Pre-annealing of metal stack precursors and its beneficial effect on kesterite absorber properties and device performance

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ABSTRACT

A variety of approaches is being used to fabricate kesterite absorbers, such as sputtering, co-evaporation and solution based techniques. Annealing at high temperatures is a common processing step to stimulate elemental mixing and grain growth. This study investigates the effect of pre-annealing of metal stack precursors at 150 °C, 200 °C, 300 °C and 450 °C on kesterite absorber and solar cell properties. Structural, morphological and vibrational properties of the thin films were investigated. It was found that pre-annealing at 450 °C exhibited a structural mixture distinct from precursors annealed at lower temperatures. The absorber showed improved thickness uniformity, compositional surface homogeneity and absence of Sn-S phases. Lower temperatures resulted in Sn-S compounds in the absorber. In situ XRD is used to monitor phase transitions during pre-annealing. It is shown that implementing a pre-annealing step can improve the absorber properties and the device efficiency. The best performing solar cell had a 4.02% efficiency and was achieved by pre-annealing the precursor layer at 450 °C.

1. Introduction

Kesterite, or Cu_2ZnSnS_4 (CZTS), has been proposed as a sustainable alternative to CIGS, since it consists of earth abundant and non-toxic materials. Additionally, it has a direct optical bandgap between 1 and 1.5 eV and an absorption coefficient above 10^4 cm^{-1}. Kesterite thin films are typically aimed to be in the compositional region of 0.76–0.90 for Cu/(Zn + Sn) and 1.1–1.3 for Zn/Sn. It was shown before that off-stoichiometric films result in devices with better electronical properties as opposed to stoichiometric films [1]. Because of the narrow stoichiometric region of CZTS, off stoichiometric films are more likely to have secondary phases. Secondary phases have a detrimental effect on device performance. This was found for example with the presence of SnSe in CZTSe selenium based films [6]. Etching methods aim to remove phases such as CuS/Se, ZnS/Se and SnS/Se. However, they introduce an additional processing step which is less favorable for industrial use [2–5]. A variety of chemical and physical deposition techniques can be used to obtain films in this compositional range; sputtering [7], co-evaporation [5], spray-pyrolysis [8] and solution based spin coating [9]. Most of the processing methods involve a high temperature annealing step in order to stimulate elemental mixing and grain growth.

Several research groups are using metal stacks as a precursor for CZTS films in which the metal stack is ordered in different ways, *e.g.* Mo/Sn/Cu/Zn [10,11], Mo/Zn/Sn/Cu [12], Mo/Zn/Cu-Sn [13] or Mo/CZT [14–16]. To prevent Sn loss this element is usually deposited as the bottom layer [17]. Cu can easily diffuse in both Zn and Sn when it is in the middle [17]. Zn is a volatile compound and is sometimes placed at the bottom to prevent evaporation during the process. Co-deposition of the metals is another approach and may improve homogeneity because of the readily mixed compound [18].

As part of a processing strategy, several groups have incorporated a soft annealing or pre-annealing step, which occurs with or without adding sulfur or selenium. This pre-annealing is implemented to stimulate diffusion and intermixing of the metals, such that reaction pathways for CZTS become dominant and compositional homogeneity of the film is promoted. An overview of studies that include a pre-annealing method is given in Table 1.

In this study, a pre-annealing strategy is being implemented with regard to the metal precursor with Cu/(Zn/Sn) = 0.8 and Zn/Sn = 1.2. Separate precursors are pre-annealed at 150 °C, 200 °C, 300 °C and 450 °C. The effect of alloy formation on the structural and morphological properties of sulfurized films is investigated. In particular, the

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Table 1
Overview of studies where a similar pre-annealing of metal precursors was performed before commencing the sulfurization/selenization process.

Stacking order	Deposition technique	Atmosphere (Gas/P)	Time (min.)	Pre-annealing Temperature (°C)	PCE	S/Se	References
Mo/CZT	Electro co-deposition	Ar/H$_2$ (95/5%)	30	350	–	Se	[19]
Mo/CZT	Electro co-deposition	Ar	10	350	2.64%	Se	[14]
Mo/CZT	Electro co-deposition	Ar	–	450	3.74%	S	[15]
Mo/CZT	Electro co-deposition	Ar	60	250/300/350	–	S	[16]
Mo/Cu/Sn/Zn	Electrodeposition	Inert gas / 1000 Pa	30	300	8.2%	Se	[20]
Mo/Cu-Sn/Zn	Electrodeposition	N$_2$	20	350	–	S	[21]
Mo/Cu/Sn/Cu/Zn	Electrodeposition	N$_2$	3	270	–	S	[17]
Mo/Zn/Cu-Sn	DC sputtering	Ar / 10^5 Pa	60	350	4.4%	S	[13]
Mo/Sn/Cu/Zn	DC sputtering	N$_2$	30	240	2.81%	S	[22]
Mo/Sn/Cu/Zn	DC Sputtering	Ar / 10^5 Pa	10	150/200/300/450	4.02%	S	*This work*

relation between Cu-Sn and Sn in the precursors and Sn-S compounds in the absorber is investigated. The effect of Sn-S compounds on device performance of pure sulfide CZTS is also studied. Finally, XRD was explored as an *in situ* tool during pre-annealing to monitor the occurrence of Sn-S compounds.

2. Experimental methods

2.1. Pre-annealing and absorber formation

The metallic stacks were prepared by DC magnetron sputtering using the deposition ordering glass/Mo/Sn/Cu/Zn. This sequence was chosen assuming that Cu diffuses easily into Sn and Zn and prevents Sn loss. Precursor films with compositional ratios of Cu/(Zn + Sn) = 0.8 and Zn/Sn = 1.2 were prepared. Additional results of copper stoichiometric films (Cu/(Zn + Sn) = 1.0) can be found in Supplementary information. Pre-annealing was performed by placing the sample in a quartz crucible in a three zone tube furnace. A background pressure of 1 bar Ar was used. A ramping rate of 20 °C/min was used and the samples were naturally cooled down. The annealing temperature was held steady for 10 min. The time of ramping and natural cooling down is not included in the 10 min.

The sulfurization process took place in the same type of furnace. Separate tubes were used for pre-annealing and sulfurization in order to avoid preliminary inclusion of sulfur into the metal stack. In both annealing processes the tubes were flushed with Argon twice before starting. Samples were placed in a graphite box alongside 50 mg of finely ground sulfur powder (Alfa Aesar, 99.995%). A ramping rate of 20 °C/min and a background pressure of 1 bar of Ar was used. The sulfurization was performed at 550 °C for 30 min and the samples were cooled down naturally.

2.2. Thin film characterization and solar cells

The compositional, structural, morphological and vibrational properties were studied respectively with x-ray fluorescence spectroscopy calibrated with ICP-OES (XRF, Fisherscope XVD), x-ray diffraction (XRD, Siemens D500 diffractometer) in θ–2θ configuration, scanning electron microscopy (SEM, ZEISS Series Auriga) using 5 kV and Raman spectroscopy with λ_{exc} = 633 nm. The Raman spectra were corrected with a Si reference line at 520 cm^{-1}. For the XRF measurement, 16 different points were taken on each sample. The average values were used to calculate the compositional ratios. The standard deviation of the ratio was approximately 0.05.

The absorbers were treated with an HCl etching method [3] in order to remove ZnS from the surface. Subsequently, 50 nm of CdS was deposited by a chemical bath deposition, followed by sputtering of 50 nm undoped ZnO and 250 nm of ITO with 90% of In$_2$O$_3$ and 10% of SnO$_2$ (CT100 Sputtering System, Alliance Concepts). No additional heating is used during sputtering, temperatures will be approximately 100–150 °C. The solar cells were scribed in 3 × 3 mm^2 sections. Solar

device characteristics were studied with a solar simulator (Abet 3000) under one sun illumination.

3. Results & discussion

3.1. Composition of alloyed precursor thin films

The compositional ratios of the pre-annealed precursors are depicted in Fig. 1. The Zn/Sn ratio follows a decreasing trend at elevated pre-annealing temperatures. Some zinc loss is expected due to its high volatility and for being the top layer of the metal precursor stack.

3.2. Structural properties of precursors and absorbers

XRD patterns of the annealed films are depicted in Fig. 2 as false-color intensity plots. Fig. 2A and B show patterns of the pre-annealed precursors and absorbers, respectively. Elemental Sn is present up to 450 °C (arrow 1) in the precursors. The intensity evolution of elemental Sn (arrow 1) is in accordance with the evolution of the Sn peaks at 44–46°. In stoichiometric films, elemental Sn is only present up to 150 °C (see SI Fig. S5). The persistence of elemental Sn is expected in copper poor films, because there is higher competition between Zn and Sn to alloy with Cu than in stoichiometric films.

There is a broad contribution of Cu-Sn and Cu-Zn alloys in the 43° region (arrow 2). For higher temperatures, these peaks become more pronounced and narrow, indicating further crystallization of the alloys after pre-annealing at 200 °C and 300 °C. Note that above the melting point of Sn (230 °C), liquid Sn might facilitate intermixing.

Between 300 °C and 450 °C significant structural changes occur in the precursor film which is visible across the whole pattern. From the Cu-Sn phase diagram it can be seen that above 408 °C a transition from Cu$_6$Sn$_5$ → Sn(l) + Cu$_3$Sn takes place [23]. The Cu$_3$Sn reflection is observed at 42° (arrow 3). Because Cu$_6$Sn$_5$ dissolves, it is plausible that Cu$_5$Zn$_8$ becomes dominant in the 43° region. However, the reverse
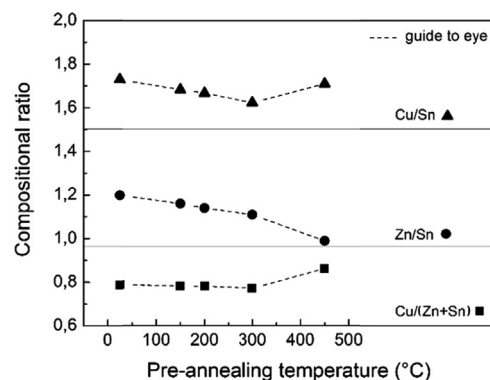

Fig. 1. Comparison of compositional ratios of copper poor precursors with respect to pre-annealing temperatures. The dashed trend line serves as a guide to the eye.