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Effects of the metallic target compositions on the absorber properties and the performance of $Cu_2ZnSnSe_4$ solar cell devices fabricated on TiN-coated Mo/glass substrates

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ABSTRACT

$Cu_2ZnSnSe_4$ (CZTSe) films have been fabricated by sputtering of Cu–Zn–Sn metallic targets on the TiN-coated Mo/glass substrates, followed by selenization at 500–600 °C for 1 h under a compensation disk. Three targets of A, B, and C, with different ratios of Cu, Zn, and Sn elements were fabricated by hot pressing the constitutive powder mixture. The effects of the target's compositions on the growth behavior, microstructural characteristics, and electrical properties of CZTSe films have been investigated. Influence of the target's composition outshined the CZTSe films in grain growth, film composition, electrical properties, and solar cell performance. The CZTSe films deposited from target B of [Cu]/[Zn]/[Sn] at 2/1/1 had a [Cu]/([Zn]+[Sn]) ratio of 1.01, large grains of 2.5–5.0 μm, and high mobility of ~80 $cm^2 V^{-1} s^{-1}$ and its fabricated solar cell device had the efficiency of 2.6%, as compared to the TiN-free device with 0.58% efficiency.

1. Introduction

Earth-abundant $Cu_2ZnSnSe_4$ (CZTSe), Cu_2ZnSnS_4 (CZTS), or $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells have shown the energy conversion efficiencies of 8–10% [1–3]. CZTS-based solar cell systems have the potential to be the $Cu(In,Ga)Se_2$ (CIGS) replacements. All those devices with outstanding efficiency had their absorbers with dense microstructure and large grain size of 1–2 μm.

Sputtering is a cost-effective technique for thin-film deposition. This technique also has been applied for fabricating CZTSe solar cells. Co-sputtering with three ceramic targets followed by the selenization at 580 °C under the SnS and S_2 atmospheres had achieved the 7.75% CZTSSe solar cell devices [4]. Sequential sputtering of Sn, Cu, and Zn films followed by sulfurization or selenization has achieved the 3.2–7.5% cell efficiencies [5–7]. Co-sputtering with Cu, SnS, and ZnS targets led to an efficiency of 6.77% device [2]. Combining the sulfide sputtering and the metal co-evaporation, a 6.0% efficient device was obtained [8]. The record efficiency of 9.7% CZTSe solar cell device fabricated by the vacuum sputtering of Cu, Zn, and Se layers and the selenization with H_2Se have just announced by IMEC in July, 2013 [9]. The common feature of the previous CZTSe sputtering studies is the utilization of multiple sputtering targets. Single metallic target sputtering for CZTSe is not popular because many target compositions need to be tested in order to find the appropriate composition.

A selenization procedure of Cu–Zn–Sn metallic films in the presence of a ($SnSe_2$ + Se) compensation disk has been developed to transform metallic into selenized films with large grains of 1–6 μm [10]. Considering the interfacial reaction to form $MoSe_2$, the TiN barrier layer has been proposed for an 8.4% efficient CZTSe solar cell [11]. MoS_2 has been observed at the prolonged co-sputtering at 560 °C with the Cu–Sn alloy and Zn targets in the H_2S atmosphere [12]. The interfacial reaction is quite difficult to be controlled precisely without device degradation. Here, we have grown the CZTSe films by depositing Cu–Zn–Sn films with sputtering of single metallic Cu–Zn–Sn targets on the TiN-covered Mo/glass substrates, followed by post-selenization at 500–600 °C for 1 h. Three targets with different Cu, Zn, and Sn ratios have been used to deposit the different CZTSe films for comparative purpose.

2. Experimental

To fabricate CZTSe absorbers, the Cu–Zn–Sn metallic films were firstly deposited on the unheated TiN-coated Mo/glass substrates by direct-current (DC) sputtering at 80 W for 1 h with single Cu–Zn–Sn metallic targets. The working distance of DC sputtering was kept at 15 cm. Then the as-deposited films were selenized at 500, 550, and 600 °C for 1 h together with a compensation disk

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Table 1
Composition molar ratios of three different targets containing Cu, Zn, and Sn.

Target	[Cu]	[Zn]	[Sn]
A	1.5	1	1
B	2	1	1
C	1.8	0.9	1.0

containing ($SnSe_2$ + 30 wt% Se) powder to provide the required Se vapor and convert the metallic into selenide films. The targets with 2-in. diameters for depositing Cu–Zn–Sn films were formed by mixing Cu, Zn, and Sn powders, followed by hot pressing. In order to achieve better CZTSe composition, the Cu–Zn–Sn compositions of three targets have been attempted and they are listed in Table 1. The processes of selenization have been carried out by the one-step or two-step procedure. For the one-step procedure, the as-deposited films together with compensation discs were directly heated to 500–600 °C with raising temperature of 10 °C/min and duration of 1 h. For the two-step procedure, the temperature first increased to 300 °C with a holding time of 30 min, followed by increasing selenization temperature to 600 °C and holding for 1 h. During the selenization, Cu–Zn–Sn films were loaded in a lid-covered ceramic crucible together with compensation discs. For solar cell devices, a 50 nm-thick CdS buffer layer was deposited on the CZTSe absorber layer by the chemical bath deposition at 70 °C for 30 min in a solution of cadmium acetate, thiourea, ammonium chloride, and ammonia. The 50 nm-thick ZnO and 500 nm-thick ITO layers were deposited by radio-frequency (RF) sputtering at 200 °C for different durations. For RF sputtering, the power was 60 W, the working distance was 10 cm, and the sputtering atmosphere was argon with a flow rate of 40 ml/min. The deposition time was 30 min for ZnO and 60 min for ITO film. The silver paste was used for electric contacts.

Phase identification of CZTSe layers was analyzed by X-ray diffractometry (XRD, Rigaku D/Max-RC). A field-emission scanning electron microscope (SEM, JEOL JSM 6500F) equipped with energy dispersive spectroscopy (EDS) was used for microstructural characterization and composition analysis. A Hall measurement system (HMS 2000, ECOPIA, Korea) was used to measure the resistivity, mobility, and carrier concentration of the selenized films deposited on the pyrex glass substrates. The illuminated *J–V* characteristic of the device was measured by a standard AM1.5 illumination meter.

3. Results and discussion

Fig. 1 shows SEM images of the CZTSe films deposited by DC magnetron sputtering of metallic Cu–Zn–Sn target A, followed by one-step selenization at (a) 500 °C, (b) 550 °C, and (c) 600 °C for 1 h in the presence of a compensation disk of ($SnSe_2$ + 30%Se). The 500 °C-selenized CZTSe film was porous and showed small grains. No densification was observed at low selenization temperature of 500 °C. With increasing the selenization temperature to 550 °C, the film had bigger and island-like grains but was still rough. Reaching to 600 °C, the CZTSe films showed the good microstructure with a large-grained and pore-free surface. After selenization at 600 °C, grains of 1–2 μm in size were obtained. These CZTSe films were characterized for their elemental composition by the EDS analysis. The [Cu]/([Zn] + [Sn]), [Zn]/[Sn], and [Se]/([Cu] + [Zn] + [Sn]) ratios were 0.54, 1.92, and 1.09, respectively, for the 500 °C-selenized, 0.75, 1.03, and 1.42 for the 550 °C-selenized, and 0.62, 1.42, and 1.16 for the 600 °C-selenized films. The Cu deficiency and a [Zn]/[Sn] ratio of 1.15–1.25 in CZTSe have been frequently mentioned for good absorber layers [13,14]. Here, our films strongly deviated from the expected compositions. The large difference in target's and film's composition made us decide to change the one-step to the two-step selenization.

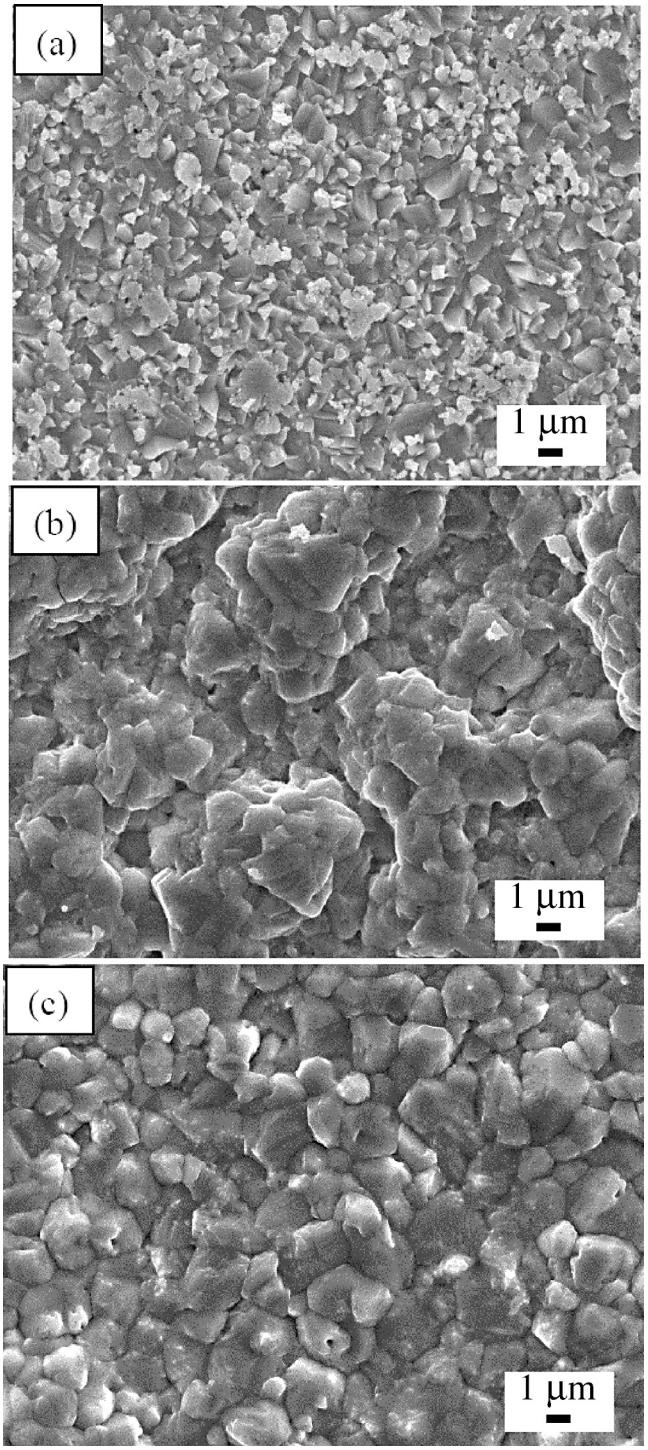

Fig. 1. SEM images of the CZTSe films deposited by DC magnetron sputtering of metallic Cu–Zn–Sn target A, followed by one-step selenization at (a) 500 °C, (b) 550 °C, and (c) 600 °C for 1 h.

Fig. 2 shows SEM images of the CZTSe films after selenization at (a) 500 °C, (b) 550 °C, and (c) 600 °C for 1 h with a two-step procedure. The two-step selenization obtained continuous, smooth, and dense CZTSe films after heating at 550 °C (Fig. 2(b)), while the one-step one remained discontinuous, rough, and porous (Fig. 1(b)). Obviously, the two-step procedure assists to get the improvements in densification and grain growth after selenization at and above 550 °C. After selenization at 600 °C, grains of 2–3 μm in size were obtained. It is suggested that the two-step selenization procedure