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*Published in:*

Book of Abstracts. DTU's Sustain Conference 2015

*Publication date:*

2015

*Document Version*

Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*

Cazzaniga, A. C., Engberg, S., Ettliger, R. B., Crovetto, A., & Schou, J. (2015). Pulsed laser deposition (PLD) of the solar cell materials CZTS and CTS. In Book of Abstracts. DTU's Sustain Conference 2015 [E-36] Lyngby: Technical University of Denmark (DTU).

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## Pulsed laser deposition (PLD) of the solar cell materials CZTS and CTS

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**Background:** The world demand of electricity supply at a Tera-Watt scale means that there is a need for earth abundant and non-toxic materials. Therefore, many efforts are currently devoted to exploit the full potential of the absorber layer  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  (CZTS), which has a similar structure and similar band-gap as  $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$  and is fully made by earth-abundant materials. The record efficiency of CZTS solar cells has been greatly improved during the last few years, reaching 12.6% with a sulfo-selenide blend and with a 50 nm thick buffer layer of CdS. While these results are very encouraging, Se- and Cd- free solutions are still at an early stage of development. Regarding the pure sulfide  $\text{Cu}_2\text{ZnSnS}_4$ , the annealing step is very critical for the physical quality of the absorber layer. Many difficulties are related to the high volatility of sulfur and of its binary compounds.

**Idea:** The idea is to make the annealing process more controllable and reproducible by using a cap layer on top of the CZTS before the annealing. The cap layer should prevent decomposition reactions and assist in self-balancing the stoichiometry. For this purpose we have selected a thin layer of ZnS.

- ZnS can serve as buffer layer.
- ZnS is made of earth abundant material, unlike CdS.
- ZnS withstands high temperatures, so it can be annealed together with the CZTS layer.

We compare the results of annealing the bilayer CZTS/ZnS to the annealing of a single CZTS layer. In the first case, the enhancement in the crystalline quality of both layers is clearly visible from the x-ray diffraction patterns and SEM images.

**Experimental technique:** We deposit a bilayer of CZTS/ZnS onto Mo-coated Soda Lime Glass by using Pulsed Laser Deposition (PLD). The laser is operating at 248 nm, 10 Hz and 3 J/cm<sup>2</sup>. The targets were made of stoichiometric, sintered powder; Depositions were carried out under high vacuum ( $p \sim 1 \cdot 10^{-6}$  mbar) and the substrate temperature was fixed at 300° C. Annealing was done in a tube furnace in a  $\text{N}_2 + \text{S}_2$  atmosphere at 550° C for 30 minutes.