



Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: [www.elsevier.com/locate/tsf](http://www.elsevier.com/locate/tsf)

# Influence of hydrogen sulfide annealing on copper–zinc–tin–sulfide solar cells sputtered from a quaternary compound target

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## ARTICLE INFO

Available online xxxx

### Keywords:

Cu<sub>2</sub>ZnSnS<sub>4</sub>  
Sputtering  
Quaternary target  
Sulfurization temperature  
MoNa

## ABSTRACT

With a theoretical efficiency around 30% and an optimized band gap for sunlight absorption, Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) is a promising, earth-abundant, material for thin film solar cells. Sputtering CZTS from a quaternary compound target is a quick and potentially industrial-scaled process that has not been investigated deeply yet. Our approach is based on an in-line vacuum system for the complete device. CZTS is sputtered from a compound target on a sodium molybdate (MoNa) pre-sputtered stainless steel substrate, and then annealed in high-pressure H<sub>2</sub>S atmosphere. A 1 μm thick absorber is obtained within 7 minute sputtering. Top layers are then deposited, without vacuum breaking. The effects of different annealing temperatures on the absorber morphology and composition are investigated. It is observed that recrystallization already occurs at 420 °C and that crystallinity improves with increasing temperature up to 550 °C. However, micro-sphere formation underneath the film degrades the corresponding solar cell performance dramatically above 510 °C. It is shown that sodium is needed in order to enhance recrystallization of CZTS but the MoNa layer thickness seems not to be a critical parameter. Scanning electron microscopy, X-ray diffraction, X-ray fluorescence and current–voltage measurement were used to characterize the samples.

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## 1. Introduction

The development of clean and affordable electricity sources is one of the major stakes of current research projects in energy technologies. Earth-abundant Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) absorber exhibits an optimal bandgap for sunlight absorption [1] and a theoretical efficiency around 30%. Encouraging results were obtained in the last few years with a record efficiency close to 10% for pure sulfide compound [2] but a lot of improvements are required to reach efficiency levels close to the related high performance copper–indium–gallium–diselenide (CIGS).

Both vacuum and non-vacuum processes were investigated in order to deposit high quality CZTS layers. Among vacuum based approaches, sputtering is a well-known and potentially industrial scaled process. CZTS solar cells based on a sputtered absorber exhibit relatively low efficiencies, close to 8% for the record cell [3–5], which denotes a very high improvement potential. Developing a fast and exclusively sputtering-based process is a potential route towards fast development of CZTS solar cells.

Sputtering CZTS from a quaternary compound target is a quick and reproducible process, in agreement with the industry needs. This process has been investigated by Katagiri et al. in the early 2010s and a 5.24% efficiency cell was achieved at this time [6]. This deposition method usually involves two steps. First, copper, zinc, tin and sulfur are deposited via compound sputtering. The absorber is then annealed at high temperature, typically slightly above 500 °C. During this annealing phase, CZTS recrystallizes and kesterite grains are formed helped by sodium diffusion from the substrate. Investigating the influence of sodium content as well as annealing temperature on the absorber morphology and on the cell performance is hence of first interest in order to achieve higher efficiency devices.

## 2. Experimental details

Stainless steel substrates are used in order to handle fast temperature changes. To prevent substrate atoms from diffusing into the upper layers, a diffusion barrier is then deposited. A sodium molybdate (MoNa) layer is sputtered subsequently from a 10% sodium molybdate MoNa target and acts as a sodium seed layer to enhance recrystallization during annealing. Finally, the molybdenum back contact is sputtered. All these steps are performed using Midsummer's DUO sputtering tool and form the so-called pre-sputtering phase. Pre-sputtered stainless steel substrates are then ready to be processed.

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Inspired from the already mature CIGS process, Midsummer's CZTS solar cells are based on a cadmium-free, all-sputtering approach [7]. The different layers that form the solar cell are successively deposited using an in-line vacuum sputtering tool from Ulvac called SMO. Originally designed for the optical disk industry, the SMO was re-built in order to match CZTS solar cell development requirements. Its architecture is based on a main vacuum chamber surrounded by 7 sputtering stations. Articulated arms equipped with a resistive heating system allow us to transport successively the pre-sputtered substrate from one sputtering station to the following one. CZTS is first sputtered from a quaternary compound target (22% Cu, 16% Zn, 12% Sn, 50% S). The absorber layer annealing is performed in an especially modified vacuum chamber. A 50 nm thick  $\text{In}_2\text{S}_3$  layer is subsequently deposited and form the PN junction. The ZnO/indium–tin–oxide window layers are sputtered on top of the buffer. To finalize the device, a silver grid is screen-printed on top of the solar cell and cured at 240 °C.

Fabricated sample specifications are available in Table 1. Three samples of each type were fabricated in order to assess the reproducibility of the process. It was observed that samples of the same type showed very similar morphology and performance.

For the first part of this study, substrates with different MoNa layer thicknesses were used to evaluate the influence of sodium on the absorber morphology and properties. A 15 minute annealing at 510 °C was used in this series.

A 15 minute long annealing with different heating powers provided to the arm heaters was chosen in the second part of this study. Different annealing temperatures in the range of 420 to 560 °C were tested to investigate the evolution of the absorber morphology and the corresponding cell parameters with increasing temperature. The annealing atmosphere was maintained at 50 kPa Ar/10%  $\text{H}_2\text{S}$ . The annealing chamber is equipped with a glass window that allows pyrometer temperature measurement of the sputtered film during annealing. The emissivity setting of the pyrometer was set at 0.5.

The metal composition of the CZTS films was determined using a PANalytical Epsilon 5 X-ray fluorescence (XRF) tool. Cu and Zn analysis are run at 75 kV, using a Ge secondary target and the Sn analysis at 100 kV using a  $\text{BaF}_2$  secondary target. Rutherford backscattering results were used as a calibration for the XRF measurement [8]. Sulfur content of the films was determined by energy dispersive spectroscopy (EDS) at 20 kV using a Bruker AXS X flash 4030 EDS detector.

Thickness measurements and images were taken from scanning electron microscopy (SEM) of cross-sections in a Hitachi S4800 SEM at 10 kV acceleration voltage. A Siemens D500 X-ray diffraction (XRD) equipment in Bragg–Brentano focusing geometry was used to characterize the samples crystallinity and identify potential secondary phases. Cu  $\text{K}\alpha$  radiation is used in this set-up.

Current–voltage (IV) characteristics were measured on 1  $\text{cm}^2$  small cells using an Agilent 2722A Source meter and a Newport 91193-1000 solar simulator.

**Table 1**  
Samples summary.

Sample	Annealing temperature plateau [°C]	Sodium precursor layer thickness [nm]
S0	510	0
S1	510	110
S2	510	220
S3	510	330
A0	No annealing	110
A1	420	110
A2	450	110
A3	475	110
A4	490	110
A5	510	110
A6	525	110
A7	550	110

### 3. Results and discussion

#### 3.1. Sodium study

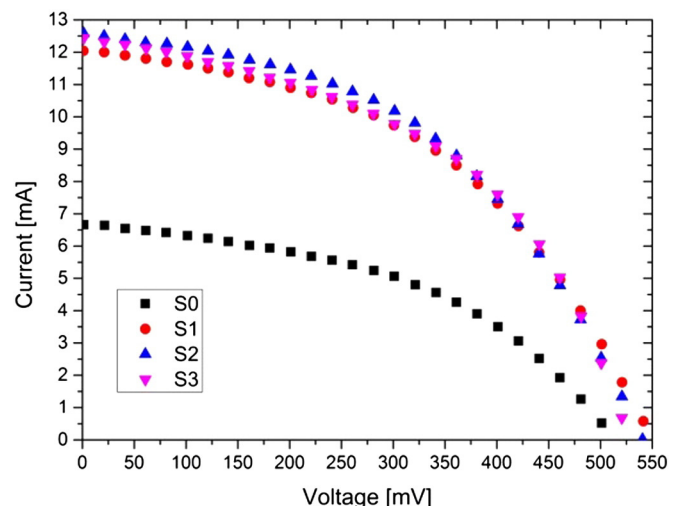
A grain size improvement can be observed with sodium precursor layer incorporation in the solar cell structure. The IV curves shown in Fig. 1 exhibit a higher short circuit current for samples S1, S2 and S3 compared to S0. These observations are consistent with the already reported absorber improvement due to sodium incorporation [9]. However there is no real trend that can be identified when the sodium precursor layer thickness is increased. Previous studies on Na supply from MoNa layers in co-evaporated  $\text{Cu}(\text{In,Ga})\text{Se}_2$  showed increasing sodium diffusion for increasing MoNa layer thickness [10]. However, it was also shown that other parameters such as MoNa layer porosity, sputtering parameters, interfaces and grain boundary density can have a strong influence on the sodium supply [11]. Our results show that the MoNa thickness above 110 nm, using constant process parameters, is not critical for device performance. Further studies on actual sodium concentration in the CZTS and variations in MoNa precursor deposition are needed to clarify if optimum sodium concentration is obtained in this process. Based on the present results a constant layer thickness of 110 nm was chosen for the annealing study.

#### 3.2. Annealing study

##### 3.2.1. Samples morphology and composition

The SEM cross-section of the as deposited film presented in Fig. 2a shows a very columnar structure of the precursors which is consistent with a low temperature deposition.

SEM cross-sections and images of the absorber back, after peeling off the layers from the back contact (Figs. 2 and 3), show a clear increase in grain size for the samples annealed at high temperature. Diffractograms for all the samples studied are shown in Fig. 4. The as-deposited CZTS sample, A0, exhibits common peaks between  $\text{ZnS}$ ,  $\text{Cu}_2\text{SnS}_3$  (CTS) and CZTS. This is similar to the structure of CZTS precursors from reactive sputtering at low temperature [12]. In that work, a cubic, disordered CZTS structure was evidenced by homogenous Cu, Zn, Sn and S distribution, absence of  $\text{ZnS}$  in UV Raman and similar XRD pattern as for the A0 sample in Fig. 4. This non-equilibrium phase could be advantageous for obtaining rapid grain growth during annealing since additional energy is provided in the phase transition to the equilibrium kesterite phase. One can notice the appearance of characteristic CZTS peaks corresponding to (101) and (110) planes for the lowest annealing temperature



**Fig. 1.** IV curves measured under 1 sun AM 1.5.

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