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# The effect of soft-annealing on sputtered Cu<sub>2</sub>ZnSnS<sub>4</sub> thin-film solar cells

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## Abstract

In this study, we investigate the effect of soft annealing on the efficiency of Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) kesterite solar cells. The absorbers were grown on Mo-coated soda-lime glass by sputter deposition of Cu, SnS, and ZnS targets and sulfurized at 585°C for 15 minutes under an N<sub>2</sub> atmosphere. Before sulfurization, the films were subjected to a soft-annealing process in a temperature range from 150°C to 350°C. All absorbers were characterized by Raman spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and current density-voltage (**J-V**). The highest device efficiency of 6.1% was obtained at a post-annealing temperature of 150°C, while the median efficiency was 5.04% ( $\sim 20\%$  higher than the reference). Further increase in the soft-annealing temperature lowers device efficiency. The Raman spectra of the CZTS absorbers show a strong Raman peak at 337 cm<sup>-1</sup>, a less intense peak at 288 cm<sup>-1</sup>, and no secondary phases were detected. Interestingly, we find that soft annealing affects Cu/Zn disorder in the CZTS absorbers, with a higher ordering observed at 150°C, which coincides with the highest device efficiency. Finally, our results reveal that soft annealing does not significantly affect the samples' composition. Moreover, SEM images show that the impact of the soft-annealing temperature on the average grain size and morphology is insignificant.

**Keywords:** soft annealing, CZTS, kesterite, sputtering

# 1 Introduction

Developing efficient and low-cost photovoltaic (PV) systems is vital in facing the environmental and energy crisis. The PV industry is a rapidly growing field ready to provide clean energy, with PV production being doubled every year since 2002 and with PV capacity rising from 3.7 GW in 2004 to 225 GW in 2015, with an addition of ~90 GW in 2016-2019 and a prediction of additional capacity of ~120 GW in 2020-2025. [1],[2],[3] The most widespread solar cells are fabricated from silicon (Si), which is an earth-abundant material, and have reached a market share of 95% of the total PV production in 2020.[4] Silicon PVs are based on mature technologies and the efficiencies of different types of Si solar cells exceed 26.7% and 24.4% for monocrystalline and polycrystalline Si solar cells, respectively.[4],[5] However, Si has an indirect bandgap and, as a consequence, this requires a thick material layer (optimal is ~100 μm for c-Si [6]) to absorb enough solar radiation.[7] In addition, high-quality crystals are required to achieve high device efficiencies, which raises the total cost of Si modules.[7] Alternatives to Si modules have become thin film solar cells, which rely on direct band gap materials and significantly reduce the material thickness required to adsorb solar radiation (up to a few hundred nanometers).[7],[8] In the solar cell industry, thin-film PVs have a market share of approximately 5%, with CdTe and CuIn(Ga)(Se)<sub>2</sub> (CIGS) solar cells being the most prevalent.[4],[9] Thin-film solar cells present high conversion efficiencies, with CdTe reaching 21% and CIGS 23.35%. [5] Other materials that are used for thin film solar cells and show significant efficiencies are GaAs (29.1%) and organic/inorganic perovskites (21.6%). [5] Some of these materials (CdTe, GaAs, CIGS) consist of scarce elements (In, Ga, Te) that may cause problems for future large-scale production, as well as toxic ones (Se) that may possess environmental hazards.[10],[11],[12] A potential substitute for CIGS, which is more environmentally friendly and uses abundant elements, is kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS).[10]

In CZTS, indium, gallium, and selenium are replaced by tin, zinc, and sulfur. Selenium is commonly added to form Cu<sub>2</sub>ZnSnSe<sub>4</sub> (CZTSe) or a mixed sulfo-selenide phase Cu<sub>2</sub>ZnSn(S<sub>x</sub>Se<sub>1-x</sub>)<sub>4</sub> (CZTSSe), which are also considered to be promising candidates for thin-film solar applications but having a lower bandgap than that of a pure sulfide compound.[13] CZTS has a direct bandgap of 1.4–1.5 eV, a high absorption coefficient ( $\geq 10^4 \text{cm}^{-1}$ ), and p-type conductivity.[14],[15] Its crystal structure is similar to chalcopyrite CIGS, and, generally, the most common structures are kesterite and stannite. The first phase is dominant for producing thin film solar cells, as the kesterite phase is more thermodynamically stable, and the formation energy is lower than that of stannite.[10],[16] Deposition of CZTS can be performed by various vacuum-based techniques, such as thermal evaporation (12.6% efficiency [17]), sputtering (11.01% efficiency), pulsed laser deposition (5.4% efficiency [18]), and non-vacuum based techniques, such as electrodeposition (7.3% efficiency [19]), or molecular inks (4.65% efficiency [20]), which allow large scale

production at a lower cost [21]. These fabrication methods generally include a high-temperature annealing step to achieve grain growth and elemental intermixing.[22]

CZTS is still in its development phase, and the power conversion efficiency has not yet exceeded the levels of commercial thin-film absorbers, with the highest reported efficiency of 11% (for CZTSe- and CZTSSe-based thin films, the efficiency rises to 11.6% and 12.6%, respectively).[5],[23] This moderate efficiency is primarily due to a high open-circuit voltage ( $V_{OC}$ ) deficit. The low  $V_{OC}$  results from the Cu/Zn disorder, a non-optimized interface between CZTS and CdS buffer layer [24], and poor back electrical contact between Mo and CZTS, intensifying the recombination processes.[16],[25] Moreover, the presence of secondary phases lowers the  $V_{OC}$  and fill factor, and lattice/structural defects (grain boundaries) compromise crystallinity and efficiency of the CZTS cells.[8],[26],[27]. Several methods have been proposed to increase the performance of CZTS; recently, a so-called 'soft-annealing' process was proposed.[28] An implementation of the 'soft-annealing' method, a pre-annealing treatment at a lower temperature than the final annealing, has been shown to improve the crystalline structure and device performance.[14],[29] It is reported that solar cells obtained from soft-annealed  $\text{CuInS}_2$  (CIS) films have higher efficiency (5%) than those from CIS films without soft annealing (1.5%).[23] Moreover, prevention of Sn loss in CZTS may be achieved through soft annealing before sulfurization.[10],[14] One study on CZTSe thin films suggests the best properties are achieved after soft annealing at a temperature of 250°C for a studied temperature range from 200 to 350°C.[30] Also, the highest efficiency of 12.5% of CZTSSe has used soft-annealing in Se-rich atmosphere.[28]

In this study, we explore the influence of the soft-annealing method applied to kesterite sputtered precursors at temperatures of 150°C, 200°C, 250°C, 300°C, and 350°C for 45 minutes under an  $\text{N}_2$  atmosphere, followed by sulfurization at 585°C for 15 minutes. To access films' properties, we have performed characterization using Raman spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and current density-voltage ( $J$ - $V$ ) measurements. Our study suggests that the soft-annealed absorbers at 150°C present the highest median (5.04%) and overall efficiency (6.1%), whereas a lower cation disorder occurs for this sample. The average grain size does not show significant differences among the soft-annealed absorbers and the reference (*i.e.*, without soft annealing), in contrast to the grain standard deviation, which is lowest at 150°C and rises with a further increase in soft-annealing temperature.

## 2 Experimental

### 2.1 Sputtering deposition of CZTS

The deposition of CZTS precursors ( $\sim 300$  nm) was conducted via co-sputtering of Cu, SnS, and ZnS targets, each one with a diameter of 2 in, on Mo-coated soda-lime glass substrates. The base pressure inside the sputtering chamber was  $1 \times 10^{-7}$  mbar, and during the sputtering process, the pressure was kept constant at  $4 \times 10^{-3}$  mbar. The targets were placed at a distance of 7 cm from the substrate and at an angle of  $63^\circ$  between the substrate plane and the normal of the target surface. A DC power supply was applied for Cu and a radio-frequency (RF) power supply for SnS and ZnS targets. The power density varied between 0.48-0.58 W/in<sup>2</sup> for Cu, 2.63-2.94 W/in<sup>2</sup> for SnS, and 3.42-4.62 W/in<sup>2</sup> for ZnS to control the composition of the precursors. The deposition time was 15 minutes.

### 2.2 Soft-annealing of precursors

For the soft-annealing, the samples were positioned inside a graphite box and placed inside a quartz tube in the middle of a tube furnace. The quartz tube was evacuated and flushed with N<sub>2</sub> (5.0N purity from Air Liquide) three times to eliminate oxygen and water residues, reaching a base pressure of  $2 \times 10^{-3}$  mbar, after which it was filled with N<sub>2</sub> to a pressure of 175 mbar at room temperature. The as-deposited precursors were soft-annealed at various temperatures (150°C, 200°C, 250°C, 300°C, and 350°C) for 45 minutes with a ramping rate of 20°C/min. The samples were cooled down in the graphite box outside the tube furnace from 100°C and below. The corresponding samples were named "150°C", "200°C", "250°C", "300°C", and "350°C", respectively. One of the precursors from the same batch was not subject to this procedure to have a reference sample for this study.

### 2.3 Sulfurization of soft-annealed precursors

The second stage includes the final annealing under the same conditions for all the samples, including the reference one. First, the samples were placed inside a graphite box, and elemental sulfur and tin were added to graphite crucibles to create sulfur- and tin-rich atmosphere, with contents of  $\sim 50$  mg and  $\sim 5$  mg, respectively. Second, they were placed inside the quartz tube, with the pumping/purging sequence repeated, and finally, the quartz tube was filled with up to 175 mbar N<sub>2</sub> at room temperature. The temperature and time were 585°C and 15 minutes, and the ramping rate was 20°C/min. The final cooling of all absorbers was conducted inside the furnace, with an open lid at 300°C and below.

## 2.4 Fabrication of CZTS solar cells

The annealing process was followed by the chemical etching of the absorbers in 10 wt.% ammonium sulfide ((NH<sub>4</sub>)<sub>2</sub>S) solution for 5 minutes. After this, chemical bath deposition was used to deposit a 50 nm thick CdS buffer layer, with cadmium sulfate (CdSO<sub>4</sub>) as cadmium source, thiourea (CH<sub>4</sub>N<sub>2</sub>S) as a sulfur source, ammonium hydroxide (NH<sub>4</sub>OH) as the complexing agent, and ammonium chloride (NH<sub>4</sub>Cl) as a buffer solution. During the deposition, the temperature was maintained at 70°C. Lastly, intrinsic ZnO (i-ZnO) of 50 nm in thickness and 350 nm-thick aluminum-doped zinc oxide (AZO) were deposited by sputtering at a temperature of 150°C. Finally, the solar cells were manually scribed to create a nominal cell with an area of approximately 0.09 cm<sup>2</sup> (3 mm × 3 mm).

## 2.5 Characterization methods

Raman measurements at 532 nm excitation laser were performed in a home-built confocal Raman spectroscopy system. The samples were illuminated through a 40× objective lens (NA=0.75), type Nikon CFI Plan Flour. The spectrometer used was Spectra Pro HRS-750 scanning monochromator from Princeton Instruments, equipped with a liquid-nitrogen-cooled, ultra-low noise Pylon CCD camera, type PyLoN:100BR. For the Raman measurements, a grating of 1200 gr/mm was selected. Raman spectra were collected with an acquisition time of 10 s for each frame and five frames averaging. The peaks that indicate distinct CZTS phases were identified and the presence of the secondary phases was investigated. Raman spectra at 785 nm were acquired using a Renishaw inVia Reflex confocal Raman spectrometer. The measurements were carried out in a back-scatter configuration, and the spectra were calibrated using Si at 520.5 cm<sup>-1</sup> Raman peak. Raman spectra were collected using low power of 150 μmW to avoid sample damage, and 15 s acquisition time, 10 spectra averaged. The Cu/Zn disorder was calculated with the use of the intensity of the peaks at 288 cm<sup>-1</sup>, 302 cm<sup>-1</sup>, 337 cm<sup>-1</sup>, 368 cm<sup>-1</sup>, and 376 cm<sup>-1</sup>, as discussed in Section 3.2. The films' morphology and composition were performed on Quanta FEG 200 SEM equipped with Oxford X Max EDS detector. CZTS grain size was determined with the help of ImageJ software, and the EDX spectra were analyzed using AZtec v3.3 software. Furthermore, the *J-V* measurements were performed under near Standard Test Conditions (STC, 1000 W/m<sup>2</sup>, AM1.5 and 25°C) using a Newport class ABA steady-state solar simulator. The setup was calibrated with the use of a 2×2 cm<sup>2</sup> Mono-Si reference cell from ReRa, certified by the Nijmegen PV Measurement Facility, with a known output at STC conditions, for an irradiance (at a specific spot the samples were placed), to be as close to 1000 W/m<sup>2</sup> as possible. For each *J-V* curve, 150 points were collected with 2 ms required time between two measurements. It should be noted that all the characterization above was conducted on the samples after sulfurization.

## 3 Results and discussion

### 3.1 $J$ - $V$ measurements

Figure 1 shows the  $J$ - $V$  parameters and the  $J$ - $V$  curves of the soft-annealed absorbers and the reference, including the efficiency (Fig. 1a), short-circuit current density,  $J_{SC}$  (Fig. 1b), the fill factor, FF (Fig. 1c), and the open-circuit voltage,  $V_{OC}$  (Fig. 1d). The soft-annealed devices at 150°C exhibit the highest median efficiency (5.04%), which is  $\sim 20\%$  more than the reference (4.16%). The highest solar cell efficiency achieved at the soft-annealing temperature of 150°C is 6.1% (see Table 1). This efficiency increase is due to a rise in  $V_{OC}$  of  $\sim 25\%$  compared to the reference sample (from 0.425 V to 0.582 V). Higher soft-annealing temperatures reduce the overall performance of the solar cells, which can be seen from a decline in all the parameters (for example, the  $V_{OC}$  drops by nearly  $\sim 40\%$  for 350°C devices). The FF is above 55% for all the devices, except for the device processed at 350°C, which drops at 50.3%. The best-performing cell has a  $J_{SC}$  of 20 mA/cm<sup>2</sup>, comparable with state-of-the-art devices (e.g., Yan *et al.*[31] reported 21.7 mA/cm<sup>2</sup>). Note that no antireflective coatings were used in this work. However, the other soft-annealed absorbers have lower  $J_{SC}$  values than the state-of-the-art CZTS mentioned previously.

**Table 1:**  $J$ - $V$  parameters of the most efficient solar cells from the soft-annealed absorbers and the reference.

Sample	Efficiency (%)	$J_{SC}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	Fill Factor (%)
Reference	5.17	20.4	0.425	59.7
150°C	6.09	17.5	0.582	59.4
200°C	5.38	15.3	0.564	62.3
250°C	3.04	12.2	0.425	58.8
300°C	3.19	11.9	0.459	58.6
350°C	3.34	15.6	0.434	50.3