High-energy deposition methods for CZTS and CTS solar cells

Ettlinger, Rebecca Bolt; Cazzaniga, Andrea Carlo; Canulescu, Stela; Normann, K.; Schou, Jørgen; Pattini, Francesco; Rampino, Stefano; Gilioli, Eduardo

Publication date:
2017

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

Link back to DTU Orbit

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
High-energy deposition methods for CZTS and CTS solar cells

R. B. Ettlinger¹, A. Cazzaniga¹, S. Canulescu¹, K. Normann², J. Schou¹, F. Pattini³, S. Rampino³, and E. Gilioli³

¹DTU Fotonik, Technical University of Denmark, 4000, Roskilde
²DTU Energy, Technical University of Denmark, 4000, Roskilde
³IMEM-CNR, PR 43124, Parma, Italy

*E-mail: reet@fotonik.dtu.dk

Copper zinc tin sulfide and copper tin sulfide have been studied widely for the last few years as potential alternatives to Cu(In,Ga)Se₂ (CIGS) for the absorber layer in thin film solar cells. While CIGS is vulnerable to fluctuations in the price and availability of the rare element In, Cu₂ZnSnS₄ (CZTS) and Cu₂SnS₃ (CTS) contain only Earth-abundant elements. However, whereas CIGS solar cells have reached an efficiency of 22.6 % [1], the maximum CZTS solar cell efficiency is 9.4 % [2] and the maximum CTS efficiency is 4.6 % [3]. The fabrication of high-quality layers of CZTS and CTS remains a challenge. We have investigated two high-energy deposition methods for these materials: pulsed laser deposition (PLD) and pulsed electron deposition (PED), which have been highly successful for the deposition of complex oxides such as the superconductor YBa₂Cu₃O₇-x. PED has also been successfully used to make CIGS solar cells with over 17 % efficiency [4]. We were the first to make CZTS by PED and CTS by PLD. Both PED and PLD rely on ablation of a target material in vacuum by a high-energy pulse; the ablated material forms a thin film on the surface facing the target (Fig. 1). An important advantage is that the high energy of the ablated material permits a low growth temperature (270 °C for CIGS by PED compared to 500-600 °C for equilibrium CIGS processing). Indeed, deposition of CZTS and CTS films at ~ 300 °C resulted in crystalline films where normal processing methods require 550-580 °C. However, the films lacked S, contained secondary phases like ZnS, Sn₂S₃, and CuS, and the composition changed gradually over the micrometer film thickness (Fig 2.). We propose that this difficulty in controlling the film composition stems from differential evaporation of the starting materials in the solid target.

Fig. 2: The principle of PED. The electron discharge voltage is 10-20 kV. In PLD the electron gun is replaced by a pulsed laser that enters through a quartz window and Ar is not required.

Fig. 1: SIMS (secondary ion mass spectroscopy) profile showing an increase in the Cu/(Zn+Sn+S) ratio from front to back in a CZTS film made by PLD at 300 °C. Inset: SEM cross section of the same film.