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

Cazzaniga, Andrea Carlo; Crovetto, Andrea; Ettlinger, Rebecca Bolt; Canulescu, Stela; Canulescu, Stela; Pryds, Nini; Yan, Chang; Sun, Kaiwen; Hao, Xiaojing; Hansen, Ole; Schou, Jørgen

Publication date: 2017

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Pulsed laser deposition (PLD) of a CZTS-absorber for thin solar cells with up to 5.2 % efficiency

A. Cazzaniga¹, A. Crovetto², R. B. Ettlinger¹, S. Engberg¹, S. Canulescu¹, N. Pryds³, C. Yan⁴, K. Sun⁴, X. Hao⁴, O. Hansen² and Jørgen Schou¹

¹ DTU Fotonik, Technical University of Denmark, DK-4000 Roskilde, Denmark.  
² DTU Nanotech, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark.  
³ DTU Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark  
⁴ University of New South Wales, Sydney, NSW 2052, Australia

Introduction:

Pulsed laser deposition (PLD) is usually considered as a technique, by which a complicated material can be transferred from a target to a substrate with the same stoichiometry. It is widely used in scientific labs, in particular for production of complex oxide films. 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. We are investigating PLD of thin films of chalcogenide materials Cu₂ZnSnS₄ (CZTS) and Cu₂SnS₃ (CTS), which are promising candidates for absorber layers of earth-abundant thin-film solar cells. The material transfer is found highly non-stoichiometric, contrary to what is commonly believed with PLD. We investigate deviations from stoichiometry and find out that:

1) Copper content increases with increasing fluence.
2) Droplets density and size increase with laser fluence.

Experimental: We deposit a thin layer of CZTS (or CTS) onto Mo-coated Soda Lime Glass by Pulsed laser Deposition (PLD) in high vacuum. The targets are made of sintered powders and are not single phase. They contain mostly binary phases CuS, ZnS and SnS, which have different thermal properties and vapor pressure. The CZTS films were deposited with PLD at room temperature at DTU and treated with standard annealing at 560 °C at UNSW. PLD allows single step deposition of materials of complex stoichiometry from the highly nonthermal removal of target material. Crystallinity of the film can be enhanced even at modest substrate temperatures as compared to other techniques such as evaporation deposition due to the non-thermal energy of the arriving atoms.

Discussion:

Results shown here are published in:  
A. Cazzaniga et al.  

Fig. 1: The fluence on the target was 0.6 J/cm² with a spot size of 4 mm².  
Fig. 2: The different phases over a typical length scale of a few hundred µm are clearly visible.

Fig. 3: Non-stoichiometric material transfer as function of laser fluence. Copper content varies significantly, while Zn and Sn are kept in stoichiometric proportion (within EDX detection limit, grey bar). S content not shown for clarity.

Fig. 4: Droplets on films at different fluence. No peaks detected in XRD, indicating the films and the droplets are amorphous.

Fig. 5: The champion CZTS film deposited with PLD at RT and subsequently annealed at 560 °C.

Fig. 6: J-V curve of the champion device at 1 sun.