Unified numerical solver for modeling metastability and reliability of CdTe solar cells

D Vasileska[1], A Shaik[1], D Guo[1], C Ringhofer[1], D Brinkman[2], D Krasikov[3] and I Sankin[3]

[1]Arizona State University, USA, [2]San Jose State University, USA, [3]First Solar, USA

CdTe is the most successful thin-film PV (TFPV) technology in the market to date. Recent advances in CdTe TFPVs have boosted module efficiency from 12% to beyond 18% and these results were achieved on the basis of costly empirical research and development that was only weakly supported by theoretical guidance. There are two primary directions of improvement for this technology: (1) *improvements in efficiency*, primarily the open-circuit voltage (Voc), and (2) *reduction of metastabilities and long-term degradation rates*. The remaining challenges are: (1) understanding of *doping formation*, which is clouded by the presence of self-compensation and a multitude of defects, (2) understanding of *recombination*, which is challenged by the presence of external and internal (GB) interfaces, and (3) understanding of *degradation* that is influenced by the fact that all of the above can change under field conditions. In parallel, the empirical evolution to cell efficiencies above 21% was enabled through the increased use of band-gap grading in the absorber structures, which further complicates the defect physics of the material and makes our ability to predict performance or stability ever more challenging. *The above mentioned problems must be treated to the degree that they can become predictive to polycrystalline device behaviour and replace empirical "trial and error" with an "engineering by design" approach.* Therefore, the need for the Unified Numerical Solver depicted in Figure 1 which bridges physics across multiple length and time scales. Species under investigation are described by sets of low-level parameters that include (depending on the model level) formation energy, ionization energies and diffusion coefficients for different charged states, solubility limits, grain boundary segregation parameters, etc. System evolution for a given set of stressors (temperature, light, and bias) is calculated based on provided initial conditions (distributions). The solver outputs the distributions of charged and neutral dopants and recombination states. Given device geometry and band structure of semiconductors, the solver uses these distributions to simulate IV, CV, and CV trends that could be confirmed experimentally on real device structures.

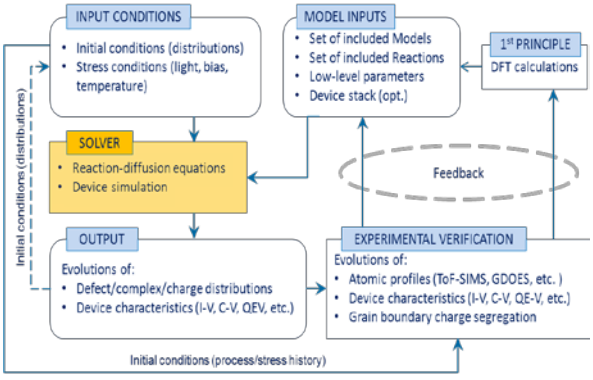

Figure 1: Schematic block-diagram illustrates the use of the solver to tune the model and study CdTe device metastability.

We have demonstrated functional prototypes of 1D and 2D Unified Numerical solvers that have already provided unique insight into physical processes behind doping formation and metastabilities observed in thin-film CdTe devices. In particular, we have explained the long-standing mystery of "Cu solubility limits" in CdTe by the difference in the formation energies of Cu-related defects in the CdTe absorber and the Cu source layer. Thus we were able to accurately simulate atomic Cu profiles obtained in as-fabricated devices for different annealing/quenching conditions. We have also determined the role of donor-acceptor pairs (DAP) in the diffusion of Cu, when the dissociation energy of Cu(i)-Cu(Cd) complex was found to dominate

Cu migration in CdTe. When simulating Cu diffusion profiles obtained at different annealing conditions, we found pronounced discrepancy between fitted and DFT-calculated values of Cu diffusion barrier (0.7eV vs. 0.46eV, correspondingly). To explain this contradiction, we have analyzed the energy path for dissociation of Cu complex and found exact match to effective Cu diffusion barrier fitted by the Unified Solver. Experimental data overlayed with simulation curves and DFT analysis are shown in Fig.2. Yet another interesting discovery we have made, that shed some light on the nature of metastabilities in CdTe absorbers, is illustrated in Fig. 3. Experiment performed on Colorado State University samples suggested that under zero bias, atomic concentration of Cu in CdTe absorber can drop by 50% over several weeks at field temperature (e.g., 65°C). At the same time, total net acceptor concentration in the bulk remains positive showing changes in the range of < 1e15cm-3, which means bulk regions lose both Cu donors and Cu acceptors. Since only interstitial Cu donor ions can diffuse at such low temperatures, this observation has led to conclusion that in the presence of Cd(i), Cu/Cd exchange reactions happen at high rate already at 65°C. DFT calculations performed to explain observed phenomena have confirmed this hypothesis.

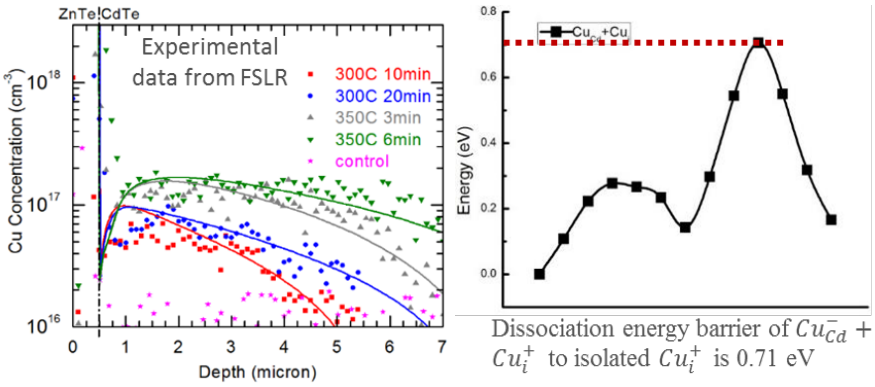

Figure 2: DFT-calculated dissociation energy barrier of Cu(i)-Cu(Cd) is 0.71eV (right plot) that corresponds to effective diffusion barrier fitted from experimental data (left plot). Note that DFT-calculated diffusion barrier for the Cu(i) is only 0.46eV.

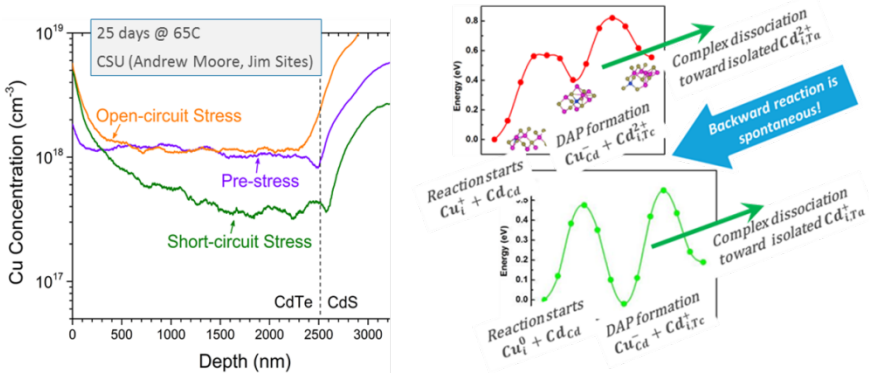

Figure 3: Results of DFT calculations (right plot) in our previous work using Unified Numerical Solver explain observed instability of Cu doping (left plot) in the presence of interstitial Cd.

We consider the presented Unified Numerical Solver as the best scientific approach to study formation and evolution of defects responsible for the performance of TFPV device as it accounts for all the components depicted in Fig. 1.