Thin films of CZTS and CZTO for solar cells produced by pulsed laser deposition

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CZTS solar cells absorbers produced by sputtering or pulsed laser deposition

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Currently CZTS sulfide absorbers for solar cells with the highest efficiency have all been produced by vacuum techniques which thus seem to be superior to solution processing for CZTS cells. Sputtering and pulsed laser deposition are typical vacuum techniques, which are employed for solar cell absorbers of complicated stoichiometry. Both techniques are well-known for stoichiometric transfer of chemical compounds such as metal oxides and nitrides from a target to a substrate. The two techniques are non-thermal since the emitted atoms from the target are quite energetic and may have an energy distribution with a tail up to more than 10 eV. This non-thermal arrival energy is also known to be beneficial for growth of layers with high crystallinity.

In the photovoltaic literature there seems be a limited number of examples of a comparison between the absorbers and cells produced by either sputtering deposition (SD) or pulsed laser deposition (PLD) except for an inconclusive study without production of solar cells by Sun et al. [1].

We have recently produced solar cells by co-sputtering deposition and PLD with a record efficiency of 6.6 % for SD, while that by PLD reached 5.2 % [2]. While the efficiency was comparable, there were several processing differences, in particular in the thermal annealing steps. It is not clear how different the ideal thermal profiles for the two techniques are under similar deposition conditions, i.e., same type of Mo-coated substrate and precursor films of the same thickness and composition.

Furthermore, for single-target SD the composition of the films can be very difficult to tune because of preferential sputtering from the growing film induced by the arrival of fast atoms or ions from the target. In contrast, for standard PLD (with a single target) the composition can be varied by adjusting the laser fluence, since the transfer of copper atoms from target to film is increasing with fluence (and with 0.8 J/cm2 as the optimum fluence) [2,3].

We will discuss a few other PLD experiments: The CZTS-films can be doped with additional elements, e.g. by Ag using doped targets without any additional complications in the PLD process. Also the production of oxide precursor films is comparatively easy with an oxide target for PLD, while it is not yet clear how successful a detour via metal oxides to sulfides would be for co-SD.

Detailed results for the comparison between films made by SD and PLD as well as examples PLD-films of other compositions will be shown in this contribution.

[1] L. Sun et al., Journal of Crystal Growth 361 (2012) 147–151
[2] A. Cazzaniga, A. Crovetto et al., Solar Energy Materials & Solar Cells 166 (2017) 91–99
[3] J. Schou et al., Applied Physics A) 124 (2018) 78