

## ABSTRACT

Thin film photovoltaic modules based on  $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS) thin films possess attributes that enable them to compete effectively with silicon-based modules. These attributes are stability, high efficiency, and low material cost. A very promising industrial related process to produce the chalcopyrite absorber layers involves the selenization of metallic precursors. However, recent literature suggests that it is extremely difficult to incorporate an appreciable amount of gallium into the active region of the CIGS thin film. Regardless of its location in the precursor stack, gallium has been observed to segregate to the back of the film during the high temperature selenization step. Consequently, the resulting films are phase-segregated with  $\text{CuGaSe}_2$  near the Mo electrode and  $\text{CuInSe}_2$  at the film surface.

In this study, the incorporation of gallium and sulfur into  $\text{CuInSe}_2$  thin films was systematically investigated to establish a scientific and engineering base for the fabrication of homogeneous  $\text{CuIn}(\text{Se,S})_2$  and  $\text{Cu}(\text{In,Ga})\text{Se}_2$  quaternary alloys with optimum band gap values between 1.1 and 1.2 eV. The selenization of selenium-containing (i.e.  $\text{Cu/InSe}$ ,  $\text{InSe/Cu}$  and  $\text{InSe/Cu/InSe}$ ) precursors in elemental Se vapour at temperatures around  $550^\circ\text{C}$  resulted in  $\text{CuInSe}_2$  thin films with superior structural properties. In an attempt to increase the band gap of these films, the selenium species were replaced by sulfur species during a solid-state diffusion process. Alternatively, gallium was introduced into the structure by replacing the  $\text{InSe/Cu/InSe}$  precursors with  $\text{InSe/Cu/GaSe}$  precursors. Important process parameters such as the deposition temperature of precursor elements, the selenization temperature in elemental Se vapour, as well as the concentration of gallium in the alloys were optimized during subsequent studies. From these systematic studies optimum experimental conditions were determined for the deposition of homogeneous  $\text{Cu}(\text{In,Ga})\text{Se}_2$  thin films. The monophasic nature of the quaternary alloys was confirmed by XRD studies, revealing a shift in the lattice spacing due to the homogeneous incorporation of gallium into the chalcopyrite lattice. Completed solar cell devices revealed open-circuit voltages above 500mV, which confirmed the increase in the band gap value of the absorber films.