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Over 11 % efficient eco-friendly kesterite solar cell: Effects of S-enriched surface of $Cu_2ZnSn(S,Se)_4$ absorber and band gap controlled (Zn,Sn)O buffer

Jiwon Lee [a,1], Temujin Enkhbat [a,1], Gyuho Han [a], Md Hamim Sharif [a], Enkhjargal Enkhbayar [a], Hyesun Yoo [b], Jin Hyeok Kim [b], SeongYeon Kim [a,c], JunHo Kim [a,*]

[a] Department of Physics, Incheon National University, Incheon, 22012, Republic of Korea
[b] Department of Material Science and Engineering, Chonnam National University, Gwangju, 61186, Republic of Korea
[c] Chemistry and Nanoscience Center, National Renewable Energy Laboratory, Golden, CO, 80401, USA

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ABSTRACT

For high efficiency kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cell, CdS thin film was usually used as a buffer layer. However, due to the toxicity of Cd and pollution problems involved from the solution-based chemical bath deposition, eco-friendly high efficiency CZTSSe solar cell with Cd-free buffer is necessary. As an Cd-free buffer layer, we investigated (Zn,Sn)O (ZTO) film deposited by sputtering method. In order to achieve high power conversion efficiency, we controlled energy band gaps of CZTSSe absorber as well as ZTO buffer, which was required to optimize conduction band offset (CBO) between the absorber and the buffer and to increase open circuit voltage (V_{oc}) and fill factor (FF). The CBO was optimized by controlling the band gap of ZTO. By varying the Sn/(Zn + Sn) ratio and its deposition temperature, band gap of ZTO was successfully adjusted. Experimental and computational calculation results showed that solar cell performance was strongly affected by the CBO between absorber and buffer. Besides CBO matching, larger band gap of ZTO improved short circuit current density (J_{sc}) with enhanced external quantum efficiency value in blue photon spectrum range. As an additional way to improve power conversion efficiency of solar cell, band graded CZTSSe absorber was developed by using spray-based two-step process. The sprayed CZTSSe film was engineered to have S-enriched surface, which makes surface band gap widened and surface passivated, and resultantly increases V_{oc}, J_{sc} and fill factor (FF). By controlling band gaps of both CZTSSe absorber and ZTO buffer, we obtained 11.22% environment-friendly CZTSSe solar cell without MgF_2 anti-reflection coating.

1. Introduction

Kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) has attracted great attentions in chalcogenide solar cell community. Compared to organic-inorganic hybrid perovskite solar cell and $Cu(In,Ga)Se_2$ (CIGS) solar cell, CZTSSe is comprised of non-toxic and low-cost earth abundant elements, which has big advantages over the module scale production in large capacity [1–5]. In terms of characteristics of photo-absorber material, CZTSSe has high photo absorption coefficients more than 10^4 cm^{-1} in visible spectrum range and its band can be tunable by cation alloying or anion alloying from 1 eV to 1.9 eV, which are desirable for high efficiency solar cell and also for the application of tandem solar cell.[2,4] At present champion CZTSSe solar cell is reported to have power conversion efficiency (PCE) of ~12.6% with CdS buffer [6,7]. Considering toxicity of Cd and hazardous waste from chemical bath deposition (CBD) process, environment-friendly CZTSSe solar cell with Cd-free buffer is required for the spread of its applications [8,9].

Cd-free buffers have been studied for long time in CIGS solar cell community [10–19]. Zn(O,S) [12,13], In_2S_3 [14,15], (Zn,Sn)O [16,17], (Zn,Mg)O [18,19], and (Zn,Ti)O [20] are successfully developed as a Cd-free buffer layer for high efficiency CIGS solar cells. Up to now, the champion CIGS cell with PCE of 23.35% employs Zn(O,S) buffer instead of CdS buffer. From the development history of CIGS solar cells, we can think of possibility that CZTSSe solar cell with Cd-free buffer surpasses

* Corresponding author.
E-mail address: jhk@inu.ac.kr (J. Kim).
[1] These authors contributed equally to the work.

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