



# High photo-conversion efficiency $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ thin-film solar cells prepared by compound-precursors and metal-precursors

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## ABSTRACT

$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  (CZTSSe) thin-film solar cells have been fabricated by various methods. Sputtering is one of the vacuum processes that can be used for the growth of the precursors. In this study, CZTSSe thin-films that were fabricated using metal-precursors and with a high efficiency of 12.3% were examined in a comparison with CZTSSe thin-films that were fabricated using compound-precursors, whose efficiency is 9.1%. Especially, the Kelvin probe force microscopy (KPFM) analysis and local current measurement by conductive atomic force microscopy (c-AFM) show that their local electrical properties indicate completely opposite results. The grain boundaries (GBs) has a downward surface potential bending, and this repelled the minority carriers into the intragrain (IGs) in the sample from the metal-precursors. Therefore, we originally verified the differences between the carrier behaviors and the current flows on the surface.

## 1. Introduction

Due to its low cost and high power conversion efficiency (PCE), kesterite-type  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  (CZTSSe) is considered a promising material for thin-film solar cells. Its band gap ( $E_g$ ) of 1.0–1.5 eV is suitable and tunable, and its absorption coefficients are  $\sim 10^4 \text{ cm}^{-1}$  [1–3]. The latest report on CZTSSe solar cells shows the accomplishment of a high PCE of 12.6% for which an IBM-developed hydrazine-based nonvacuum process was used [4]. Using the sputtering method, DGIST achieved a PCE of 12.3% [5]. Nonetheless, compared with the 22.6% PCE of the  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$  (CIGS) solar cells [6], the further improvement of CZTSSe is warranted.

The radio frequency (RF) and direct current (dc) sputtering procedures with compound and metal targets, which have already been demonstrated for the CIGS solar cells, are one of the CZTSSe deposition methods in vacuum system. It has been reported that compound sources such as zinc sulfide (ZnS) and tin disulfide ( $\text{SnS}_2$ ) provide an improved adhesion between a substrate and a light absorber layer [7–11]. A dense nonvoid morphology has been observed on the surface-stacking order of copper (Cu)/ $\text{SnS}_2$ /ZnS [7]. A thicker layer showed an explicitly decreased circuit-current density and fill factor due to the high series resistance in the CZTS thin-film solar cell [12]. According to a recent report on sputtering-fabricated CZTSSe solar cells, the use of pure metal targets achieved a high efficiency [5]. It is critical to investigate the

various absorber-layer conditions for the enhancement of the CZTSSe conversion efficiency to a PCE of more than 20%.

The role of grain boundaries (GBs) on polycrystalline absorber layer for thin-film solar cells have been controversial. The researches on GBs in CIGS thin-films have discussed, and then those in kesterite thin-films are being established. One of the view-points on GBs is that they take a role as electron-hole pair recombination center [13,14]. According to Li *et al.*, they reported that localized defect states at the GBs can be caused by high density of defect states, theoretically. The other view is GBs behave as a benign carrier collection region, where the minority carrier collection occurs, probed via KPFM and c-AFM measurement [15,16]. Particularly, GBs in CZTSSe have been probed to determine the presence of an interesting electrical behavior. Li *et al.* and Kim *et al.* reported that GBs act as an efficient carrier-collection region [15,17]. Kelvin probe force microscopy (KPFM) and conductive atomic force microscopy (c-AFM) measurements have shown that the minority-carrier collection occurs at the GBs in the CZTSSe thin-films [15]. More recently, however, the CZTSSe thin-film surface showed a carrier behavior that is quite different from those of the reported researches. Xin *et al.* investigated lithium (Li)-doped CZTSSe thin-films, and the GBs were passivated by the Li ions. Thus, the GB work function can be larger than that of the intragrain (IGs), and the potential at the GBs is downward [18]. Therefore, the surface potential at the GBs indicates downward bending. Sadarshiti *et al.* addressed the tin oxide ( $\text{SnO}_x$ )

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**Table 1**  
Device Characteristics of Compound-precursor CZTSSe Solar Cells [25], Metal- precursor CZTSSe Solar Cells [5].

Sample	[Cu]/([Zn] + [Sn])	[Zn]/[Sn]	V <sub>oc</sub> [V]	J <sub>sc</sub> [mA/cm <sup>2</sup> ]	Fill factor [%]	Efficiency [%]
Compound-precursor CZTSSe	0.85	1.28	0.42	35.62	60.7	9.1
Metal-precursor CZTSSe	0.70	1.35	0.52	34.98	67.2	12.3

\*Efficiency in active area (0.183 cm<sup>2</sup>).

enrichment at the GB regions via nanoscale nano-Auger mapping, despite the removal of the surface oxygen (O) by an ammonium hydroxide (NH<sub>4</sub>OH) cleansing [19]. This also can bring about the downward potential bending at the GBs. Erkan et al. examined the surface potential bending after a solution-based post-deposition treatment (PDT) of a potassium cyanide (KCN) etching and an NH<sub>4</sub>OH cleansing that resulted in a downward potential bending at the GBs [20].

In this paper, an investigation of the roles of the GBs and IGs in sputtered compound- and metal-target CZTSSe thin-films is carried out using local electrical and device characterizations. We were motivated to measure and compare kesterite thin-film from different precursor formation; one is composed of sulfide compounds and Cu metal (so called, compound-precursor sample), the other of pure metals (metal-precursor sample). This is because of the different results between compound-precursor samples [17,21,22] and metal-precursor samples, which have been studied in a series, in spite of diverse selenization, sulfurization, or sulfo-selenization conditions. Furthermore, the annealing condition has been changed in order to maintain S and Se ratio for similar thin-film properties between compound- (S-containing) and metal- (S-free) precursor samples. With additional S, the compound-precursor sample could be S-rich, resulting in a large band gap. On the one hand, if the metal-precursor samples were only selenized, Cu<sub>2</sub>ZnSnSe<sub>4</sub> thin-films would be formed. The big difference in the band gap may lead to changes in the thin-film properties; for instance, defect level etc. Therefore, we tried to focus on the characterization of kesterite thin-films having similar S/Se ratio, but different precursor materials.

Our group reported the results by analyzing high-efficient CZTSSe solar cells in terms of band gap grading [5], defect states [23], and simulation of device simulation [24]. In this research, we probed the CZTSSe thin-films at local scale to determine the solar cell performance. The surface potential was measured by KPFM, which can analyze the electric field on the thin-film surfaces. With c-AFM, local current maps were obtained, accompanied to the topography. Local current (*I*)-voltage (*V*) curves displayed the difference in conductivity between the GBs and the IGs. By comparing the local electrical properties of compound- and metal-precursor CZTSSe thin-film solar cells via KPFM and c-AFM, we could comprehend the carrier behavior in the materials. Thus, the research can help drawing up plans for the betterment of kesterite-type thin-film solar cells.

## 2. Experimental

For the fabrication of the CZTSSe thin-films, two kinds of precursor were used, as follows: compound-precursors including ZnS, tin sulfide (SnS), and Cu, and metal-precursors from zinc (Zn), tin (Sn), and Cu pure-metal targets.

### 2.1. Thin-film fabrication via the compound-precursors

The ZnS/SnS/Cu-precursor layer was sequentially deposited on a 600-nm-thick molybdenum (Mo)-coated soda-lime glass (SLG) by the sputtering of 99.99%-pure Cu, SnS, and ZnS targets [25]. The thicknesses of the precursor layers are 337 nm for the ZnS, ~ 400 nm for the SnS, and ~200 nm for the Cu. The precursors were first deposited using a stacked-sputtering method, and they were then annealed with selenium (Se) metal in a furnace at 570 °C for 20 min in a furnace. Argon

(Ar) gas was then introduced into the sealed furnace, and the pressure was increased to atmospheric pressure. The CZTSSe-absorber layers were covered with a 50-nm-thick cadmium sulfide (CdS)-buffer layer using a chemical-bath deposition (CBD). A 50-nm intrinsic ZnO layer and a 300-nm aluminum (Al)-doped ZnO layer were then deposited using RF sputtering. Finally, a 500-nm Al collection grid was deposited on top of the device via thermal evaporation. [S]/([S] + [Se]) ratio was ~0.09 [25].

### 2.2. Thin-film fabrication via the metal-precursors

The metal-precursors for the CZTSSe-absorber layer were deposited on the Mo layer using 99.99%-pure Cu-, Sn-, and Zn-sputtering targets with the stacking order of Cu (170 nm)/Sn (268 nm)/Zn (188 nm)/Mo. The Mo layer was deposited on a SLG substrate via dc-magnetron sputtering using a Mo target with a purity of 99.99%. For the sulfo-selenization process, the precursors were placed in a graphite box with SeS<sub>2</sub> and Se source whose SeS<sub>2</sub>/Se ratio was 0.38%. The annealing process that was conducted in an Ar-filled rapid thermal process (RTP) is conducted at slightly above 1 atm at 510 °C for 18 min. A 50-nm-thick CdS-buffer layer was deposited via CBD. Subsequently, a 50-nm-thick intrinsic ZnO layer was deposited via sputtering, a 300-nm-thick Al-doped ZnO layer was deposited via sputtering, and a 500-nm-thick Al collection grid was deposited via thermal evaporation [5]. Due to front band gap grading, [S]/([S] + [Se]) of the CdS-CZTSSe interface was 0.11, and that amid the CZTSSe thin-films was about 0.065 [5]. More detailed [S]/([S] + [Se]) ratio depending on the thin-film depths are shown in Ref. [5].

The device parameters of the samples are shown in Table 1. About the efficiency measurements, the total area of the two samples was 0.185 cm<sup>2</sup>, and the active area of them was 0.183 cm<sup>2</sup>. Therefore, the difference of the efficiencies in between total area and active area will be less than 1%.

### 2.3. Characterization

The local electronic properties of the thin-films were studied using KPFM. The n-Tracer commercial atomic force microscopy (AFM) instrument (NanoFocus, Inc, n-Tracer) was used for the KPFM and c-AFM measurements. The bare CZTSSe absorber surfaces were scanned, which were not gone through any solution-based treatment. Before measurement, the samples were kept in a desiccator whose humidity is maintained with 20% ± 5%. During measurement, samples were kept in a glove box. A clean surface and controlled environment were kept during the measurement by operating it in the glove box, whose humidity and oxygen concentration are under 1.0 ppm. The temperature inside the glove box is room temperature in nitrogen atmosphere at slight over 1 atm. The surface potential of the sample was measured in the noncontact mode using an alternating current (ac)-voltage amplitude of 1.0 V. Notably, the samples were not damaged by the carrying out of such measurements, and the lock-in amplifier was operated with a sensitivity of 100 mV/nA. The surface current map was operated in the contact mode, and the scan area is 3 × 3 μm<sup>2</sup>. Local *I*-*V* curves were obtained from the contact between the sample surface and the platinum (Pt)/iridium (Ir)-coated silicon (Si) tip for which a bias from -10 to 10 V was applied.

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