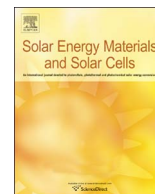




Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Increase in conversion efficiency of above 14% in $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ (β -CIGS) solar cells by Na_2S incorporation through the surface of β -CIGS film

Ji Hye Kim^a, Seung Tae Kim^a, Liudmila Larina^a, Byung Tae Ahn^{a,*}, KiHwan^b, Jae Ho Yun^b

^a Department of Material Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 34141, South Korea

^b Photovoltaic Team, Korea Institute of Energy Research, Daejeon 34129, South Korea

ARTICLE INFO

Keywords:

Thin-film solar cells
Cu(In,Ga)₃Se₅
 β -CIGS
Co-evaporation process
 Na_2S incorporation

ABSTRACT

Little work has been reported on the performance improvement of the β -CIGS solar cell itself even though the β -CIGS phase can have an ideal band gap for high-conversion efficiency solar cells. We incorporated Na_2S to β -CIGS film by supplying Na_2S to three different stages: on the $(\text{In,Ga})_2\text{Se}_3$ layer, on the α -CIGS layer, and on the β -CIGS layer in the three-stage co-evaporation process. The purpose of Na_2S incorporation was to control the carrier concentration and passivate grain boundaries in β -CIGS film. With Na_2S incorporation on the β -CIGS surface, both the Cu and Se concentrations at the β -CIGS surface were greatly reduced and the Na-depleted subsurface area that existed in the referenced β -CIGS film without Na_2S was eliminated. The carrier concentration determined at 100 kHz was lowest with Na_2S incorporation on the β -CIGS surface, while that determined at 1 MHz was similar with various Na_2S supply stages. The open-circuit voltage and fill factor greatly increased in the β -CIGS solar cell with the Na_2S incorporation. The cell conversion efficiency with Na_2S incorporation on the β -CIGS layer improved from 10.3% to 14.2% without AR coating, which is a record efficiency in β -CIGS solar cells at this time.

1. Introduction

$\text{Cu}(\text{In,Ga})\text{Se}_2$ (α -CIGS) and related materials have been studied for thin film solar cells since their high absorption coefficient and adjustable band gap can achieve a high conversion efficiency. Recently, several groups reported a cell efficiency of more than 20% with alkali treatment on the CIGS surface [1,2]. The increase efficiency was assigned to the modification of the surface chemical composition of CIGS absorber and optoelectronic properties at the CIGS/buffer interface induced with treatment. Chirila et al. have shown that the sequential post-deposition treatment with sodium (NaF-PDT) and potassium fluoride (KF-PDT) lead to the remarkable decrease in the concentration of the Cu at the α -CIGS surface and affect the interface properties of the resulting p-n junction [1]. The depletion of the Cu and Ga at the CdS/CIGS interfaces was confirmed by XPS depth profile analysis and ion exchange process was proposed as underlying mechanisms. To further clarify the favorable effect of the PDT on the power conversion efficiency. Reinhard et al. investigated the influences of alkali post deposition treatments with NaF and/or KF on the CIGS films grown on flexible polyimide foils [3]. The removal of Na from the bulk and the formation of a Cu-depleted, K-enriched layer on the surface after KF PDT were confirmed by nondestructive advanced techniques. After the

post-deposition treatment, the concentration at the α -CIGS surface was greatly reduced [1]. It was suggested that the alkali element modified the surface of the α -CIGS layer [3].

A Cu-depleted surface layer was also found on the surface layer of CIGS film by annealing at low temperature in a Se, O, or S atmosphere [4]. The surface layer was identified as the $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ (β -CIGS) phase [4]. The β -CIGS layer on α -CIGS film is considered as an epitaxial layer and acts as a hole blocking layer, resulting in the improvement of cell performance and reproducibility. The intentional deposition of a surface β -CIGS layer on α -CIGS film increased cell efficiency of α -CIGS solar cells [5,6]. In particular, Nishimura et al. achieved a 19.8% efficiency with the help of a β -CIGS surface layer on α -CIGS film [7]. Even though the β -CIGS plays an important role in α -CIGS cell, the study of the β -CIGS solar cell itself has not been extensive. Nakada et al. developed a multi-step process for CIGS film growth with intentionally incorporated Na_2Se to an increase of the p-type conductivity [8]. The application of the Na control technique enables a remarkable increase the hole concentration of the CIGS-based films up to the 10^{16} – 10^{17} cm^{-3} for a wide range of Cu/(In + Ga) ratios 0.4–0.8). The application of developed β -CIGS absorber leads to the cell efficiency of 13.5% with $J_{\text{SC}} = 35.2$ mA/cm^2 , $V_{\text{OC}} = 567$ mV, and $\text{FF} = 67.7\%$. [8]. A cell efficiency of 13.5% for β -CIGS-based solar cells was reported by T. Nakada [8].

* Corresponding author.

E-mail address: btahn@kaist.ac.kr (B.T. Ahn).

<https://doi.org/10.1016/j.solmat.2017.12.022>

Received 21 August 2017; Received in revised form 11 November 2017; Accepted 17 December 2017

0927-0248/ © 2017 Published by Elsevier B.V.

The crystal structure of β -CIGS is a stannite-like structure with Cu vacancy and In_{Cu} defects [9,10]. The Cu/(In + Ga) ratio in the β -CIGS ranges from 0.3 to 0.65 [10]. The band gap of the β -CIGS phase can be adjusted from 1.17 to 1.9 eV by increasing the Ga composition [10,11] and it usually exhibits p-type conductivity because of the formation of a Cu-poor CIGS thin film [12].

β -CIGS film was prepared by a three-stage co-evaporation with various Cu/(In + Ga) ratios [13], and a 10.3% efficiency was reported by improving the morphology with Se flux control and reducing the surface Cu composition with Se annealing at low temperature [14]. The presence of Na in CIGS-based thin film solar cells plays important roles in material and device properties. It was reported that Na depletion in CIGS increases the resistivity of CIGS film [15]. With Na incorporation in a β -CIGS solar cell, the cell performance greatly improved in β -CIGS film [8]. In the literature, Na was incorporated in-situ during the second-stage of a three-stage co-evaporation process using Na_2S as a doping source.

In our experiment, we conducted a systematic study by incorporating Na through three different stages: after the first stage, after the second stage, and after the third stage using Na_2S as the doping source. We then systematically investigated the most effective Na incorporation for β -CIGS solar cells. This study achieved a cell conversion efficiency of above 14%, the highest value at the moment.

2. Experimental

2.1. Film growth and cell fabrication

β -CIGS films with a thickness of 2 μm were grown on Mo-coated soda-lime glass substrate by a co-evaporation process. The evaporation rates of Cu, In, Ga, and Se were 1.0, 3.0, 2.5 and 16 $\text{\AA}/\text{s}$, respectively. In the first stage, the substrate temperature was maintained at 350 $^\circ\text{C}$ to form the $(\text{In,Ga})_2\text{Se}_3$ (IGS) layer by In, Ga, and Se co-evaporation. In the second stage, the substrate temperature was elevated to 550 $^\circ\text{C}$ in 5 min and then Cu and Se were co-evaporated. At this stage, a Cu-rich CIGS (α -CIGS) film was formed in situ by a direct reaction with the $(\text{In,Ga})_2\text{Se}_3$ film and the evaporated Cu and Se. In the third stage, In, Ga, and Se elements were evaporated to make β -CIGS layers at the same substrate temperature. Then, the samples were cooled down to 350 $^\circ\text{C}$ in a Se atmosphere.

Na was incorporated into the CIGS film by depositing a 6-nm thick Na_2S layer during the three-stage co-evaporation process at the three different stages: ① Na_2S deposition on the IGS layer at 350 $^\circ\text{C}$, ② Na_2S deposition on the $\text{Cu}(\text{In,Ga})\text{Se}_2$ (α -CIGS) layer at 550 $^\circ\text{C}$, and ③ Na_2S deposition on the β -CIGS layer at 550 $^\circ\text{C}$. The three Na_2S incorporation stages ①, ②, and ③ are marked in the schematic three-stage co-evaporation process shown in Fig. 1. Note that both Na_2S and Se were co-evaporated during Na_2S evaporation. The deposition rate of Na_2S was adjusted to be 1 $\text{\AA}/\text{s}$, and the rate was measured using Quartz crystal microbalance before experiment. The deposition time of Na_2S on IGS at 350 $^\circ\text{C}$ and on α -CIGS and on β -CIGS was 1 min each. For 350 $^\circ\text{C}$ deposition on IGS layer, the Na_2S might exit on the IGS surface at 350 $^\circ\text{C}$ and then diffuse away through CIGS film during the subsequent α -CIGS formation and β -CIGS formation at 550 $^\circ\text{C}$. For 550 $^\circ\text{C}$ deposition on α -CIGS layer at 550 $^\circ\text{C}$, Na_2S can diffuse away during β -CIGS formation at 550 $^\circ\text{C}$. For 550 $^\circ\text{C}$ deposition on β -CIGS layer, Na_2S diffuse into the β -CIGS surface during Na_2S deposition and during cooling. In the first two cases Na_2S could be dissolved into β -CIGS layer and the third case Na_2S could either dissolved on CIGS surface or exist as very thin layer. The elemental analysis and its effect on the electrical properties were reported in this paper.

The overall composition was controlled by adjusting the deposition time and evaporation rates. The Ga/(In + Ga) and Cu/(In + Ga) composition ratios of the β -CIGS films, as determined by an energy dispersive spectrometer (EDS), were approximately 0.44 and 0.42,

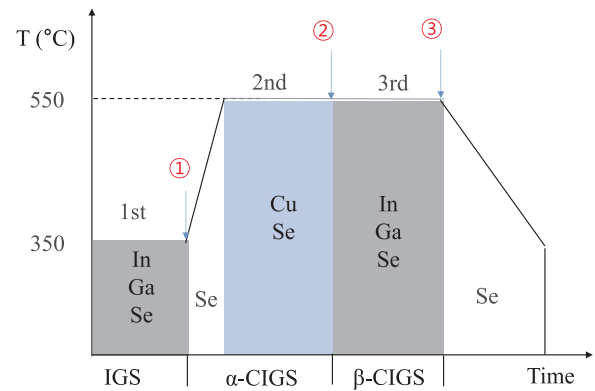


Fig. 1. A schematic three-stage co-evaporation process for $\text{Cu}(\text{In,Ga})_3\text{Se}_5$ (β -CIGS) film with Na_2S incorporation at various stages: on the $(\text{In,Ga})_2\text{Se}_3$ layer (①), on the $\text{Cu}(\text{In,Ga})\text{Se}_2$ (α -CIGS) layer (②), and on the β -CIGS layer (③).

respectively.

In order to control the top surface composition (a Cu depleted surface) of grown β -CIGS films, the films were subjected to the low temperature annealing in a Se environment. For this purpose, the CIGS film and Se pellet were placed in graphite box and then taken into quartz tube furnace. The tube was filled with N_2 gas and the pressure was set at 500 Torr. An annealing of the absorbers was conducted at 200 $^\circ\text{C}$ during 5 min.

For the solar cell fabrication, a CdS buffer layer with a thickness of 50 nm was deposited by a chemical bath deposition technique. The ZnO window layer was deposited by RF magnetron sputtering in a bi-layer structure that consisted of a 50-nm thick intrinsic ZnO layer and a 400-nm thick Al-doped ZnO layer. The metal electrode was deposited by thermal evaporation of Al through an aperture mask. No antireflective coating layer was applied on the cell.

2.2. Film and cell characterization

The morphology and microstructure of the films were examined using scanning electron microscope (SEM). The crystal structure was examined by thin-film X-ray diffraction (XRD) measurements using a Rigaku ATSXG diffractometer. The chemical states of the films were characterized by X-ray photoelectron spectroscopy (XPS). The XPS spectra were taken using a Multilab 2000 spectrometer equipped with monochromatic Al $K\alpha$ (1486.65 eV) X-ray source. The samples were held with Cu clips, which were grounded to the sample stage. In the XPS, the binding energy scales were calibrated using the binding energy positions of the C 1s core level at 284.8 eV and the Au 4f 7/2 core level at 84.0 eV. Experimental values have the precision limited to ± 0.1 eV. The analysis depth of XPS is around of ~ 3 nm and we considered the 3 nm as "surface" for absorbers.

The depth analysis of the films was gained by combining AES using a Perkin Elmer PH 4300 system with simultaneous sputtering. The sputtering was done with Ar-ions at the acceleration energy of 3 kV. Quantitative analysis was done with the PHI MultiPakV8.2b software package from the manufacturer. The compositional sensitivity of the AES technique is limited to about 0.1 at%. The photoluminescence (PL) spectra of the β -CIGS films were measured at 10 K using a He-Ne ion laser with an excitation wavelength of 633 nm using a liquid nitrogen cooled CCD detector. The depth profiles of the Na element in the β -CIGS films were studied by secondary ion mass spectroscopy (SIMS) measurements using Cs^+ as a primary ion with an acceleration voltage of 10 kV at room temperature. I-V measurements of the devices with an active area of 0.43 cm^2 were performed under air mass 1.5 G spectrum with the intensity of 100 mW/cm^2 . C-V measurement were conducted using Agilent model 4284 precision meter at 100 kHz and 1 MHz.

Download English Version:

<https://daneshyari.com/en/article/6534305>

Download Persian Version:

<https://daneshyari.com/article/6534305>

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