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Effect of potassium fluoride post-deposition treatment on Cu(In,Ga)Se₂ thin films and solar cells fabricated onto sodalime glass substrates



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ABSTRACT

In this study, we investigated the effect of potassium fluoride post-deposition treatment (KF-PDT) on Cu(In_{1-x}Ga_x)Se₂ (CIGS) thin films and solar cells fabricated onto sodalime glass (SLG) substrates. Secondary Ion Mass Spectrometry (SIMS) analysis showed that the K increased in the entire CIGS layer after KF-PDT, however Na seemed no change because of a large amount of K and Na diffused from SLG substrates. X-ray photoelectron spectroscopy (XPS) analysis revealed that the KF-PDT depleted Cu, whereas increased K and Ga at the near surface CIGS layer, before the rinsing process. Removal of native oxides from KF-treated CIGS thin film was observed based on rinsing solutions. Ammonia aqueous solution removed Ga compounds more efficiently from KF-treated CIGS thin film than that of distilled water. Time-resolved photoluminescence (TRPL) revealed that the carrier lifetime and PL intensity greatly increased after KF-PDT, resulting in the reduction of photo-generated carrier recombination. The V_{oc} loss ($E_g/q - V_{oc}$) decreased from 0.52 to around 0.44 V for KF-treated CIGS solar cells with band gap (E_g) of 1.06–1.23 eV. Electron beam-induced current (EBIC) analysis indicated that the effective carrier collection of the CIGS solar cells widened toward the Mo back-contact side after KF-PDT. This phenomenon could be attributed to the increase in carrier lifetime. C-V measurements suggested that KF-PDT not only increased hole concentration but also passivated bulk defects.

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1. Introduction

The effect of an alkali-metal incorporation into Cu(In_{1-x}Ga_x)Se₂ (hereafter referred to as CIGS) thin films and solar cells has been intensely investigated. Incorporation of Na into CIGS improves the conversion efficiency of solar cells and modules by increasing the carrier concentration and modifying the quality of the interface junction [1–7]. Researchers at the National Renewable Energy Laboratory (NREL) [1] and Aoyama Gakuin University (AGU) [8] observed that K improves the efficiency of CIGS solar cells by increasing the majority carrier concentration. These groups added K compounds such as KF and K₂Se before or during CIGS deposition. The NREL group proposed the mechanism of increased net hole concentration, in which the formation of donor point defects (In_{Cu}) is inhibited by a finite substitution of K (or Na) for the In_{Cu} antisites to form neutral K (or Na)_{Cu}.

Recently, the Swiss Federal Laboratories for Materials Science and Technology (EMPA) developed a novel way of incorporating K into CIGS thin films by treating the films with KF after deposition, which is known as KF post-deposition treatment (KF-PDT). It has

opened the experimental potential for higher CIGS solar cell efficiencies [9–20]. The EMPA group reported that KF-PDT reduces the Cu and Ga concentration at near-surface region of CIGS layer deposited onto alkali-free polyimide substrates, which leads to significant increase in the open circuit voltage (V_{oc}). They interpreted the cause for increased V_{oc} as a formation of a very dense shallow donor-type Cd_{Cu} during the chemical bath deposition (CBD)-CdS process [9,12]. In addition, KF-PDT enables a significant reduction in the thickness of the CdS buffer layer without the commonly observed losses in device parameters [9–15]. Due to the Cu-deficient compounds at the very-near-surface region, a shift of the valence band to lower binding energies has been observed [18]. The Centre for Solar Energy and Hydrogen Research (ZSW) group found that the KF-PDT process maximizes the efficiency of CIGS solar cells with a higher Ga content compared to the traditional value, which suggests that this new process could be used to develop solar cells with efficiencies beyond the record values reported so far [14,15]. Moreover, the NREL group reported that the V_{oc} of the solar cells fabricated by the two-step selenization process could be improved with the use of KF-PDT [20]. The compositional investigations with KF-PDT have been performed mainly for CIGS thin films deposited onto the alkali-free substrates in order to avoid the diffusion of Na and K from SLG substrates. The SIMS measurements were carried out by ZSW group with KF

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treated CIGS thin films deposited on alkali-free alumina (Al_2O_3) substrates [16,17]. EMPA group also used alkali-free polyimide substrates for XPS measurements [9–13]. However, the effect of KF-PDT on CIGS thin films deposited on SLG substrates may differ from that of alkali-free substrates. We thus investigated the influence of KF-PDT on CIGS films and solar cells in actual device structure in which the sodalime glass is used as a substrate. In the present work, the crystallographic morphology, chemical composition, carrier concentration, minority carrier lifetime of KF-treated CIGS thin films and solar cells deposited on SLG substrates were analyzed using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), time-resolved photoluminescence (TRPL), electron beam-induced current (EBIC), current-voltage (J - V), and capacitance-voltage (C - V) measurements.

2. Experimental

2.3–2.5 μm thick CIGS absorber layers were deposited by three-stage co-evaporation process at a maximum substrate temperature of 520 °C. Nine 30 mm \times 30 mm Mo-coated soda-lime glass (SLG) substrates were set on a 10 cm \times 10 cm substrate holder that was subsequently inserted into water-cooling molecular beam epitaxy system (EIKO Engineering Co., Ltd., EW-500). After CIGS deposition, the substrates were removed from the vacuum chamber into air. An inductively coupled plasma (ICP) spectroscopy (SPS 7700, Seiko, Japan) was used to measure the average composition of the film. The KF-PDT process was performed on air-exposed CIGS samples in presence of Se vapor of 3.1×10^{-3} Pa. The KF source and substrate temperatures were kept at 550 and 350 °C, respectively. The KF shutter was opened for 2 min, and the Se shutter was opened for 10 min at a substrate temperature of 350 °C and then closed when the substrate temperature decreased to 300 °C. The depth profiles of the CIGS absorber layers were obtained by SIMS (PHI ADEPT-1010, Physical Electronics, Chanhassen, MN, USA). EBIC (Hitachi S-4800 FE-SEM) analysis was performed to investigate the minority carrier collection at an accelerating voltage of 5 keV. Photoluminescence (PL) was measured at room temperature using a TRPL system (C12132, Hamamatsu Photonics K. K., Japan) with a YAG laser ($\lambda=532$ nm, 1.1 mW for excitation). The PL intensity and minority carrier lifetime were evaluated using a solar cell structure with a ZnO ($E_g=3.3$ eV)/CBD-CdS ($E_g=2.4$ eV)-covered CIGS absorber layer to avoid degradation caused by air exposure. Therefore the CdS deposition was performed as quickly as possible after the CIGS deposition.

Prior to fabricating the solar cells, the KF-treated CIGS thin films were rinsed in distilled water to remove residual K compounds. CBD-CdS buffer layers were deposited onto the CIGS layers using a CdSO_4 (0.015 M)– NH_3 (2.2 M)– $\text{CH}_4\text{N}_2\text{S}$ (1.5 M) aqueous solution [21]. During the CBD process, solution temperature was increased from room temperature (RT) to 65 °C. Radio-frequency

(RF) sputtering was used to deposit 100-nm-thick non-doped ZnO and 300-nm-thick ZnO:Al (2 wt% Al_2O_3 -doped ZnO) thin films on the CBD-CdS layer at room temperature. The solar cell was completed with the evaporation of a Ni/Al front grid. An antireflection (AR) coat of MgF_2 was deposited on the ZnO:Al layer for several selected high-efficiency solar cells. Thus, the completed CIGS solar cell structure was $\text{MgF}_2/\text{Ni}/\text{Al}/\text{ZnO:Al}$ (300 nm)/ZnO (100 nm)/CBD-CdS (~ 60 nm)/CIGS/Mo/SLG. The device area of the solar cell was measured using a digital microscope (VH-6300, Keyence, Japan). The J - V characteristics were measured using a solar simulator (Class A spectrum match, YSS-80, Yamashita Denso Corporation, Japan) with AM1.5 and 100-mW/cm² illumination at 25 °C. The solar simulator was calibrated using a standard Si cell. The deviation in cell efficiency of our in-house and NREL measurements was around 1% [22-Supplementary, Table 1]. The J - V measurement system and conditions, used in this experiment, were the same as those presented in our previous publication [22]. C - V profiles were recorded using a 4200-SCS parameter analyzer (Keithley Instruments, Cleveland, OH, USA) at 100 kHz in the dark at room temperature. XPS measurement was performed using a Quantera scanning XPS microprobe (PHI) with monochromatic Al K α (1.5 keV) X-ray radiation. Ar ion-beam sputter etching was performed using a differentially pumped ion gun operating at 2.0 keV and a sputtering rate of 5 nm/min for SiO_2 . The energy resolution of the instrument was a FWHM (Full Width at Half Maximum) of 0.9 eV using the Ag 3d_{5/2} peak of 368.2 eV [23]. To avoid peak-shifting due to specimen charge-up, the surface of the specimen was grounded. No significant peak shifts caused by charge-up were observed in any of the measurements.

3. Results and discussion

Fig. 1(a) and (b) show the SEM images of the CIGS (No. 150110) absorber layer without and with KF-PDT, respectively. White dot-like particles were observed on the surface of the CIGS thin films after KF-PDT but were no longer visible after a distilled water rinsing; instead, nanoholes of similar shape were formed on the faceted CIGS surface, as seen in Fig. 1(c). Wide range XPS spectra confirmed that K and F signals were observed for KF-treated CIGS as shown in Fig. 1(d). The white dot-like particles might have been the KF compounds. Fig. 2 illustrates the SIMS depth profiles of all the relevant elements of the CIGS (No. 141227, $E_g=1.18$ eV) thin film solar cells fabricated with (solid lines) and without (dotted lines) KF-PDT. It is evident from Fig. 2 that the high concentration of K in the entire region is based on the KF-PDT, whereas no significant change in atomic concentration was recorded for Na. The behavior of Na atoms in our present work differed from that reported by the EMPA group, which found that Na concentration significantly decreased due to the ion exchange with K after KF-PDT [9,10]. This discrepancy may result from the different incorporation paths of Na into CIGS films. EMPA group added

Table 1

Cell parameters and V_{oc} loss of CIGS solar cells shown in Fig. 5(a). Cu/(In+Ga)=CGI, Ga/(In+Ga)=GGI.

CIGS No	CGI	GGI	E_g (eV)	KF-PDT	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	DD Device area (cm ²)	$(E_g/q)-V_{oc}$ (V)
150216	0.89	0.25	1.06	without	36.8	0.522	0.650	12.4	0.501	0.53
				with	36.9	0.611	0.699	15.8	0.503	0.44
150210	0.86	0.37	1.14	without	35.2	0.581	0.662	13.6	0.510	0.55
				with	35.2	0.694	0.736	18.0	0.513	0.44
141227	0.90	0.40	1.18	without	33.6	0.650	0.733	16.0	0.499	0.53
				with	33.5	0.722	0.744	18.0	0.517	0.46
150110	0.78	0.57	1.23	without	30.9	0.717	0.757	16.7	0.517	0.51
				with	31.2	0.760	0.755	18.0	0.516	0.47

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