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# Precise-tuning the In content to achieve high fill factor in hybrid buffer structured $Cu_2ZnSn(S, Se)_4$ solar cells

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ABSTRACT

The doping of indium into absorber layer has been proven to be beneficial for hybrid buffer structured $Cu_2ZnSn(S, Se)_4$ (CZTSSe) solar cells, but it is difficult to precisely control the doping content only relying on In diffusion from $In_2S_3$ emitter. Herein, we use the solution method to prepare In-substituted CZTSSe layer by directly doping $In_2Se_3$ into metal chalcogenides precursor solution. The doping content can be precisely controlled and the influences of indium doping on cell performance are systematically discussed. Mott-Schottky and resistivity measurements indicate that the carrier concentration and charge transport process are monotonically enhanced with increasing In/(In + Sn) content (0 at.%, 3 at.%, 6 at.% and 12 at.%). The improvements of series resistance also lead to a monotonic increase of fill factor (*FF*) from 52.1% to 64.8%. Due to the larger recombination at high doping content, the 6 at.% In content device finally contributes the highest power conversion efficiency of 8.47%. It is expected that a precisely controlled indium doping could further improve cell performance for efficient hybrid buffer structured devices.

## 1. Introduction

As an alternative to the well known $Cu(In, Ga)(S, Se)_2$ (CIGS), $Cu_2ZnSn(S, Se)_4$ (CZTSSe) is a direct band gap material and has attracted more considerable attention in thin film solar cells, due to its low toxicity, abundance of composition elements and the potential commercial value (Lee et al., 2016; Yang et al., 2016, 2014; Emrani et al., 2013; Kumagai et al., 2015; Jung et al., 2016). Benefiting from the similar crystalline structure to CIGS, kesterite CZTSSe solar cell has high absorptivity for photons from visible to near-IR spectral range and could achieve the theoretical efficiency of up to 31% (Winkler et al., 2014; Tian et al., 2015; Buckley et al., 2016). As single phase stability could only be achieved at a much narrow region in the $\mu_{Cu}$-$\mu_{Zn}$-$\mu_{Sn}$ chemical potential space, the CZTSSe material is more vulnerable to have large number of defects, leading to its record power conversion efficiency 12.7% remarkably lower than that of the CIGS device (22.6%) Kim et al., 2014; Jackson et al., 2016. Researches demonstrate that open-circuit voltage $V_{oc}$ deficits ($E_g/q$–$V_{oc}$) and fill factor (*FF*) losses induced by the defects are the dominant issue for CZTSSe solar cell. For instance, the highest *FF* of CZTSSe solar cell is 70.8% (Kim et al., 2014), while the best *FF* of CIGS device is 81.2% (Repins et al., 2008).

The multivalent Sn (+II and +IV oxidation states) in CZTSSe solar cell is proven to create deep level defects and thus limit the device performance (Kumar et al., 2015; Larramona et al., 2015; Erkan et al., 2015). Partial substitution of Sn with cations Ge could efficiently reduce these defects, increase minority carrier lifetime and broaden the band gap of CZTSSe absorber (Gershon et al., 2013; Giraldo et al., 2015; Collord and Hillhouse, 2016; Bag et al., 2012; Khadka et al., 2016). Though this shift in band gap contributes an increase of $V_{oc}$, a remarkable loss in short circuit current ($J_{sc}$) is also induced and the Ge-substituted CZTSSe device could only present 9.14% efficiency (Bag et al., 2012). Recently, Mitzi et al. successfully enhanced the overall device performance based on a hybrid emitter structure of CZTSSe/CdS/ $In_2S_3$ due to the improvement of electrical transport properties of CZTSSe layer and the band alignment at the CZTSSe/buffer interface (Kim et al., 2014). They proposed that a great deal of indium from the $In_2S_3$ emitter diffused into CZTSSe layer, increased the carrier density and improved the $V_{oc}$ deficit via the formation of $In_{Sn}^{-}$ shallow defects (Kim et al., 2014; Ge et al., 2014). Furthermore, Giraldo's group prepared Cu/Sn/Cu/Zn metal stack by DC-magnetron sputtering deposition, and deposited In layer on top to dope the In concentrations ranging from 0 to $2.6 \times 10^{20}$ $cm^3$ (Giraldo et al., 2016). They demonstrate that In is uniformly introduced in CZTSe, not

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affecting the main elements distribution, but leading to the formation of a bilayer structure. However, despite these indium doping methods may be more attractive in the future, it is hard to precisely control the doping content and uniform distribution in CZTSSe layer and ensure the repeatability of cell performance only relying on the diffusion of In (Fig. 1).

Herein, we use solution method to prepare the In substituted CZTSSe layer by doping $In_2Se_3$ in metal chalcogenides ($Cu_2S$, ZnS and SnSe) precursor solution. The advantage of this approach is that the doping indium can be precisely controlled and uniform dispersion in the prepared CZTSSe layer (Fig. 1). Different In content CZTSSe device with hybrid emitter (soda lime glass/Mo/CZTSSe/$In_2S_3$/CdS/i-ZnO/ITO/Ag) are fabricated. After device performance characterization, we show a significant increase in carrier density with the increase of In content, and the *FF* is improved from 52.1% to 64.8%. This further supports that a precisely controlled In content in CZTSSe layer could further enhance cell performance for efficient hybrid emitter structured CZTSSe device, without $V_{oc}$ and $J_{sc}$ losses.

## 2. Experimental section

### 2.1. Materials

$Cu_2S$ (99.5%), ZnS (99.99%), SnSe (99.99%), Se (99%) and $In_2Se_3$ (99.99%) were purchased from Alfa Aesar. Ethylenediamine anhydrous (AR, 99%), dithioglycol ($HSCH_2CH_2SH$, AR), cadmium sulfate (AR) and thiourea (AR) were purchased from Aladdin. All the chemical reagents were used as received.

### 2.2. Formation of CZTS precursor solution

The CZTSSe precursor solution was prepared under inert atmosphere in an argon-filled glove box. $Cu_2S$ (0.0875 g, 1.10 mmol), ZnS (0.0729 g, 0.693 mmol), SnSe + $In_2Se_3$ (0.621 mmol), Se (0.0150 g, 0.190 mmol), 1,2-ethylenediamine (5 ml) and 1,2-ethanedithiol (0.5 ml) were added into a 25 ml argon filled round bottom flask (the ratio of In/(In + Sn) are about 0 at.%, 3 at.%, 6 at.%, 12 at.%), accompanied with stirring and heating for 12 h at 70 °C. Noting that the fresh solution must be immediately used due to its instability.

### 2.3. Deposition and selenization of In-substituted CZTSSe films

The Mo layer was sputtered via two-step processes under the base pressure of $4 \times 10^{-6}$ Torr. The first step is carried out under sputtering power of 80 W with Ar pressure of 6.5 mTorr for 30 min, and the second step is carried out under sputtering power of 170 W with Ar pressure of 3.0 mTorr for 30 min. The CZTSSe precursor films were deposited on Mo substrate (sputtered on soda-lime glass, 700 nm thick) by spin coating method. The spin coating process was kept at 3000 rpm for 20 s and then the deposited CZTSSe films were pre-heated at 350 °C for 3 min. The above processes were repeated for seven times until the film thickness reaches 850 nm, as seen in Fig. S1 (supporting information: Fig. S1). The obtained precursor film was placed in a graphite box and selenized at 540 °C for 15 min in the mixed selenium/nitrogen atmosphere by a rapid thermal processing (RTP) tube furnace (OTF-1200x-4-RTP), which is mainly composed of a Infrared Light Heating and a Slide Cooling system. This RTP furnace is capable of achieving a max. heating rate >50 °C/s and a cooling rate >10 °C/s and its digital photograph is shown in Fig. S2 (supporting information: Fig. S2). The $In_2S_3$ and CdS layers were both deposited by chemical bath deposition according to previous literature (Kim et al., 2014; Ge et al., 2014). Subsequently, 50 nm i-ZnO layer and 200 nm ITO layer were sputtered onto the surface of CdS layer. Both the ZnO and ITO layers were prepared by direct current (DC) magnetron. The sputtering power, pressure and sputtering time were 80 W, 5 mTorr and 25 min for i-ZnO layer and 75 W, 1 mTorr and 15 min for ITO layer, respectively. Finally, a 100–150 nm Ag electrode was deposited by thermal evaporation. The active area of the hybrid emitter structured device is 0.21 $cm^2$.

### 2.4. Characterizations

X-ray diffraction data was conducted using Philips X' PertPro (Cu-K$\alpha$1 radiation $\lambda$ = 1.5406 Å). The surface and cross-section topography of the selenized CZTSSe films were taken on the field emission scanning electron microscope (SEM, JSM-5600LV). The cross-section of the fabricated device and In doping content of the CZTSSe layer were further performed on another SEM equipped with an energy dispersive X-ray analyzer (EDX, FEI Nova NanoSEM 450/EDAX). In order to identify and monitor varying depths of CZTSSe films, multiwavelength excitated Raman measurements were performed on Renishaw, RM–1000, combining with 532 nm, 633 nm and 785 nm excitation lines. The power excitation density was around 50 W/$cm^2$. Thermogravimetric analysis (TGA) was performed under the nitrogen atmosphere by the TG/DTA 6200 thermogravimetric analyzer (SII, Inc). The *J–V* curve were measured by the solar simulator (Newport, USA, Orielclass A, 91195A-SYS) under AM 1.5G, 100 mW $cm^{-2}$ illumination. The Zhuoli SCS10-X150-DSSC system was used to measure the external quantum efficiency (EQE) spectrum. Mott–schottky plots and Electrochemistry impedance spectroscopy were measured by using electrochemical test station, where the frequency is $10^4$ Hz and $10^2$–$10^6$ Hz, respectively.

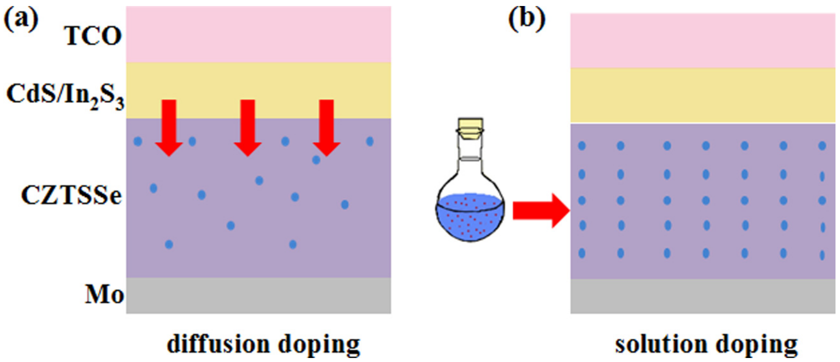

**Fig. 1.** Schematic diagram of different In doping approach in hybrid buffer structured CZTSSe solar cells. (a) Diffusion doping and (b) solution doping.