Surface & Coatings Technology 240 (2014) 281–285

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Reactive sputtering of Cu_2ZnSnS_4 thin films — Target effects on the deposition process stability

Tomáš Kubart *, Tove Ericson, Jonathan J. Scragg, Marika Edoff, Charlotte Platzer-Björkman

Ångström Solar Center, Solid State Electronics, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden

ARTICLE INFO

Article history:
Received 16 September 2013
Accepted in revised form 19 December 2013
Available online 29 December 2013

Keywords:
Reactive sputtering
H_2S
Sulfides
CZTS
Cu2ZnSnS4
CuSn sputtering

ABSTRACT

Cu_2ZnSnS_4 (CZTS) is a promising material for thin film solar cells which contains only abundant elements. This work focuses on the stability of elemental composition of films deposited by reactive sputtering of CuSn alloy targets in H_2S. Long equilibration times of several hours were observed. The main reason is the formation of a thick Cu_2S layer on the target surface. Especially in areas with low erosion rate, the Cu_2S thickness reaches up to 700 μm and is accompanied by a preferential loss of Sn from the target. Based on the results, it is suggested that the formation of Cu_2S may be limited either by more uniform erosion of the target surface or by reduction of the H_2S partial pressure.

1. Introduction

Kesterite $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTS) attracted recently significant attention as a promising alternative material for thin film solar cells [1,2]. CZTS contains only abundant elements and at the same time, solar cells with efficiencies over 11% have already been demonstrated [3]. The best efficiencies so far have been reached for materials synthesized using a two-step approach. In the first step, a precursor film containing all the elements including chalcogen is deposited at relatively low temperature. CZTS is formed during a subsequent annealing step. Direct synthesis of CZTS at elevated temperature is challenging because of poor temperature stability of the material [4]. Because of the narrow homogeneity range of CZTS [1] strict control of the metal concentrations in the precursor films is essential. At the same time, it is beneficial to incorporate the chalcogen already at this stage.

One of the techniques suitable for deposition of CZTS precursors is reactive magnetron sputtering. Sputtering is a versatile, widely used deposition technique which can be easily scaled for industrial production and it has been extensively used for synthesis of CZTS [2,5–8]. In reactive sputtering, a suitable gas serves as the chalcogen source [9]. Metallic sputtering targets can then be used which are cheaper and easier to manufacture and handle than compounds. Because of the requirements on the compositional control, alloy targets may be an attractive option. Reactive deposition process with H_2S has been successfully employed in our laboratory [10]. So far, the best solar cells have reached efficiency of 7.9%, which is comparable with the best pure sulfide CZTS devices [11]. Detailed characterization of solar cells prepared using our process is presented elsewhere [12].

The reactive process with chalcogens, however, exhibits some challenges with respect to the stability of elemental composition. In this work, the variations in the metal composition of sulfide precursors reactively sputtered from CuSn and Zn targets are analyzed in order to develop a stable deposition process. Variations in the film composition are linked to changes at the surface of the sputtering target. Since no ternary phases exist in the Cu–Sn–Zn system [13], a behavior similar to CuSn is also expected for ternary CuSnZn alloy sputtering targets. In the present experimental configuration, the Zn concentration could be readily adjusted by changing the power on the Zn target. The Cu to Sn ratio, however, was determined by the target composition and was therefore the main focus of this study.

2. Experimental

Films were deposited in a von Ardenne CS600 S deposition system. The system is equipped with two Lesker Torus 4 HV magnetrons with the target diameter of 100 mm in co-sputtering configuration mounted 45° off-axis at a distance of about 160 mm from the substrate. A shutter is placed in front of the substrate holder. 6 mm thick targets of CuSn alloy (65/35 at.% and 99.999% purity) and Zn (purity 99.994%) were used. The DC power supplies were Hüttinger PFG 3.000 supplies that were operated in constant power mode and connected to the targets through Advanced Energy Sparc-le pulsing units operated at a frequency of 20 kHz. Typically, a power of 560 W and 600 W was applied to the CuSn and Zn target, respectively. The system was pumped by a turbomolecular pump to a base pressure below 4×10^{-4} Pa (3×10^{-6} Torr). Argon (99.9997%) and H_2S (99.5%)

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* Corresponding author.
E-mail address: Tomas.Kubart@angstrom.uu.se (T. Kubart).

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http://dx.doi.org/10.1016/j.surfcoat.2013.12.042

were introduced through mass flow controllers and the working pressure was kept at 0.67 Pa (5 mTorr).

The films were deposited onto Mo coated soda lime glass placed on a rotating substrate holder. The metal composition was analyzed by means of X-ray fluorescence (XRF) using a PANalytical Epsilon 5 calibrated by Rutherford backscattering as described elsewhere [9]. To determine the deposition rates, measured intensities were converted to atomic areal densities taking signal attenuation into account. The sputtering target surfaces were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) in a LEO 440 with an EDAX EDS system. An acceleration voltage of 20 kV was used for the EDS measurements. Detailed analysis of the target cross-sections was carried out using a LEO 1550 field emission gun SEM with an AZTEC EDAX EDS system again using 20 kV acceleration voltage.

3. Results and discussion

Long term evolution of the Cu to Sn ratio in the deposited films is shown in Fig. 1 as a function of the total sputtering time. Unless stated otherwise, the depositions were carried out in a pure H_2S atmosphere. Each data point represents one deposition with a typical thickness of about 1 μm. Although the deposition conditions were kept constant, there are substantial variations in the film composition. The graph can be divided into three regions based on the spread of the Cu to Sn ratio. Initially in region I, between 0 and 12 h, a standard deposition routine was used. This resulted in large variations in the Cu/Sn ratio in the range from 1.4 to 2. The origin of these variations is discussed in the section dealing with short term process stability. Adjustments of the deposition routine led to significantly improved stability and the ratio stayed within 1.68 to 1.85 in region II, from 12 to 22 h of sputtering.

Although the deposition process wasn't altered any more, a pronounced change in the composition occurred at the time of 22 h. The Cu/Sn ratio was very variable and well above the composition of the sputtering target (1.86) after this change, in region III. The origin of such behavior is analyzed in the section dealing with long term variations.

In order to assess the influence of the time between depositions, the data from Fig. 1 is shown versus the date of each deposition in Fig. 2. There is a long dwell of nearly two months separating the second and third regions. This indicates that there might be two possible mechanisms, one responsible for the short term variations within each region, the other causing a more pronounced drift over a longer time. It should be noted that simultaneous sputtering of Zn does not have any significant influence on the Cu/Sn ratio.

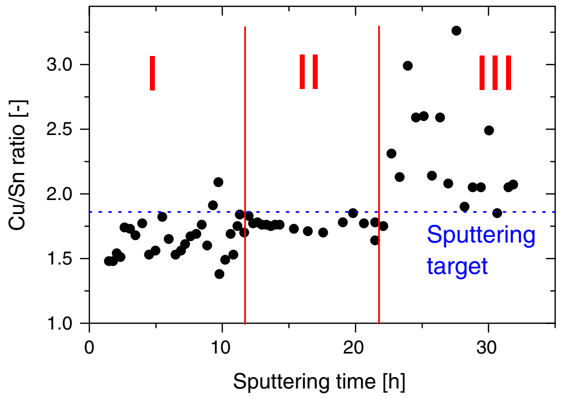

Fig. 1. Cu/Sn ratio in the deposited films as measured by XRF vs. cumulative sputtering time. The Cu/Sn ratio of the CuSn target, 1.86, is depicted by the dashed line. The data are divided into three regions as discussed in the text.

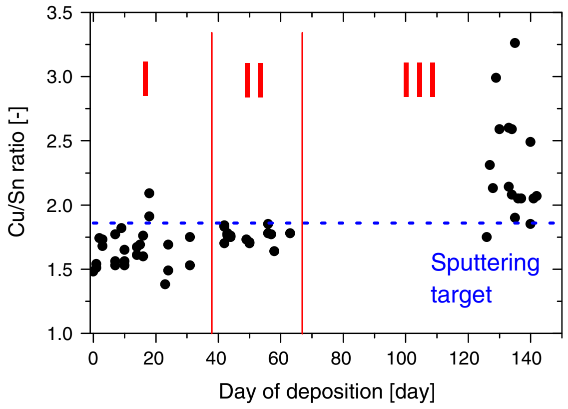

Fig. 2. Data from Fig. 1 displayed vs. the day of deposition. There was a long dwell between regions II and III.

3.1. Short term variations

Initially, in region I, a standard deposition routine was employed consisting of three steps: target cleaning in an Ar atmosphere, followed by presputtering in H_2S with the shutter closed, and then the deposition. This is a standard approach in reactive sputtering used to ensure a reproducible deposition process by first removing any possible contaminants from the target surface in Ar, and then establishing a steady state in the presence of reactive gas before starting a deposition. As shown in Fig. 1, this led to substantial variations in the film composition.

Thornton et al. analyzed the behavior of a Cu target sputtered in an Ar + H_2S mixture. The relatively long times of up to 1 hour which were required for process stabilization were attributed mainly to the conditioning of the sputtering target surface, with the other surfaces in the sputtering chamber having little effect on the resistivity of resulting CuS_x films [14]. In order to evaluate the influence of target conditioning, the following experiment was performed: The target was sputter cleaned in Ar until a stable discharge voltage was reached. Ar was then replaced by H_2S at a mass flow of 30 sccm. The target was then sputtered at a power of 560 W and every hour a 20 min deposition was performed.

The resulting film composition and relative deposition rates calculated from XRF intensities is shown in Fig. 3. The deposition rates were determined from atomic areal densities and were normalized to the deposition rates of the last sample, deposited after 9 h of sputtering. The absolute deposition rate of Cu and Sn for this sample was $1.03 \cdot 10^{15}$ and $5.64 \cdot 10^{14}$ atoms cm^{-2} s^{-1}, respectively. The deposition rate in Ar was about ten times higher than for sputtering in H_2S. Assuming constant sticking probability of metals and neglecting the

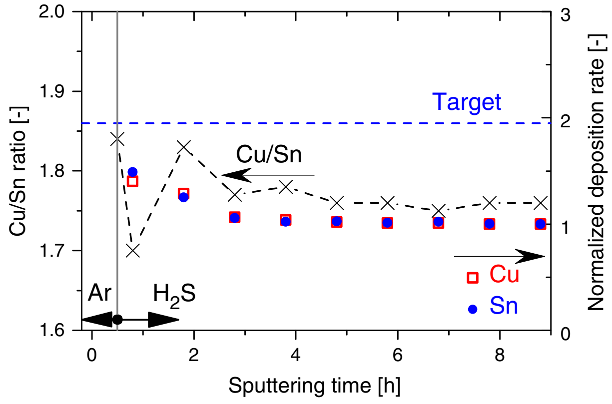

Fig. 3. Evolution of the Cu/Sn ratio in the films (dashed line) and the normalized deposition rates of Cu and Sn (points) determined by XRF. H_2S was introduced at a time of 0.5 h. The nominal target composition of 1.86 is depicted by dashed line.