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Controlled back slope of Ga/(In+Ga) profile in Cu(In,Ga)Se_2 absorber fabricated by multi layer precursor method for improvement of its photovoltaic performance

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ABSTRACT

Cu(In,Ga)Se_2 (CIGS) absorbers with several Ga/III, Ga/(In+Ga) ratio, profiles were deposited by the so-called "multi layer precursor method" consisting of Ga-Se/In-Se/Cu-Se stacks. The effects of average Ga/III ratios and back slopes of the Ga/III profiles on the photovoltaic performance were investigated. The optimum average Ga/III ratio of approximately 0.36 leads to the appropriate average band-gap energy as well as sufficiently long carrier lifetime in CIGS absorber, thus enhancing open-circuit voltage. In addition, the back slope of 0.50 μm^{-1}, defined as the ratio of the change in Ga/III ratio to the change in the depth range from 1 to 2 μm from CIGS surface, induces back surface field of 0.34 V/μm, thereby increasing short-circuit current density. Ultimately, the CIGS absorber on flexible stainless steel substrate with the double graded Ga/III profile (the average Ga/III of 0.36 and the back slope of 0.50 μm^{-1}) was fabricated by the multi layer precursor method. This results in the 14.36%-efficient CIGS solar cell on the flexible substrate without an anti-reflective layer.

1. Introduction

Renewable and sustainable energy resources have attracted considerable attention as alternatives to other sources of energy such as fossil fuels and nuclear energy [1]. Photovoltaic technology is deemed one of the most promising technologies for future energy. Nowadays, wafer-based single crystalline and multi-crystalline silicon solar cells play an essential part in the photovoltaic market; however, silicon wafers are fabricated by an expensive process, accounting for over half of the cost of the finished solar cells [1]. Thin-film solar cells on foreign substrates are therefore considered as less expensive alternatives [1]. One of the most intriguing thin-film solar cells is based on polycrystalline chalcopyrite Cu(In,Ga)Se_2 (CIGS), where its conversion efficiencies (η) of 20.8% with a small area and 18.7% for mini-module have been demonstrated [2]. The CIGS solar cells with high efficiencies have been reported to be achieved by both the 3-stage method and the 1-stage process [3–6]. Manufacturing solar cells on flexible substrates is highly interesting, as it can be applied to the roll-to-roll process, with the ability to reduce production cost and increase its throughput in comparison to the in-line process utilized in the solar cells on rigid glass substrates. The most promising flexible substrates are stainless steel (SUS) and polyimide substrates. In this report, the SUS substrate is used owing to its high temperature durability, as compared with polyimide substrates (typically below 500 °C) [3]. It was reported by Pianezzi et al. that the CIGS solar cell with the efficiency of 17.7% was obtained on stainless steel foil under a modified 3-stage method [7].

When CuInSe_2 is alloyed with Ga to form CIGS thin films, the wider band-gap energy (E_g) of the CIGS absorber can better match the solar spectrum, thus enhancing open-circuit voltage (V_{OC}), but decreasing short-circuit current density (J_{SC}) [8]. It is known that the proper Ga profile, namely double graded Ga profile, in CIGS absorber increases both V_{OC} and J_{SC} of its solar cell, thus enhancing the η [3,4]. Therefore, the optimization of Ga profiles, which are usually expressed in terms of Ga/III profiles, has been extensively investigated, where Ga/III denotes Ga/(In+Ga).

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In this contribution, CIGS films on both rigid soda-lime glass (SLG) and flexible SUS substrates with a number of Ga/III profiles were fabricated by the so-called “multi layer precursor method”, employing multi-layer co-evaporation of material sources [9–11]. In the method, CIGS crystallization and the Ga/III profiles are primarily manipulated by annealing process [12] and the thicknesses of its precursor layers, respectively. Not only were the average Ga/III ratios throughout CIGS films systematically examined to improve the V_{OC}, but also the influence of the back slopes of Ga/III profiles was scrutinized to enhance the J_{SC}, thereby enhancing the η of the CIGS solar cells on flexible SUS substrates.

2. Experimental procedure

In this literature, CIGS solar cells on rigid SLG and flexible SUS substrates with an aperture area of 0.14 cm^2 were fabricated with various Ga/III profiles in the absorbers. The aperture area includes active material, busbars, and fingers [13]. A structure of the CIGS solar cell on SLG substrate is SLG/molybdenum (Mo)/CIGS/cadmium sulfide (CdS)/zinc oxide (ZnO)/In_2O_3:Sn (ITO)/NiCr-Al grid, while that of the CIGS solar cell on SUS substrate is SUS/Fe diffusion barrier layer (BL)/Mo/CIGS/CdS/ZnO/ITO/NiCr-Al grid. After covering clean SLG substrate with Mo layer, and SUS substrate with BL and Mo layers, CIGS films were deposited by the multi layer precursor method [9,12], offering the fast fabrication process (low-cost production) by shortening the deposition time of the precursor layers. In the method, Ga-Se/In-Se/Cu-Se compound precursors were prepared at substrate temperature varying from 250 to 350 °C (low T_{SUB}), observed by pyrometer. Those precursor layers are depicted in Fig. 1(a). The sample was subsequently annealed in Se flux at substrate temperatures changing from 500 to 550 °C (high T_{SUB}) for the Cu rich CIGS film, as exhibited in Fig. 1(b). Finally, the sample was capped by the evaporation of In, Ga, and Se at the same temperature to obtain slightly Cu poor CIGS film, as depicted in Fig. 1(c). Sodium (Na) was introduced into the CIGS layers on SUS substrates to improve cell performance [14,15]. The Na induction process will be discussed elsewhere. The various Ga/III profiles in CIGS absorbers were mainly obtained by the manipulation of the thicknesses of Ga-Se and In-Se compound precursors. The Ga/III profiles were acquired by dynamic-secondary ion mass spectroscopy (D-SIMS), and the average Ga/III ratios were then calculated from the Ga/III profiles throughout the CIGS film. The minimum Ga/III point is defined as the lowest Ga/III ratio in the Ga/III profile. According to D-SIMS measurement, Fe is not presented in all CIGS films on SUS substrates in this work (not shown). The final material composition ratios in the resulting films, measured by energy dispersive spectroscopy, are Cu/(In+Ga) ratios of 0.78–0.81, Ga/III ratios of 0.30–0.43, and Se/metal ratio of 1.00. Cross-sectional images of CIGS films were investigated by scanning electron microscopy (SEM). All CIGS films in this article are the (220/204)-oriented CIGS absorbers, characterized by X-ray diffraction (XRD). The CIGS films were furthermore measured by time-resolved photoluminescence (TRPL) with laser power density and wavelength (λ) of 1 mW/cm^2 and 532 nm, respectively (Hamamatsu C12132). Estimated penetration depth of the laser light into CIGS film is about 100 nm. The minority-carrier lifetime (τ) in CIGS films, shortly called carrier lifetime, was estimated from the fitting of their TRPL decay curve by using $I(t)=A1\exp(-t/\tau_1)+A2\exp(-t/\tau_2)$, where t is the time after a laser pulse excitation, $I(t)$ is the luminescence intensity at time (t), and A1 and A2 are the coefficients. The τ_1 and τ_2 are the fast and slow components of the TRPL lifetimes. The fast component τ_1 and slow component τ_2 are ascribed to the recombination at interface and bulk regions within a range of about 100 nm from the CIGS surface, respectively [11].

After depositing the CIGS film, the KCN etching (1 wt.%, 1 min) was conducted to remove Cu_xSe secondary phase located on the surface of CIGS films [16–18]. A CdS buffer layer was then prepared by chemical bath deposition on resulting CIGS film. ZnO as a window layer and ITO as a transparent conductive oxide layer were deposited by sputtering. After the formation of top NiCr-Al grid, cell parameters, J_{SC}, V_{OC}, fill factor (*FF*), and η, were evaluated from the current density-voltage (*J-V*) characteristic based on an aperture area of 0.14 cm^2 under Air Mass 1.5 G illumination (100 mW/cm^2). External quantum efficiency (EQE) was measured by a conventional lock-in detection system. After capacitance-voltage measurement, the width of space charge region (SCR) was calculated to be about 320 nm as reported in our previous work [9]. Average Ga/III ratio in SCR (near CIGS surface) was subsequently estimated from Ga/III profile in the range of 200 nm from CIGS surface to assure that it is in SCR. Moreover, the back slope of Ga/III profile (BS) is defined as a ratio of the change in Ga/III ratio to the change in the depth range from 1 to 2 μm from CIGS surface. The equivalent E_g was estimated from the actual Ga/III ratio using the equation $E_g(x)$ [eV]$=1.044+0.735x-0.223x(1-x)$, where variable x denotes the content ratio of Ga/III [11,19].

3. Results and discussion

3.1. Influence of average Ga/III ratio in CIGS absorber on its photovoltaic performance

First, CIGS absorbers on rigid SLG substrates with different average Ga/III ratios, calculated throughout the absorbers, were characterized by the τ_2, deduced from the TRPL decay curve. Fig. 2(a) illustrates two TRPL decay curves of the CIGS layers on SLG substrates with the average Ga/III ratios of (I) 0.33 and (II) 0.48, respectively. It is revealed that τ_2 of 7.33 ns for (I) average Ga/III ratio of 0.33 is longer than that of 2.39 ns for (II) average Ga/III ratio of 0.48. Fig. 2(b), therefore, demonstrates τ_2 as a function of

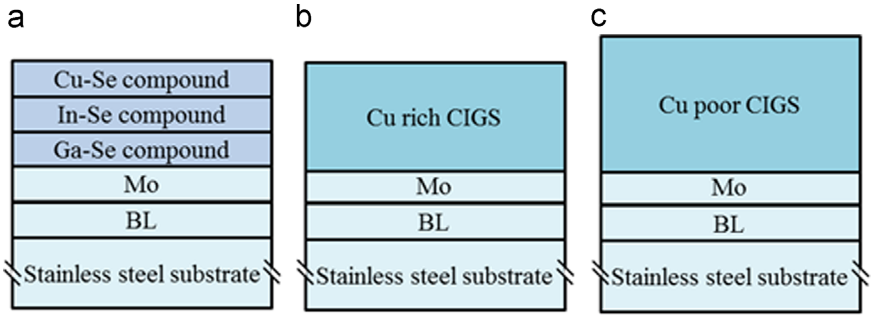

Fig. 1. Schematics of the resulting samples on SUS substrates; (a) SUS/BL/Mo/Ga-Se compound/In-Se compound/Cu-Se compound, (b) SUS/BL/Mo/Cu rich CIGS, and (c) SUS/BL/Mo/Cu poor CIGS.