Thin films of CZTS prepared by Pulsed Laser Deposition

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Introduction:
We are investigating the properties of the chalcogenide semiconductor Cu₂ZnSnS₄ as an absorber layer for earth-abundant thin-film solar cells. The physics behind the working principles of CZTS-based devices is not yet fully understood, including the relation between electro-optical and structural properties. In order to understand the underlying physics it is necessary to identify and optimize the most critical parameters that affect the structural properties. Here we illustrate how the deposition of a thin layer of ZnS (~ 60 nm) on top of a 700 nm Cu-rich CZTS absorber layer (as obtained with Pulsed Laser Deposition of a single stoichiometric target) can dramatically enhance the material properties during the annealing. While on one hand Cu-rich composition is always related to low efficiency of the photovoltaic device, on the other hand it is understood that Cu-rich precursors favor the synthesis of CZTSe crystals (see: Cu-Rich Precursors Improve kesterite solar cells, M. Mousel et al., Adv. Energy Mater. 2014, 4, 1300543).

Experimental:
We deposit a bilayer of CZTS/ZnS onto Mo-coated Soda Lime Glass by using Pulsed laser Deposition (PLD). The laser works at 248 nm, 10 Hz and with a fluence of 1 to 3 J/cm². The targets were made of stoichiometric, sintered powder and the substrate was placed at distance of 40 mm. Depositions were carried out under high vacuum ($p \approx 1 \times 10^{-6}$ mbar) and substrate temperature was fixed at 300°C. Annealing was done in a tube furnace in N₂ + S₂ atmosphere at 550°C for 30 minutes. Why using PLD? PLD allows us to make single step deposition of materials of complex stoichiometry. Films of 700 nm can be fabricated in less than 1 hr and the crystallinity can be enhanced at modest substrate temperatures compared to other deposition techniques.

Next goals
- Change the thickness of the ZnS layer and discuss the change in low Temperature Photoluminescence.
- Change the position of the ZnS layer.
- Estimate the content of ZnS secondary phase (High resolution TEM-EDX analysis)

(*) When the 60nm ZnS layer is placed below the 700 nm Cu rich CZTS layer, the XRD pattern shows unwanted secondary phases.

Fig. 1: Left: the usual annealing in sulfurized atmosphere. Right: the ZnS layer suppresses SnS evaporation during the annealing and provides a reservoir for Zn.

Fig. 2: (Left) X-ray diffraction pattern of the single layer CZTS as deposited (at 300°C) and after annealing. (Right) same diffraction pattern for the bi-layer CZTS/ZnS, again as deposited and after annealing.