



# Sulfurization of co-evaporated $\text{Cu}_2\text{ZnSnSe}_4$ thin film solar cells: The role of Na

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## ABSTRACT

The sulfurization of co-evaporated  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) thin films is studied. In this work, a relationship between the Na concentration and the further S incorporation in the CZTSe absorber layer is found. Na is added by a NaF precursor layer before CZTSe co-evaporation and/or by diffusion from the soda-lime glass substrate. Higher Na concentrations result in bigger grain sizes, higher S/(S + Se) atomic ratios and photovoltaic devices with higher  $V_{OC}$ , as investigated by SEM, GIXRD, Raman and I-V measurements. Results using an alternative substrate as ceramic verify the importance of the control of the Na content, which alters the carrier concentrations and elements distribution with much higher S and Na concentrations at the surface in this particular case. By using this methodology, it is possible to tune the kesterite band gap energy by the creation of S-gradient through the absorber thin film. This may provide a new approach for the control of  $\text{Cu}_2\text{ZnSn(S,Se)}_4$  growth and development of high efficiency kesterite solar cells. Efficiencies of 5.5% and 6.4% are obtained using ceramic and SLG substrates respectively (without antireflection coatings and without grids).

## 1. Introduction

$\text{Cu}_2\text{ZnSn(S,Se)}_4$  (CZTSSe) has been shown as a promising candidate as absorber layer for thin film solar cells. A maximum efficiency of 12.6% has been achieved [1]. This performance is very low in comparison to the highest conversion efficiency of  $\text{Cu(In,Ga)Se}_2$  (CIGSe) solar cell of 22.9% [2]. The main limitation of kesterite-based solar cells is the open circuit voltage deficit (defined as  $E_g/q - V_{OC}$ , where  $E_g$  is the absorber band gap energy,  $q$  is the elementary charge and  $V_{OC}$  is the open circuit voltage). One of the reasons of this drawback is the non-optimal quality of kesterite absorber and the presence of secondary phases [3,4]. The existence of electrostatic potential fluctuations in the CZTSSe absorber layer could be another important factor that deteriorates the solar cell efficiency [5,6]. The interface recombination with the unfavourable alignment of the conduction band minimum (CBM) at the CZTSSe/buffer interface leads to a decreased performance [3].

Goushi et al. [7] achieved an enhanced  $V_{OC}$  of  $\text{Cu(In,Ga)(S,Se)}_2$  (CIGSSe) devices using the sulfurization after selenization (SAS)

method. Solar Frontier reported CIGSSe-based solar cells with 22.3% efficiency using this SAS process [8]. Nowadays, this company has achieved 19.8% CIGSSe mini-modules using such a method [9]. With this SAS method, an enlarged surface bandgap by S-incorporation in CIGSe is obtained with a reduction of defects, lowering the valence band maximum (VBM) at the vicinity of the CIGSe surface region. Experimental and modelling results have demonstrated this effect, leading to an enhanced  $V_{OC}$  [10,11]. Nevertheless, it is difficult to apply this method for kesterite absorber layers successfully. It seems that the mechanism of S diffusion into CIGSSe matrix and CZTSSe are quite different. Cai et al. [12] have shown that the sulfurization of the surface of the kesterite absorber layer leads to a widening surface bandgap with an improved device performance and  $V_{OC}$ . The sulfur-modified surface of kesterite was achieved by introducing  $\text{H}_2\text{S}$  gas during cooling stage of the selenization process of stacked metallic precursors [12].

On the other hand, it is well known that the inclusion of alkali elements in CIGSSe absorber layers enhance the  $V_{OC}$  and improve the final photovoltaic devices [2,13,14]. Recently, the influence of alkali

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elements, particularly of Na, on the kesterite absorber layer has been studied [15–20]. However, these effects are still under discussion. First, there is still some controversy in the influence of Na in the grain growth and the crystallization of the absorber layers. Repins et al. [15] reported the improvement of the photovoltaic parameters of co-evaporated kesterite devices by the introduction of a NaF precursor layer without affecting the grain size, as well as Abzieher et al. [19] found that the larger grain size in solution-based kesterite absorbers are not necessary related with the Na presence. On the contrary, some research groups state the positive effect of the presence of Na, regardless the different Na addition processes, in the crystallization and in the grain growth [16,20]. Regarding the alkali impact on the photovoltaic parameters, Li et al. [17] showed that the presence of Na causes an increase of the  $V_{OC}$  and FF due to an increment of the hole density, making the acceptor levels shallower. However, Na produces lower  $J_{SC}$  owing to a narrower depletion width and a decrease in the carrier lifetime. Xie et al. [18] also reported the importance of Na content and Na in-depth profile, especially in the CZTSSe/CdS region of the solar cells, for the device performance. Very recently, Haass et al. [21] has found the importance of the adjustment of Sn content and alkali concentration for each alkali metal, Li, Na, K, Rb and Cs, achieving efficiencies higher than 11% by using Li. In general, it has been reported the favorable effect of alkali metals in the improvement of kesterite devices, but there is not a clear explanation about the alkali inclusion mechanisms and the final compounds formed. In this regard, Sutter-Fella et al. proposed a selenization mechanism in which the presence of Na raises the chemisorption of Se species forming  $Na_2Se_x$  phases that are responsible of the grain growth [20]. Whereas Xie et al. proposed the formation of  $Na_2Se(S)$  and also Na-containing species with high vapor pressures as  $Na_2CO_3$ ,  $Na_2O$  or  $NaSe(S)O_3$ , since they observed large Na loss at the absorbers surface [18].

The objective of this work is to investigate the incorporation of S into co-evaporated CZTSe layers without using any  $H_2S/H_2Se$  toxic gases, and to study the role of Na on S incorporation. The sulfurization of CZTSe at 550 °C leads to the formation of CZTSSe. Here, we have demonstrated a relationship between the Na added, via diffusion from the substrate or via evaporation of a NaF precursor layer before the co-evaporation process, and the S content incorporated into the kesterite material. In this way, we show a new approach to generate the optimal S/(S + Se) ratio and gradient through the kesterite absorber layer. This work shows that the control of Na is a key parameter to enhance  $V_{OC}$  and the final CZTSSe-based device performance. Finally, this investigation has been extended to photovoltaic (PV) devices grown on ceramic substrates, increasing the range of applications, for example for Building Integrated PV (BIPV) concepts.

## 2. Materials and methods

### 2.1. Deposition of $Cu_2ZnSn(S,Se)_4$ thin films

$Cu_2ZnSnSe_4$  thin films were deposited onto  $5 \times 5 \text{ cm}^2$  Mo/soda-lime glass (SLG) or Mo/ceramic substrates by co-evaporation of Cu, Sn, ZnSe and Se at nominal substrate temperature between 275 and 325 °C. A scheme of the co-evaporation system is shown in Fig. 1. The substrates are heated by lamps localized on top of the back substrate side. The substrate temperature was measured by a thermocouple behind the substrate. The temperatures are given as measured in the experimental set-up. The substrate was rotated during deposition to improve the film uniformity. A quartz crystal microbalance was used to determine the Se evaporation rate before starting the process.

The co-evaporation process consisted of three stages. First, Se was evaporated onto Mo/substrate for around 3 min. Secondly, all the elements were co-evaporated simultaneously for around 33 min. After that, in order to achieve a Cu-poor composition, Sn, ZnSe and Se were co-evaporated the same time as used in the second stage of the co-evaporation process. The low substrate temperature used was to avoid

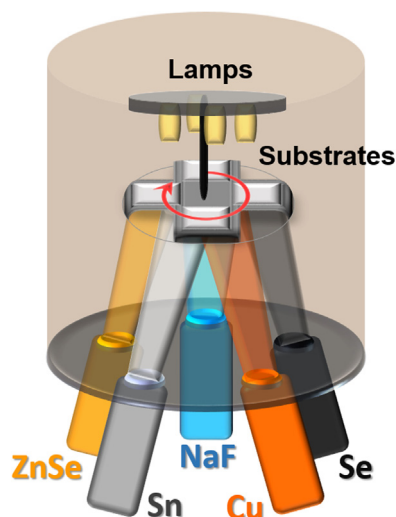


Fig. 1. Illustration of the high vacuum co-evaporation chamber.

the losses of SnSe. As-grown CZTSe thin films were annealed at 550 °C for 30 min in Ar atmosphere at pressure of  $9.5 \times 10^4$  Pa under excess of sulfur. For that purpose, the as-co-evaporated CZTSe thin films were placed in a partially closed graphite box of 56 mm  $\times$  70 mm  $\times$  20.5 mm with a hole of 1 mm diameter in the lid, and inserted into a quartz tube furnace [22]. In order to have an overpressure of sulfur, 22 mg of pure elemental sulfur (99.999%) were also supplied into the graphite container. The heating rate was of 20 °C/min and the cooling rate was 10 °C/min in all the cases.

Table 1 summarizes the composition measured by Energy Dispersive X-ray spectroscopy (EDX) of the samples grown by different co-evaporation processes. Samples 1 and 2 come from the same co-evaporation process carried out at nominal substrate temperature of 325 °C using different substrate materials, SLG and ceramic respectively. Sample 3 was co-evaporated onto Mo/SLG at lower nominal substrate temperature of 275 °C.

As it has been mentioned before, generally, the addition of Na on CZTSSe has a positive effect on the final solar cells. Because of the low substrate temperature used during these co-evaporation processes, and therefore the reduced Na diffusion from the SLG towards the absorber layer, around 15 nm NaF layer was evaporated prior to the CZTSe co-evaporation in the same vacuum chamber at room temperature for samples 1 and 2. The ceramic substrate used in this work is commercial ecological porcelain stoneware ceramics, which was developed using a ceramic paste formulation with the addition of industrial wastes (recycled glass, sludges and chamote). This was coated with vitreous enamels containing quantities of  $Na_2O$  corresponding to 1 wt%, which act as Na source. As reported by Becerril-Romero et al. [23], the average roughness lies in the range of 15–20 nm for concentrations between 2 wt% and lower of 20 wt% of  $Na_2O$ . Although it is high in comparison to SLG (7 nm), these values are acceptable for PV applications. This alters the surface morphology of the substrates creating undulations, pinholes and cracks. However, in [23], a flat surface was observed for a concentration of  $Na_2O$  of 2 wt%. As mentioned above, here we work with enamel containing only 1 wt% of  $Na_2O$  and despite the low Na concentration, it is visible the rougher surface of the Mo on the ceramic compared to that on SLG substrate. It is worth mentioning that the higher roughness and thickness of the ceramic substrate than for the SLG produce variations in the Mo layer growth and could lead to a decrease in the nominal temperature of the Mo/ceramic structure during the co-evaporation process.

Sample 3 was grown without adding any extra Na concentration apart from that diffusing from the SLG substrate. For that, we could assume that the Na content obtained from the out-diffusion of the SLG

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