SISGR: Defect Studies of CZTSSe & Related Thin Film Photovoltaic Materials
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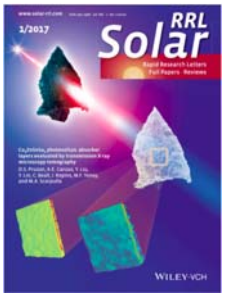
Program Scope

The research objectives of this project centered around investigations of the basic properties of $Cu_2ZnSn(S,Se)_4$ especially the electronic defects in the bulk, at the interface with heterojunction partners used in solar cells, and at the polycrystalline grain boundaries. In the course of the project we addressed many specific sub-areas in 17 peer reviewed publications listed at the end of this report (2 more are also in preparation). The impact of this research is to generate basic but critical materials knowledge about this emerging alloy system that may be capable of photovoltaic efficiency on par with CdTe and CIGS but at lower cost and having the benefit of avoiding constraints on scale-up from rare and expensive elements using earth abundant elements. In the final phase of this project, Prof. Scarpulla worked with Dr. Kirstin Alberi at NREL and rigorously solved a theoretical problem that is general across all semiconductors – the prediction of point defect concentrations in the presence of excess carriers.

Recent Progress (other topics have been summarized in past reports)

Origins of electronic disorder in CZTS

We completed our data processing and analysis of a large data set of transmission x-ray microscopy tomography taken at SSRL on layers of CZTSe deposited as thin polycrystalline films. Also, we collaborated with NREL transmission electron microscopy scientists on CZTSSe singles. Many techniques have revealed evidence of electronic disorder (both fluctuating potentials and bandgaps) in CZTSSe alloys. We used these real-space compositional measurements to investigate the origins and lengthscales of these energetic variations.



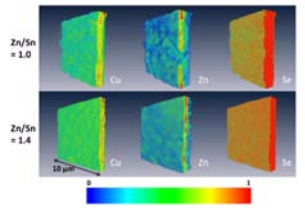
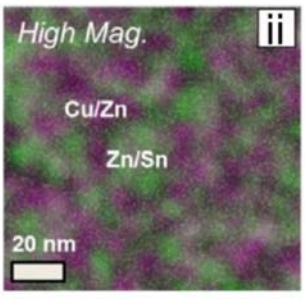


Figure 2. Final elemental compositional intensity maps for CZTSe films for samples with Zn/Sn = 1.0 and Zn/Sn = 1.4. Intensities in both samples are normalized on the same scale from 0 (blue) to 1 (red) based on the highest concentration in the Se layers. Primarily qualitative analysis is done on these reconstructions, including surface roughness, relative concentrations and individual elemental distributions.

In the x-ray tomography work, we were able to simultaneously measure a unique combination of spatial resolution near 200 nm and area of study 10's of um. Additionally, the SSRL beamline allowed us to generate element-specific tomographic reconstructions of the samples. We then analyzed the Cu and Zn spatial densities and showed that these two elements in particular tended to be anticorrelated on the lengthscale of grains. In other words, the origins of compositional and thus electronic inhomogeneity are not simply at the atomic scale in point defects but also at the scale of the microstructure – adjacent grains appear to have significantly different stoichiometry. These are novel findings that broaden the scope of understanding. The work was chosen for the cover article for Solar RRL.

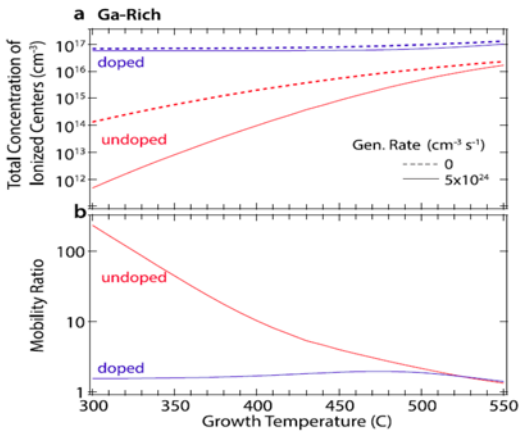
Similarly, our TEM study revealed novel results on a different lengthscale. In this work we obtained single crystals of CZTS from a collaborator in Japan and studied the compositional fluctuations on nm lengthscales with direct imaging. These bulk crystal samples were very slowly cooled from the growth temperature so approach the thermodynamic ground state for the Cu_2ZnSnS_4 material, somewhat in contrast to polycrystalline thin films deposited in vacuum which are used for thin film solar cells. In these single crystalline regions, we found statistically-significant composition variations for Cu, Zn, and Sn on 20 nm



lengthscales – similar to what might be expected for spinodal decomposition. This shows that even on the smallest lengthscales of a few unit cells CZTS is inhomogeneous.

Theory of the Influence of Excess Carriers on Point Defect Formation

For nearly a century since the work of Kroger, it has been understood that the equilibrium concentrations of point defects in semiconductors and insulators are determined by the Fermi level (which is the chemical potential of both electrons and holes in equilibrium). For example, the formation enthalpy of a donor defect will increase with increasing n-type doping (higher Fermi level) and decrease with increasing p-type doping (lower Fermi level). Especially in compound semiconductors with wide bandgaps, this effect can lead to doping limits, high compensation of extrinsic doping, and formation of undesirable trap states.



(top) Predicted concentrations of Ga antisites as function of temperature for n-type doped and unintentionally-doped GaSb. Solid lines are for illuminated and dashed for dark. (bottom) Ratio of electron mobility for illuminated growth vv dark growth as function of temperature for undoped nad doped cases.

Working with Dr. Kirstin Alberi (NREL), we developed a full, rigorous theory of how excess carriers affect the formation enthalpy of defects, allowing cases beyond thermal equilibrium in the dark such as while currents are flowing or under illumination or ionizing radiation) to be analyzed. In these cases, there are separate quasi-Fermi levels representing the chemical potentials of electrons and holes. The theory essentially merges the established quasi-chemical formalism for defect populations with detailed balance for the rates of capture and emission from the defect's charge transition level. The essential physics is that the excess carriers change the occupation statistics of the defect charge states compared to the thermal equilibrium case.

The most important prediction of the theory is that in the case of compensating defects (i.e. acceptor-like defects in n-type doped material) are suppressed by the presence of excess carriers. Thus it suggest that growing or annealing semiconductors with above-bandgap illumination or with current injection can yield qualitatively different results in material properties than those typically obtained with thermal equilibrium methods. Also, it should be relevant in understanding how materials change over time when used in devices – for example in LEDs where high concentrations of carriers are injected during operation. The initial paper using GaSb as a model system (because only one defect, the Ga antisite, occurs in significant concentrations) was published in Scientific Reports and follow-up papers with slight improvements to the model and considering wide bandgap materials are in review and preparation.

Conclusions

This project was successful in elucidating some of the fundamental materials properties of $Cu_2ZnSn(S,Se)_4$ materials and their origins. It also allowed the development of a new theory of interactions between

Journal Publications (each publication listed here acknowledges project DE-SC0001630)

D.S. Pruzan, Y. Liu, A.E. Caruso, Y. Lin, C. Beall, I. Repins, M.F. Toney, M.A. Scarpulla.
Grain to Grain Composition fluctuations in $Cu_2ZnSnSe_4$ thin film solar cells measured by transmission x-ray tomography
Solar RRL, 1(1) 1600024 (2017). DOI: http://dx.doi.org/10.1002/solr.201600024 . (Front cover article)

A Nagaoka, MA Scarpulla, and K Yoshino
Na-doped Cu_2ZnSnS_4 single crystal grown by traveling-heater method
Journal of Crystal Growth **453**, 119-123 (2016). DOI: http://dx.doi.org/10.1016/j.jcrysgro.2016.08.014

Jeffery A. Aguiar, Mehmet E. Erkan, Dennis Pruzan, Akira Nagaoka, Kenji Yoshino, Helio Moutinho, Mowafak Al-Jassim, and Michael A. Scarpulla
Cation ratio fluctuations in Cu_2ZnSnS_4 at the 20 nm length scale investigated by analytical electron microscopy
Physica Status Solidi A 213: 2392–2399 (2016) DOI: http://dx.doi.org/10.1002/pssa.201600060 .

K. Alberi and M.A. Scarpulla
Suppression of native defect formation during semiconductor processing via excess carrier generation
Scientific Reports **6**, 27954 (2016). DOI: http://dx.doi.org/10.1038/srep27954

Mehmet Eray Erkan, Vardaan Chawla, and Michael A. Scarpulla
Reduced defect density at CZTSSe/CdS interface by atomic layer deposition of Al_2O_3
J. Applied Physics **119**, 194504 (2016). DOI: http://dx.doi.org/10.1063/1.4948947

Matthew M. Nowell, Mike A. Scarpulla, Naba R. Paudel, Kristppher A. Wieland, Alvin D. Compaan, and Xiangxin Liu
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Akira Nagaoka, Ryoji Katsube, Shigeru Nakatsuka, Kenji Yoshino, Tomoyasu Taniyama, Hideto Miyake, Koichi Kakimoto, Michael A. Scarpulla, and Yoshitaro Nose
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J. Crystal Growth, **423** pp. 9-15 (2015). http://dx.doi.org/10.1016/j.jcrysgro.2015.04.012

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Solution growth of chalcopyrite compounds single crystal
Renewable Energy **79**, pp. 127–130 (2015). http://dx.doi.org/10.1016/j.renene.2014.10.015

Mehmet Eray Erkan, Vardaan Chawla, Ingrid Repins, and Michael A. Scarpulla
Interplay between surface preparation and device performance in CZTSSe solar cells: Effects of KCN and NH_4OH etching
Solar Energy Materials and Solar Cells **136** 78-85 (2015); http://dx.doi.org/10.1016/j.solmat.2015.01.006

Hui Du, Fei Yan, Matthew Young, Bobby To, Chun-Sheng Jiang, Pat Dippo, Darius Kuciauskas, Zhenhuan Chi, Elizabeth A. Lund, Chris Hancock, Win Maw Hlaing OO, Mike A. Scarpulla and Glenn Teeter,

Investigation of combinatorial coevaporated thin film Cu_2ZnSnS_4. I. Temperature effect, crystalline phases, morphology, and photoluminescence
Journal of Applied Physics **115**, 173502 (2014); http://dx.doi.org/10.1063/1.4871664

Elizabeth A. Lund, Hui Du, Win Maw Hlaing OO, Glenn Teeter, and Michael A. Scarpulla
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A Quasichemical Model of Native Point Defect Equilibrium in Cu_2ZnSnS_4 (CZTS) and Application to One-Zone Annealing
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W.M. Hlaing Oo, J.L. Johnson, A. Bhatia, E.A. Lund, M.M. Nowell, and M.A. Scarpulla
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2016 Conference Record of the IEEE Photovoltaic Specialists Conference
2016-November,7750024, pp. 2195-2199

Comparison and interpretation of admittance spectroscopy and deep level transient spectroscopy from co-evaporated and solution-deposited Cu2ZnSn(Sx, Se1-x)4 solar cells
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Effects of back contact resistance, depletion width and relaxation time distributions in admittance spectroscopy of CZTSe devices Caruso, A.E., Pruzan, D.S., Lund, E.A., Scarpulla, M.A.
2015 2015 IEEE 42nd Photovoltaic Specialist Conference, PVSC 2015 7356015

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Caruso, A.E., Pruzan, D.S., Kosyak, V., (...), Repins, I., Scarpulla, M.A.
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