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## High-energy deposition methods for CZTS and CTS solar cells

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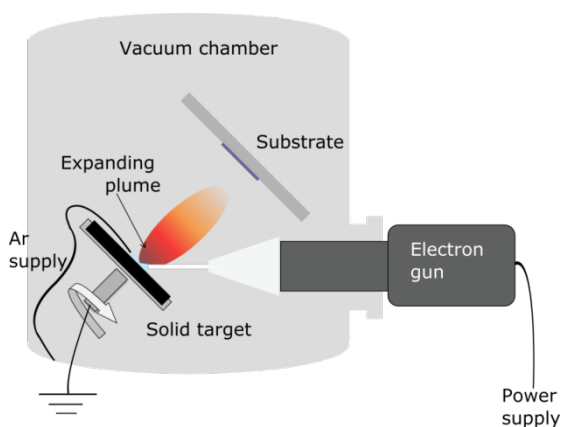
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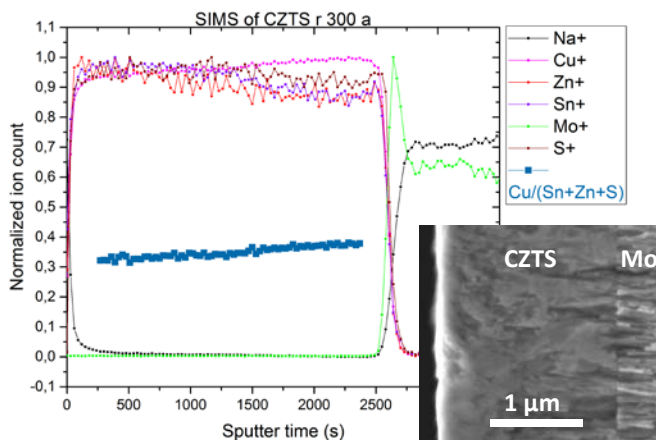
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Copper zinc tin sulfide and copper tin sulfide have been studied widely for the last few years as potential alternatives to Cu(In,Ga)Se<sub>2</sub> (CIGS) for the absorber layer in thin film solar cells. While CIGS is vulnerable to fluctuations in the price and availability of the rare element In, Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) and Cu<sub>2</sub>SnS<sub>3</sub> (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 YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>. 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, Sn<sub>2</sub>S<sub>3</sub>, 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.

[1] Green et al. (2017) Prog. Photovolt: Res. Appl. **25**:3–13  
 [3] Nakashima et al. (2015) Appl. Phys. Express **8**: 042303

[2] Tajima et al. (2017) Prog. Photovolt: Res. Appl. **25**:14–22  
 [4] Mazzer et al. (2016) Energies **9** (3) 207