ABSTRACT

Hages, Charles J. Ph.D. Purdue University, August 2015. Development and Characterization of Nanoparticle-based Kesterite Solar Cells. Major Professor: Rakesh Agrawal.

Kesterite solar cells based off of the $Cu_2ZnSn(S,Se)_4$ (CZTSSe) material system are a promising technology for earth-abundant photovoltaic applications. Thin-film absorbers fabricated from kesterite materials demonstrate a tunable band gap ideal for photovoltaic applications, high absorption coefficient ideal for low material usage, and success with low-cost, scalable, solution-based processing techniques. However, CZTSSe solar cells achieve low power-conversion efficiencies relative to other successful solar absorber technologies with cubic/tetragonal crystal structure, such as c-Si, GaAs, CdTe, and $Cu(In,Ga)Se_2$. In this work, the development of kesterite-based solar cells from nanocrystal inks is discussed in terms of understanding and improving device performance for this material system.

Herein, an overview of CZTSSe solar technology, nanoparticle synthesis, thin film formation, and optoelectronic characterization is presented, illustrating the challenges associated with the formation of high-quality quaternary semiconductors. Detailed optoelectronic and material characterization is used to develop an understanding of the fundamental limitations to improved device performance, with general applicability to the CZTSSe material system; namely, detailed analysis of the origin of voltage limitations commonly reported for CZTSSe solar cells is considered. Fundamental device performance limitations are associated here with a high propensity for detrimental defect formation in CZTSSe absorbers. Ultimately, an improved understanding of these device performance limitations and their association with the absorber material properties is used to develop novel thermal processing techniques to improve the absorber transport

properties. Optimized absorber processing has resulted in the fabrication of record performance nanocrystal-based CZTSSe solar cells.

In addition to novel CZTSSe absorber processing, modification of the absorber properties is also presented in terms of alloyed-kesterite materials based off of the CZTSSe material system. Namely, the development of Ge-alloyed $Cu_2Zn(Sn,Ge)(S,Se)_4$ (CZTGeSSe) and Ag-alloyed $(Ag,Cu)ZnSnSe_4$ (ACZTSe) absorbers is described. CZTGeSSe and ACZTSe are shown to demonstrate promise as alternative kesterite material absorbers due to improved optoelectronic properties and device performance relative to CZTSSe. Record device performance is reported here for CZTGeSSe and ACZTSe solar cells.

Lastly, detailed optoelectronic characterization – including current-voltage, quantum efficiency, and capacitance spectroscopy – is used to develop novel analysis methodologies for non-ideal diodes. This work demonstrates how traditional optoelectronic characterization analysis techniques, commonly applied to CZTSSe solar cells, can result in misinterpretation of device limitations if non-ideal diode behavior is not accounted for in the diode analysis. Here, a consideration of the complex material properties in the developed optoelectronic characterization analysis methods has resulted in improved accuracy in understanding fundamental device performance limitations in kesterite solar cells.