Critical role of Zn/Sn ratio to enhance Cu-Zn-Sn-S solar cell efficiency by suppressing detrimental $Cu_{2-x}S$ secondary phase

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ABSTRACT

The co-existing secondary phases, in off-stoichiometric Cu-Zn-Sn-S (CZTS) solar cells, are one of the main causes of performance gap between earth abundant CZTS and matured Cu-In-Ga-Se (CIGS) solar cells technology. Highly metallic Cu-S based secondary phases provide shunting paths to the current flow and critically affect the device performance. Several chemical etchants have been developed and used to remove conductive $Cu_{2-x}S$ phase from CZTS absorber surface before device fabrication. Present work is mainly focused to tune the Zn/Sn composition ratio in co-sputtered CZTS active layer to suppress the formation of $Cu_{2-x}S$ phase during the growth itself to eliminate the additional step of etching in device fabrication. Significant reduction of $Cu_{2-x}S$ secondary phase was observed with decreased Zn/Sn ratio, which resulted in more than 3 times efficiency enhancement for the final composition. The fabricated solar cell in the stacking order of Ag/ITO/i-ZnO/CdS/CZTS/Mo/SLG with optimum composition showed an efficiency of 6.11% without any antireflection coating. Controlling the Zn/Sn ratio resulted in an effective and virtuous solution to avoid the detrimental secondary phases like $Cu_{2-x}S$, which conventionally required a chemical etching treatment.

1. Introduction

Cu_2ZnSnS_4 (CZTS) quaternary compound is the most sought earth-abundant absorber material for thin film solar cells. In addition to being economically and ecologically viable, CZTS possesses desirable properties such asp-type conductivity, large absorption coefficient, $\alpha > 10^4$ cm^{-1}, and an optimum band gap of ~ 1.5 eV [1]. The past several years have spotted tremendous improvements in the performance of CZTS devices with different synthesis techniques like sputtering, co-evaporation, co-electrodeposition and various solution processed methods [2–5]. Mitzi and his co-workers reported a record efficiency of 12.6% [5] for hydrazine based solution processed CZTSSe solar cell. Solar cells employing Se-free co-electrodeposited CZTS absorber with conventional CdS buffer have shown an efficiency of 9.4% [6]. So far, the highest efficiencies of CZTS devices are reported for the solution processed cells. However, solution based methods involve the usage of hazardous chemicals that are environmentally not favorable and may raise practical issues restricting large scale deployment [7]. Despite all the efforts made, there is a huge performance disparity between CZTS and its counterpart CIGS ($Cu_2InGaSe_2$) with highest reported efficiency of 22.6% [8].

One of the major challenges in the synthesis of CZTS is its narrow phase stability which leads to the formation of secondary phases such as Cu_2S, ZnS, SnS, SnS_2 and Cu_2SnS_3 [9,10]. Chemical instability of CZTS during prolonged annealing profiles and corresponding Sn loss at elevated temperatures leads to the formation of Cu-S based secondary phases [11,12]. Sn loss at elevated temperatures is attributed to vaporization of highly volatile SnS_2 as a by-product of SnS and S vapor [13]. This Sn loss thereby favors the segregation of deleterious $Cu_{2-x}S$ secondary phase in the active layer and at absorbing-buffer layer interface [14]. Cu-S based $Cu_{2-x}S$ phases are highly detrimental for the device performance as they form the shunting paths and result in concealing of photo generated electron-hole pairs [15]. High content of $Cu_{2-x}S$ phases often lead to non-performing solar cell devices [16]. There are only few studies on the investigation of the segregation and evolution of Cu-S based secondary phases which provide an effective solution to avoid these deleterious phases [9]. Moreover, people have tried controlling Sn loss by maintaining high sulfur and SnS partial pressures, which limits the formation of Cu-S based secondary phases but often results in ZnS secondary phase formation [13,17].

To improve the CZTS surface and consequently the CZTS/CdS interface, chemical etching is commonly performed [18]. Several etchants

including KCN have been developed to remove $Cu_{2-x}S$ metallic phases, the main cause of shunting and interface recombination in CZTS solar cells. KCN etching in CZTS(Se) has significantly improved the efficiencies. However, KCN is highly toxic and reactions with KCN sometimes produce harmful gases like HCN. Also, etching affects the chemical composition at the surface of the film which disturbs the compositional uniformity [19]. Recently, KCN/KOH treatment of CZTSe absorber layer is carried out to remove $Cu_{2-x}Se$ secondary phases as a part of interface engineering and efficiency of > 5% is achieved [20]. Fairbrother et al., have achieved highest efficiency of 5.2% by selective removal of $Cu_{2-x}S$ phases and ZnS secondary phase using KCN and HCl respectively in CZTS solar cell [21]. Usage of harmful chemicals during etching may restrict the large scale production of CZTS solar cells. Also, formation of air voids are often reported after etching [22]. Thus, development of safe method to avoid detrimental $Cu_{2-x}S$ phases for highly efficient CZTS solar cells is required.

Chemical composition of absorber layer plays a crucial role in the formation of secondary phases during post heat treatments [14]. Previous reports suggest that Cu-poor and Zn-rich compositions are favorable for high efficiency CZTS devices [23]. Copper-poor conditions are usually judged on the basis of Cu/(Zn + Sn) ratio of the total sample composition being less than 1. However, the ratio of Cu/(Zn + Sn) can deviate to a value higher than 1 even in a Cu-poor CZTS phase if the secondary phase such as ZnS is not accounted for [24]. Thus, it is argued that Cu/Sn and Zn/Sn ratios are more appropriate for determining the composition of CZTS absorber layer [24]. Controlling Cu/Sn ratio is a bit difficult being in copper poor region but the precise control of Zn/Sn ratio is possible [14]. There are recent reports on the importance of Zn/Sn ratio in CZTS based solar cell devices where it plays a vital role in controlling charge carrier concentration and depletion region width of the CZTSSe solar cell device [7,25]. Zn/Sn ratio also influences the formation of defects and defect clusters as their formation energies are sensitive to Zn content of the CZTS film [26]. An optimal Zn/Sn ratio in CZTS absorber tends to reduce secondary phases and defects formation. Threshold value of Zn/Sn ratio above which all the excess Zn segregates in the form of ZnS secondary phase is given to be 1.09 (± 0.04), for zinc-rich CZTSSe solar cells [24]. However, the role of Zn/Sn ratio in controlling secondary phases is not extensively studied and thus demands more attention as it controls the Sn loss during annealing which is one of the main causes of Cu-S phase formation [14].

In this work, role of Zn/Sn ratio was studied to restrain the $Cu_{2-x}S$ formation during growth itself instead of relying on post treatments of chemical etching. Zn/Sn ratio was tuned in two steps by first varying density of Zn precursor to estimate a nominal CZTS stoichiometry. In second step, power density of Sn precursor was adjusted to fine tune the Zn/Sn ratio. This allowed a precise control over Zn/Sn ratio without affecting Cu/(Zn + Sn) ratio of CZTS layer. Zn/Sn composition ratio was observed to play critical role in defining the CZTS properties and in suppressing highly metallic $Cu_{2-x}S$ secondary phase. Efficiency enhancement was observed to be more than 3 times, as efficiency increases from 1.8% to 6.11% with fine tuning of Zn/Sn ratio. The main cause of efficiency enhancement is the suppression of $Cu_{2-x}S$ conductive phase present on the CZTS surface. $Cu_{2-x}S$ suppression eventually increases the shunt resistance which further enhances the fill factor (FF) of the device and finally leads to higher efficiency. For highest efficiency device, Zn/Sn ratio was 1.10, which is very close to the reported threshold value of 1.09 (± 0.04) above which ZnS segregates due to excess Zn content [24]. It implies that CZTS composition with highest efficiency is free of ZnS segregation. This work provides a simple and innocuous approach to control highly detrimental Cu-S based phases without any need for additional step of etching of the CZTS surface, which may alter material properties at the interface. To the best of our knowledge, critical role of Zn/Sn ratio in controlling $Cu_{2-x}S$ phases has not been implicitly reported so far.

2. Experimental

2.1. CZTS absorber film growth

CZTS films were synthesized in a two-step fabrication method which involves precursor deposition followed by heat treatment in the presence of H_2S and Argon ambient, 5% + 95% respectively. Soda lime glass (SLG) substrates were cleaned thoroughly before CZTS deposition by ultrasonication in DI water followed by acetone and propanol for 30 min each. Finally, the substrates were put for UV cleaning to avoid any microbial impurities. Molybdenum (Mo) was deposited on cleaned substrates of area 1.5×1.5 cm^2 at DC sputtering power density of 5.92 W/cm^2. The CZTS films were then deposited on Mo coated soda lime glass (SLG) substrate by co-sputtering of Cu, ZnS, and SnS$_2$ targets each of 2″ diameter. The deposition chamber was pumped down to a base pressure of 7.5×10^{-7} Torr. After that 20 sccm of Ar gas (purity 99.99%) was injected into the system. CZTS film deposition was performed at 6 mtorr at room temperature providing RF power to ZnS and SnS$_2$ targets and DC power to Cu target. The two step process was used for co-sputtering of CZTS precursor that proved to be beneficial for a better control of composition. Samples S01, S02 and S03 were prepared keeping ZnS RF power density as 3.70 W/cm^2, 4.94 W/cm^2 and 6.17 W/cm^2, whereas SnS$_2$ and Cu powers were fixed at RF power density of 1.97 W/cm^2 and DC power of 1.48 W/cm^2, respectively. The details of the deposition parameters for sample S01, S02 and S03 are given in Table 1. First set of deposition provided the initial idea of ZnS and Cu sputtering power that resulted in near stoichiometric compositions with slightly higher Zn/Sn ratio. For further tuning of Zn/Sn ratio, another set of samples S04 and S05 were deposited with SnS$_2$ RF power density of 2.46 W/cm^2 and 2.96 W/cm^2, respectively. Whereas, powers of ZnS and Cu precursors were same as that of sample S01. Deposition time was optimized through quartz crystal monitor (INFICON) to achieve a final thickness of ∼ 1 μm which was further confirmed by a profilometer. Substrates were rotated at 11 rpm during deposition to improve the uniformity of the CZTS layer. After deposition, samples were annealed in a quartz tube furnace at 510 ˚C for 3 h with 5% H_2S and 95% N_2 atmosphere. No etching has been processed on the CZTS films prepared during this study.

2.2. Absorber layer characterizations

The crystallinity of the films was studied using grazing incident X-ray diffraction (GIXRD) using PANalytical X-pert pro multipurpose diffractometer equipped with high intensity CuKα (0.1504 nm) radiation. Whereas, the phase identification of the material is carried out using Raman spectroscopy with excitation laser of wavelength 532 nm. Scanning electron microscope (SEM-ZEISS) was used to study the surface and cross-section morphologies of the device. Composition of the sulfurized samples was determined by energy dispersive spectroscopy (EDS) analysis operated at 20 kV. Photoluminescence (PL) spectra was recorded at room temperature by a 532 nm laser excitation. The oxidation states of different elements in CZTS films are studied by X-Ray Photoelectron spectroscopy (XPS) using a Versaprobe PHI 5000 scanning system employing Al Kα X-rays. X-ray florescence (ZSX PrimusIV Japan) was used to study elemental mapping of the CZTS film.

Table 1
List of prepared CZTS active layer samples in Set I from co-sputtering process with sputtering power densities of different targets.

Sample	Power density ZnS (W/cm^2)	Power density Cu (W/cm^2)	Power density SnS$_2$ (W/cm^2)
S01	3.70 RF	1.48 DC	1.97 RF
S02	4.94 RF	1.48 DC	1.97 RF
S03	6.17 RF	1.48 DC	1.97 RF