Chemical Composition Control of Evaporated Cu_2ZnSnS_4 Solar Cells

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Abstract: This paper focuses on chemical composition issue of evaporated Cu_2ZnSnS_4 (CZTS) absorber and potential solutions to it. The chemical composition of the CZTS absorber was estimated by energy dispersive spectroscopy (EDS) and a solution-based Inductively Coupled Plasma Mass Spectroscopy (ICPMS). It discloses a chemical non-uniformity issue spatially on even the same sample and confirms Sn loss issue. It also reveals that substrate option affects composition control.

Keywords: Composition control, evaporation, CZTS.

1. INTRODUCTION

CZTS is promising as it replaces rare and expensive In, Ga in commercial $CuIn_XGa_{(1-X)}Se_2$ (CIGS) solar cells with earth-abundant and cheap Zn, Sn, which could reliably support terawatt renewable electricity consumption [1]. Meanwhile it shares similar properties with CIGS. CZTS at this stage mainly imitates the processing of CIGS as a shortcut for development. Co-evaporation is proved a successful technique in achieving the record 21.7% CIGS solar cell efficiency [2]. Besides this, sequential evaporation of the elements or compound often shows strong inhomogeneity and multi-phases [3]. Additionally, a close to stoichiometry pure sulphide CZTS solar cell has achieved 4.1% by one step co-evaporation without further sulfurization [4]. Moreover, chemical composition is one of the major factors to influence efficiency [5]. Therefore, co-evaporation of CZTS and chemical composition inhomogeneity of the evaporated film is investigated in this paper.

Chemical composition non-uniformity is not an issue for CIGS solar cell, however may form a major challenge for CZTS solar cells. CIGS has a wide range of tolerance of the anion-to-cation off-stoichiometry [6]; however, CZTS has a narrow chemical composition window for a single phase CZTS absorber [7]. Meanwhile, empirically a sweet chemical range for high efficiency CZTS solar cells has been identified: ratio of Cu/(Zn+Sn)=0.8-0.9 and Zn/Sn=1.2-1.3 [5]. It implies the tolerance for the composition variation: (0.9-0.8)/0.8=12.5% for Cu/(Zn+Sn) and (1.3-1.2)/1.2=8.33% for Zn/Sn. As Cu/Sn ratio appears to be also important [8], it was also included in this study. Even at compositions in this range, the efficiencies reported by different groups could have a difference above 10% [5]. This paper is to reveal whether composition uniformity is an issue for future CZTS production.

2. EXPERIMENTAL DETAILS

The 5×5cm^2 size soda lime glass substrate had ~ 1000nm thick Mo coated on it with a sheet resistance of ~ 0.15 Ω/□. The substrate was subjected to in-situ CZTS co-evaporation in a Mantis evaporator at substrate temperature of ~ 500 ºC and substrate rotation rate of ~ 15 revolutions/min (with one exception for improving uniformity by increasing rotation rate to ~ 20rpm). The Mantis chamber was equipped with Cu, Zn, Sn effusion cells (Veeco manufactured) and sulphur cracker. As composition was intentionally varied to check the composition uniformity under different compositions, the detail parameters are irrelevant for the discussion in this paper and will not be listed in this paper.

The chemical composition of the majority of the CZTS absorber films are measured by EDS, and only a few requiring high precision are tested by solution based ICP measurement. For EDS measurement, all samples was divided into 5 measurement regions: the centre region and 4 other corner regions. Each region had three measurements spots. And in total 15 spots were measured for each sample. Only the average result and the standard deviation of each sample will be reported.

3. RESULTS AND DISCUSSION

3.1. Spatial Uniformity

Figure **1** shows the chemical composition profile of in-situ co-evaporated CZTS absorber on a 5×5cm^2

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sample. It indicates the centre has more uniform chemical composition distribution than on the corner in general. And the average Cu/(Zn+Sn) has a standard deviation of 3.2% which means an variation of ± 3.2%. So the fluctuation would be 6.4% well below the tolerance for Cu/(Zn+Sn); And the average Zn/Sn has a standard deviation of 12.3%, which is well above the tolerance already. Actually Cu/Sn can be deduced once Cu/(Zn+Sn) and Zn/Sn are known, Cu/Sn here is just for a reference as Cu/Sn ~ 2 is generally considered good for efficiency.

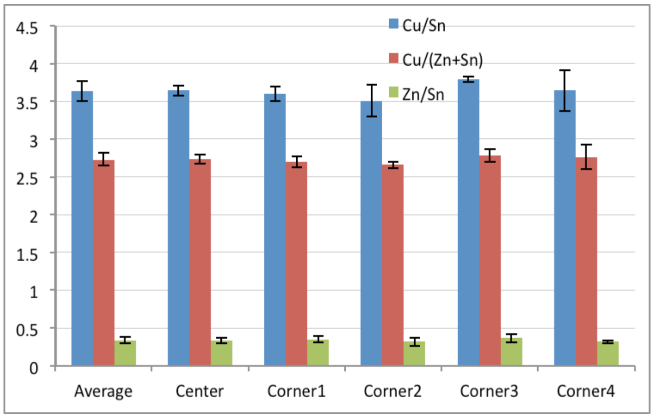

Figure 1: The chemical composition profile of in-situ co-evaporated CZTS absorber on a 5×5cm^2 sample (The vertical axis is ratio if not specified). The sample is divided into 5 regions: the centre plus 4 corners. Compositions are measured on 15 spots in total with each region 3 samplings.

Figure **2** demonstrates chemical composition profiles of one step co-evaporated CZTS absorbers with different compositions: Cu rich Zn poor, Cu rich Zn rich, Cu poor Zn poor, Cu poor Zn rich. Especially for Cu poor Zn rich samples, rotation rate at 20rpm improves the chemical composition uniformity substantially.

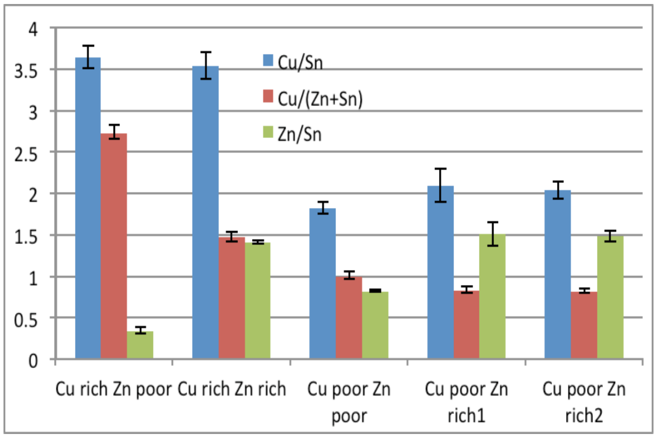

Figure 2: The chemical composition profile of in-situ co-evaporated CZTS absorbers on 5×5cm^2 sized samples. Cu poor Zn rich1 and Cu poor Zn rich2 were deposited at rotation rate of 15rpm and 20rpm, respectively.

To check whether the composition uniformity is in the tolerance range, the standard deviation of each samples and allowed standard deviation tolerance is compared in Figure **3**. It indicates that Cu rich Zn rich and Cu poor Zn poor samples are within the tolerance. And increasing the rotation rate from 15rpm to 20 rpm also makes the variation close enough to the allowed range.

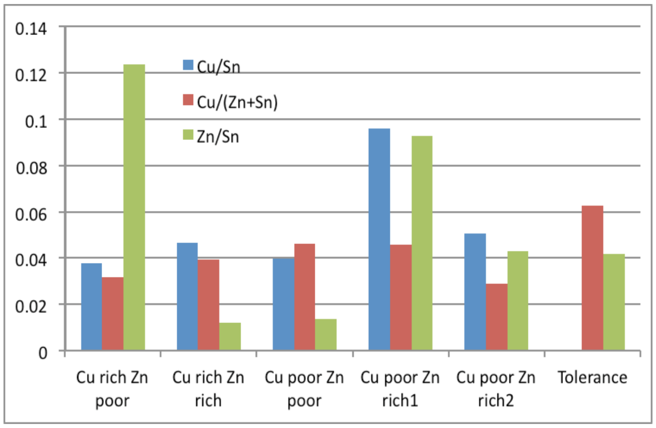

Figure 3: Standard deviation of the chemical compositions of examined samples in comparison with the allowed tolerance (the vertical axis is standard deviation).

As the target composition is Cu poor Zn rich, high rotation rate is suggested for enhancing composition uniformity.

3.2. Mo Substrate Versus Soda Lime Glass Substrate

Figure **4** illustrates chemical composition of CZTS absorbers on Mo and glass substrates in the same

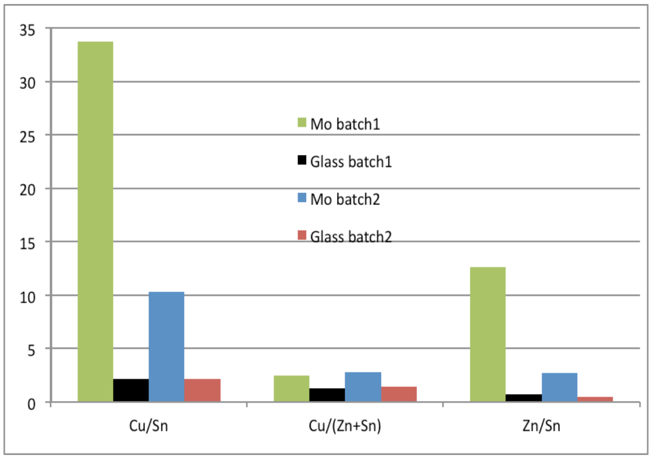

Figure 4: Chemical composition of CZTS on Mo and glass substrates in the same batches. The composition is measured by ICP. Mo batch1 and glass batch1 substrates are put into the evaporator chamber in the same time; Mo batch2 and glass batch2 are put into the chamber in the same batch.

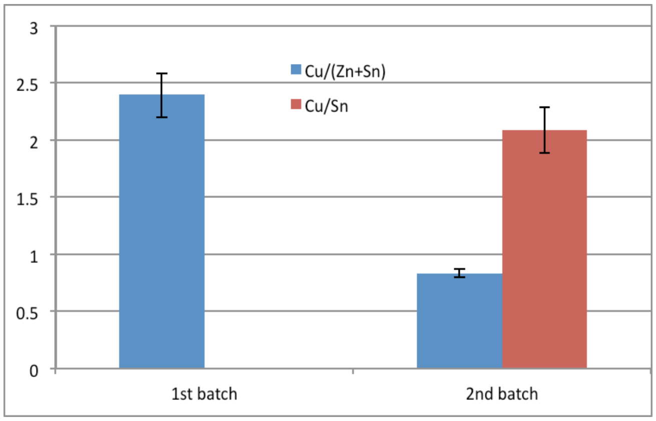

Figure 5: Chemical compositions of the CZTS absorbers deposited in two continuous batches under the same processing condition. Negligible Sn is detected in the first batch, therefore is ignored in the picture.

deposition batches. It indicates that the chemical compositions are quite different for CZTS absorbers on Mo and glass substrates even they were put in the evaporator for deposition simultaneously. This necessitates individual optimization process for each type of substrates.

3.3. Elemental Loss Issue

Zn and SnS has very high vapour pressure and is very difficult for these atoms to stick on high temperature substrate [9]. To reduce Zn loss, high S pressure is necessary; though this may lead to high Sn loss. S cracker valve and shutter are generally opened~10 minutes prior to opening shutters of Zn, Sn, Cu. Figure **5** shows chemical compositions of the CZTS absorbers deposited in two continuous batches under the same processing condition. It reveals no detectable Sn in the first batch; however Sn concentration is almost in the target range for the second batch. This implies that Sn was readily lost once opening shutter because the whole chamber was filled with S molecules and SnS was formed upon evaporated Sn evaporating out of the crucible. SnS has a very high vapour pressure and hardly sticks on the high temperature substrate without adequate Sn supply in the chamber atmosphere. For the second batch deposition, Sn was already in the atmosphere. To control Zn, Sn loss and therefore the composition of the absorber, appropriate S and Sn pressure control is suggested to be implemented. Otherwise, Sn shutter needs to be opened first and then immediately followed by shutter opening of Cu, S, Zn because S and Zn have high vapour pressure and relatively easily fill the chamber once evaporated. To resolve the Zn loss issue, ZnS may also be suggested as the Zn source instead of metal Zn evaporant because ZnS has much lower evaporation pressure than Zn.

4. CONCLUSIONS

The chemical composition control issues have been identified for CZTS: standard deviation of Zn/Sn on a 5×5cm^2 CZTS sample is ~ 9% well above the allowed one ~ 4% with the substrate rotation at 15rpm during deposition; Mo and SLG substrates results in quite different composition even in the same deposition batch; Sn loss is significant with high S pressure prior to opening Sn shutter. Solutions for the first issue is simply increasing the substrate rotation rate; for the second one, it is to optimize deposition parameters individually for each class of substrates; the final one is implementing S, Sn pressure control or a sequential shutter opening procedure prior to co-evaporation while in the meantime replacing Zn evaporant with ZnS. In summary, the chemical control issue can be resolved and may not form a severe challenge for commercializing CZTS solar cell technology.

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