Renewable Energy 76 (2015) 575–581

Contents lists available at ScienceDirect

Renewable Energy

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

Estimation of open-circuit voltage of $Cu(In,Ga)Se_2$ solar cells before cell fabrication

Jakapan Chantana [a,*], Daisuke Hironiwa [a], Taichi Watanabe [b], Seiki Teraji [b], Kazunori Kawamura [b], Takashi Minemoto [a]

[a] Department of Electrical and Electronic Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan
[b] Environment and Energy Research Center, Nitto Denko Corporation, 2-8 Yamadaoka, Suita, Osaka 565-0871, Japan

A R T I C L E I N F O

Article history:
Received 8 February 2014
Accepted 21 November 2014
Available online

Keywords:
Copper indium gallium selenide
Solar cell
Open-circuit voltage
Grazing incidence X-ray diffraction
Raman spectrum
Photoluminescence

A B S T R A C T

$Cu(In,Ga)Se_2$ (CIGS) absorbers with several Ga/III, Ga/(In + Ga), profiles were fabricated by the so-called "multi layer precursor method" under the control of Ga flux rate during film's deposition. Open-circuit voltage (V_{OC}) of CIGS solar cell is principally dependent on average band-gap energy (E_g) in space-change region (SCR) of below 1.3 eV. This average E_g in SCR, principally controlled by average Ga/III ratio in SCR, is estimated by the peak position of (220/204)-oriented CIGS films on soda-lime grass (SLG) substrates investigated by grazing incidence X-ray diffraction (GIXRD) with 0.1° incident angle, whereas the average E_g in SCR is predicted by Raman or photoluminescence (PL) peak positions of CIGS absorbers on both SLG and stainless steel (SUS) substrates. Ultimately, with the average E_g in SCR of below 1.3 eV, the (220/204) peak position (GIXRD) can be well used as a predictor of the V_{OC} on rigid SLG substrates. On the other hand, Raman peak and PL peak positions can be well utilized as indicators of the V_{OC} on not only rigid SLG but also flexible SUS substrates before solar cell fabrication. These are fast and non-destructive methods to evaluate the Ga content, E_g near CIGS surface, and corresponding V_{OC} for high cell performance.

1. Introduction

Productions of solar cell and solar module are the promising technologies of the renewable energy sources [1]. Thin-film solar cells on foreign substrates are deemed less expensive alternatives [1,2]. One of the most promising thin-film solar cells for low-cost production and high efficiency is predicated on polycrystalline chalcopyrite $Cu(In,Ga)Se_2$ (CIGS), where its conversion efficiencies of above 20% with a small area have been reported [3,4]. The addition of Ga into $CuInSe_2$ (CIS) is found to significantly improve photovoltaic performance because of the ability to engineer the band-gap energy (E_g) of CIGS from around 1.0 eV for pure CIS (Ga-free) to about 1.7 eV for pure $CuGaSe_2$ (In-free) [5]. The alloying of Ga primarily enhances conduction-band minimum (E_C), while valence-band maximum (E_V) is slightly affected [6]. In this contribution, CIGS solar cells on both rigid soda-lime glass (SLG) and flexible substrates with different E_gs of their absorbers, mainly controlled by Ga content, are consequently scrutinized. The solar cell on flexible substrate has attracted an interest, as it can be applied to the roll-to-roll process with the ability to reduce production cost and increase its throughput in comparison with the in-line process used in the solar cell on rigid SLG substrate. Stainless steel (SUS) substrate as a flexible substrate is utilized in this work owing to its high temperature durability, as compared with polyimide substrates (typically below 500 °C) [7]. It is well known that double graded Ga profile in CIGS absorber material induces double graded E_g profile, thereby enhancing open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), and conversion efficiency (η) of CIGS solar cells [8–11]. The Ga profiles are usually expressed in terms of Ga/III profiles, where Ga/III denotes Ga/(In + Ga) ratio.

V_{OC} of CIGS solar cells is considered as one of the most important parameters for improvement of the η. It is reported that the V_{OC} is well correlated to CIGS crystal quality and local E_g near CIGS absorber surface [9,10,12]. Motivated by the three-stage deposition process [13,14], CIGS films in this work were prepared by the so-called "multi layer precursor method", using multi layer co-

* Corresponding author. Tel./fax: +81 77 561 4836.
E-mail addresses: jakapan@fc.ritsumei.ac.jp (J. Chantana), hironiwa@fc.ritsumei.ac.jp (D. Hironiwa), taichi_watanabe@gg.nitto.co.jp (T. Watanabe), seiki_teraji@gg.nitto.co.jp (S. Teraji), kazunori_kawamura@gg.nitto.co.jp (K. Kawamura), minemoto@se.ritsumei.ac.jp (T. Minemoto).

http://dx.doi.org/10.1016/j.renene.2014.11.073
0960-1481/

Abbreviations

CIGS	$Cu(In,Ga)Se_2$
CIS	$CuInSe_2$
E_C	conduction-band minimum
E_V	valence-band maximum
SLG	soda-lime glass
SUS	stainless steel
E_g	band-gap energy
SCR	space-charge region
Average Ga/III ratio in SCR	average Ga/(In + Ga) content ratio calculated in a range of 100 nm from front Ga/(In + Ga) profile
Average E_g in SCR	average E_g calculated in a range of 100 nm from front E_g profile
D-SIMS	dynamic-secondary ion mass spectroscopy
GIXRD	grazing incident X-ray diffraction
PL	photoluminescence
TRPL	time-resolved photoluminescence
ODLTS	optical deep level transient spectroscopy
BL	Fe diffusion barrier layer
Low T_{SUB}	deposition temperature of precursor layers
High T_{SUB}	annealing temperature
EQE	external quantum efficiency
BSF	back surface field

evaporation of material sources, offering fast process, namely low-cost production [12]. Under this method, CIGS crystal quality, i.e., the large and homogeneous CIGS grains obtained owing to the proper annealing temperature, which was kept constant, is almost identical; however, local E_g near CIGS surface, mainly manipulated by the Ga content near the surface, was adjusted by manipulating Ga flux rate during the deposition. Namely, all CIGS absorbers with a number of local E_gs near CIGS surface were grown under a control of Ga flux rate during the film's deposition, while other deposition conditions were identical. According to our previous work [12], the correlation coefficient of V_{OC} with the depth range from CIGS surface for calculating the average Ga/III ratio is close to 0.97, when the depth range near CIGS surface (or in space-charge region (SCR) of the solar cell). The result implied that V_{OC} is primarily influenced by the Ga/III, correlating to E_g, near CIGS surface (or in SCR). CIGS films with several E_g profiles, i.e., various Ga/III profiles, were prepared. E_g profiles were calculated from Ga/III profiles which were investigated by dynamic-secondary ion mass spectroscopy (D-SIMS). It is known that Ga/III ratio can be observed by corresponding CIGS peak positions of grazing incident X-ray diffraction (GIXRD) and Raman spectra [15–17]. It is furthermore considered that photoluminescence (PL) peak position should be varied with the change of Ga/III ratio in resulting CIGS films.

In this literature, the relationship between V_{OC} and the average E_g in SCR, mainly controlled by the average Ga/III in SCR, was therefore investigated, where the average E_g in SCR is estimated from E_g profile in a depth of 100 nm from the CIGS surface, which was calculated from Ga/(In + Ga) profile by D-SIMS measurement. In addition, the correlations between the average E_g in SCR and the corresponding CIGS peak positions, which were investigated from GIXRD, Raman, and PL measurements, were examined. Finally, these peak positions are proposed as indicators of V_{OC} without solar cell fabrication in order to evaluate CIGS absorber quality for high cell performance, which are fast and non-destructive monitors.

2. Experimental procedure

In this work, E_g of CIGS films were mainly controlled by Ga/III ratio. CIGS films on both rigid SLG substrates (SLG/Molybdenum (Mo)) and flexible SUS substrates (SUS/Fe diffusion barrier layer (BL)/Mo) were therefore fabricated with various Ga/III profiles for several E_g profiles. After covering clean SLG with back electrode of Mo layer and SUS with BL and Mo layers, all CIGS films were deposited by the so-called "multi-layer precursor method" [12,18,19]. In the process, co-evaporation of Ga and Se was first conducted to form Ga–Se compound precursor layer such as Ga_2Se_3 and GaSe. In and Se were then co-evaporated to form In–Se compound precursor layer such as In_2Se_3 and InSe at the substrate temperatures varying from 300 to 350 °C (low T_{SUB}) for (220/204) preferred orientation in resulting CIGS films. Cu–Se compound precursor e.g. Cu_2Se was covered on the sample by co-evaporation of Cu and Se at the same substrate temperature. The sample was consequently annealed in Se flux at substrate temperatures of 500 °C for case of SLG substrates and 550 °C for case of SUS substrates (high T_{SUB}) for copper-rich CIGS formation with Cu/(In + Ga) ratio of about 1.1. Next, the sample was capped by evaporation of In, Ga, and Se at the same temperature to obtain slightly copper-poor CIGS film. The substrate temperature was observed by the pyrometer. Sodium (Na) under the same condition was introduced into CIGS layers on flexible SUS substrates to improve cell performance [20,21]. The Na induction process will be discussed elsewhere. Final material composition ratios of all CIGS films, measured by energy dispersive spectroscopy operated at 20 kV, are a constant Cu/(In + Ga) ratio of approximately 0.80, Ga/III ratios of 0.27–0.46, and Se/metal ratio of 1.00. A number of Ga/III profiles, investigated from D-SIMS, were primarily obtained by the manipulation of Ga flux rate during the film's deposition, observed by beam flux monitor, whereas other deposition conditions were exactly alike. The quantitative analysis data of Cu, In, Ga, and Se profiles in CIGS films were obtained from the depth profiles of D-SIMS calculated using the mole fraction of an electron probe microanalysis [22]. Ga/III profiles in CIGS layers were thus estimated. The D-SIMS method is considered as a destructive method, since charge particles (secondary ions) from CIGS surface are generally removed by sputtering to measure. It moreover takes about 30 min to investigate a CIGS film by D-SIMS. The equivalent E_g profiles in resulting CIGS films were calculated from the actual Ga/III profiles using an equation $E_g(g)$ [eV] $= 1.044 + 0.735g - 0.223g(1 - g)$, where variable g denotes the content ratio of Ga/III [23], in the case of Cu/(In + Ga) ratio of 0.9, which is almost similar to a Cu/(In + Ga) ratio of about 0.80 in our CIGS films.

In the contribution, the carrier concentrations of CIGS absorbers are in a small range of 1.39×10^{16}–2.0×10^{16} cm^{-3}, obtained from capacitance–voltage measurement in the structure of the solar cell. The SCR width was then estimated to be approximately 320 nm. Consequently, average Ga/III ratio and average E_g in SCR, namely near CIGS absorber surface, was calculated from corresponding Ga/III and E_g profiles in a depth range of 100 nm from CIGS surface in order to assure that both the average Ga/III ratio and the average E_g are located in SCR. In addition, the near-surface region of CIGS absorbers with different average Ga/III ratios (i.e. average E_gs in SCR) were profoundly characterized by GIXRD, Raman, and PL measurements. The GIXRD spectrum of near-surface CIGS was obtained by PANalytical X′ Pert PRO with Cu K_α ($\lambda = 1.5405$ Å) radiation operated at 45 kV and 40 mA with an incident angle of 0.1° and step size scanning of 0.04°. Calculated penetration depth of Cu