Tin disulfide segregation on CZTS films sulfurized at high pressure

Alejandro Alvarez^a, Stephen Exarhos^a, Lorenzo Mangolini^{a,b*}

a) Mechanical Engineering Department, University of California Riverside,
900 University Avenue, Riverside, CA 92521, USA. E-mail: lmangolini@engr.ucr.edu

b) Materials Science and Engineering Program, University of California Riverside,
900 University Avenue, Riverside, CA 92521, USA

Abstract

CZTS thin films were synthesized by annealing of Zn, Cu, and Sn stacked layers under sulfur atmosphere. Pressure was controlled by varying the mass of the sulfur charges introduced into the closed annealing chamber. Films sulfurized at higher pressure show clear segregation of hexagonal SnS₂, suggesting that Sn reacts with gaseous S to form a solid-state phase, leading to an inhomogeneous 3D film morphology. Lower pressure synthesis yields uniform layers mainly composed of CZTS. Variations in film morphology suggest that different reaction pathways take place as the pressure is raised. Formation of gaseous SnS is favored at lower pressure, while nucleation of solid SnS₂ preferentially occurs at higher pressure. Influence of the cooling rate after annealing was also studied. We have found that this affects the film stoichiometry, while the film morphology did not show relevant dependence on this parameter.

Keywords: CZTS; sulfurization pressure; thin films; physical vapor deposition; photovoltaics

1. Introduction

Cu₂ZnSnS₄ is a promising material for thin film photovoltaics. CZTS is composed of earth abundant, non-toxic elements, making it an ideal candidate for the scalable and economically feasible production of thin film solar cells [1–3]. However, efficiency records lower than those achieved by the commercially available CIGS technology have kept CZTS production away from industrial levels [4,5]. Among the various CZTS synthesis processes, sulfurization of stacked layers of metallic precursors has become attractive due to its controllable stoichiometry and use of a clean, non-toxic approach [6–8]. Within this particular technique, the influence of

several parameters such as annealing temperature, annealing time, utilized substrate, preheating, and precursor stoichiometry have been thoroughly studied [9–14]. However, there are only a few studies on sulfurization pressure. The lack of information addressing this topic leads to inconsistencies associated to the role of pressure in grain size and post-annealing stoichiometry [15,16]. Additionally, procedures related to the sulfurization steps vary widely. It is therefore unreliable to reach unequivocal conclusions from results that follow different sulfurization routes. A better understanding of the chemical pathways through which CZTS is synthesized is crucial in order to identify the source of efficiency problems mainly related to low open circuit voltage and short recombination times [17]. In this manuscript we present a direct and concise analysis on the influence that sulfurization pressure has on CZTS in a closed system.

2. Materials and methods

50nm of Zn were initially deposited on a quartz substrate by RF magnetron sputtering, followed by the deposition of 80nm of Cu and 110nm of Sn by electron beam evaporation. This combination of techniques facilitates the deposition of a smooth-surface film for each metallic precursor. Five samples were independently annealed in a sealed quartz ampule (203mm long, 7mm in diameter) at 500°C for 8h. A base pressure of 1×10^{-5} Torr was achieved with an Oerlikon Leybold TURBOVAC SL 80 turbo pump. The ampules were heated in a tube furnace at a rate of 7 °C/min. After annealing, the films were let to cool down naturally for 120 minutes. One end of the ampule was gently pushed out of the heating zone in order to induce constant sulfur condensation in that region and away from the sample. The sulfurization pressure was controlled by modifying the amount of sulfur introduced into the closed system. Pressure calculations were based on the application of the ideal gas law. In accordance to previous reports, the mole fractions of the various molecular species present in sulfur vapor (S_8 to S_2) were considered for these estimations [18]. The corresponding pressure data for each mass value, listed in increasing order, is approximately 32 (1mg), 95 (3mg), 191 (6mg), 287 (9mg), and 383 (12mg) Torr. SEM/EDS analysis was performed on a FEI Nova NanoSEM 450 system equipped with an Oxford Instruments Aztec Synergy software. EDS data was obtained from diverse areas of each sample. The average stoichiometry and standard deviation were recorded. XRD

characterization was held on a PANalytical Empyrean X-ray system using CuK α radiation with a wavelength of 1.74nm. A Horiba LabRam HR instrument, equipped with a 532nm laser source, was used for Raman analysis.

3. Results

Fig. 1 shows low and high magnification SEM images of the CZTS films sulfurized at different pressures. There are no obvious morphological differences among the samples synthesized at lower pressure (Fig. 1a-1f). On the other hand, three-dimensional structures are visible in the films sulfurized at 287 and 383 Torr (Fig. 1g-1j). These features are randomly dispersed over the surface of the films. The regions in between the 3D structures are very similar to those shown in the previous samples.

at% Before sulfurization				Pressure (Torr)	at% After sulfurization						
Sample	%Zn	%Cu	%Sn		Natural cooling (120 minutes)						
1	24.4 $\pm$ 0.4	46.5 $\pm$ 0.5	29.1 $\pm$ 0.5	32	16.7 $\pm$ 1.5	22.7 $\pm$ 0.8	14.4 $\pm$ 1.2	46.2 $\pm$ 0.7	1.58	1.16	1.36
2	23.8 $\pm$ 0.4	47.0 $\pm$ 0.5	29.1 $\pm$ 0.1	95	15.4 $\pm$ 1.5	24.0 $\pm$ 1.0	14.5 $\pm$ 1.0	46.1 $\pm$ 1.0	1.65	1.06	1.56
3	24.4 $\pm$ 0.3	46.6 $\pm$ 0.2	29.0 $\pm$ 0.3	191	16.2 $\pm$ 1.9	23.9 $\pm$ 0.8	14.1 $\pm$ 1.4	45.8 $\pm$ 1.4	1.70	1.15	1.48
4-SA1	25.2 $\pm$ 0.9	46.1 $\pm$ 1.0	28.6 $\pm$ 0.6	287	18.1 $\pm$ 0.9	24.4 $\pm$ 0.8	12.8 $\pm$ 0.6	44.6 $\pm$ 1.2	1.90	1.41	1.35
4-SA2	25.2 $\pm$ 0.9	46.1 $\pm$ 1.0	28.6 $\pm$ 0.6	287	16.0 $\pm$ 0.4	23.7 $\pm$ 0.6	14.4 $\pm$ 0.5	45.8 $\pm$ 0.5	1.64	1.11	1.48
5-SA1	23.7 $\pm$ 0.6	46.6 $\pm$ 0.3	29.6 $\pm$ 0.6	383	17.8 $\pm$ 0.3	25.2 $\pm$ 0.4	12.7 $\pm$ 0.4	44.3 $\pm$ 0.5	1.99	1.41	1.41
5-SA2	23.7 $\pm$ 0.6	46.6 $\pm$ 0.3	29.6 $\pm$ 0.6	383	15.1 $\pm$ 0.3	23.2 $\pm$ 0.4	15.3 $\pm$ 1.1	46.5 $\pm$ 0.8	1.54	0.99	1.54
Slow cooling (240 minutes)											
6	24.4 $\pm$ 0.4	46.5 $\pm$ 0.5	29.1 $\pm$ 0.5	32	11.8 $\pm$ 1.0	20.9 $\pm$ 1.0	16.2 $\pm$ 0.9	51.0 $\pm$ 1.1	1.29	0.73	1.77
7	25.2 $\pm$ 0.9	46.1 $\pm$ 1.0	28.6 $\pm$ 0.6	287	12.6 $\pm$ 0.5	21.5 $\pm$ 1.0	15.7 $\pm$ 0.7	50.2 $\pm$ 0.8	1.37	0.80	1.71

Table 1. Summary of EDS analysis performed in all samples reported in the present manuscript.

EDS analysis is broken down in Table 1. Due to film inhomogeneity, data for samples 4 and 5 is reported under Scanning Areas 1 and 2 (SA1, SA2). SA2 includes every relevant feature in the sample, whereas SA1 does not comprise the characteristic 3D morphologies solely present in the films synthesized at higher pressures. Fig. 2a-2c show a graphic representation of the stoichiometry values reported in Table 1 while only considering data from SA1. Cu/Sn and Zn/Sn ratios (Fig. 2a and 2b, respectively) are considerably larger at 287 and 383 Torr. The Cu/Zn ratio (Fig. 2c), however, does not show a clear dependence on the sulfurization pressure. This information suggests that there is major Sn loss in SA1 as the pressure is raised. When including the 3D structures into these measurements (i.e., reporting values from SA2) the Cu/Sn, and Zn/Sn ratios (Fig. 2d and 2e, respectively) are remarkably similar. There is therefore no material loss at higher pressures, but rather a displacement of Sn into clearly defined regions of the film. Additional EDS mapping of these 3D features is displayed in Fig. 2g-2k. Strong S and Sn signals are detected in the region of interest (Fig. 2j and 2k, respectively). In contrast, Cu and Zn signals at Fig. 2h and 2i are much weaker in that particular sector.

XRD data from the as-synthesized films is shown in Fig. 3a. Peaks associated to CZTS, Cu_2SnS_3 , and ZnS are present at 28.5° , 33.1° , 47.5° , and 56.2° . Additional weak peaks at 34.6° , 50.0° , and 52.1° indicate there is minor segregation of secondary phases in all films. These reflections may be related to the $\text{Cu}_{39}\text{S}_{28}$ alloy (JCPD 036 0380) [19]. Peaks from SnS_2 at 15.0° and 32.1° become visible at 287 and 383 Torr, adding up to

the evidence of SnS_2 segregation at high pressures. The remarkable similarity among the CZTS, ZnS, and Cu_2SnS_3 XRD peaks makes it impossible to fully confirm the presence of CZTS by solely employing this characterization technique [20]. Raman analysis is a useful complimentary tool for CZTS detection. Fig. 3b shows the Raman spectrum for each of the five samples synthesized at various sulfurization pressures. Strong CZTS peaks at 337cm^{-1} and 289cm^{-1} are readily detected in all the films. As pressure increases, a hexagonal SnS_2 peak at 314cm^{-1} becomes stronger. This trend is consistent with the EDS and XRD data presented above.

4. Discussion

Previous investigations on CZTS sulfurization in closed systems emphasize the importance solid-gas phase reactions have in the chemical pathways that lead to the formation of CZTS crystals [21]. At low sulfurization pressure, the proposed mechanism consists in the formation of gaseous SnS as a result of the interaction between solid Sn with the S atmosphere. Further incorporation of SnS into the film leads to a solid-state interaction with CuS phases to form Cu_2SnS_3 . Finally, ZnS diffuses into Cu_2SnS_3 to yield CZTS. The presence of SnS_2 at high pressure suggests that the chemical route explained above is partially altered under these

anomalous conditions. Instead of forming SnS (g), interaction between Sn (s) and S (g) favors the growth of solid SnS₂ three-dimensional structures. Since these features appear in the final film morphology, it is evident that there is no further reaction between SnS₂ and other phases during the sulfurization process. Higher stability of SnS₂ (s) over SnS (g) may readily explain this phenomenon.

An additional experiment was designed in order to discard the effects that the cooling rate may have over the film morphology. Two extra samples, sulfurized at 32 and 287 Torr, underwent a slower cooling process. The overall cooling time was increased from 120 to 240 minutes. Stoichiometry values as obtained from EDS measurements are reported in Table 1 (samples 6 and 7). A larger amount of Sn and S is detected. Zn and Cu losses are also evident. Nonetheless, despite the stoichiometric variations there were no morphological changes associated to the cooling rate. Film features are very similar to those shown in Fig. 1a-1b and 1g-1h, suggesting that there is no influence of the cooling rate in the formation of SnS₂ 3D structures. It is apparent that the cooling rate is a relevant and often overlooked factor in the final stoichiometry of the film. Gaseous sulfur left in the ampule keeps reacting with the sample while cooling. These notable stoichiometric variations shed light on the great complexity related to the formation mechanisms of CZTS, in which subtle changes in any parameter play a substantial role on the final film properties.

5. Conclusions

The effects of pressure during CZTS sulfurization in a closed system was investigated. Higher pressure yields samples with evident segregation of 3D SnS₂ structures randomly dispersed along the film. Collected data suggests that the formation of these structures follows different reaction pathways to those reported for lower pressure processes. A greater chemical stability of solid SnS₂ compared to that of gaseous SnS explains the fact that the formation of SnS₂ does not lead to further interaction with other phases in the film. Additionally, the cooling rate has a substantial influence on the sample final stoichiometry. However, the surface morphology is unaffected by changes in this parameter.

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Captions

Fig. 1. Low and high magnification SEM images showing the surface morphology of the CZTS samples sulfurized at various pressures.

Fig. 2. Cu/Sn (a, d), Zn/Sn (b, e), and Cu/Zn (c, f) stoichiometry ratios of samples sulfurized at various pressures. Data from both SA1 and SA2 is included for the samples synthesized at higher pressures. (h-k) EDS mapping of the framed region in (g). S (j) and Sn (k) comprise most of the elemental stoichiometry of that specific feature.

Fig. 3. (a) XRD data showing characteristic CZTS peaks and weak Cu₃₉S₂₈ reflections in all films. Hexagonal SnS₂ reflections are observed at 287 and 383 Torr. (b) Raman analysis of samples sulfurized under various

pressure conditions. A strong CZTS signal is observed in all films. A hexagonal SnS₂ peak becomes more visible as pressure increases.