

Sodium (Na) and antimony (Sb) incorporation strategies for sequential processed CZTS solar cell

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CZTSSe(Cu₂ZnSn(S_{1-x}Se_x)₄) material is a promising candidate to replace CIGS (Cu(In,Ga)Se₂) in thin film solar cells technology as it uses only earth abundant constituents. Particularly, sulfur-based kesterite (CZTS) are of prime interest due to their wide bandgap (1.5eV) and the absence of toxic element. Despite their similar properties, CZTSSe based solar cell only achieved 12.6% efficiency [1] (9.2% for pure sulfur CZTS solar cells [2]), which is far from 22.6% efficiency achieved by CIGS [3]. Absorber doping with Alkali (Na, K) and crystallization control with Sb are some of the reasons explaining the high performances of CIGS solar cells [2]-[3], due to the defect passivation and surfactant ability of those dopants.

Therefore, this study focuses on strategies to improve sulfur based CZTS absorber synthesis with incorporation of Na and Sb to the process. CZTS solar cells are typically fabricated on soda lime glass which contain Na, K along with some other materials. To avoid non-controlled diffusion of these elements from the substrate, a SiN_x barrier layer has been used prior to absorber synthesis. The CZTS material is then synthesized on Mo back contact by sulfurization of Cu/Sn/Cu/Zn stack of precursors. Two different routes have been tested to incorporate Na in the absorber layer: first NaF (0 nm – 60 nm) has been evaporated directly before the precursor stack prior to annealing process (Na before synthesis). In the second approach, NaF is deposited on top of already synthesized absorbers and a second annealing is performed (Na after synthesis). Sb (0 nm – 20 nm) has been evaporated as well before absorber synthesis. The joint effect of Sb and Na (Na before synthesis) on CZTS crystallization has been assessed with structural characterization (XRD, SEM). The beneficial effect of Na on electrical and photovoltaic properties has been demonstrated (J-V, EQE, C-V) while the incorporation of Sb does not clearly improve the devices, despite the recent claim [5]. For example, Fig. 1 shows that the incorporation of Na is largely beneficial for solar cells, particularly if it is already present during the absorber synthesis (Na before synthesis and Na from glass).

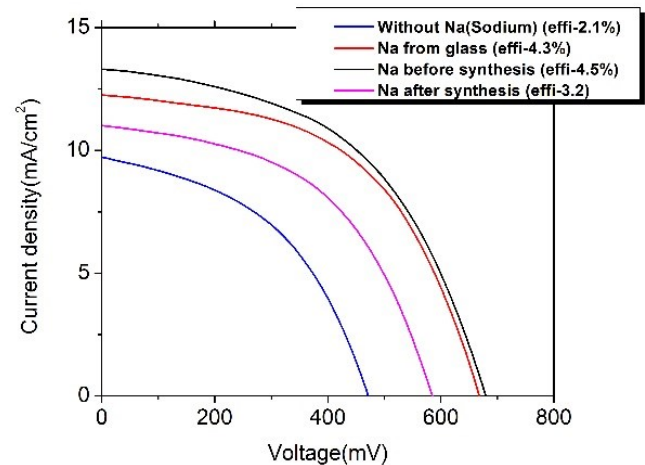


Figure 1: AM1.5 illuminated J-V curve of CZTS solar cells with different Na doping.

This new approach of Na doping on sequential process for CZTS solar cells allow to substantially improve the efficiencies of the devices and above all improve the reproducibility of the process through a precise control of the Alkali in the absorber. It will be further extended to other materials (K, Li) which already showed their ability to improve CIGS solar cells.

- [1] W. Wang *et al.*, "Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency," *Adv. Energy Mater.*, vol. 4, no. 7, p. n/a-n/a, May 2014.
- [2] H. Hiroi, N. Sakai, T. Kato, and H. Sugimoto, "High voltage Cu₂ZnSnS₄ submodules by hybrid buffer layer," in *2013 IEEE 39th Photovoltaic Specialists Conference (PVSC)*, 2013, pp. 0863–0866.
- [3] P. Jackson, R. Wuerz, D. Hariskos, E. Lotter, W. Witte, and M. Powalla, "Effects of heavy alkali elements in Cu(In,Ga)Se₂ solar cells with efficiencies up to 22.6%," *Phys. Status Solidi RRL – Rapid Res. Lett.*, vol. 10, no. 8, pp. 583–586, Aug. 2016.
- [4] M. Yuan, D. B. Mitzi, O. Gunawan, A. J. Kellock, S. J. Chey, and V. R. Deline, "Antimony assisted low-temperature processing of CuIn_{1-x}Ga_xSe₂-ySy solar cells," *Thin Solid Films*, vol. 519, no. 2, pp. 852–856, Nov. 2010.
- [5] D. Tiwari *et al.*, "Cu₂ZnSnS₄ Thin Films Generated from a Single Solution Based Precursor: The Effect of Na and Sb Doping," *Chem. Mater.*, vol. 28, no. 14, pp. 4991–4997, Jul. 2016.