Fabrication of thin film CZTS solar cells with Pulsed Laser Deposition (18/06/2019)

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This project was about making CZTS solar cells using PLD for the fabrication of the absorber layer, and using standard techniques for the rest of the device. The solar cell is a very complicated device and all the steps in the fabrication are very important. It doesn't matter if PLD brings the best absorber layer, if one has a poor device processing the outcome will be disastrous. The converse holds true exactly in the same way. Developing the device-fabrication takes time, trials and errors. Unless one has a special PLD equipment for large area deposition, PLD's sample-throughput is too low to provide enough "dummy samples" to develop device processing. If one wants to try out PLD for making solar cells with a standard PLD setup, my suggestion is to first develop device processing with an alternative technique, e.g. sputtering, and with an established material, i.e. CIGS, easier than CZTS to handle. Once device processing is under control, the small area of the samples made with PLD may be a not-too-dramatic problem. CZTS as absorber layer is a polycrystalline material with a complicated structure that tolerates deviation from exact stoichiometry. It is very difficult to characterize such kind of material since many parameters can modify the optical and electronic properties: grain boundaries, point defects, disorder and secondary phases are just a few. When the CZTS layer is integrated in the solar cell, interface physics can also become very significant to the final device efficiency. As consequence, one cannot always distinguish a "good" or "bad" CZTS only using conventional techniques (Raman, SEM, x-ray diffraction, photoluminescence...) on the absorber layer alone. The only meaningful information comes from the full solar cell operation, but at this stage everything is coupled together behind the Quantum Efficiency (QE) curve. What do I learn by reading this thesis? You will learn how to deposit a thin film CZTS absorber layer with Pulsed Laser Deposition with the desired composition. In addition, you will see how material transfer in PLD, which is generally believed to be stoichiometric, can be very much non-stoichiometric. How to do it? I suggest to do PLD on a single sintered target (2CuS.ZnS:SnS). The films are deposited at room temperature and then annealed in a furnace with some sulfur powder aside. The annealing step is as important as the PLD step to the final device efficiency. What is your best solar cells? With our own in-house device fabrication we reached a 2.6% conversion efficiency. With the absorber layer produced with our PLD setup followed by a well established annealing + device processing we reached a PLD record efficiency of 5.2%. The world record efficiency for this material is around 9%, with sputtering. Did you manage to get good quality CZTS? We cannot evaluate the performance of our annealing step. We can only demonstrate that the precursors made with PLD can be used for producing state-of-the-art solar cells. Is there anything left to do? Oh yes! Exploring the non-equilibrium properties of PLD for the production of CZTS films. This may enable one to deposit crystalline CZTS at lower substrate temperature, with no requirement for an annealing step afterwards. Preliminary results do not seem too encouraging. The main obstacle to this approach may be that droplets do not have enough thermal energy to dissociate and merge in the absorber layer. Any further suggestions? Learn by doing. Results from other group are more-often-than-not system dependent. Select your references very carefully. If the paper doesn't come from a group that has ever reported making solar cells, there is almost no point in reading it (and they are the vast majority).

Vox auctoritatis:

"[...] the thickness of annealed films was 1.7μm for CZTSSe, and 0.9μm for CZTS (significant cracks will develop for a thicker CZTS layer).", from a foot-note in IBM's [34], Dec. 2015. And I really wish they had written this before.

"[...] even rather detailed materials characterization was not able to resolve the particular chemical products that led to the large differences in device performance. The devices in this study varied from 0.3% to 7.9% efficient, but no strong differences were observed by Raman, SEM, or EDS mapping at the surfaces and back contacts. This means that the causes of the electrical differences are on a smaller scale than the resolution of these techniques and could be, for example, very finely distributed secondary phases, changes in grain boundaries, or of course, point defects.", from a paper by J. Scragg dated 2013 [29]. Which basically says that if you do not make a solar cell, you do not understand much about this material.

"Of course you can talk about XRD, at some point you've got to write something to finish your Ph.D, but people mostly care about optical and electronic properties of this material, and of course, the efficiency of the solar cell above all". Private discussion with S. Siebentritt.

"[...] you just need to have the right composition in your precursors and the annealing pretty much does the job". Private discussion with T. Teodorov, from IBM's lab.

"[...] reproducibility of the results is an issue. Reproducibility of our best solar cells is below 30%". Private discussion with S. Tajima, from Toyota's lab.

General information
Publication status: Published
Organisations: Department of Photonics Engineering, Optical Microsensors and Micromaterials
Contributors: Cazzaniga, A. C.
Number of pages: 128
Publication date: 2016

Publication information
Publisher: Technical University of Denmark (DTU)
Original language: English
Electronic versions:
Andrea_thesis_PLD_chalcogenides.pdf