Electrodeposited CIS-based Thin Films for Photoelectrochemical Hydrogen Production

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Abstract

Photoelectrochemical hydrogen production promises to be one of the most efficient solar to hydrogen conversion techniques. Large area fabrication and low-cost material requirements combine to make thin film materials a desirable option. Electrodeposition provides a low-cost, scalable technique for the production of large area thin film materials for this application. Electrodeposited $CuInSe_2$ (CIS) thin film materials have been extensively studied, however, their band gap is too low for application as a top junction in these devices. It is known that addition of Ga and S into the CIS lattice can increase the material band gap to within the desired range of 1.7 – 2.0eV[1]. The addition of sulfur in the electrodeposition process has proved to be extremely difficult. In this research, $Cu(In,Ga)Se_2$ materials were electrodeposited on molybdenum coated glass substrates, and then vapor enriched in several different atmospheres containing sulfur.

Copper in solution affects overall deposited film composition. Greater copper concentration in solution correlated to greater Cu and less Se deposited in the film. Successive depositions from the same fresh solution resulted in little change in the composition of the films. However, deposition from the same solution after sitting overnight, or from a different solution with the same composition, often resulted in deviation from the previous stoichiometry.

Annealing these precursor materials in a sulfur-containing atmosphere enriches them from the surface down. Due to diffusion limitations, sulfur is seen in higher concentration near the material surface versus the material bulk. Phase separation is evident in many of these materials, most likely due to this compositional gradient. Some materials show multiple band gap characteristics due to this effect. Figure 1 shows the XRD pattern of an enriched sample. This film shows a higher sulfur and gallium concentration at the surface. Splitting in the CIS peaks is seen, representing these variations in the lattice.

Films with a high Ga/In ratio, and S/Se = 1 show a band gap around 1.9eV, with a second apparent band gap in the CIS range. Films with a very low Ga/In ratio show a single, much lower band gap, closer to 1.1eV. All of the former films show splitting in the XRD patterns.

These materials show potential in attaining the appropriate band gap for the top junction in photoelectrochemical water splitting cells. However, consistent deposition methods, including sulfur incorporation, need further development. Phase separation and annealing losses are problems being addressed.

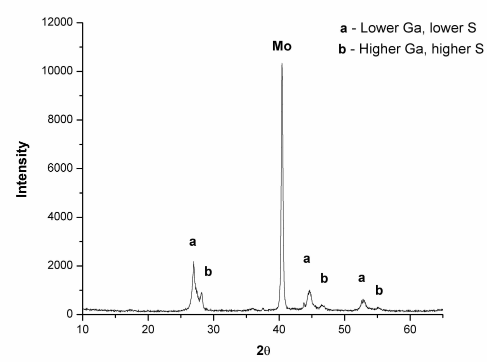

Figure 1. XRD pattern showing peak splitting due to annealing in a sulfur-containing atmosphere and consequent film inhomogeneity.

References

1. Leisch, J.E., et al., Solar Energy Materials and Solar Cells, 2003(81): p. 249-259.