BAPVC Annual Project Report

Project Title: Fundamental Modeling of Chalcopyrite Solar Cells

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Summary:

This project deals with theoretical modeling and calculation of defect properties in CIGS and CZTS absorber materials. The concentrations of dominant defects are calculated based on ab initio and stoichiometric input data, allowing for a prediction of recombination processes which lower the cell efficiency. Calculation of defect concentrations together with calculated diffusion barrier heights leads to estimation of diffusivities. The long term goal is predictive models for defect evolution, impurity kinetics and phase transformation in these materials.

Key Accomplishments:

A main challenge for the efficient application of thin film solar cells based on CIGS ($Cu_2In_xGa_{1-x}Se_4$) and CZTSSe ($Cu_2ZnSnS_xSe_{1-x}$) is gaining a more fundamental understanding of the complex intrinsic defect behavior. A central part of this project deals with the calculation of 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. Fig. 1(a) shows an example of calculated defect concentrations in the Cu-poor and Zn-rich stoichiometry range in CZTS, which is experimentally known to lead to cell efficiencies of 5-8%. The dominant defects at these compositions turn out to be the charge compensated complexes V_{Cu}+Zn_{Cu} and Zn_{Sn}+2Zn_{Cu}, as well as Cu_{Zn} antisites and Cu vacancies (V_{Cu}), both in neutral and negative charge states.

With the knowledge of defect concentrations at different charge states, the application of Shockley-Read-Hall theory allows for the calculation of recombination rates for each possible ionization process having a transition energy in the band gap. For system in Fig. 1(a) for example, the Cu_{Zn}[-/0] process is predicted to have the highest impact on the total recombination rate. This is due to the high concentration of Cu_{Zn} compared to all other defects having ionization levels in the band gap, even though the Cu_{Zn}[-/0] level is rather shallow. For CZTSSe, these predictions are compared to combinatorial experiments from the Hillhouse group.

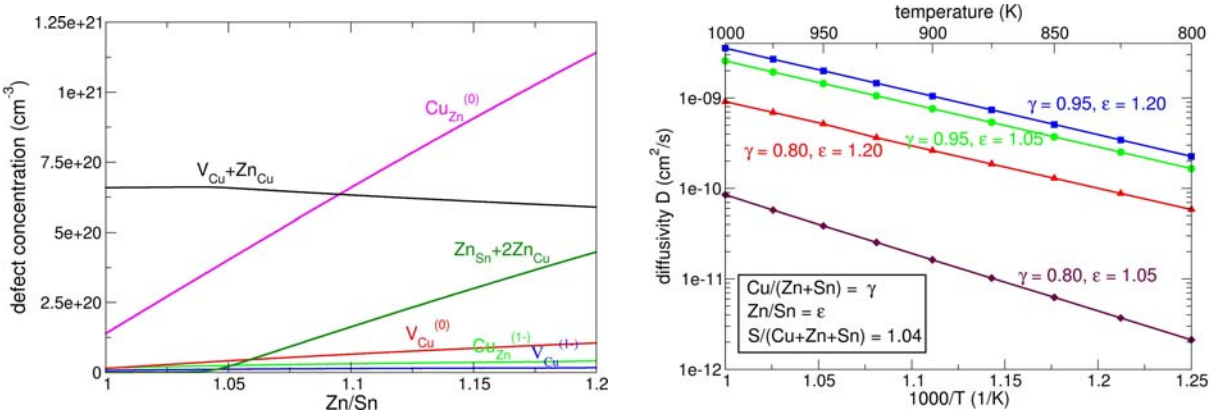

Fig. 1. (a) Concentrations of dominant defects in CZTS at Cu-poor [Cu/(Zn+Sn)=0.9] and Zn-rich conditions, a anion/cation ratio S/(Cu+Zn+Sn)=1.03, and at T=900 K. (b) Diffusivities of Cu into nearest cation Cu vacancies in CZTS as a function of temperature and stoichiometry

The knowledge of barrier heights and vacancy concentrations, calculated as described above, allows for the determination of the diffusivities of atomic components at a given temperature and stoichiometry (see Fig. 1(b)). The calculation of energy barriers with density functional theory and the nudged elastic band method leads to the result, that Cu diffusion into Cu vacancies via nearest cation neighbor hopping has the highest rate and controls the diffusion process.

A central goal of this project is to study the influence of temperature and entropy on the stability of CIGS and CZTS, and the possibility of separation into competitive phases by performing Kinetic Lattice Monte Carlo simulations. For this purpose, a catalog of energies and diffusion barrier heights has to be provided based on ab initio calculations. In CIS and CIGS, the complex composed of 2 copper vacancies and one indium on copper antisite, having a lower formation energy than the individual components, is believed to play an important role in defect behavior and the existence of ordered defect phases (e.g. $CuIn_3Se_5$ or $CuIn_5Se_8$). This has a direct influence on band gap variation and cell efficiency. To gain insight into the characteristics of this defect, the formation energies of $2V_{Cu}+In_{Cu}$ (or Ga_{Cu}) configurations in CIGS, which differ by the relative distance and position of the three constituents to each other, have been calculated with ab initio methods and compared (see Fig. 2 on the left). It can be seen, that the defect with the In_{Cu} being in a symmetry center of the two vacancies [(b)] has the lowest formation energy due to optimal charge compensation. In general, configurations in which the two negatively charged vacancies are close to each other without a positively charged In_{Cu} in between, are less favorable. In contrast to previous reports, we find little difference between the formation and binding energies of these complexes between CIS and CGS. Migration of Cu atoms into the vacancies of the defect complex is also considered (see Fig. 2 on the right). Since processes like these always create and fill a Cu vacancy, they only change the configuration of the defect complex. It is seen that the migration barrier height, calculated with density functional theory and the nudged elastic band method, depends on the environment of the moving Cu atoms. Thus, the mobility of a Cu vacancy depends on the atomic arrangement in the direction of possible movement.

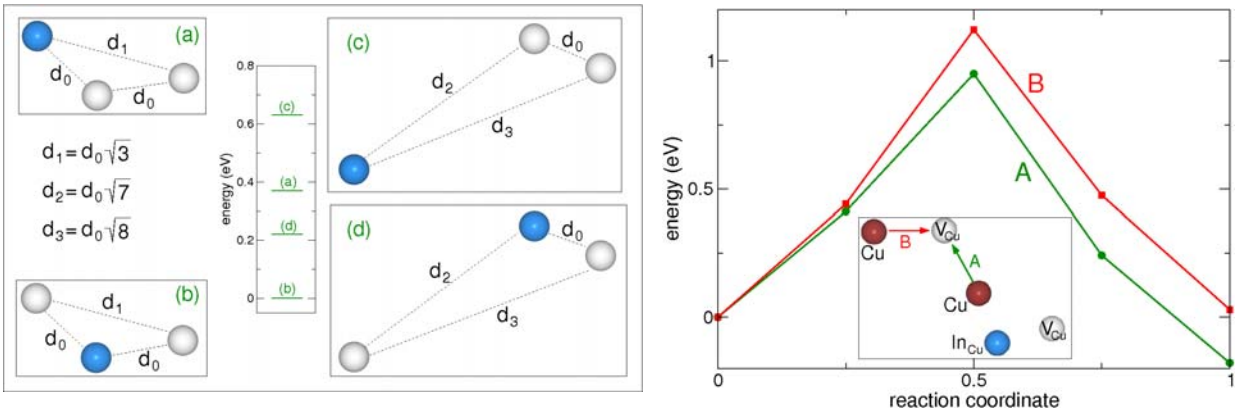

Fig. 2. Left: Comparison of the formation energies of different configurations of the defect complex $2V_{Cu}+In_{Cu}$ in CIS (V_{Cu}: white spheres, In_{Cu}: blue spheres). The configurations differ by the distances (d_0: nearest cation neighbor distance) and relative positions of the three constituents to each other. Right: Migration barrier heights of Cu into Cu vacancies belonging to $2V_{Cu}+In_{Cu}$.

Future Work:

The long term goal of this project is to develop accurate models for the energies and diffusion barriers of arbitrary configurations based on ab initio calculations and to implement these models within large scale Kinetic Lattice Monte Carlo simulations. This will allow for a prediction of atomic rearrangement, stability and phase separation as function of temperatures in CIGS and CZTSSe systems.