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journal homepage: www.elsevier.com/locate/solmatEffects of the Cu/(Ga+In) ratio on the bulk and interface properties of Cu(InGa)(SSe)₂ solar cellsDongho Lee^a, JungYup Yang^b, Young-Su Kim^a, Chan B. Mo^a, Sungchan Park^a,
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ABSTRACT

In this study, we systematically investigated the performance loss factors in Cu(InGa)(SSe)₂ (CIGS₂Se) solar cells with various Cu/(Ga+In) (CGI) ratios, which were fabricated with sputtering and sequential selenization/sulfurization processes. The effects of the CGI ratio on the CIGS₂Se solar cells were determined by measuring the current–voltage (IV) curves and junction capacitance of the solar cells, as well as by performing X-ray analysis techniques on the cells. An increase in the defect density and decrease in the free carrier density were observed in samples with high Cu concentrations (CGI ratio > 0.89), which resulted in a drastic decrease in the open-circuit voltage (V_{OC}) and fill factor (FF). The temperature-dependent IV (IVT) and X-ray diffraction (XRD) results of the bulk characterization corresponded well with the capacitance measurements for all CGI ratios. The low crystal quality and short minority-carrier diffusion length at high CGI ratios resulted in a significant bulk recombination rate. A qualitative analysis of the interface characteristics was performed with IVT measurements, and the results showed that the recombination activation energy in the samples with high CGI ratios was lower than the bandgap (E_g), decreasing the V_{OC} of these devices. For the samples with high CGI ratios, their inferior bulk and interface characteristics caused recombination to occur at the interface as well as in the bulk. However, the interface recombination rate was negligible for the samples with low CGI ratios (CGI ratio < 0.89). In addition, a CIGS₂Se solar module was fabricated on a mass production assembly line, with the size of the CIGS₂Se solar module the same as that of commercially available crystalline-Si-based solar modules. The record efficiency of a solar module with a total area of is 16.0%.

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1. Introduction

Over recent years, there has been considerable progress in the performance of thin-film solar cells composed of copper indium gallium diselenide (CIGSe), which have been commercialized in the photovoltaic market and have power conversion efficiencies close to 14% [1]. Moreover, the best efficiencies obtained for CIGSe solar cells on glass substrates, and even on polymer films, have exceeded 20%,

and the efficiencies of CIGSe solar cells are still increasing thanks to pioneering research groups and companies [2–4].

One of the most important and critical fabrication conditions for CIGSe solar cells is the ratios of the metallic elements present in the CIGSe absorber layer, such as Cu/(Ga+In) (CGI) and Ga/(Ga+In) (GGI). When the CGI ratio is near unity, the CIGSe absorber layer has a stoichiometric composition, which restricts it from acting as a p-type absorber layer because the free carriers in CIGSe-based materials are generated from the Cu vacancies (V_{Cu}). Therefore, we have to ensure that the CIGSe absorber layer acts as a p-type semiconductor when the cell is fabricated by maintaining a lower-than-stoichiometric Cu concentration, *i.e.*, a CGI ratio < 1.

Prior studies that have investigated the ratio of metallic elements were focused on co-evaporated CIGSe solar cells [5]. In such studies, CIGSe cells with over 19.5% efficiency were created with a wide range of CGI ratios (0.80–0.93), implying that the CGI ratio is

Abbreviations: AS, admittance spectroscopy; CIGSe, copper indium gallium diselenide; CGI, Cu/(In+Ga) ratio; CV, capacitance–voltage; DLCP, drive-level capacitance profiling; E_g , bandgap; FF, fill factor; J_{SC} , short-circuit current density; TCO, transparent conducting oxide; V_{OC} , open-circuit voltage

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not a critical factor for fabricating high-efficiency CIGSe solar cells with the co-evaporation process. However, there have not been many systematic investigations into the effects of the CGI ratio on CIGSe absorber layers formed by the heat treatment of metallic precursors with selenium-containing compounds or reaction gases (e.g., H_2Se or H_2S) [6, 7]. This is surprising because some commercialized CIGSe modules are produced through a precursor and selenization process, which is called the two-step process.

In this two-step process, the CIGSe layer is generally formed by the reaction between Cu, In, and Ga metallic precursors, followed by the application of H_2Se or H_2S gas. In this study, we decided to focus on the precursor conditions and their influence on the absorber layer properties after the selenization process. In particular, the CGI ratio has significant effects on the bulk characteristics and surface properties of the CIGSe absorber layer. The capacitance–voltage (CV) and drive-level capacitance profiling (DLCP) methods have been employed to identify the free carrier and defect characteristics in bulk CIGSe layers [8]. The absorber/buffer interface is another key factor in p–n heterojunction solar cells, and thus, several in-depth investigations of the interface characteristics have been performed to explain the metastability of CIGSe solar cells [8–12]. Recently, improving the interface quality has become a key issue for enhancing the performance of CIGSe solar cells, with the most promising enhancement technique being a K-based post-deposition treatment of the surface of the CIGSe absorber layer [4,13–15]. The highest efficiency of a CIGSe solar cell on a polymer film (20.4%) was achieved by treating the surface of the absorber layer with K. Potassium post-treatment etched out Cu from the absorber surface and the empty Cu site was filled by Cd during the cadmium sulfide (CdS) chemical bath deposition (CBD) process for buffer layer. This process helped reduce the thickness of the buffer layer and enhance the quantum efficiency at wavelengths below 550 nm [3]. Another effort is the back surface modification. The modification of the contact area between Mo and the absorber layer, like the rear local-contact technology in silicon-based solar cells, was employed in the CIGSe system. Vermang et al. intentionally covered the Mo back electrode with a patterned Al_2O_3 layer and deposited the CIGSe absorber layer. The absorber layer is locally contacted with the Mo electrode. This back surface treatment reduced the recombination rate around the CIGSe/Mo interface [16]. Lee et al. found the void surface passivation mechanism using the EBIC and TEM-EDX techniques. The conduction and valence band energies of the void surface were enhanced by sulfurization and the generated carriers were repelled by the high electric potential of the void surface. This electrical process can help reduce the carrier recombination around the voids in the CIGSse solar cell system. [16–17].

In this study, the effects of the CGI ratio on the performance of CIGSse solar cells fabricated with the two-step process were examined. We systematically investigated the performance loss factors by analyzing the electrical and compositional properties of CIGSse solar cells fabricated with a wide range of precursor conditions. In particular, by comparing the results of the cells with different CGI ratios, the main performance loss factors in CIGSse solar cells were determined.

The optimized precursor conditions were then applied to a large-area CIGSse solar cell, and with the two-step process, we fabricated a high-efficiency, large-area, CIGSse solar module.

2. Materials and methods

The CIGSse absorber layer was formed on Mo-coated glass. For a monolithically integrated module, we scribed the Mo layer with a high-power laser (P1). The width between the P1 scribing was optimized based on the desired current density, and thickness and

quality of the transparent conducting oxide (TCO) layer. The precursor layers were deposited on the Mo back electrode layer with a sputtering method. The substrate size is $902 \times 1602 \text{ mm}^2$. CIGSse absorber layers with a thickness of approximately 1.5–1.7 μm were formed by the reaction of the Cu–Ga/In precursors with H_2Se and H_2S gases. Sodium (Na) is an essential element for creating high-performance CIGSse solar cells and its concentration must be carefully controlled. We deposited SiO_2 barrier before sputtering the Mo back electrode layer; the Mo was deposited on the barrier layer with an in-line DC sputtering system. The 13 nm of Na-containing Cu–Ga layer (Cu–Ga:Na layer) was then deposited on the Mo back electrode layer. The Cu–Ga and In precursors were sequentially deposited on the Cu–Ga:Na layer with DC sputtering. The precursor thickness were modified by the precursor deposition time. We changed the CGI ratio in the absorber layer by varying the thickness of the metal precursors. The samples were divided into three groups: those with low (0.80–0.85), medium (0.85–0.9), and high (0.9–0.95) CGI ratios. The temperature and time of the reaction process was optimized. The chamber was heated to 480–500 °C and filled with H_2Se/N_2 gas. The 1st step, the selenization process, was then carried out for 25–35 min. The 2nd step, exposing the selenized film to the H_2S/N_2 gas, was performed at 550–580 °C for 60–90 min. The chamber was then allowed to cool to 300–350 °C after the H_2S/N_2 conditioning, and then purged with N_2 gas. The reactions were done in a specially designed reaction chamber that can endure the highly toxic H_2Se gas environment. The buffer layer, used to reduce shunt paths and increase the interface quality, was grown on the absorber layer with a chemical bath deposition (CBD) process. The CBD solution used to deposit the Zn(OH, O, S)-based buffer layer on the CIGSse absorber layer was formed by dissolving $ZnSO_4$, NH_4 , and thiourea (CH_4N_2S) in deionized (DI) water. The samples were pre-rinsed with DI water at room temperature. The CBD process was performed at 60 °C, and the thickness of the resulting buffer layer was between 3 and 5 nm.

The series connections between the unit cells separated by the P1 scribing were formed by mechanical scribing (P2). The gap between the P1 and P2 scribing should be minimized to reduce the dead area within the total module area.

The low thickness of the buffer layer meant that the entire buffer layer and the top absorber layer would have been damaged by the sputtering plasma if we had used Al-doped ZnO for the sputtering process. Therefore, B-doped ZnO (BZO) was used as the TCO layer and was fabricated with low-pressure chemical vapor deposition (LPCVD). The thickness and sheet resistance of the TCO layer were 950 nm and 11–13 Ω/\square , respectively. The final step for separating the unit cells was done by a mechanical scribing process (P3). The aperture area is 1.35 m^2 .

The unit cells used for the characterization measurements were cut from the full-size module ($902 \times 1602 \text{ mm}^2$) and the unit cell area was 0.66 cm^2 .

The composition of the absorber layer was analyzed with X-ray fluorescence (XRF) spectroscopy (Fischer Scientific), and the compositional depth profile was measured with glow discharge optical emission spectroscopy (GDOES, GD Profiler-2, Horiba Jobin Yvon) using a 4-mm-diameter anode. The GDOES intensity profiles and XRF results were calibrated with inductively coupled plasma mass spectroscopy (ICP-MS, ELAN DRC II, Perkin Elmer). The crystallinity of the CIGSse absorber layer was determined with X-ray diffraction (XRD, X'pert Pro MPD, PANalytical).

The solar cell performance was characterized under standard conditions: AM 1.5 G irradiation at 25 °C. For the temperature-dependent electrical measurements, we utilized a liquid nitrogen (LN_2) cryostat with a temperature range of 80–300 K. The sample temperature was determined by measuring the cold finger temperature with a calibrated Si diode attached to the back of the glass

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