



Performance of CZTSSe thin film solar cells fabricated using a sulfo-selenization process: Influence of the Cu composition



R.B.V. Chalapathy^a, Myeng Gil Gang^a, Chang Woo Hong^a, Ji Hun Kim^b, Jun Sun Jang^a, Jae Ho Yun^c, Jin Hyeok Kim^{a,*}

^a Department of Materials Science and Engineering and Optoelectronics Convergence Research Center, Chonnam National University, Gwangju 500-757, South Korea

^b School of Electrical Engineering and Computer Science, Gwangju Institute of Science and Technology, 123 Cheomdangwagi-ro, Buk-Gu, Gwangju 500-712, South Korea

^c Photovoltaic Research Group, Korea Institute of Energy Research, 71-2 Jang-Dong, Yuseong-Gu, Daejeon 305-343, South Korea

ARTICLE INFO

Keywords:

CZTSSe

Cu content

Sulfo-selenization

Sputtering

Thin film solar cells

ABSTRACT

In this work, earth-abundant CZTSSe thin film solar cells were fabricated by sulfo-selenization of the Mo/Zn/Cu/Sn/Cu metallic precursors. The influences of morphological and compositional properties of the absorbers on performance of solar cells were investigated by tuning Cu content in the films. The Raman analysis showed that absorbers consist of a kesterite CZTSSe phase with ZnSe as a minor secondary phase. X-ray photoelectron spectroscopy (XPS) analyses revealed that the surfaces are Cu depleted and Zn enriched compared with the bulk composition of the absorbers. The results indicate that during sulfo-selenization the Cu diffused into the film and the Zn towards the film surface. The performance of the solar cells initially improved with the increasing of the Cu content and then decreased. By tuning the Cu content in the absorbers, the minority-carrier life time improved from 0.8 to 1.6 ns. The power conversion efficiency increased from 5.1 to 8.03% with fine controlling of Cu composition of the CZTSSe absorbers. The diode-ideality factors are higher than 2, suggesting an increased interfacial recombination in the devices. The high ideality-factors A and low minority carrier life times may originate from surface and bulk related defects, which in turn limits the V_{oc} and the achievable high conversion efficiency for the CZTSSe thin film solar cells.

1. Introduction

Second generation thin film solar cells based on copper indium gallium (di) selenide $\text{CuInGa}(\text{Se})_2$ and cadmium telluride (CdTe) have emerged as promising technologies for high efficiency and low cost solar cells (Kamada et al., 2016; Green et al., 2017). However, concern over the use of expensive and toxic elements such as indium (In) and cadmium (Cd) has led researches to seek out an alternative material system. Among the various candidates, kesterite $\text{Cu}_2\text{ZnSn}(\text{SSe})_4$ (CZTSSe) has attracted much attention as an absorber for low cost thin film solar cells owing to its abundance and optimal optoelectronic properties. The high absorption coefficients and variable band gaps from 1.0 to 1.5 eV can be obtained by varying the sulfur (S)/selenium (Se) anion ratio for a solar spectrum-matching for the maximum conversion efficiency (Wang et al., 2013). So far, CZTSSe thin film solar cells with power conversion efficiencies over 12.7% and 12.3% have been reported with solution and sputtering processes, respectively (Kim et al., 2014; Yang et al., 2016a).

The conversion efficiencies achieved so far are less than those of the

CIGSSe (22.8%) thin film solar cells and are lower than achievable theoretical efficiency (Kamada et al., 2016; Siebentritt and Schorr, 2012). The low efficiency arises due to large open circuit voltage (V_{oc}) deficit of more than 500 mV. One reason for low V_{oc} is the potential fluctuations that arise due to compositional inhomogeneity of the absorbers; this factor contributes 170 mV to the V_{oc} deficit. The formation of defects at the surface and bulk of absorbers and band offsets at the interfaces enhance interfacial recombination which contributes additional losses of approximately ~ 400 mV (Gunawan et al., 2013). It is known that formation of single phase region in the Cu-Zn-Sn-S-Se system is a very narrow region, any deviation from off-stoichiometry leading to formation of secondary $\text{Cu}(\text{S-Se})_2$, $\text{Zn}(\text{S-Se})$, $\text{Sn}(\text{S-Se})_2$ and $\text{Cu}_2\text{Sn}(\text{S-Se})_3$ phases (Olekseyuk et al., 2004) in the film; these phases degrade the performance of the devices (Tai et al., 2016). The absorber surface region is critical in thin film solar cells. The morphological and compositional non-uniformity at the surface introduces defect states in the band gap and these defects increases interfacial recombination in thin film solar cells. The electronic properties of absorbers such as low carrier diffusion length, minority carrier life time and mobility reduce

* Corresponding author.

E-mail address: jinhyeok@chonnam.ac.kr (J.H. Kim).

the achievable V_{oc} and short circuit current density (J_{sc}) in the CZTSSe thin film solar cells, which limits wide applicability of CZTSSe technology (Gershon et al., 2017; Aninat et al., 2016). Reports have indicate that the composition strongly influences the electronic properties of the CZTSSe films (Tai et al., 2016; Aninat et al., 2016), so to improve the conversion efficiency further it is necessary to control the compositional in-homogeneity and defects in the absorbers.

CZTSSe thin film solar cells are fabricated using a wide variety of vacuum and non-vacuum based techniques (Gang et al., 2016; Li et al., 2016a, 2016b; Yang et al., 2017; Chen et al., 2016; He et al., 2012; Li et al., 2015; Xin et al., 2015; Haass et al., 2015; Larramona et al., 2015; Jiang et al., 2014; Yang et al., 2016a, 2016b; Guo et al., 2016; Schnabel et al., 2015; Miskin et al., 2015; Lin et al., 2015; Jung et al., 2016). Among the numerous methods for the growing of the CZTSSe absorbers, dc sputtering of metallic precursors followed by a reactive annealing in Se and S atmosphere is a preferable process (Gang et al., 2016; Yang et al., 2017). This process offers advantages over non-vacuum based chemical methods due to large area scalability and avoidance the use of highly toxic and hazardous chemicals. The properties of CZTSSe films strongly depend on the nature of precursor stacks, order and number of stacking layers. Most of the reported metallic precursor stacking order consists of Cu top layer to protect the re-evaporation of Sn from the film surface during annealing. The excessive Cu content layer at the top will lead to formation of Cu rich Cu_2S and Cu_2Se phases on the surface, which introduces shunt in the devices. In previous work, CZTSSe thin film solar cells with an efficiency of 9.2% have been fabricated using a three layer Mo/Zn/Sn/Cu metallic precursor stacks that were reacted using sulfurization/selenization (Gang et al., 2016). The use of bottom Zn layer increases the formation of fine grains at the interface, and this has a deleterious effect on the fill factor (FF) of the devices. Recently, using multi-nano ZnS/SnS/Cu precursor stacks with 15 layers, an improved performance of CZTSSe thin film solar cells with conversion efficiency of 7.0% was achieved (Yang et al., 2017). On the other hand (Chen et al., 2016) reported 7.74% CZTSSe thin film solar cell with metallic precursor consisting 9 layers. However, the use of sulfide layers requires high annealing temperatures to avoid the formation of ZnS at bottom of the film and use many layers increases the process complexity. So, it is necessary to choose optimum precursor stack to decrease the process complexity, less voids, Zn content at the bottom and to avoid the formation of Zn(S-Se) phases, Hence, in this study the precursor stack was modified by splitting the top Cu layer into two layers.

In this work, the effect of copper content on the morphological and compositional properties of the CZTSSe absorbers grown by sulfo-selenization of dc sputter deposited Mo/Zn/Cu/Sn/Cu metallic stack was studied. The Cu/(Zn+Sn) ratio was varied in order to investigate its effect on the device performances. The surface composition of the films measured using X-ray photoelectron spectroscopy (XPS) suggests that the surface is extremely Cu-poor compared with the bulk composition. The Cu-poor surface may lead to the formation of surface defects that decreases the achievable V_{oc} . With increasing the Cu content in the precursors, the absorber exhibited smooth and dense surface morphologies. The best performance of 8.17% was achieved with the Cu/(Zn+Sn) ratios of 0.65 and 0.30 for the bulk and surface compositions, respectively.

2. Experimental

2.1. Deposition of the precursor stacks and the absorber formation

The CZTSSe absorbers were grown using a two-step method. The precursor stacks with Mo/Zn/Cu/Sn/Cu sequence were deposited onto $2.5 \times 2.5 \text{ cm}^2$ Mo coated soda lime glass substrates (SLG) by dc magnetron sputtering using pure Cu, Zn and Sn metal targets. The process conditions used for precursor deposition; base pressure is 5×10^{-6} torr, working gas Ar flow rate is 30 sccm, and working pressure is

8 mTorr. The sputtering power density was fixed at $0.68 \text{ (W/cm}^2\text{)}$ for all three metals, and the deposition times were optimized to vary the Cu/(Zn+Sn) ratio in the precursors. The composition ratio in the precursors was measured using energy dispersive X-ray spectroscopy (EDX). Using field emission scanning electron microscopy (FESEM), the precursor thicknesses were measured as 680, 754, 727, and 747 nm with various Cu contents. To investigate the influence of the Cu content, the Cu/(Zn+Sn) ratio in the precursors was varied from 0.55 to 0.71 by tuning the Cu deposition time. All depositions were carried out at room temperature. The stack order was chosen to prevent the evaporation of the Sn and to reduce the Zn content at the bottom of the film. To intermix and form binary alloys, the deposited precursors were subjected to preannealing for 1 h at $300 \text{ }^\circ\text{C}$ in Ar atmosphere (760 Torr). To convert precursors into CZTSSe absorbers, the preannealed precursors were annealed in graphite box (volume $\sim 406 \text{ cm}^3$) with 196 mg of selenium (Se) and 4 mg of sulfur (S) using a rapid thermal annealing (RTA) system in an Ar atmosphere (400 Torr) with a ramp rate of $10 \text{ }^\circ\text{C/s}$. The annealing temperature was kept at $540 \text{ }^\circ\text{C}$ for 10 min. The amount of S and Se were chosen in order to synthesize absorbers with (S/Se+S) ratio < 0.25 . After the annealing, the films were cooled down to room temperature naturally.

2.2. Solar cell fabrication

CZTSSe thin film solar cells were fabricated in the configuration of Mo/CZTSSe/CdS/i-ZnO/AZO/Al. Prior to the CdS deposition; the absorbers were etched with a 0.2 M potassium cyanide (KCN) for 2 min at room temperature to remove the $Cu_2(S-Se)$ phases on the surface. After KCN etching a CdS buffer layer with a thickness approximately of 50 nm was deposited by chemical bath deposition using 0.2 M $CdSO_4$, 0.84 M ammonia, and 1.02 M thiourea at $80 \text{ }^\circ\text{C}$ for 13.30 min. Bi-layer window layers consisting of intrinsic zinc oxide i-ZnO (50 nm) and aluminum doped zinc oxide (AZO) (500 nm) were deposited at 50 and 70 W, respectively by radio frequency sputtering. An Aluminum top contact was deposited through a metal mask using dc sputtering process. Finally, the devices were mechanically isolated with an active area of 0.31 cm^2 .

2.3. Characterizations

The crystal structure and phase purity of sulfo-selenized absorbers were analyzed by using high resolution X-ray diffraction (XRD, X'Pert PRO, with Cu K_α radiation (1.5416 \AA) PANalytical, The Netherlands). The phases were also confirmed by a Raman spectrometer with a laser excitation wavelength of 532 nm (Tokyo Electronics, Japan) and with an ultraviolet (UV) laser excitation of 325 nm with a LabRam HR800 UV Raman microscope (Horiba Jobin-Yvon, France), (KBSI, Gwangju-center). The surface and cross-sectional morphologies of films were observed using a SU-70 FE-SEM (Hitachi, Japan). The composition of the precursors and the sulfo-selenized films were measured using energy dispersive energy spectroscopy (EDX) attached to the FESEM. The surface composition of the absorbers were measured with VG Multilab 2000 X-ray photoelectron spectroscopy (XPS) (Thermo VG Scientific, U. K.) with a monochromatic Mg- K_α (1253.6 eV) radiation source after Ar ion etching. The current-voltage (J-V) characteristics of solar cells were measured using a class AAA solar simulator (Sol 31, Oriol, USA) under standard illumination of 100 mW/cm^2 at room temperature. Prior to the measurement solar simulator was calibrated with a Si reference solar cell. External quantum efficiency (EQE) measurements were performed with a QE system (PV Measurements Inc., USA). Time resolved photoluminescence (TRPL) measurements were performed on completed solar cells using Fluorescence spectrophotometer in the wavelength region from 300 to 1400 nm.

Download English Version:

<https://daneshyari.com/en/article/7936002>

Download Persian Version:

<https://daneshyari.com/article/7936002>

[Daneshyari.com](https://daneshyari.com)