

A. Cazzaniga, A. Crovetto, S. Canulescu, R. B. Ettliger, N. Pryds, Ole Hansen and J. Schou\*  
The Technical University of Denmark, DTU Fotonik, Risø Campus, DK-4000 Roskilde,  
Denmark

A. Crovetto, O. Hansen

The Technical University of Denmark, DTU Nanotech, DK-2800 Kgs. Lyngby, Denmark

C. Yan, K. Sun, X. Hao

School of Photovoltaic and Renewable Energy Engineering, University of New Wales, NSW  
2052, Sydney, Australia

### **Pulsed laser deposition (PLD) of the CZTS absorber for thin solar cells with up to 5.2% -efficiency**

CZTS ( $\text{Cu}_2\text{ZnSnS}_4$ ) is a promising material for a solar cell absorber and consists of abundant and environmentally friendly elements. The efficiency of a cell based on this material has increased from 2% in 2001 to 9.4 % in 2015 [1].

Pulsed laser deposition (PLD) is usually considered as a technique, by which a material with a complicated stoichiometry can be transferred from a target to a growing film in a vacuum chamber. It is widely used in scientific labs, in particular for production of complex oxide films [2]. PLD is a non-equilibrium film deposition technique, and since the energy source is outside the deposition chamber, the parameter space is huge for all physical parameters such as the background gas pressure, the substrate temperature, the target-substrate distance and the laser fluence.

For complicated compounds which are produced from sintered, multi-element targets, the composition of the films can deviate significantly from that of the target, depending on the laser fluence. By tuning the laser fluence with a 248-nm excimer laser beam on a sintered CZTS target ( $2\text{CuS}:\text{ZnS}:\text{SnS}$ ), the metal ratios in the film can be controlled and the film made slightly copper-poor. A film of thickness of 400 nm was deposited in high vacuum ( $p < 5 \cdot 10^{-6}$  mbar) on a Mo-coated soda lime glass substrate at room temperature. At low fluence below  $1 \text{ J/cm}^2$  the copper content in the film is low, while at high fluence the films become copper-rich. At a fluence  $0.7 \text{ J/cm}^2$  we have achieved a ratio  $\text{Cu}/(\text{Sn}+\text{Zn}) \sim 0.85$  which is in the right regime for an operating solar cell [3,4].

A drawback of PLD is the generation of micron-sized droplets on the surface which typically originates from violent heating of the surface and the adjacent layers by the laser beam [5]. At the low fluence,  $0.6\text{-}0.8 \text{ J/cm}^2$  used here, the number of droplets turned out to be relatively low, (and any sign of droplets turned out to disappear after sulfurization).

The sulfurization and the final deposition of the buffer and window layers were carried out at School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, NSW 2052, Sydney, Australia [3]. The best cell with an effective area of  $21 \text{ mm}^2$  and only a 400-nm thick CZTS layer had a remarkably high efficiency of 5.2 %, a  $V_{oc} = 616 \text{ mV}$ , a  $J_{sc} = 17.6 \text{ mA/cm}^2$  and a fill factor of 48 %. This efficiency is the highest one from a cell obtained with an absorber layer of CZTS produced by PLD until now [3]. Despite the thin absorber, there are no signs that material and junction quality are significantly lower than that of thicker absorbers: grain size, carrier lifetimes, collection efficiency, shunt resistance, and dark saturation current are all similar to (thicker) benchmark CZTS solar cells.

- [1] S. Tajima et al. , Prog. Photov. Res. Appl. (2016), in press.
- [2] Pulsed laser deposition of thin films, ed. R. Eason, Wiley (2007)
- [3] A. Cazzaniga, A. Crovetto et al. submitted to Solar Energy Materials and Solar Cells
- [4] K. Ito Copper Zinc Tin Sulfide-based thin film solar cells, Wiley (2015)
- [5] Chen, in: Pulsed laser deposition of thin films, Wiley (1994) p. 167.