

Tailoring the Properties of CZTS Thin Films through Cation Substitution and Thermal Annealing

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Abstract: Pure sulfide kesterite ($\text{Cu}_2\text{ZnSnS}_4$ or CZTS) is a promising absorber material for next-generation photovoltaic (PV) technologies, especially for tandem and indoor applications. These quaternary chalcogenides offer tunable optoelectronic properties, an earth-abundant elemental composition, low cost, and high chemical stability [1]. However, the intrinsic bandgap of CZTS (≈ 1.5 eV) is suboptimal for tandem and indoor PV applications, which require a wider bandgap in the range of 1.65-1.9 eV. Alloying strategies based on cation substitution provide a flexible approach for engineering the structural, morphological, and optoelectronic properties. In particular, combining Ag alloying with alkaline metal incorporation enables effective tuning of these properties, offering a promising route for bandgap widening and absorber optimization [2,3].

In this study, Ag-alloyed $(\text{Ag,Cu})_2\text{ZnSnS}_4$ (ACZTS) thin films were fabricated on SLG/Mo substrates using a chemical solution process based on molecular precursor solutions. The films were deposited by spin coating, followed by drying. After ACZTS film deposition, Na-Li was incorporated by spin-coating an alkali precursor solution onto the absorber, followed by drying. The films were then heat treated under an argon atmosphere with solid sulfur at temperatures between 600 and 660 °C to promote crystallization. Complete solar-cell devices were fabricated using a CdS buffer layer (CBD), ZnO/ITO window layers (sputtering), and Ag front contacts.

The impact of Ag and Na-Li incorporations, as well as heat-treatment temperatures, on the structural, morphological, and optoelectronic properties was systematically investigated. Structural and morphological (SEM/EDS, XRD and Raman) together with optical measurements and current-voltage (J-V) characteristics revealed enhanced grain growth, improved cation stoichiometry, bandgap widening (>1.5 eV) and kesterite crystal structure. The heat treatment temperature was found to strongly influence crystallinity and grain morphology. Na-Li incorporation significantly improves the solar-cells efficiency.

These results highlight ACZTS as a promising wide-bandgap absorber for tandem and indoor photovoltaic applications. Ag alloying and Na-Li co-doping provide complementary strategies to tune the bandgap and crystal structure, while enhancing absorber quality and device performance.

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