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Investigation of factors limiting efficiency in Cu(In,Ga)Se_2 thin film solar cells during rapid evaporation process

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ABSTRACT

Rapid evaporation is crucial in the low-cost manufacturing of Cu(In_xGa_{1-x})Se_2 (CIGS) thin-film solar cells. This form of evaporation deteriorates cell performance in an open-circuit voltage and fill factor. Cell performance is strongly dependent on the deposition process and properties of the thin films. With respect to evaporation rates, analyses of electrical properties, film composition, grain structure, and phase characteristics were conducted to investigate limits on the efficiency of evaporated CIGS thin-film solar cells. CIGS solar cells evaporated at different deposition rates were compared. Raman spectroscopy was used to characterize the residual phases deteriorating the cell performance of these solar cells. Sodium (Na) profiles measured using secondary-ion mass spectrometry revealed that with higher CIGS evaporation rates, Na diffusion in the CIGS layers is lower. Rapidly evaporated CIGS led to two features, residual phases of the CIGS remained and Na concentrations near the surface were insufficient. This result implies that a shortfall in the p-type carrier density during rapid evaporation is a critical factor negatively affecting the efficiency of CIGS thin-film solar cells.

1. Introduction

Thin-film Cu(In_xGa_{1-x})Se_2 (CIGS) is a promising material for photovoltaics because its coefficient of absorption for solar radiation is high [1]. Recently, CIGS thin-film solar cells have achieved the highest efficiencies of 21.7% among thin-film solar cells [2]. Another merit of CIGS thin film is its suitability for producing monolithically integrated structures which offer high output voltage, high productivity, and low production cost [3]. The specific feature of the evaporation method in CIGS is its flexibility in processing with regard to evaporation rate, evaporation sequence, and substrate temperature in each sequence. From the manufacturing point of view, the evaporation rate determining throughput is one of the most important issues. However, grain growth and elemental inter-diffusion in CIGS were not sufficiently improved during rapid evaporation. The solar cells deteriorated in an open-circuit voltage (Voc) and in a fill factor (FF) [4].

In evaporated CIGS, multi-graded methods such as the three-stage method [5–7] and the bi-layer method [8–10] have been generally applied to achieve high efficiency. Regarding these methods, the step involving the compositional change from the Cu-rich phase to the Cu-poor phase is reportedly the most important for film composition, grain growth structures, and phase characteristics [4]. The bi-layer method is more promising because its deposition sequence is simple. In terms of industrial mass production, this simple deposition sequence makes it possible to design compact evaporation equipment and thereby enables cost reduction of solar modules. Therefore, detailed analyses of thin-film properties concerning the CIGS evaporation rate in bi-layer method are required. In particular, the ordered vacancy compound (OVC) such as Cu(In,Ga)$_3$Se$_5$ and Cu$_2$(In,Ga)$_4$Se$_7$ [11], and residual phases such as Cu_xSe, In_xSe and Ga_xSe not fully transformed into the chalcopyrite structure are significant in determining semiconductor properties.

In this work, we analyzed defect-related factors limiting the efficiency of evaporated CIGS thin-film solar cells by varying evaporation rates. Electrical properties, film composition, grain structures, and phase characteristics [11–13] were evaluated with these CIGS solar cells. The characteristic defects of the rapid evaporation method are also discussed.

2. Experimental details

2.1. Device development

The thin-film solar cells were formed on soda lime glass (SLG) substrates using a sputtered molybdenum (Mo) back contact, a co-evaporated CIGS absorber, a chemical bath to deposit a cadmium sulfide (CdS) buffer, a sputtered zinc oxide (ZnO)

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window, and aluminum (Al) surface contacts. Mo back contacts with thickness of 600 nm were deposited by dc-magnetron sputtering. The CIGS absorber layers were grown using the bi-layer method at various evaporation rates from 30 to 100 nm/min. After depositing a Cu-rich layer using Cu, In, Ga, and Se, a layer of In, Ga, and Se was then formed. The maximum substrate temperature was set at 580 °C. All CIGS layers were approximately 2-μm thick. The samples using seven different deposition rates were fabricated and categorized in three types: (a) high-rate (HR) cells deposited with 100 nm/min, (b) medium-rate (MR) cells deposited with 50 nm/min, and (c) low-rate (LR) cells deposited with 30 nm/min. For reference, cells of the three stage method were deposited with 20 nm/min. The CdS buffer layers and the ZnO window layers were deposited with thicknesses of 50 and 300 nm, respectively.

2.2. Evaluation and characterization

The average composition of the layers was determined from energy dispersion X-ray fluorescence measurements under settings of 50 kV, 60 mA, and spot size of 10 mm ϕ. The compositional changes and the amount of sodium (Na) incorporated in the CIGS layers were measured by secondary-ion mass spectrometry (SIMS) using Cs^+ as a primary ion of 5 kV with the spot size of 54 × 54 μm^2. The morphology of CIGS was measured with a scanning electron microscope (SEM) using an accelerating voltage of 5 kV. V_{OC}, J_{SC} (short-circuit current density), FF, R_{sh} (shunt resistance) evaluated by current density-to-voltage (J–V) measurements characterized the performance of the solar cells. The J–V measurements were conducted under AM 1.5G conditions: 25 °C, 100 mW/cm^2 in-house. The cell performances were analyzed based on the median values of eight cells. The Raman spectra were obtained using laser excitation at 532 nm wavelength with a Raman microscope to characterize the specific phases: chalcopyrite CIGS peak at around 175 cm^{-1}, OVC peak at around 154 cm^{-1} [11], In_xSe peak at around 219 cm^{-1}, Ga_xSe peak at around 240 cm^{-1} [12], and Cu_xSe peak at around 259 cm^{-1} [13] were defined. The laser power was set to 1.0 mW. The peak intensities were normalized using the chalcopyrite CIGS peak at around 175 cm^{-1}.

3. Results and discussion

3.1. Cell performance

Fig. 1 plots cell efficiencies for different CIGS evaporation rates. Cell efficiencies were inversely proportional to the evaporation rates. The J–V curves of solar cells, LR, MR, and HR, are compared in Fig. 2. The LR cell had a larger Voc and FF than the MR cell, however, the $V_{OC} \times J_{SC}$ value was almost the same. The main reason for the decreasing efficiency was FF deterioration. Low FF mainly resulted from low R_{sh}. The values of R_{sh} were 441 Ωcm² for the HR cell, 2668 Ωcm² for the MR cell, and 4500 Ωcm² for the LR cell. Furthermore, the cell efficiency of the HR cell was approximately 1.0% lower than that of the MR cell, mainly due to J_{SC}. Insufficient carrier transformation originating in the CIGS thin film is one of the reasons for decreasing J_{SC} [14]. The origin of these negative factors in CIGS thin films during evaporation process is discussed below.

3.2. CIGS thin film analysis

3.2.1. CIGS grain growth

Cross-sectional structures of the three samples (Fig. 3) show no significant visible differences. Regarding the range of evaporation rates, the duration did not specifically restrict CIGS grain growth. Therefore, the grain growth structure was not the direct cause of the deterioration of cell performance.

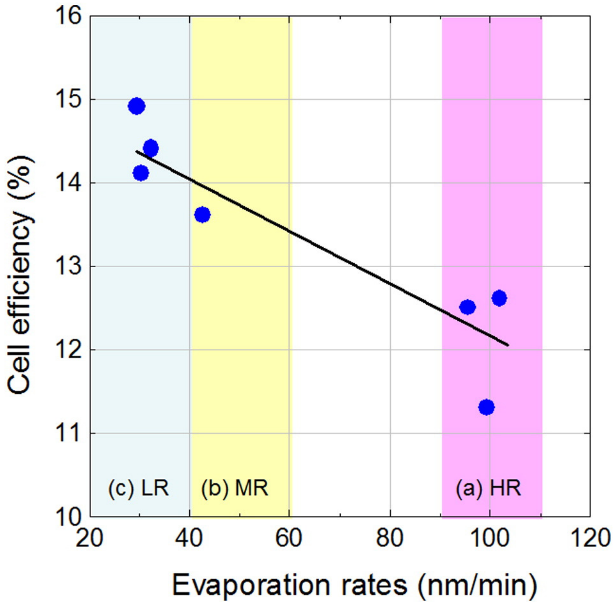
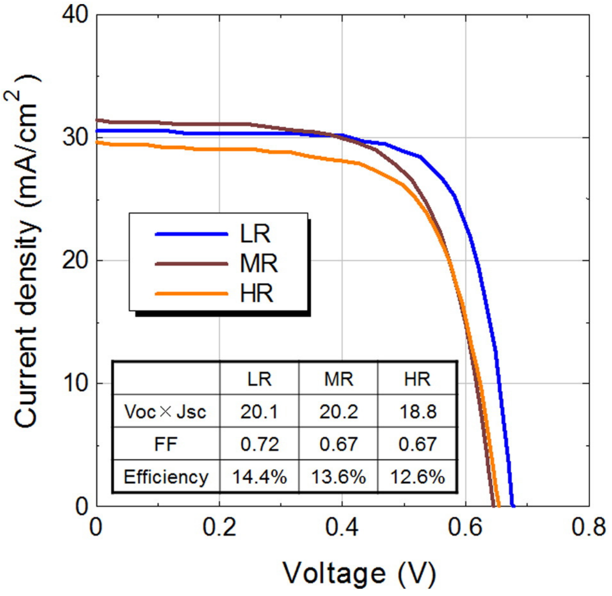


Fig. 1. Plots of the cell efficiencies at various CIGS evaporation rates. Cell type is characterized according to the evaporation rate used in CIGS deposition: (a) high-rate (HR), approximately 100 nm/min; (b) middle-rate (MR), approximately 50 nm/min; and (c) low-rate (LR), approximately 30 nm/min. The cell performances were plotted with the median values of eight cells.

3.2.2. Film composition

In general, the low-resistance Cu-rich CIGS solar cells containing residual Cu_xSe phase show low R_{sh} [15]. In this study, the film composition ratios of Cu/III of LR and HR cells were 0.89 and 0.88, respectively, where III refers to the concentration of In and Ga. Both were Cu-poor CIGS solar cells. Furthermore, SIMS depth profiles were obtained to investigate the compositional changes in the CIGS layers. Fig. 4 shows that Cu/III and Ga/III of LR and HR cells. Cu-rich phases were not present anywhere in either the LR or HR cells. Cu/III and Ga/III were clearly reduced at the surface of HR cells, however, this phenomenon has been observed often even in the reference cells developed by the three-stage method;



	LR	MR	HR
Voc × Jsc	20.1	20.2	18.8
FF	0.72	0.67	0.67
Efficiency	14.4%	13.6%	12.6%

Fig. 2. Current density-voltage curves of three types of CIGS thin film solar cells fabricated on SLG substrates. Measurements were carried out at 25 °C under AM 1.5G (100 mW/cm²) illumination (in-house measurements).