

High Bandgap Copper Indium Gallium Disulfide Materials for Solar-Assisted Water Splitting

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Photoelectrochemistry (PEC) is one of the most efficient methods to produce alternative fuels, although the efficiency, cost, and durability of lab-scale systems are currently not at the level required to make this technology economically feasible. The chalcopyrite material class, typically identified by its most popular alloy $\text{Cu}(\text{In,Ga})\text{Se}_2$, provides exceptionally good candidates to meet the requirements identified for cheap, sustainable solar fuels production. As we recently reported¹, co-evaporated 1.6 eV CuGaSe_2 offers very high-saturated photocurrent densities ($20 \text{ mA}\cdot\text{cm}^{-2}$ in pH 0 under AM1.5G illumination), long durability (up to 400 hours), and relatively high Faradaic efficiency ($>85\%$ for non-catalyzed systems). Although CuGaSe_2 has the highest bandgap of the copper chalcopyrite class, its optical characteristics are still too close to that of amorphous silicon (a-Si), a low-cost material our research team has identified as an ideal photovoltaic *driver* in a monolithic hybrid photoelectrode device. Nevertheless, a solar-to-hydrogen efficiency of 3.7% was achieved using a co-planar integration scheme, where CuGaSe_2 was connected in series with three a-Si solar cells. In order to improve the water-splitting efficiency further, novel chalcopyrite alloys with bandgap greater than 1.6 eV must be developed.

In the present communication, we report on our effort to synthesize 1.8-2.2 eV band-gap chalcopyrite materials for PEC water splitting. Specifically, we investigate the impact of sulfur on the optical and photoelectrochemical characteristics of the copper chalcopyrite material class. Using co-evaporated 1 μm -thick CuGaSe_2 as baseline system, we demonstrate that selenium can be substituted by sulfur using a simple annealing step. With this protocol, a dramatic change in optical properties was observed, with a bandgap increase from 1.6 eV (CuGaSe_2) to 2.4 eV (CuGaS_2), in good agreement with theoretical predictions². Then,

by simply adjusting the indium content in the film during the initial growth process, the bandgap of sulfurized copper chalcopyrite was decreased from 2.4 eV [$\text{GGI}=\text{Ga}/(\text{Ga}+\text{In})=1$] to 2.2 eV ($\text{GGI}\approx 0.8$) and finally to 2.0 eV ($\text{GGI}\approx 0.7$), as presented in Fig. 1. X-ray photoelectron spectroscopy analysis performed on the 2.0 eV CuInGaS_2 material indeed confirmed the all selenium at the surface of the films was replaced with sulfur. Additional Raman scattering analysis (Fig. 2) pointed out that the majority of the 2.0 eV bandgap film bulk was sulfurized, although a small fraction of CuInGaSe_2 remained ($[\text{Se}]<2\%$, as evidenced by energy dispersive X-ray spectroscopy). Preliminary PEC analyses reveal an anodic shift of the flatband potential with increasing bandgap. This suggests that the bandgap modification in sulfurized films primarily stems from a downward shift of the valence band, an ideal situation for p-type PEC systems.

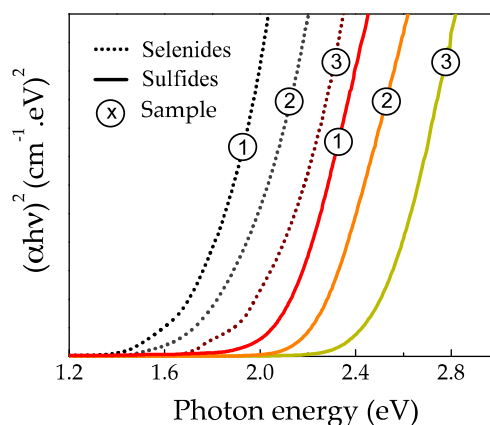


Fig.1. Tauc plots of CuInGaSe_2 thin films with GGIs of ~ 0.7 (①), ~ 0.8 (②) and 1 (③) before (dashed lines) and after (solid lines) sulfurization.

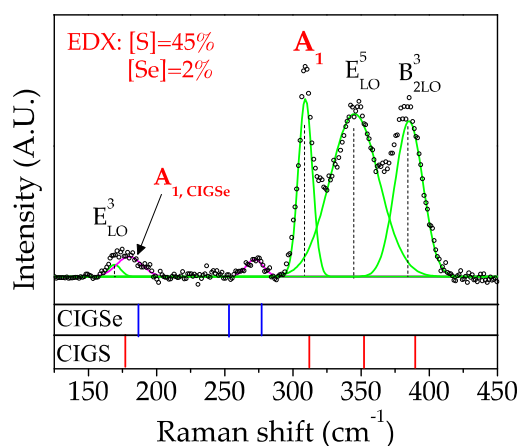


Fig.2. Raman scattering spectrum measured on a CuInGaSe_2 sample ($\text{GGI}=0.7$), after sulfurization.

¹ N. Gaillard, D. Prasher, J. Kaneshiro, S. Mallory, and M. Chong, *MRS Spring Meeting*, Z2.07 (2013).

² M. Bär, W. Böhne, J. Rohrich, E. Strub *et al.*, *Appl. Phys. Lett.* 96, 3857 (2004).