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*Publication date:*  
2014

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Ettlinger, R. B., Crovetto, A., Bosco, E., Rasmussen, P., & Schou, J. (2014). *Pulsed laser deposition of Cu-Sn-S for thin film solar cells*. Poster session presented at World Conference on Photovoltaic Energy Conversion 6, Kyoto, Japan.

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## Pulsed laser deposition of Cu-Sn-S for thin film solar cells

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### ABSTRACT

Thin films of copper tin sulfide were deposited from a target of the stoichiometry Cu:Sn:S ~1:2:3 using pulsed laser deposition (PLD). Annealing with S powder resulted in films close to the desired Cu<sub>2</sub>SnS<sub>3</sub> stoichiometry although the films remained Sn rich. X-ray diffraction showed that the final films contained both cubic-phase Cu<sub>2</sub>SnS<sub>3</sub> and orthorhombic-phase SnS.

### 1. INTRODUCTION

The ternary chalcogenide Cu<sub>2</sub>SnS<sub>3</sub>, like the more widely researched material Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS), can be used as the absorber layer of thin film solar cells [see, e.g. 1, 2]. Pulsed laser deposition is a well-recognized deposition method for compound materials and several groups have used it to deposit CZTS [see, e.g., 3]. We have deposited Cu<sub>2</sub>SnS<sub>3</sub> at temperatures below 300 °C, where, however, a number of secondary phases formed. A loss of S and Sn is anticipated with higher deposition or annealing temperature, as needed to obtain good crystal quality [1, 2]. Therefore a Sn and S enriched target was used to deposit precursor films, which were annealed with S powder. The resulting films contain cubic-phase Cu<sub>2</sub>SnS<sub>3</sub> with a stoichiometry near the desired Cu:Sn:S ratio of 2:1:3.

### 2. METHODS

#### 2.1 Pulsed laser deposition

Pulsed laser deposition was done using a 355 nm Nd:YAG laser with 5-7 ns pulses at 10 Hz. The laser beam was rastered across a rotating target in vacuum ( $p < 5 \cdot 10^{-6}$  mbar) and the ablated material was deposited on substrates placed 4.5 cm from the target (Fig. 1); the substrates were fused silica or molybdenum-coated soda-lime glass (Mo/SLG). All depositions took place at room temperature. The target was a sintered pellet of copper and tin sulfides (PVD products). The laser spot size was 2.5 mm<sup>2</sup>, the fluence varied from 0.7-2.8 J/cm<sup>2</sup>, and the film thickness varied

from ~1300 nm to ~4200 nm. Annealing was done with S powder in a graphite box held inside a quartz tube with >100 mbar N<sub>2</sub>. The temperature was ramped to 500 °C at 12 °C/min, then to 570 °C at 1 °C/min. It remained above 570 °C for 10 min, reaching a maximum of 580 °C, after which the system cooled naturally.

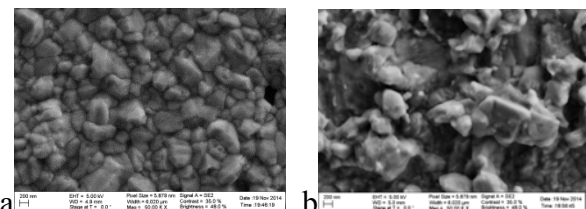
#### 2.2 Characterization

Scanning electron microscopy was performed at 5 keV using the secondary electron detector of a SEM equipped with a field emission gun (FE-SEM, Supra 60VP, Zeiss). Energy dispersive X-ray spectroscopy (EDX) was performed in this SEM using a silicon drift detector (X-Man<sup>N</sup> 50, Oxford Instruments) and a beam voltage of 15 kV. On films, full area scans were made at 1000x magnification; on targets, 250x magnification was used. Several measurements were averaged for each sample. The element ratios were calculated using Cu K-lines with Oxford Instruments' Aztec software. When the Mo contribution to the S peak was detectable, the Mo peak was deconvoluted from the spectrum.

X-ray diffraction was done in Bragg-Brentano mode with a Bruker D8 powder diffractometer using a step size of 0.01° and a measurement interval of 1.5 s/step. K<sub>α2</sub> radiation was subtracted from the data using the program EVA. The diffraction peaks were identified manually and matched to JCPDS files.

### 3. RESULTS

#### 3.1 Morphology



**Fig. 1** SEM images of annealed Cu-Sn-S films on Mo/SLG. **a**: deposited at 2.2 J/cm<sup>2</sup>, precursor ~1320 nm thick; **b**: deposited at 0.7 J/cm<sup>2</sup>, precursor ~4200 nm thick. Magnification 50k.

As-deposited films displayed an underlying film dotted with round droplets, similar to CZTS films produced by PLD [4]. The laser fluence had little influence on film appearance.

After annealing, several films contained relatively large grains and visible pinholes (Fig. 1 a) while one thicker film deposited at lower fluence appeared rougher with less well-defined grains (Fig. 1 b). The films with large grains are similar in appearance to  $\text{Cu}_2\text{SnS}_3$  films annealed in a similar manner by Chino et al. [2].

### 3.2 Energy dispersive X-ray spectroscopy

The composition of the Sn- and S-enriched target, as-deposited films and annealed films is shown in Fig. 2. Measurements on as-deposited films were made on films on fused silica substrates, whereas annealed films were deposited on Mo/SLG. As-deposited films on Mo/SLG were generally a few absolute percent more Sn and S rich than those on fused silica.

The as-deposited films were Sn- and S-poor compared to the target. The composition did not depend significantly on fluence or laser spot size. Annealing decreased the Sn content while increasing the S content slightly. The stoichiometry of the annealed films is close to  $\text{Cu}_2\text{SnS}_3$ ; the thickest film is closest. All the films retained an excess of Sn.

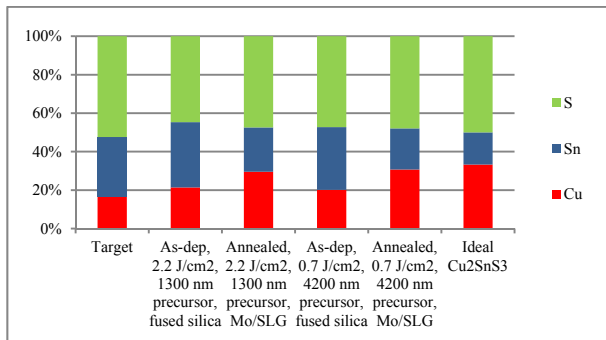


Fig. 2 Composition from EDX of target and selected films.

### 3.3 X-ray diffraction

As-deposited films on fused silica displayed no obvious X-ray diffraction peaks; films on Mo/SLG were assumed to be similar. After annealing, films form  $\text{Cu}_2\text{SnS}_3$  (cubic phase) alongside SnS (orthorhombic) (Fig. 3). The thick film shown in Fig. 1 b is dominated by cubic-phase  $\text{Cu}_2\text{SnS}_3$ , while the thinner films were dominated by SnS (orthorhombic phase).

### 4. Discussion and conclusion

As seen from the EDX data, S and Sn was lost relative to the target during pulsed laser deposition at room temperature. Annealing further caused loss of Sn, probably in the form of SnS, where the S loss was compensated by the S powder. The pinholes seen in the thinner films (Fig. 1 a) may be evidence of SnS

evaporation [1]. Compared to the thickest film, the pinholes may appear clearly in the thinner films due to more uniform crystallization. The relatively small X-ray diffraction peaks for the thick film may indicate that it is not fully crystallized but contains amorphous regions.

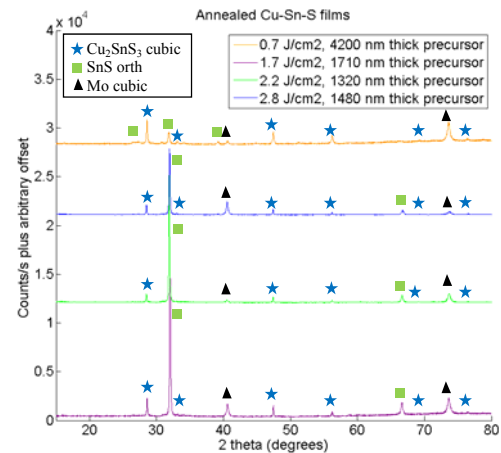


Fig. 3 X-ray diffractograms of films of different thickness made at different fluences. Cubic  $\text{Cu}_2\text{SnS}_3$ : JCPDS 89-2877; orthorhombic SnS: JCPDS 39-354; cubic Mo: JCPDS 42-1120

In summary, using a Sn- and S-enriched target for pulsed laser deposition of copper tin sulfide, we obtained near-stoichiometric  $\text{Cu}_2\text{SnS}_3$  thin films after annealing with S above 570 °C. However, the films remain Sn rich and contain SnS. In future work a less enriched target may be used.

### REFERENCES

- [1] N. Aihara, H. Araki, A. Takeuchi, K. Jimbo, and H. Katagiri, "Fabrication of  $\text{Cu}_2\text{SnS}_3$  thin films by sulfurization of evaporated Cu-Sn precursors for solar cells", *Phys. Stat. Sol. C*, **10**, No. 7-8, 1086-1092 (2013).
- [2] K. Chino, J. Koike, S. Eguchi, H. Araki, R. Nakamura, K. Jimbo, H. Katagiri, "Preparation of  $\text{Cu}_2\text{SnS}_3$  Thin Films by Sulfurization of Cu/Sn Stacked Precursors", *Jpn J Appl Phys* **51**, 10NC35 (2012).
- [3] A. V. Moholkar, S. S. Shinde, G. L. Agawane, S. H. Jo, K. Y. Rajpure, P. S. Patil, C. H. Bhosale, and J. H. Kim, "Studies of compositional dependent CZTS thin film solar cells by pulsed laser deposition technique: An attempt to improve the efficiency", *J. Alloys Compounds*, **544**, 145-151 (2012).
- [4] S. M. Pawar, A. V. Moholkar, I. K. Kim, S. W. Shin, J. H. Moon, J. I. Rhee, and J. H. Kim, "Effect of laser incident energy on the structural, morphological and optical properties of  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) thin films", *Current Appl. Phys.* **10**, 565-569 (2010).