

## ABSTRACT

Koeper, Mark J. PhD, Purdue University, May 2017. Solution Processing of Thin Film Kesterite Photovoltaics. Major Professor: Rakesh Agrawal.

Renewable energy technologies are increasingly the focus of new electrical power generation due to many concerns, including global warming, environmental pollution, and limitations of carbonaceous fuel reserves. Solar irradiance is the largest renewable energy resource available and therefore developing photovoltaics, the direct conversion of photons to electrical power, is an important area of research. Currently, silicon based photovoltaics dominate the market. In order to reduce capital costs and material usage, solution processing of thin film solar cells is currently under investigation. Here, nanoparticle based solar cells are studied as this solution processing technique provides a path to roll-to-roll fabrication and is shown to achieve high power conversion efficiencies (p.c.e.).

$\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  (CZTSSe) has been the focus of extensive research as an earth abundant, thin film solar cell material. However, CZTSSe is primarily limited in achieving high p.c.e. due to Cu-Zn related defects. In depth admittance spectroscopy is used to study the metastable behavior of CZTSSe indicating that one of the main defects, likely related to the Cu-Zn disorder, is formed during carrier injection. It is also demonstrated that this defect, as well as an additional lower energy defect, exhibit voltage independent activation energies which is interpreted as these defects originated from the bulk.

In depth optical and electrical analyses is presented on CZTSSe films with different processing conditions, including baseline conditions, oriented CZTSSe films, and low temperature annealing of CZTSSe (the latter shown to reduce Cu-Zn disorder). It is shown that oriented films increase defect densities creating worse performing solar

cells, and the orientation originates from large, sporadic grains. Low temperature annealing is demonstrated to change the defect properties such that the higher energy defect in admittance moves to higher activation energies, but the devices are still limited by high defect densities. This suggests novel processing conditions will not improve CZTSSe efficiencies.

Since alternate processing conditions do not decrease the Cu-Zn disorder, substituting Cu with Ag is also explored. Analyses indicates this cation replacement leads to improved defect properties consistent with reduced cation disorder, increased grain growth, and increased band gap values closer to the optimal value. However, despite these beneficial impacts the resulting photovoltaic solar cells demonstrate decreasing p.c.e. which is believed to be related to decreasing minority carrier concentrations.

Solution processing of copper free  $\text{Ag}_2\text{ZnSnSe}_4$  (AZTSe) films are also studied as a low defect, n-type absorber layer. It is shown the heating ramp rate is critical to forming phase pure films, and therefore a rapid thermal processor is critical to forming these films from nanoparticle based technologies. Initial research demonstrates 0.3% p.c.e., which while low indicates potential. Additionally, it is demonstrated that this material is not limited by similar defects observed in CZTSSe further indicating its promise.

Finally, suggested future research projects are presented with the goal of improving AZTSe films and nanoparticle based technologies in general. AZTSe based absorber layers is currently in the initial stages of development and therefore there is much to understand about its physical growth mechanisms, electrical, and optical properties. Additionally, a guide to semiconductor and photovoltaic characterization using electrical and optical analytical tools is presented.