Fabrication and device characterization of potassium fluoride solution treated CZTSSe solar cell

Tanka Raj Rana [a], JunHo Kim [a], [*], Jun-Hyoung Sim [b], Kee-Jeong Yang [b], [**], Dae-Hwan Kim [b], Jin-Kyu Kang [b]

[a] Department of Physics, Incheon National University, 119 Academy-ro, Yeonsu-gu, Incheon, 22012, Republic of Korea
[b] Convergence Research Centre for Solar Energy, DGIST, 333 Techno jungang-daero, Dalseong-gun, Daegu, 42988, Republic of Korea

ARTICLE INFO

ABSTRACT

Post deposition treatment (PDT) for $Cu_2ZnSn(S,Se)_4$ (CZTSSe) was carried out by simply dipping the absorber into the KF solution at 80 °C. The dipping time of absorber in KF solution was found to be crucial to device parameters of CZTSSe solar cell. The K-doping improved the solar cell efficiency from 4.4% to 7.6% by 1 min dipping whereas the longer than 5 min dipping solar cells showed distorted kink J-V curves. The activation energy of CZTSSe solar cell was increased upto 1 min KF treatment from 0.83 eV to 0.92 eV which indicates interface recombination is reduced significantly. However, the activation energies of 5 min and 10 min dipping solar cells were found to be 0.81 eV and 0.63 eV where dominant recombination was interface recombination. Furthermore, trap energies of 49 meV and 298 meV of pristine CZTSSe solar cell were modified to 33 meV and 117 meV for 1 min treated CZTSSe solar cell. Trap energies of 5 min were calculated to be 112 meV and 147 meV. The proper KF doping passivated the shallow as well as deep defects of CZTSSe solar cell which is reflected in photovoltaic performances directly.

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1. Introduction

The kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cell is emerging as promising replacement for the $Cu(In,Ga)Se_2$ (CIGS) solar cell which includes expensive and rare earth elements, In and Ga. CZTSSe, consisting of earth abundant and nontoxic elements, has suitable photovoltaic properties such as high absorption coefficient ($\alpha > 10^4 \, cm^{-1}$) and tunable band gap energy 1–1.5 eV [1,2]. Although CZTSSe has promising photovoltaic properties, it showed still lower solar cell performance than CIGS. The world champion CZTSSe solar cell fabricated by hydrazine-based process demonstrated power conversion efficiency (PCE) of 12.6%, whereas CIGS reached up to the best PCE of 22.6% [3,4,5]. Especially, the open circuit voltage (V_{OC}) deficit is now major limiting factor in the development of CZTSSe solar cell. Series of experiments to overcome low V_{oc} of CZTSSe solar cell have been done, which are aimed to reduce deep point defect and secondary phases. The close ionic size of Cu, Zn and Sn is responsible for the cation

disorder in kesterite CZTSSe, which induces deep defects in CZTSSe and results in severe band tailing and potential fluctuation. The cation disorder can be reduced by replacing Cu or Zn with larger sized atoms like Ag for Cu, Cd for Zn [6,7]. Along with cations substitution, doping with alkali metals and antimony also has shown beneficial effects on CZTSSe improving crystallinity and charge carrier concentration [8-13].

Recently, CIGS has shown jump in record efficiency by using the post deposition treatment (PDT) of alkali elements. At the beginning, it was believed that diffused Na from soda lime glass (SLG) to CIGS increased the PCE by improving structural properties of GIGS during the film growth. However, CIGS grown on Na-free substrate with subsequent addition of Na also showed high PCE [14-16]. This benign effect of Na on solar cell performance motivated further study of alkali doping into CIGS and CZTSSe. CIGS solar cell doped with the other alkali elements such as Li, K, Rb and Cs also showed positive effects on photovoltaic performance.

Several reasons have been proposed to explain the beneficial effects of alkali doping. Na-doping improves PCE of CIGS solar cell by passivating the defects in interface and grain boundaries and by increasing carrier concentrations [17-19]. KF PDT modifies the absorber surface into Cu-depleted surface containing large

* Corresponding author.
** Corresponding author.
E-mail addresses: jhk@inu.ac.kr (J. Kim), kjyang@dgist.ac.kr (K.-J. Yang).

amounts of K. On the modified surface, thinner CdS buffer layer can grow with good quality, which results in increase of short circuit current density (J_{sc}) by reducing external quantum efficiency (EQE) loss in blue photon region [20,21]. The interface recombination between CdS/CIGS was also found to be significantly reduced by using KF PDT, which is explained by lowering VBM [22] with the reduction of the charge recombination, K (Na) doping increase the PCE of CZTSSe solar cell with improvement of open circuit voltage (V_{oc}), fill factor. Alkali metals doping especially with Na and K having smaller radii compared to other heavy alkali metals resulted in larger CZTSSe grain sizes which enhanced carrier density by reducing carrier recombination [12]. Furthermore, K-doping provides an opportunity for optimization of n-type window layer by which J_{SC} can be improved due to collection of high energy photons [12]. Alkali doping is reported to enhance p-type conductivity with increased hole density in the absorber, for which several mechanisms are proposed. Grain boundary (GB) mechanism states that Na is segregated at GB of CIGS with high concentration [23-25], which passivates the donor like defects at GB such as In_{cu}, V_{Se} resulting in the increase of net hole concentrations [23,24,26-28]. However, Na doping is also observed to increase hole concentration of grain interior throughout CIGS layer, which has driven to propose new mechanism: Na-dopants creates new accepter by forming Na_{In} (Na_{Ga}) antisites or by eliminate the donor sites In_{Cu} (Ga_{Cu}), which increase the hole concentration. But formation of antisites Na_{In} (Na_{Ga}) and reduction of donor sites In_{Cu} (Ga_{Cu}) are not favorable according to the first principle calculations [29-31]. So another mechanism is proposed, where Na-dopants forms electrically inactive Na_{Cu} in CIGS due to lowest formation energy at higher temperature [32]. Na_{Cu} is unstable at low temperature so Na diffuses out leaving Cu unoccupied forming V_{Cu} in CIGS grain [33,34]. The Na on absorber surface is dissolved out during rinsing process for absorber, by which Cu-depleted surface is produced. Thus, surface and GBs of CIGS are usually Cu-depleted by alkali doping. V_{Cu} is shallow acceptor in CIGS with ionization level about 30 meV above valence band maximum (VBM) which enables the intrinsic p-type conductivity [20,35]. Formation energy for K-doping is higher than that for Na-doping at the same lattice so that K is difficult to be incorporated into CIGS [32]. However, K-doping leads to the formation of K-enriched surface layer (Cu-free, K-In-Se compounds). Experimental results showed that large amounts of K could be doped into CIGS grains at higher temperatures [36-38]. KF PDT is usually carried out after Na-doping, and then Na is replaced by K and Na may diffuse towards the surface and Mo back contact layer. V_{Cu} is increased in CIGS grain because of out-diffusion of Na and K after rinsing and cooling. Thus p-type conductivity is enhanced after KF PDT [32]. Besides effects mentioned above, K-doping in CZTS is reported to enhance (112)-preferred growth and suppress the secondary phase of ZnS [39].

Various techniques can be adopted for alkali incorporation into the absorber layer. The alkali elements could be doped during synthesis of absorber or by PDT of absorber layer [40-42]. The most common method till now is utilization of co-evaporation process. The introduction of alkali elements to the absorber can be controlled systematically by evaporation, which is very effective for alkali free flexible substrate. There are also different methods reported for alkali treatment by evaporation such as KF or NaF, which are evaporated onto CIGS absorber layer in the presence of Se at higher temperature and treated with or without subsequent selenization [20,43,44]. A few of solution method are reported for potassium doping into CZTS (CZTSSe), where alkali source is added to the precursor solution of CZTS (CZTSSe) and it is spin-coated on to the film [12,40]. But in our experiment here, we carried out the PDT process simply by dipping in the KF aqueous solution, which is similar to KCN etching process. This solution process could be

attractive method for CZTSSe absorbers fabricated by using vacuum- and non-vacuum-based method, which can be applied as an alternative to toxic KCN etching process also. We performed KF PDT for CZTSSe and studied its effect on solar cell efficiency along with characterization of the modified surface of CZTSSe. To understand the modification of defects during KF treatment, electrical characterizations of solar cells such as c-f-T and J-V-T were employed.

2. Experimental

CZTSSe solar cells were fabricated by RF sputtering process. The devices consisted of SLG/Mo/CZTSSe/CdS/i-ZnO/AZO structure and fabrication process for each layer was same as previous report except KF treatment [45]. The precursor was made of Cu/SnS/ZnS/Mo and post-annealed by using RTP process at 510° C for 20 min using only selenium source [45]. We carried out KF treatment experiment to post-selenized CZTSSe absorbers. The absorbers layers were dipped into the solution composed of deionized water and 4.5 wt % potassium fluoride KF at 80 °C using hot plate. We varied KF treatment time such as 30 s, 1 min, 5 min and 10 min. After dipping the absorbers, we cleaned the samples with di-water and further layers CdS/i-ZnO/AZO were deposited to make the completed devices. So, we fabricated five types of solar cells i.e. pure CZTSSe (reference), 30 s KF treated CZTSSe solar cell (A), 1 min KF treated CZTSSe solar cell (B), 5 min KF treated CZTSSe solar cell (C) and 10 min KF treated CZTSSe solar cell (D).

2.1. Characterization

The surface morphologies of films were studied by using by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-7001F). The structural properties of the films were characterized by X-ray diffraction (XRD) with a high resolution XRD machine (Rigaku, Smart LAB) equipped with Cu-K$_z$ source ($\lambda = 1.5412$Å). To investigate phase purity precisely, we measured Raman spectra by using a Raman scattering system (Spectro co.) equipped with an excitation laser of $\lambda = 532$ nm (irradiation power on sample < 1 mW). The X-ray photoelectron spectroscopy (XPS) was performed by using PHI 5000 Versa Probe II. The current density−voltage (J-V) curve of the CIGS solar cell was measured by using source meter (Keithley 2400) under AM 1.5G filtered illumination of 1000 Wm^{-2} Xe lamp (Abet Technology), which was calibrated with Si reference cell. The J-V characteristics were studied in the temperature range (300 K−90 K) under dark, white and filtered light illumination. The external quantum efficiency (EQE) was measured by using Xe light source and monochromator combined with light chopper and lock-in amplifier (McScience Inc.). Admittance spectroscopy (AS) was performed to analysis defect in the solar cells using LCR meter (E4980A, Agilent) which probes from 20 Hz to 2 MHz in the temperature range of 300 K-90 K. All C-f scans were carried out at an ac voltage of 30 mV under the dark condition. The same LCR meter was used to measure capacitance-voltage (C-V) profile.

3. Result and discussion

3.1. Characterization of KF treated CZTSSe absorber layer

The surface morphologies of bare CZTSSe and KF treated CZTSSe are shown in Fig. 1(a) and (b-e), respectively. The post-selenized CZTSSe showed compact and good crystalline texture. Fig. 1(b−e) presents the SEM images of KF treated CZTSSe for 30 s, 1 min, 5 min and 10 min. The small pores were formed on the CZTSSe surface and few white dot like particles were observed for 30 s and 1 min KF treated samples. The white dot like particles could be KF compounds. But for longer treated like 5 min and 10 min samples