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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_2SnS_3 stoichiometry although the films remained Sn rich. X-ray diffraction showed that the final films contained both cubic-phase Cu_2SnS_3 and orthorhombic-phase SnS.

1. INTRODUCTION

The ternary chalcogenide Cu_2SnS_3, like the more widely researched material Cu_2ZnSnS_4 (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_2SnS_3 at temperatures below 300 ºC, 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_2SnS_3 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 ($p < 5*10^{-6}$ 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^2, the fluence varied from 0.7-2.8 J/cm^2, 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_2. The temperature was ramped to 500 ºC at 12 ºC/min, then to 570 ºC at 1 ºC/min. It remained above 570 ºC for 10 min, reaching a maximum of 580 ºC, 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^N 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. $K_{\alpha 2}$ 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

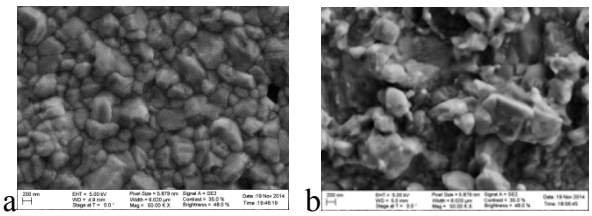

Fig. 1 SEM images of annealed Cu-Sn-S films on Mo/SLG. **a**: deposited at 2.2 J/cm2, precursor ~1320 nm thick; **b**: deposited at 0.7 J/cm2, precursor ~4200 nm thick. Magnification 50k.

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 Cu_2SnS_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 Cu_2SnS_3; the thickest film is closest. All the films retained an excess of Sn.

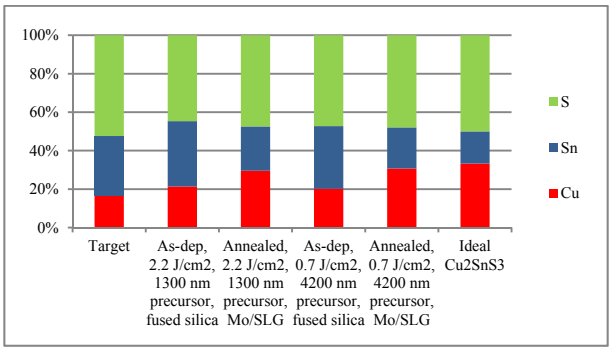

Fig. 2 Composition from EDX of target and selected films.

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 Cu_2SnS_3 (cubic phase) alongside SnS (orthorhombic) (Fig. 3). The thick film shown in Fig. 1 b is dominated by cubic-phase Cu_2SnS_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.

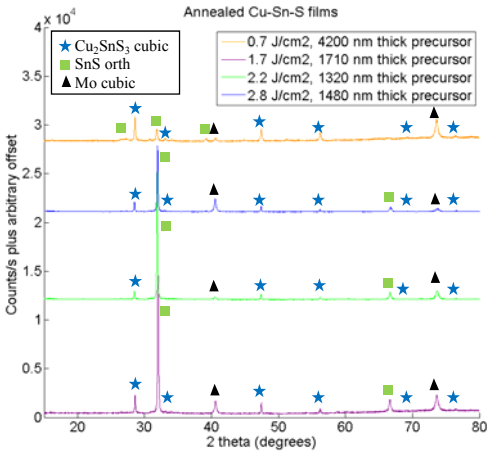

Fig. 3 X-ray diffractograms of films of different thickness made at different fluences. Cubic Cu2SnS3: JCPDS 89-2877; orthorhombic SnS: JCPDS 39-354; cubic Mo: JCPDS 42-1120

In summary, using a Sn- and S-enriched target for pulsed laser deposition of copper tin sulfide, we obtained near-stoichiometric Cu_2SnS_3 thin films after annealing with S above 570 ºC. However, the films remain Sn rich and contain SnS. In future work a less enriched target may be used.

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