 . V_{oc} , J_{sc} , FF , R_s , R_{sh} of the CZTS-based solar cell with $\eta = 5.74\%$ without DIW-soaking process were 662 mV, 15.7 mA/cm^2 ,

*E-mail address: e0987@mosk.tytlabs.co.jp

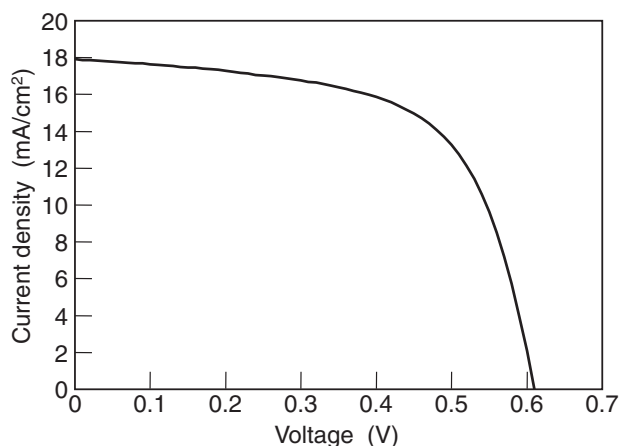


Fig. 2. J - V characteristic of the best performance CZTS-based thin film solar cell under AM 1.5 and 100 mW/cm^2 illumination after light soaking for 5 min. $\eta = 6.77\%$, $V_{oc} = 610\text{ mV}$, $J_{sc} = 17.9\text{ mA/cm}^2$, $FF = 0.62$, $R_s = 4.25\ \Omega$, and $R_{sh} = 370\ \Omega$.

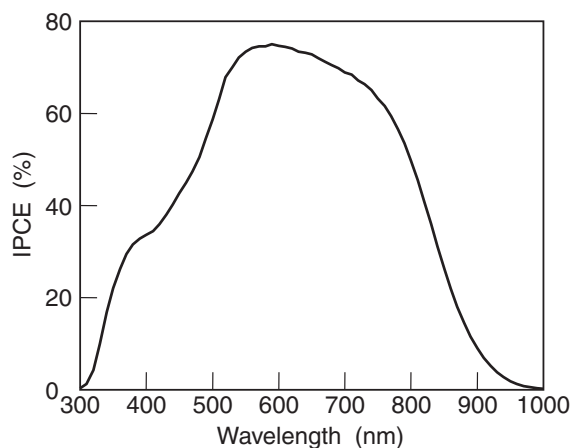


Fig. 3. IPCE spectrum curve of the best CZTS-based solar cell shown in Fig. 2. IPCE is higher than 60% in the 510–760 nm wavelength range.

0.55, $9.04\ \Omega$, and $612\ \Omega$, respectively. It is inferred that J_{sc} and FF of the CZTS-based solar cells were improved through lowering of the series resistance by DIW-soaking. Figure 3 shows the incident photon-to-photocurrent conversion efficiency (IPCE) spectrum curve of the best CZTS-based solar cell (same device in Fig. 2). The spectral region higher than 60% in IPCE was from 510 to 760 nm. The decline of IPCE spectrum with wavelength from 350 to 450 nm is caused by optical absorption of the CdS buffer layer.

It was found that the DIW-soaking after forming the CZTS absorber layer was important to improve the efficiency of CZTS-based solar cells. Therefore, to confirm clearly the effect of the DIW-soaking, we studied the components of the CZTS layer before and after soaking SLG/Mo/CZTS for 4 h in DIW. We measured inplane distributions of the components in the CZTS layer before and after 4-h-DIW-soaking by electron probe X-ray micro analysis (EPMA). Figures 4 show inplane distributions of oxygen in the CZTS layer before and after 4-h-DIW-soaking. Bright point-like areas of higher concentration of

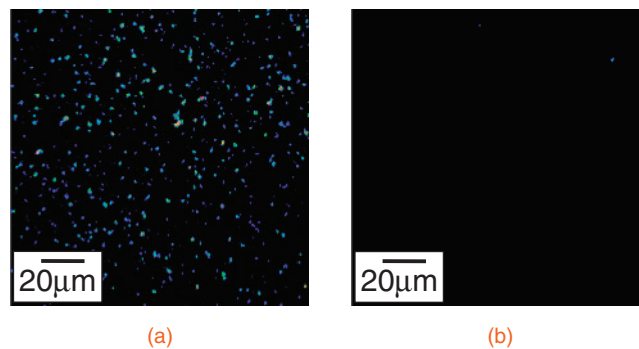


Fig. 4. Inplane distributions of oxygen in the CZTS layer before 4-h-DIW-soaking (a) and after 4-h-DIW-soaking (b). Bright point-like areas in (a) are higher concentration areas of oxygen. In (b), bright point-like areas are not almost confirmed.

oxygen are scattered in the CZTS layer before 4-h-DIW-soaking [Fig. 4(a)]. In contrast, concentration of oxygen in the CZTS layer fell below measurable limit of the EPMA instrument by 4-h-DIW-soaking in almost whole region [Fig. 4(b)]. Since oxygen is probably present in the form of metal oxide in the CZTS layer, one bright point-like area in Fig. 4(a) is considered one small metal oxide particle. Disappearance of the bright point-like areas by 4-h-DIW-soaking [Fig. 4(b)] shows that the metal oxide is easy to dissolve in water. It was found that DIW-soaking had the effect of preferential etching for the CZTS absorber layer. Since the metal oxide apparently does not absorb light effectively like CZTS, removing the oxide from CZTS layers is preferable to improve the conversion efficiency of solar cells by increasing the area where the CdS buffer layer directly touches the CZTS absorber layer. We presumed that increasing the direct contact area between the CZTS absorber layer and CdS buffer layer resulted in lowering of R_s of the CZTS-based solar cells.

In conclusion, CZTS-based thin film solar cells over 6.7% efficiency have been fabricated for the first time using preferential etching technique for CZTS absorber layers. This result suggests that the CZTS-based solar cell is promising for the next generation solar cells.

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