

BAPVC Annual Project Report

Project Title: Fundamental Modeling of Chalcopyrite Solar Cells

PI: Scott T. Dunham, University of Washington, Seattle

E-mail: dunham@ee.washington.edu

Summary:

This project deals with theoretical modeling and calculation of the properties of defects in CIGS and CZTS absorber materials. The long term goal is predictive models for defect evolution, impurity kinetics and phase transformation in these materials to enable optimization of fabrication processes for maximum cell efficiency and reliability. A tool for calculation of the concentrations of dominant defects has been developed based on ab initio calculations combined with stoichiometric input data, while calculation of barrier heights leads to estimation of diffusivities. Monte Carlo simulations are used to connect these results to nanoscale ordering and impurity redistribution, with results connected to device simulation to predict impact on performance.

Key Accomplishments:

Fundamental understanding of the complex behavior of impurities and point defects in CIGS ($\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$) and CZTSSe ($\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$) under realistic processing conditions is essential for effective applications in thin film solar cell devices. Last year, the group developed a tool for calculation of the concentrations of intrinsic lattice defects at given CZTS and CIGS stoichiometries. A method was developed that makes use of defect formation energies from ab initio calculations combined with mass action relations between the defects to enable calculation of concentrations of defects in all accessible charge states under a given set of stoichiometric constraints and processing temperature. This year, that method was extended to allow for use of an arbitrary combination of stoichiometric constraints and chemical potentials in the presence of impurities such as sodium, potassium, and cadmium and associated extrinsic defect complexes. In addition, migration barrier heights calculated with the nudged elastic band method provide insight into the effect of the local lattice structure on the diffusion of dominant point defects. Figures 1 and 2 illustrate typical results. Figure 1 shows the behavior of dominant defect concentrations in $\text{Na}+\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ for $x = 0.9$ under varying anion/cation ratio ω for Cu-poor conditions and a typical sodium concentration of 0.1%. In this case, the defect concentrations summed over all charged states are shown, and the material transitions from n-type to p-type at $\omega=1.024$. Figure 2 compares the energy barriers for nearest-neighbor copper vacancy-mediated diffusion of Cu, Na_{Cu} , and K_{Cu} computed with density function theory and the nudged elastic band method. Our results for various CIGS compositions within the stable range of chemical potentials suggest that the formation of $\text{Na}_{\text{III}}^{2-}$ and $\text{K}_{\text{III}}^{2-}$ donors (where III = In or Ga) either dominates or directly competes with the formation of neutral Na_{Cu}^0 and K_{Cu}^0 substitutionals, respectively. Moreover, the low barrier for diffusion of sodium and potassium via hopping on the copper sublattice may provide an energetically favorable pathway through which the local valence structure is repaired.

One of the major goals of this project is to understand ordering and phase separation in CIGS. Determination of phases in CIGS can be attained by canonical Monte Carlo simulations. The group has performed a comparative analysis of a wide range of functional forms to approximate

the energy of arbitrary CIGS configurations. These configurations include those with intrinsic defect clusters such as the complex containing two copper vacancies and a group-III-on-Cu antisite, which may be responsible for the existence of ordered defect phases. These energy functional models are used as the basis for the canonical Monte Carlo simulation. The results of these simulations have been used to generate classes of stable CIGS configurations at various temperatures, revealing the formation of indium/vacancy-rich regions as illustrated in Fig. 3.

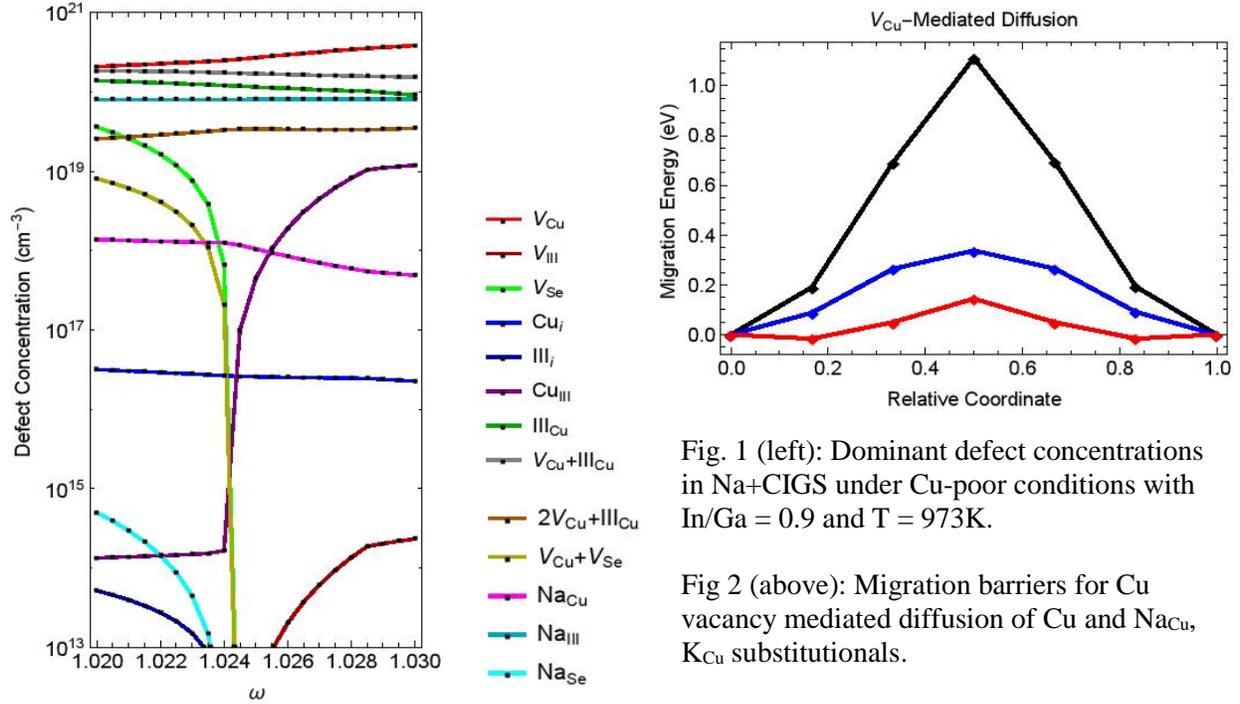


Fig. 1 (left): Dominant defect concentrations in Na+CIGS under Cu-poor conditions with In/Ga = 0.9 and T = 973K.

Fig 2 (above): Migration barriers for Cu vacancy mediated diffusion of Cu and Na_{Cu}, K_{Cu} substitutionals.

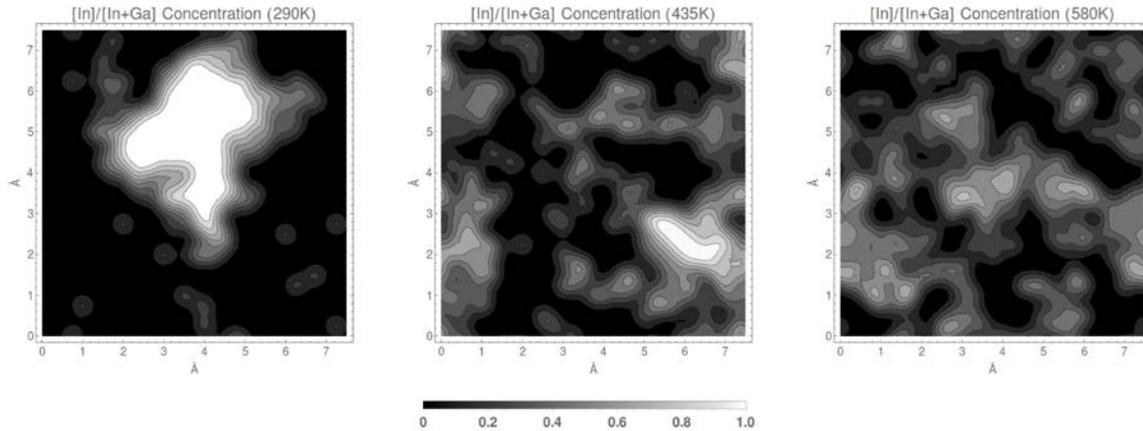


Fig. 3. Contour plot of In fraction after MC simulation at 290K, 435K and 560K for systems with 1800 cation sites (3600 total sites), an average [In]/[In+Ga] fraction of 25%, and an average vacancy concentration of 2.5% of cation sites.

Future Work:

The plan for the coming year is to extend the analysis to a broader range of impurities and explore the impact of impurity diffusion and phase separation on CIGS device performance.