Unified Numerical Solver for Modeling Device Metastabilities in CdTe Thin-Film PV

Dragica Vasileska[1], Igor Sankin[2], James Sites[3], Da Guo[1], Andy Moore[3], Daniel Brinkman[1], Dmitry Krasikov[2], Stephan Lany[4], Abdul Shaik[1]

[1]*Arizona State University*, [2]*First Solar*, [3]*Colorado State University*, [4]*NREL*

Project Objective: *The Unified Solver proposed to be developed as part of this project will enable the analysis of polycrystalline PV devices at an unprecedented depth. Greater depth, however, implies a greater challenge in obtaining accurate values in the Solver inputs. In this project, input parameters will be taken from the literature or derived from first-principle calculation, and will be fine-tuned through validation experiments. Systematic approaches to calculate the key input parameters will be developed. While the uncertainty in the input parameters may present the most significant risk to this project, a working Solver will allow us to validate results and chemical trends in a targeted approach. The existence of GBs cannot be ignored and will be embraced as a critical feature in the Solver. Additionally, a device solver will be an integral component of the Unified Solver, since drift and diffusion processes are influenced by the presence of electric fields, which may well be influenced by GBs and other impurities. A closed solution to the entire system will be developed.*

Need for PREDICTS

Without "unified infrastructure", disciplines do not interact at critical levels:

Device Characterization: Needs accurate models to be interpreted correctly

Semiconductor models: Lack knowledge of impurity distributions and parameters

Kinetic equations: Can calculate distributions, but need parameters and Fermi level

DFT: Can calculate low-level parameters but neither direct or indirect verification available

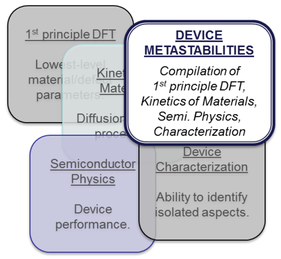
A multi-level Unified solver allows:

DFT to feed to material kinetics and semiconductor models

Material kinetics and semiconductor equations solved as self-consistent system in time and quasi-3D domain

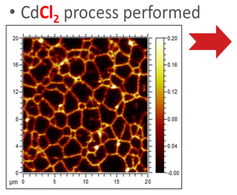
Experiment feeds back to theory, verifies models and calibrates parameters

Stage is set for understanding and accurate prediction of metastable phenomena



Prototypical Fabrication Sequence of CdTe Solar Cells:

- CdTe film deposition
- CdCl_2 process performed



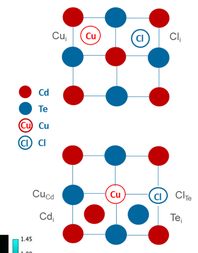
- Passivation process involving $CdCl_2$ treatment is crucial to the device performance.
- The success of the treatment remains mysterious:
  - How Cl works?
    - Grain growth and recrystallization.
    - Passivate deep traps.
    - Optimize carrier collection.
  - How Cl gets there?
    - Why Cl segregates along the grain boundaries?

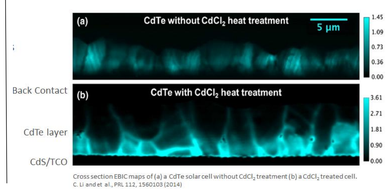
2D Simulation a MUST!

- Film is coated with ZnTe:**Cu** followed by an annealing at a certain temperature to form a back contact
  - Cu on substitutional site → **ACCEPTOR** (p-type dopant)
  - Cu on interstitial site → **DONOR** (n-type dopant)

Physical Model

- Intrinsic Defects in CdTe:
  - **Cd_i(0/2+), V_{Cd}(0/2-),** Te_i, Cd_{Te} …
- Extrinsic Defects in CdTe:
  - Cu Defects
    Cu_i(0/+), Cu_{Cd}(0/-), Cd_i-Cu_{Cd}(0/+) …
  - Cl Defects
    Cl_i(0/±), Cl_{Te}(0/+), Cl_{Te}-V_{Cd}(0/-) …
  - Cu-Cl Complexes
    Cl_{Te}-Cu_{Cd}(0), Cl_i-Cu_{Cd}…





Cross section EBIC maps of (a) a CdTe solar cell without $CdCl_2$ treatment (b) a $CdCl_2$ treated cell. C. Li and et. al., PRL 112, 156010 (2014)

Cl decoration of Grain Boundaries

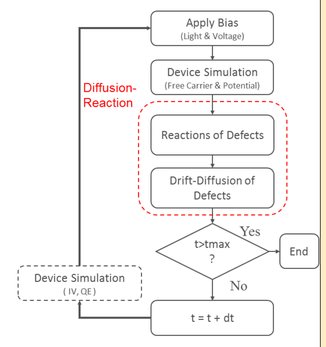
Mathematical Model

- Implicit Reaction Scheme isolated from Diffusion-Reaction Equations
  - Avoid negative concentration
  - Maintain conservation

$$\frac{\partial[X]}{\partial t} = R_X, \frac{\partial[X]}{\partial t} = J_X$$

- Solution of Drift-Diffusion Equations
  - Scharfetter-Gummel discretization
  - Implicit Euler time discretization
  - LU-Decomposition/Backslash

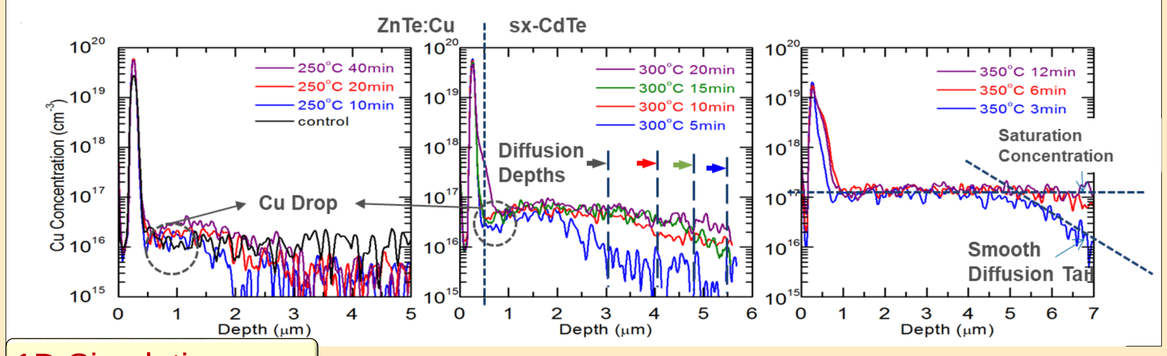
$$\frac{\partial[X]}{\partial t} = \frac{X_i^{new} - X_i^{old}}{\Delta t} = D_X\left(\frac{d[X]}{dx} + \frac{[X]}{kT}\frac{d[q\varphi + G]}{dx}\right)$$



*Reactions are solved sequentially in PREDICTS for both 1D and 2D case.

Experimental Data

Single Crystal CdTe Anneal



DFT Calculations

Goal: Develop defect diffusion theory. Calculate the defect properties such as:

- defect formation energy,
- ionization energy,
- defects interaction energy,
- diffusion path,
- diffusion energy barrier, etc.,

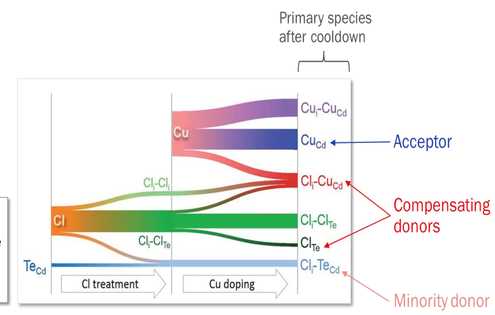
in both bulk and grain boundaries.

Bimolecular defect reactions formalism: $R_1 + R_2 \rightarrow P$

	Cl_i^{-1}	Cl_i^{+1}	Cl_{Te}^{+1}	Te_i^{0}	Te_i^{+2}	Te_{Cd}^{0}	Te_{Cd}^{+2}	Cu_i^{+1}	Cu_{Cd}^{0}	Cu_{Cd}^{-1}	Cd_i^{+2}	V_{Cd}^{-2}
Cl_i^{-1}	-0.04											
Cl_i^{+1}	-0.82	-0.72										
Cl_{Te}^{+1}	-1.02	+0.37	+0.02									
Te_i^{0}	-0.58	+1.07	-0.65	+0.44								
Te_i^{+2}	+0.49	-0.46	+0.32	-1.42	-0.85							
Te_{Cd}^{0}	-0.24	-1.46	-0.44	-1.45	-1.49	0.54						
Te_{Cd}^{+2}	-1.88	-0.88	+0.16	-1.23	-0.68	-0.79	-0.03					
Cu_i^{+1}	-0.04	-0.33	+0.01	-0.47	-0.11	-0.57	+0.05	+0.16				
Cu_{Cd}^{0}	-0.58	-0.48	-0.41	-0.65	-1.09	-0.72	-0.68	-0.40	-0.23			
Cu_{Cd}^{-1}	+0.62	-0.65	-0.52	-0.20	-1.31	-0.04	-0.74	-0.37	-0.22	-0.07		
Cd_i^{+2}	+1.08	-0.14	+0.04	-0.54	+0.12	-0.48	+0.58	+0.02	-0.33	-1.00	+0.02	
V_{Cd}^{-2}	+0.56	-0.63	-0.74	-0.26	-2.12	0.33	-0.47	-1.50	N/A	N/A	-2.60	+0.55

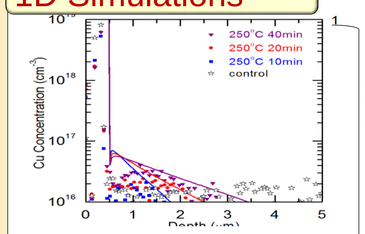
Calculated enthalpies of reactions between the point defects

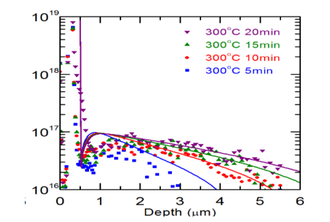
- ✓ 216-atoms supercell, HSE06
- ✓ VASP, MedeA® sofware environment
- ✓ Ohio Supercomputer Center

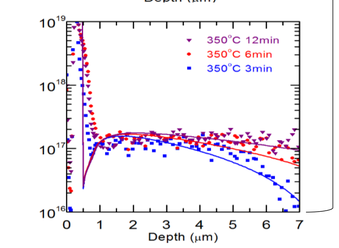


D. Krasikov and I. Sankin, "Defect interactions and the role of complexes in the CdTe solar cell absorber", *J. Mater. Chem. A*, 2017, Vol. 5, pp. 3503-3513.
(***contributed talk at Spring MRS Meeting 2017***) Dmitry Krasikov, I. Sankin, A. Alemu, "Influence of Defects Interactions on the Properties of CdTe:Cl,Cu Solar Cell Absorber".

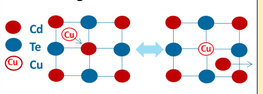
1D Simulations





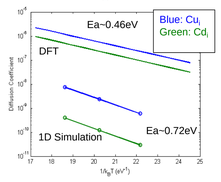


Cu_i & Cu_{Cd} defect system investigated first:

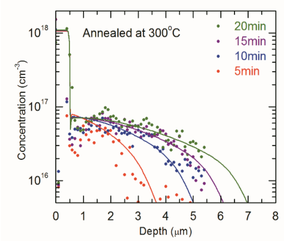


$$Cu_i^{+} + Cd_{Cd} \underset{Backward}{\overset{Forward}{\leftrightarrow}} Cu_{Cd}^{-} + Cd_i^{2+}$$

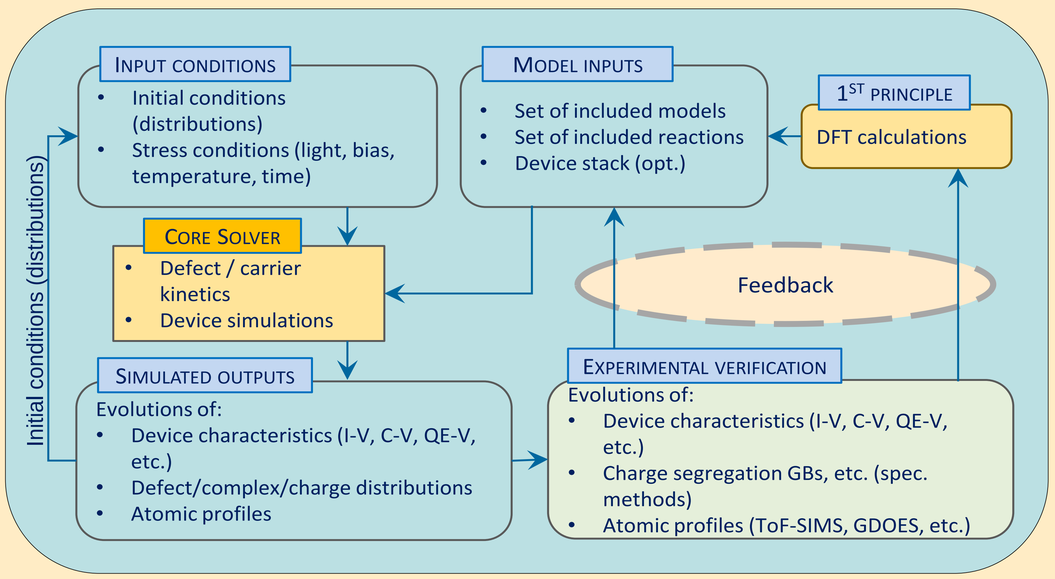
- Saturation behavior established as equilibrium of defect chemistry.
- Smooth diffusion tail formed by internal electric field.
- Cu drop near interface achieved by Cu back diffusion during cool down.
- Compensation between Cu_i/Cd_i and Cu_{Cd}, 3x10^{15} cm^{-3} hole density.



- Discrepancy presented between DFT and fitted diffusion parameters.
- The employed diffusion barrier (0.72eV) was found to be close to the DFT calculated dissociation energy of Cu_i-Cu_{Cd}, 0.71eV
- Expand our model with formation and dissociation of Cu complexes.



Da Guo, Daniel Brinkman, Abdul R. Shaik, I. Sankin, D. Krasikov, Christian Ringhofer and Dragica Vasileska, "Modeling Metastability in CdTe Solar cells due to Cu Migration", Springer, Book Ed. by Roderick Melnik, in press (22 pages).



Dissemination on nanoHUB.org

1D solver: 53 Users + 1 Citation

2D solver: 45 Users

2D Effort: Grain Boundaries

Used Slotboom Variables $u_i = X_i e^{\frac{\theta_i \varphi}{U_T}}$

Used Finite Element Method

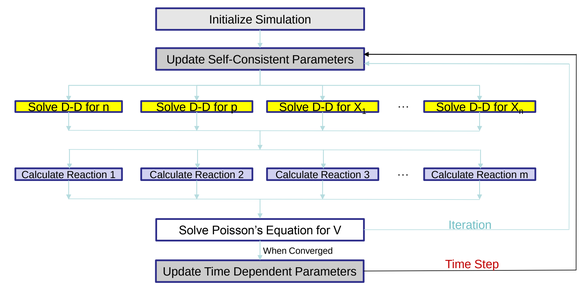
$$\int_\Omega \partial_t X_i v dx = \int_\Omega \nabla \cdot \left(\mu_i U_T e^{-\frac{\theta_i \varphi}{U_T}} \nabla u_i\right) v dx$$
$$= -\int_\Omega \mu_i U_T e^{-\frac{\theta_i \varphi}{U_T}} \nabla u_i \cdot \nabla v dx + \int_{\partial\Omega} \mu_i U_T e^{-\frac{\theta_i \varphi}{U_T}} \nabla_n(u_i) v dx$$

Time Splitting

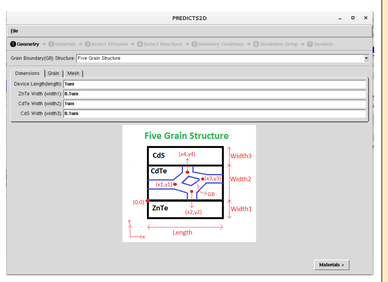
$$\boldsymbol{X'}_i^{k+1} = \left(\frac{\boldsymbol{M}}{\Delta t} - \mathbf{A_i}\boldsymbol{\varphi}\right)^{-1} \frac{\boldsymbol{M}}{\Delta t} \boldsymbol{X}_i^k$$
$$\boldsymbol{X}_i^{k+1} - \boldsymbol{X'}_i^{k+1} = \Delta t \, \boldsymbol{R}_i\left(\boldsymbol{X}_i^{k+1}\right)$$

Efficient Implementation.
•Scales linearly with the number of Defects
•Scales linearly with the number of Reactions

*Grain Boundaries treated as region with different diffusivity.



- Grain boundary geometry and mesh generation can be done entirely via the GUI
- All geometric parameters can be set by the user.
- Allowed geometries:
  - Single Crystal
  - Channel (Vertical GB)
  - Horizontal GB
  - Crossed GBs
  - Forked GB
  - Five Grains (shown)



D. Brinkman *et al.*, "Self-Consistent Simulation of CdTe Solar Cells with Active Defects", J. Appl. Phys. **118** (3), 035704 (2015)

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