PVRD-FASP: A Unified Solver for Modeling Carrier and Defect Transport in Photovoltaic Devices

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Abstract—In this article, we present a simulator for modeling transport of charge carriers and electrically active defect centers in solar cells by treating them on an equal footing, which allows us to address metastability and reliability issues. The exact nonlinear differential equations set solved by our solver is presented. The formulation of such differential equations, namely the continuity equations, drift-diffusion equation, and Poisson equation, for studying charge and defect transport is explained. The parameters needed for forming the differential equations are taken from first principle calculations. The solver is verified with test cases built on PN heterojunctions, Cu diffusion in single crystal CdTe and comparing Silvaco simulations with our numerical results.

Index Terms—Defect chemical reactions, drift-diffusion-reaction solver, implicit Euler with Newton iteration, PN heterojunction, transient solutions for continuity equation.

I. INTRODUCTION

THIN-FILM cadmium telluride (CdTe) photovoltaics are quickly maturing into a viable clean-energy solution through demonstration of competitive costs and performance stability with existing energy sources. Over the last half decade, CdTe solar technology has achieved major gains in performance; however, there are still aspects that can be improved to progress toward their theoretical maximum efficiency. Perhaps equally valuable as high photovoltaic efficiency and a low levelized cost of energy is device reliability. Understanding the root causes for changes in performance is essential for accomplishing long-term stability [1]. Understanding the underlying reasons of those instabilities is unclear due to the lack of the ability to characterize materials at atomistic levels and the lack of interpretation from the most fundamental material science point of view. The “migration of Cu” as a most common cause of metastability in CdTe solar cells has been investigated rigorously over the past twenty years. Multiple hypotheses suggesting degradation of CdTe solar cell devices due to the interaction and evolution of point defects and complexes were proposed, and none of them received strong theoretical and experimental confirmation until recently [1]. It should be emphasized that measured atomic impurity profiles in CdTe provide very little intelligence on active doping concentrations. The same elements could form different energy states, which could be either donors or acceptors, depending on their position in the crystalline lattice. Defects interact with other extrinsic and intrinsic defects. For example, changing the state of an impurity from an interstitial donor to a substitutional acceptor often is accompanied by generation of a compensating intrinsic interstitial donor defect. Hence, a simulation tool is needed that addresses the above processes and treats the carriers and the defects on the same footing to address the problems of metastability and reliability. Also, the tool must use first principle parameters as most educated input guess.

Several solvers [2]–[7] exist in the literature to study the charge carrier transport but only a few solvers [6]–[8] address the problem of defect transport. The electrically active defect centers obey the same fundamental physics equations as the charge carriers, namely continuity, drift-diffusion, and the Poisson equation. Thus, charge carriers and defects can be treated on an equal footing. The generation–recombination term in the continuity equation for charge carriers includes radiative and nonradiative processes: Shockley–Read–Hall (SRH) process, Auger process, etc. The same term in the continuity equation for arbitrary defects is not well known. Moreover, this term is strongly dependent on the interactions between both charge carriers and other defect species. In this article, we model these interactions as defect chemical reactions and use reaction-kinetic theory to write the generation–recombination terms in the continuity equation for both carriers and defects. The main physical parameters required for the continuity equation are the reaction rate constants, the diffusion constants, and the activation barriers. These values are generally calculated using density functional theory (DFT) and are taken from reference papers or from our own work [9]–[12].
Solving the semiconductor equations with these generation and recombination terms requires numerical integration of a system of nonlinear stiff differential equations of order one in time and order two in space. In this article, we use numerical algorithms for efficiently and accurately solving such a system of differential equations.

In systems with tens of electrically active defects, the amount of reactions and defect parameters is large and an ad hoc method of incorporating the input parameters for defects is not suitable. To circumvent this problem, we developed a user-friendly software tool (called “PVRD-FASP” = FSLR, ASU, SJSU, and Purdue) that allows one to easily incorporate different defect species along with their specific properties.

In Section II of this article, we formulate and present the theory we use to write the system of nonlinear differential equations for modeling transport of charge carriers and defects. We also briefly comment on the numerical algorithms employed in our solver. In Section III, we give four applications for solver validation.

1) Comparison of 0-dimensional (0-D) numerical simulations with analytical expressions for the generation–recombination process.

2) Calculation of copper point defect thermodynamic doping limit and comparison with known results.

3) Comparison of a light IV curve for a heterojunction CdTe solar cell with Silvaco.

4) Comparison of Cu diffusion in single crystal CdTe with experiment using four different annealing recipes.

Finally, we present our conclusions, remarks, and future works.

II. THEORY

The partial differential equations for describing the transport of charge carriers and arbitrary point defects are mathematically given as follows:

$$\frac{\partial u_i}{\partial t} = -\nabla \cdot J_i^t + G_i - R_i$$  \hspace{1cm} (1)

$$J_i^t = -\frac{D_i}{kT} \nabla (\mu_i^{ecp})$$  \hspace{1cm} (2)

$$-\nabla \cdot (\varepsilon \nabla \phi) = q_0 \sum_i z_i u_i$$  \hspace{1cm} (3)

where \(i\) is the index of the species (either charge carrier or point defect), \(u_i\) is the concentration, \(J_i^t\) is the diffusion flux, \(\mu_i^{ecp}\) is the electrochemical potential, \(G_i - R_i\) is the net of generation and recombination rates, \(D_i\) is the diffusivity, \(z_i\) is the ionization number of the charge state with sign of the \(i\)th species, \(k\) is the Boltzmann constant, \(T\) is the temperature, \(\varepsilon\) is the permittivity, \(\phi\) is the electrostatic potential, and \(q_0\) is the charge of an electron. The electrochemical potential \(\mu^{ecp}\) is defined as follows:

$$\mu^{ecp} = \mu^{cp} + q\phi = G_f^0 + q\phi + kT \ln \left( \frac{\mu}{N_s} \right)$$  \hspace{1cm} (4)

where \(G_f^0\) is the formation energy of the species, \(N_s\) is the maximum volumetric number density of microstates the species can occupy. The above definition for chemical potential is based on the formation energies and configuration entropies in dilute limit approximation [11], [13]. We can easily recover the standard semiconductor equations for charge carriers from the above differential equations (see Appendix A).

Next, we describe how to compute generation and recombination terms for both charged carriers and defects using defect chemical reaction kinetic theory.

A. Generation and Recombination Term

As said earlier, the generation and recombination rate terms in (1) is well known for charge carriers but unknown for point defects. In this article, we represent the interactions between charge carriers and defect species as a defect chemical reaction [14]. We employ reaction kinetics to determine their time evolution. In this article, we consider only the defect chemical reactions involving at most two reactants and at most two products (i.e., bimolecular reactions). This approximation is always valid in the dilute limit, and most of the higher order interactions can be approximately modeled by chemical reactions with at most two reactants or two products. With these assumptions we can write the generation recombination rate term as follows:

$$G_i - R_i = \frac{du_i}{dt}_{\text{reactions}} = U^T Q U + P^T U + K^i$$  \hspace{1cm} (5)

where \(U\) is the column vector with concentration of all species (point defects and charge carriers), \(Q\) is the matrix corresponding to the reaction rate constants of second-order reactions, \(P\) is the reaction rate constant row vector of first-order reactions, and \(K^i\) is rate constant of zero-order reactions involved by the species of index \(i\).

With this form we can write the net rate as a reaction operator \(R(U)\) as follows:

$$R(U) = U^T Q U + P U + K$$  \hspace{1cm} (6)

where \(Q\) is an \(M \times M \times M\) tensor, \(P\) is an \(M \times M\) matrix, \(K\) is an \(M \times 1\) vector. One major advantage of writing \(R(U)\) in this form is that the Jacobian of the reaction operator can be explicitly calculated in the form

$$J_R(U) = (Q + Q^T) U + P.$$  \hspace{1cm} (7)

More details about such representation can be found in Appendix B.

Another advantage of using the point defect chemical reaction kinetics is that we can show generation and recombination rate terms for charge carriers are easily recovered from the formulation using simple algebra and thermodynamic reaction equilibrium constant. For more details on this, see Appendix C.

B. Reaction Models

Although thermodynamics provides the ratio of forward and backward rate constants (equilibrium constants), we still must find one of the rate constants. For this we must use appropriate reaction models. For reactions with single reactant or product we mostly use a barrier limited reaction. If the reactions involve two species, in either reactants or products, then the reaction
model will be based on the type of interacting forces occurring between the involved species. For a general reaction given as
\[ A^{z_A} + B^{z_B} \xrightarrow{K} C^{z_C} + D^{z_D} \]  
where \( z \) can be 0 (being single product) and 1 (being two products), \( z_X \) being the ionization of species \( X \), the diffusion-controlled reaction rate constant [15] is given as follows:
\[ K = 4\pi R_{\text{capt}}(D_A + D_B) \exp \left(-\frac{E_A}{kT}\right) \]
where \( R_{\text{capt}} \) is the capture radius, \( D_X \) is the diffusivity of species \( X \), \( E_A \) is the activation energy of reaction \( (E_A \geq 0) \) representing the probability of a collision resulting in the formation of product. The various types of reaction models, used in the solver, are described below.

1) Diffusion Limited With Attraction Model: This model is used when the two reactants or products have opposite charges, i.e., \( z_A \times z_B < 0 \). In such a case, there is Coulombic force of attraction between the species and hence activation barrier is zero. Also, the capture radius is given by the Onsager radius which is the radius at which the Coulombic energy is equal to the thermal energy. We consider an approximation of well-ordered lattice without significant perturbations of permittivity by high density of native defects or lattice disorder. Then, we can calculate Onsager radius as follows:
\[ R_{\text{Onsager}} = \frac{q^2 |z_A z_B|}{4\pi \varepsilon kT}. \]  
Hence, the rate constant is given by
\[ K = q^2 |z_A z_B| \frac{D_A + D_B}{\varepsilon kT}. \]

2) Thermal Generation–Recombination Model: This model is used when the reaction is given by
\[ \text{Null} \xrightarrow{K_f} e^- + h^+. \]

The backward rate is equated to the band-to-band recombination rate coefficient \( B \) of the material. Currently, we assume that coefficient \( B \) is independent of temperature, although few papers [16], [17] show it as being temperature dependent.

3) Capture Radius Limited Model: This model is used for reactions when \( z_A \times z_B \geq 0 \) and assumes the activation energy of the reaction to be zero. Thus, the rate constant is given as follows:
\[ K = 4\pi R_{\text{capt}}(D_A + D_B). \]

The user needs to specify the capture radius \( R_{\text{capt}} \).

4) Capture Cross Section Limited Model: If one of the reactant of (8) is charge carrier, then the sum of diffusivities can be approximated as follows:
\[ D_A + D_B \approx D_{e/h}. \]

Also, it is common to represent charge carrier capture reaction rate constant as product of capture cross section and thermal velocities. Thus, the rate constant is given as follows:
\[ K = \sigma_{e/h} v_{th,e/h}. \]

In case of diffusion limited with attraction model with charge carrier the capture cross section of carrier is given as follows:
\[ \sigma_{e/h} = \frac{4\pi R_{\text{Onsager}} D_{e/h}}{v_{th,e/h}}. \]

For capture radius limited model, with charge carrier as reactant, the user needs to input the capture cross section parameter.

5) Barrier Limited Model: This model is used for reactions with single reactant and product. The rate constant is given as follows:
\[ K = \nu \exp \left(-\frac{E_b}{kT}\right) \]
where \( \nu \) is the attempted frequency of reaction (prefactor) and \( E_b \) is the barrier height.

C. Other Models

Parameters, like diffusion coefficients, band gap, reaction rate constants, etc., involved in the differential equations are temperature dependent. In the previous section, we showed the reaction rate models. Other models used in this article are given below.

1) Varshini Model: This model is used to account the band gap changes in semiconductor as a function of temperature. The model equation for the band gap as a function of temperature is as follows [18]:
\[ E_g(T) = E_0 - \alpha \frac{T^2}{T + \beta} \]
where \( E_0 \) is the 0K band gap, \( \alpha \) and \( \beta \) are fitting parameters.

2) Diffusion Barrier Model: The diffusion coefficient is assumed to have Arrhenius relationship with temperature given as follows:
\[ D(T) = D_0 \exp \left(-\frac{E_D}{kT}\right) \]
where \( E_D \) is the diffusion barrier energy.

This completes the description of physical models used in solver.

D. Numerical Methods

Equations (1)–(3) are solved numerically by discretizing them in space and time. We use finite volume discretization for space and forward Euler method for time discretization. Furthermore, we employ time operator splitting for transport and reaction operators. For transport operator, we apply Scharfetter–Gummel discretization and linearize the Poisson equation. The self-consistency is achieved through Gummel iteration. For reaction operator, we use implicit time scheme with Newton iteration.

III. APPLICATION/VALIDATION OF SOLVER

In this section, we describe four types of simulations to validate the solver.
concentrations (see Appendix G) fast thermal generation and recombination processes drive the holes as 0, for a total time of 1e25 s. This simulation shows how to run a 0-D simulation with initial concentration of electrons and holes.

### A. 0-D Simulation of Thermally Generated Electrons and Holes

In this simulation, we take reaction (12) in CdTe material and run a 0-D simulation with initial concentration of electrons and holes as 0, for a total time of 1e25 s. This simulation shows how fast thermal generation and recombination processes drive the system toward equilibrium. For this simulation, we can write the exact analytical expression for the time evolution of the concentrations (see Appendix G)

\[
p(t) = n(t) = n_i + \frac{2}{n_i + \frac{n(0)}{n_i - n_i}} \exp(2K_b n_i t) - \frac{1}{n_i}.
\]

Here, \(n_i = \frac{K_f}{K_b}, K_f, K_b\) are forward and backward rates of (12), \(n(0)\) is the initial electron and hole concentration, and \(t\) is the time. The numerical values are given in Table I. We can compare the numerical solution and analytical solution and validate the numerical algorithm for the 0-D solver. The comparison results are shown in Fig. 1.

### B. 0-D Simulation Study of Copper Defects in CdTe

In this article, we use the solver to study the thermodynamic limits of copper defect concentrations in CdTe. The simulation follows the work from reference [19] (APL). The authors, Yang et al., calculate the formation energies, defect transition levels under different conditions for \(\text{Cu}_0^0\), \(\text{Cu}_+^0\), and their charge states, and by finding the solution of a constrained equilibrium problem together with charge neutrality condition, they compute the thermodynamic limits of doping concentration of copper defects using analytical expressions. The equations applied in [19] are as follows:

\[
\begin{align*}
[CuC^0] &= N_{CuC} \times \frac{g_0 e^{-\Delta H_f(CuC^0)/k_B T}}{g_0 e^{-\Delta H_f(CuC^0)/k_B T} + g_{+1} e^{-\Delta H_f(CuC^0)/k_B T}} \\
[CuC^-] &= N_{CuC} \times \frac{g_0 e^{-\Delta H_f(CuC^-)/k_B T}}{g_0 e^{-\Delta H_f(CuC^-)/k_B T} + g_{+1} e^{-\Delta H_f(CuC^-)/k_B T}} \\
[Cu^0] &= N_{Cu_i} \times \frac{g_0 e^{-\Delta H_f(Cu_i^0)/k_B T}}{g_0 e^{-\Delta H_f(Cu_i^0)/k_B T} + g_{+1} e^{-\Delta H_f(Cu_i^0)/k_B T}} \\
[Cu_i^+] &= N_{Cu_i} \times \frac{g_0 e^{-\Delta H_f(Cu_i^+)/k_B T}}{g_0 e^{-\Delta H_f(Cu_i^+)/k_B T} + g_{+1} e^{-\Delta H_f(Cu_i^+)/k_B T}} \\
[CuC^0] + [CuC^-] + [Cu^0] + [Cu_i^+] &= N_{CuC} + N_{Cu_i} \\
&= N_{Cu}[CuC^-] + [e^-] = [Cu_i^+] + [h^+] 
\end{align*}
\]

where \(N_{Cu}\) is the total copper concentration, \(N_{CuC}\) is the total copper at cation defect concentration, \(N_{Cu_i}\) is the total interstitial copper defect concentration, \([X]\) and \(\Delta H_f(X)\) are the concentration and formation enthalpy of the defect species \(X\) and \(g\)'s are the degeneracy factors. With the calculated enthalpies for defects and self consistently solving (21), the authors were able to compute the thermodynamic doping limits for the Cu defects in CdTe.

We applied our solver to do the same computation but with the reaction formalism. The reactions employed to reproduce the results are as follows:

\[
\begin{align*}
\text{Cu}_i^0 &\rightleftharpoons \text{Cu}_0^0 \\
\text{CuC}_0^0 &\rightleftharpoons \text{CuC}_-^0 + h^+ \\
\text{CuC}_-^0 &\rightleftharpoons \text{CuC}_0^0 + e^- \\
\text{Cu}_i^0 &\rightleftharpoons \text{Cu}_i^+ + e^- \\
\text{Cu}_i^+ &\rightleftharpoons \text{Cu}_0^0 + h^+.
\end{align*}
\]

The formation energies, degeneracies, capture rates are all the same as that of [19] for the Cd-poor case and we ran a simulation varying total copper concentration from 1e15 to 1e19. We got the comparison results as shown in Figs. 2 and 3. The slight differences can be accounted for the finite precision arithmetic errors as evident from Fig. 4. Thus, this comparison results show that the reaction formalism assumed in our solver is valid and encompasses relevant defect chemistry results from the literature.

### C. 1-D Simulation of Heterojunction CdTe Device

In this article, we use the solver to study a CdTe-based solar cell and compare the results with Silvaco simulations. The device structure is shown in Fig. 5. The structure consists of four layers: 0.2 μm of zinc telluride (ZnTe), 1 μm of CdTe, 0.4 μm of cadmium sulfide (CdS), and finally 0.4 μm of transparent...
conducting oxide (TCO). The doping of each layer is shown in Fig. 5. The ZnTe layer has p-type doping of 1.7e18 cm⁻³, CdTe has p-type doping of 1e14 cm⁻³, CdS has n-type doping of 1e16 cm⁻³ and TCO has doping of 1.2e17 cm⁻³. The bias applied is with respect to TCO at ZnTe. The light is AM1.5G and is illuminated from TCO side.

We built the same structure in Silvaco and with our solver using the same material parameters. In our solver we specify the SRH processes and radiative processes through the reactions given as follows:

\[
\begin{align*}
\text{Null} &\rightleftharpoons e^-_c + h^+_v \\
N_D^0 &\rightleftharpoons N^+_D + e^-_c \\
N_D^+ &\rightleftharpoons N^0_D + h^+_v \\
N_A^- &\rightleftharpoons N^+_A + h^+_v \\
N_A^+ &\rightleftharpoons N^0_A + e^-_c.
\end{align*}
\] (23)

The donor dopant \( N_D \) are in CdS and TCO and acceptor dopant \( N_A \) are present in ZnTe and CdTe layers, respectively, with the concentration described above.

The capture rates and all material parameters are kept same for both our simulation and Silvaco simulation. We computed the IV curves and compared them, as shown in Fig. 6, with Silvaco simulations of an identical structure. We see that we have achieved very close match in short-circuit current between our simulation (27.26 mA/cm²) and that of Silvaco simulation (27.01 mA/cm²).

The open-circuit voltage in our simulation is very close to 0.86 V, whereas that of Silvaco simulation is around 0.86 V. This comparison further validates our formalism and methodology to study point defects and charge carriers on equal footing.

D. 1-D Simulation of Cu Diffusion in Single Crystal CdTe

In this article, we perform copper diffusion in single crystal CdTe and compare it with the experimentally measured Cu SIMS data as given in [20]. We perform the numerical simulation with four different annealing recipes namely 3 min anneal at 350 °C, 6 min anneal at 350 °C, 10 min anneal at 300 °C, and 20 min anneal at 300 °C. The simulation structure consists of a 0.5 μm ZnTe layer doped with Cu and an acceptor concentration of 1e19 cm⁻³ and 19.5 μm sx-CdTe layer. The Cu species present in ZnTe are assumed to form a neutral complex \([\text{Cu}_\text{C}^-\text{Cu}_\text{i}]^0\) with concentration 2.5e20 cm⁻³. Previous simulations [20] assumed an effective model in the ZnTe layer that maintains an acceptor doping of 1e19 cm⁻³. The current solver does not need the effective model and the Cu complex is closer to the real structure of the Cu:ZnTe layer. The reactions considered for this study are given in Table II.

The reactions in ZnTe are complex dissociation, radiative generation and recombination, and SRH reactions for acceptors. Reaction 3 in CdTe is the Cd knock off reaction which is the main reaction involved in the Cu acceptor formation in CdTe considered in this article. The other reactions are the carrier capture reactions involved with defects that resulted in the knock-off reaction and dissociation reaction. The first principle numbers are taken from [10] and [21]. Since first principle parameters are not available for the point defects considered in ZnTe, we assumed similar numbers as that of CdTe. We varied the formation energies in ZnTe and CdTe for Cd\(_i\) defect and \([\text{Cu}_\text{C}^-\text{Cu}_\text{i}]^0\) complex formation energy in ZnTe to match the experimental secondary ion mass spectrometry (SIMS) data.
Fig. 5. Schematics of heterojunction CdTe device simulation.

TABLE II

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Reactions in ZnTe Layer</th>
<th>Reactions in CdTe Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Cu₂Cu₃]⁺ ↔ Cu⁺ + Cu⁺⁺ (DLWA)</td>
<td>[Cu₂Cu₃]⁺ ↔ Cu⁺ + Cu⁺⁺ (DLWA)</td>
</tr>
<tr>
<td>2</td>
<td>Null ↔ e⁻ + h⁺ (TGR)</td>
<td>Null ↔ e⁻ + h⁺ (TGR)</td>
</tr>
<tr>
<td>3</td>
<td>NA⁺ ↔ NA⁺ + h⁺ ; NA⁺ ↔ NA⁺ + e⁻ (DLWA, CXL)</td>
<td>Cu⁺ + Cd⁺⁺ ↔ [Cu⁺Cd⁺⁺]⁺ ↔ Cu⁺⁺ + Cd⁺⁺ (CRL, DLWA)</td>
</tr>
<tr>
<td>4</td>
<td>Cu⁺ ↔ Cu⁺ + h⁺ ; Cu⁺ ↔ Cu⁺⁺ + e⁻ (CXL, DLWA)</td>
<td>Cu⁺ ↔ Cu⁺ + h⁺ ; Cu⁺ ↔ Cu⁺⁺ + e⁻ (CXL, DLWA)</td>
</tr>
<tr>
<td>5</td>
<td>Cu⁺ ↔ Cu⁺ + e⁻ ; Cu⁺ ↔ Cu⁺⁺ + h⁺ (CXL, DLWA)</td>
<td>Cu⁺ ↔ Cu⁺ + e⁻ ; Cu⁺ ↔ Cu⁺⁺ + h⁺ (CXL, DLWA)</td>
</tr>
<tr>
<td>6</td>
<td>Cd⁺⁺ ↔ Cd⁺ + h⁺ ; Cd⁺⁺ ↔ Cd⁺⁺ + e⁻ (CXL, DLWA)</td>
<td>Cd⁺⁺ ↔ Cd⁺ + h⁺ ; Cd⁺⁺ ↔ Cd⁺⁺ + e⁻ (CXL, DLWA)</td>
</tr>
<tr>
<td>7</td>
<td>Cd⁺⁺ ↔ Cd⁺ + h⁺ ; Cd⁺⁺ ↔ Cd⁺⁺ + e⁻ (CXL, DLWA)</td>
<td>Cd⁺⁺ ↔ Cd⁺ + h⁺ ; Cd⁺⁺ ↔ Cd⁺⁺ + e⁻ (CXL, DLWA)</td>
</tr>
</tbody>
</table>


Fig. 6. Comparison of IV curves for CdTe solar cell.

Our simulation shows that we need not vary the diffusion barriers as was done in [20].

Comparisons of measured copper profiles and numerical simulations for samples prepared by 350 °C 3 min anneal recipe, 350 °C 6 min anneal recipe, 300 °C 10 min anneal recipe, and 300 °C 20 min anneal recipe are shown in Fig. 7, Fig. 8, Fig. 9, and Fig. 10, respectively. We see that our simulation result closely matches the experimentally measured profiles in the CdTe layer. The measurements near the start of the ZnTe layer show a decrease in Cu concentration which can be attributed as an artifact of SIMS measurement.

The numerical simulation results are not taken after the cool down to room temperature although the measurements are taken at room temperature. Simulations of cooldown process is still in progress, however we do not expect the resulting Cu profiles to change significantly from those presented in Figs. 7–10.

Fig. 7. Copper profile comparison with 3 min 350 °C anneal recipe.
Fig. 8. Copper profile comparison with 6 min 350 °C anneal recipe.

Fig. 9. Copper profile comparison with 10 min 300 °C anneal recipe.

Fig. 10. Copper profile comparison with 20 min 300 °C anneal recipe.

IV. CONCLUSION

Photovoltaic solar cells based on CdTe represent the largest segment of commercial thin-film module production worldwide. Recent improvements have matched the efficiency of multicrystalline silicon while maintaining cost leadership. Further investigations on the role of defects (point-like or grain boundaries) can shed light on the chemical and physical processes occurring within the cell, thus enabling one to improve efficiency, minimize metastabilities, and help slow down aging of the cells and modules.

For this purpose, a drift-diffusion-reaction simulator (PVRD-FASP) was developed within our team. The simulator allows modeling of the charged carriers and active defects on equal footing. The theoretical model used in this simulator is presented here as well as key numerical details. Our new reaction simulator was validated through several simulation examples. The 0-D solver was verified via comparison with available published data on thermodynamic calculations of copper defects in CdTe. The solver was verified on the simulation of CdTe/CdS heterojunction solar cell made. The dark and light IV characteristics of the cell calculated with our solver were compared with Silvaco simulation results. Perfect matching between the two simulation experiments was obtained. Finally, the drift-diffusion-reaction solver was tested on real experimental data of Cu diffusion into single-crystal CdTe. Again, very good agreement with SIMS profiles with different annealing recipes was obtained. We conclude that the PVRD-FASP solver can robustly perform relevant and diverse simulations to study diffusion/activation of dopants, device performance, and other physically relevant processes.

APPENDIX A

STANDARD SEMICONDUCTOR EQUATIONS FOR CHARGE CARRIERS FROM ELECTROCHEMICAL FORMULATION

For charge carriers, we can simplify the differential equations given in (1)–(3) as follows:

\[
\begin{align*}
\frac{\partial n}{\partial t} &= -\nabla \cdot J_n + G_n - R_n \\
J_n &= -D_n \frac{kT}{n} \nabla \left( G^0_{f,n} - q_0 \phi + kT \ln \left( \frac{n}{N_C} \right) \right) \\
\frac{\partial p}{\partial t} &= -\nabla \cdot J_p + G_p - R_p \\
J_p &= -D_p \frac{kT}{p} \nabla \left( G^0_{f,p} + q_0 \phi + kT \ln \left( \frac{p}{N_V} \right) \right)
\end{align*}
\]

\[
\nabla \cdot (\varepsilon \nabla \phi) = -p + n - N_D + N_A. \tag{24}
\]

\[
\begin{align*}
\nabla \cdot (\varepsilon \nabla \phi) &= -p + n - N_D + N_A
\end{align*}
\]

Using the formation energies of the free carriers [see (62)], we can simplify the flux equations as follows:

\[
\begin{align*}
J_n &= -D_n \frac{kT}{n} \nabla (-\chi - kT \ln N_C) - \mu_n n \bar{E} - D_n \nabla n \\
J_p &= -D_p \frac{kT}{p} \nabla (\chi + E_g - kT \ln N_V) + \mu_p p \bar{E} - D_p \nabla p
\end{align*}
\]

\[
\begin{align*}
J_n &= -\mu_n n \bar{E} - D_n \nabla n \\
J_p &= \mu_p p \bar{E} - D_p \nabla p \tag{26}
\end{align*}
\]

where we used the definition of electric field and Einstein relationship between diffusivity and mobilities. The above equations are the standard semiconductor equation for heterostructures (see [22]) and in case of homogeneous structures the first gradient term is zero. Thus, the equation reduces to

\[
\begin{align*}
J_n &= -\mu_n n \bar{E} - D_n \nabla n \\
J_p &= \mu_p p \bar{E} - D_p \nabla p
\end{align*}
\]

which are the standard equations for charge carriers in semiconductors.
APPENDIX B
DETAILS ON GENERATION RECOMBINATION RATES FROM DEFECT CHEMICAL REACTIONS

The rate equation for a general defect chemical reaction (27) with at most two reactants or products

\[ aA + bB \xrightleftharpoons[K_i]{K_b} cC + dD \]  

is given as

\[
\frac{d[A]}{dt} = \frac{1}{a} \frac{d[B]}{dt} = \frac{1}{b} \frac{d[C]}{dt} = \frac{1}{c} \frac{d[D]}{dt} = K_i[A]^a[B]^b - K_b[C]^c[D]^d. \tag{28}
\]

The above rate equation is still complex, and we further restrict ourselves to stoichiometric coefficients \(a, b, c\), and \(d\) of either \(d = 1\) or \(d = 0\). Although this looks like a strong simplification to the domain of defect chemical reactions, it is still enough to cover the defect chemical interactions of interest.

If any of the species is involved in more than one reaction, then the rate equation for that species will have contributions from reaction rates of both the first reaction and the other reaction. For example, if the reaction system is given as follows:

\[ A + B \xrightleftharpoons[K_{i1}]{K_{b1}} C + D \tag{29} \]
\[ A \xrightleftharpoons[K_{i2}]{K_{b2}} E + F \tag{30} \]
\[ \text{Null} \xrightleftharpoons[K_{i3}]{K_{b3}} A + G \tag{31} \]

then the rate equation for the time evolution of species \(A\) is given as follows:

\[
\frac{d[A]}{dt} = -K_{i1}[A][B] + K_{b1}[C][D] - K_{i2}[A]
+ K_{i2}[E][F] + K_{i3}[A][G]. \tag{32}
\]

The above rate equation can be elegantly represented as follows:

\[
\frac{d[A]}{dt} = U^TQ_AU + P_AU + K_A \tag{33}
\]

where \(U\) is a concentration (column) vector of length 7 given as follows:

\[ U = ([A], [B], [C], [D], [E], [F], [G])^T. \tag{34} \]

\(Q_A\) is a \(7 \times 7\) sparse matrix with nonzero elements

\[ q_{12}^A = q_{21}^A = -\frac{K_{i1}}{2} \]
\[ q_{34}^A = q_{43}^A = \frac{K_{b1}}{2} \]
\[ q_{56}^A = q_{65}^A = \frac{K_{b2}}{2} \]
\[ q_{17}^A = q_{71}^A = -\frac{K_{i3}}{2}. \tag{35} \]

\(P_A\) is a row vector of length 7 with nonzero elements

\[ p_1^A = -K_{f2} \tag{36} \]

and \(K_A\) is the constant term given as \(K_{f3}\).

The representation given by (33) can be extended to any number of species and we can write the corresponding \(Q, P, K\) variables as functions of reaction rate constants. Consider a general reaction rate equation

\[
\frac{du_i}{dt} = \sum_{k=1}^{M} \sum_{j=1}^{M} a_{jk}^iu_ju_k + \sum_{j=1}^{M} b_{j}^iu_j + c^i \tag{37}
\]

for \(i = 1, 2, \ldots, M\), where \(M\) is the total number of species and \(a, b, c\) are the reaction rate constants in which the species \(i\) is involved. Then, the parameters \(Q^i, P^i, K^i\) can be calculated as follows:

\[ q_{jk}^i = q_{kj}^i = \begin{cases} \frac{1}{2}a_{jk}^i & \text{if } j \neq k \\ a_{kk}^i & \text{if } j = k \\ 0 & \text{otherwise} \end{cases} \tag{38} \]
\[ p_{ji}^i = b_{j}^i, \quad K^i = c^i. \tag{39} \]

Thus, the generation–recombination term can be expressed as follows:

\[ G_i - R_i = \frac{du_i}{dt}\text{reactions} = U^TQ^iU + P^iU + K^i. \tag{40} \]

APPENDIX C
SYSTEMATIC CORRESPONDENCE WITH RADIATIVE AND SRH GENERATION RECOMBINATION RATES

For a radiative process, the generation and recombination term in the continuity equation of charge carriers can be expressed as follows:

\[ G - R = b(n_e^2 - n_p). \tag{41} \]

Considering the radiative process interactions, the equivalent reaction is as follows:

\[ \text{Null} \xrightleftharpoons[K_i]{K_b} e^- + h^+_v \tag{42} \]

where \(e^-\) and \(h^+_v\) denote a free electron in conduction band and a free hole valence band of the material. Hence, the rate equation is given as follows:

\[
\frac{d[e^-]}{dt} = \frac{d[h^+_v]}{dt} = K_f - K_b[e^-][h^+_v] \]
\[ = K_b \left( \frac{K_f}{K_b} - [e^-][h^+_v] \right). \tag{43} \]

If the ratio of forward rate to backward rate is \(n_e^2\), we can easily see that (41) and (43) are equivalent. The thermodynamics of reactants and products results in exactly this condition in the ratio. See (63).

For SRH processes, the generation and recombination on a single defect in steady-state is given as in (23)

\[ G - R = \frac{(n_i^0p_1 - np)}{\frac{n_e^2}{n_e} + \frac{p_i^0}{p_i}}. \tag{44} \]
The equivalent reaction representing the SRH process in case of acceptor type species can be written as follows:

\[ \text{A}^0 + \frac{K_{f1}}{K_{b1}} \rightarrow \text{A}^- + h_v^+ \]

\[ \text{A}^- + \frac{K_{f2}}{K_{b2}} \rightarrow \text{A}^0 + e^- \, . \]  

(45)

The rate equations can be written as follows:

\[ \frac{d[A^0]}{dt} = -\frac{d[A^-]}{dt} = -K_{f1}[A^0] + K_{b1}[A^-]\left[h_v^+\right] + K_{f2}[A^-] - K_{b2}[A^0]\left[e^-\right] \]

(46)

\[ \frac{d[e^-]}{dt} = K_{f2}[A^-] - K_{b2}[A^0]\left[e^-\right] \]

(47)

\[ \frac{d[h_v^+]}{dt} = K_{f1}[A^0] - K_{b1}[A^-]\left[h_v^+\right] \, . \]  

(48)

From (46) we note that \([A^0] + [A^-]\) is constant in time (say \([A]^\text{tot}\)). Hence, in steady-state, we have

\[ [A^0] = \frac{K_{f2} + K_{b1}p}{K_{f1} + K_{f2} + K_{b1}p + K_{b2}n}[A]^\text{tot} \]

\[ [A^-] = \frac{K_{f1} + K_{b2}n}{K_{f1} + K_{f2} + K_{b1}p + K_{b2}n}[A]^\text{tot} \]  

(49)

where \([h_v^+] = p\) and \([e^-] = n\) is used for notational simplicity. Using (49) in (47) and (48) with few algebraic simplifications we can write

\[ \frac{dp}{dt} = \frac{dN_c}{dt} = \frac{K_{f1}K_{f2} - K_{b1}K_{b2}np}{K_{f1} + K_{f2} + K_{b1}p + K_{b2}n} \, . \]  

(50)

Now if the ratio of the reaction rates is restricted as

\[ \frac{K_{f1}}{K_{b1}} = \frac{p_1}{n_1} = N_c e^{-\frac{\chi + kT}{kT}}, \quad \frac{K_{f2}}{K_{b2}} = \frac{n_1}{p_1} = N_c e^{-\frac{\chi - kT}{kT}} \]  

(51)

then (50) can be simplified further as follows:

\[ G - R = \frac{(n_1p_1 - np)}{n_1p_1 + p_1n_1}[A]^\text{tot} \]  

(52)

which is equivalent to (44). Equation (51) will hold based on the thermodynamics of reactants and products as shown in the following section. A similar equivalence can be shown for donor type centers as well.

A. Thermodynamic Relationship Between Forward and Backward Rate Constants

Consider a general reaction

\[ \sum_{i=1}^{N} x_i X_i \rightleftharpoons \sum_{j=1}^{M} y_j Y_j \]  

(53)

with \(N\) reactants and \(M\) products. At thermodynamic equilibrium the difference in the chemical potentials of reactants and products should be zero. Thus, we have

\[ \Delta G = \sum_{i=1}^{N} x_i \mu_{X_i} - \sum_{j=1}^{M} y_j \mu_{Y_j} \]  

(54)

where \(\Delta G\) is the Gibb’s free energy change of reaction, \(\mu\) is the chemical potential of the species which can written from (4) neglecting the electrostatic potential as follows:

\[ \mu_{X_i} = G^0_{f,X_i} = kT \ln \left( \frac{[X_i]}{N_{s,X_i}} \right) \, . \]  

(55)

Note that the chemical potential here is defined as the sum of species formation energy and its configurational entropy in the dilute limit as expressed in [12] and [13]. Thus, at equilibrium, we have

\[ \sum_{i=1}^{N} x_i G^0_{f,X_i} + kT \ln \left( \frac{[X_i]}{N_{s,X_i}} \right) \]

\[ = \sum_{i=1}^{N} \left( y_j G^0_{f,Y_j} + kT \ln \left( \frac{[Y_j]}{N_{s,Y_j}} \right) \right) \, . \]  

(56)

Upon simplification, we obtain

\[ \prod_{j=1}^{M} \left[ \frac{[Y_j]}{[X_j]} \right]^{y_j} = \prod_{j=1}^{M} \frac{N_{s,Y_j}}{N_{s,X_j}} \exp \left( - \frac{\Delta_r G^0}{kT} \right) \]  

(57)

where \(\Delta_r G^0\) is the standard enthalpy change of reaction or standard reaction Gibb’s energy defined as follows:

\[ \Delta_r G^0 = \sum_{j=1}^{N} y_j G^0_{f,Y_j} - \sum_{i=1}^{M} x_i G^0_{f,X_i} \, . \]  

(58)

We also know that at equilibrium, we have

\[ K_f \prod_{i=1}^{N} \frac{[X_i]}{[X_i]}^{x_i} = K_b \prod_{j=1}^{M} \frac{[Y_j]}{[Y_j]}^{y_j} = 0. \]  

(59)

Hence, using (57) and (59), we can write the equilibrium constant as follows:

\[ K_{eq} = \left( \frac{M}{\prod_{j=1}^{M} N_{s,Y_j}} \prod_{i=1}^{N} N_{s,X_i} \right) \]  

\[ \exp \left( - \frac{\Delta_r G^0}{kT} \right) \, . \]  

(60)

Therefore, the reaction rate constants follow a fixed ratio. Applying this for the recombination reaction (12), we have

\[ K_f = \left( \frac{N_{s,h^+}}{N_{s,e} N_{s,h^+}} \right) \exp \left( - \frac{G^0_{f,e} + G^0_{f,h^+}}{kT} \right) \, . \]  

(61)

The number of microstates for electrons in the conduction band and holes in the valence band are \(N_{C}\) and \(N_{V}\), respectively. The formation energies of electrons in the conduction band and holes in the valence band (referenced from vacuum level) is

\[ G^0_{f,e} = -\chi, \quad G^0_{f,h^+} = \chi + E_g \]  

(62)

where \(\chi\) is the electron affinity of the material and \(E_g\) is the band gap of the material. Thus, we have the ratio

\[ \frac{K_f}{K_b} = \left( \frac{N_{e}}{N_{s,h^+}} \right) \exp \left( - \frac{E_g}{kT} \right) \, . \]  

(63)
For the reactions in (45), we have
\[
\frac{K_{f1}}{K_{b1}} = \frac{N_{s,A^-} N_{s,h^+}}{N_{s,A^0}} \exp \left( -\frac{G_{f,A^-}^0 + G_{f,h^+}^0 - G_{f,A^0}^0}{kT} \right)
\]
\[
\frac{K_{f2}}{K_{b2}} = \frac{N_{s,A^0} N_{s,e^-}}{N_{s,A^-}} \exp \left( -\frac{G_{f,A^0}^0 + G_{f,e^-}^0 - G_{f,A^-}^0}{kT} \right)
\]
(64)
(65)
where the formation energies are given as follows:
\[
G_{f,A^-}^0 = E_{f,A^-} - \chi - E_g
\]
\[
G_{f,A^0}^0 = E_{f,A^0} - \text{sign}(A^-) E_T - \chi - E_g
\]
\[
G_{f,e^-}^0 = -\chi, \quad G_{f,h^+}^0 = \chi + E_g.
\]
(66)
Here \(\text{sign}(A^-)\) is the sign of the charge on the species, \(E_T\) is the trap level (transition level from 0/-; see [10]) with respect to vacuum and \(E_{f,A^0}\) is defect formation energy of neutral species calculated through DFT (see Appendix D for details on how transition levels of species are related to the formation energies of its corresponding neutral species). Assuming the microstates for neutral and charged species are nearly same, we arrive at
\[
\frac{K_{f1}}{K_{b1}} = N_v \exp \left( -\frac{\chi + E_g + E_T}{kT} \right) = N_v \exp \left( \frac{E_v - E_T}{kT} \right)
\]
\[
\frac{K_{f2}}{K_{b2}} = N_c \exp \left( -\frac{-\chi - E_T}{kT} \right) = N_c \exp \left( -\frac{E_c - E_T}{kT} \right)
\]
(67)
where we have used the relations
\[
E_c = -\chi, \quad E_v = -\chi - E_g
\]
(68)
Hence, thermodynamics guarantees that the SRH process is recovered from our reaction formulation, i.e., the thermodynamics guarantees the equivalence as a chemical defect reaction.

**APPENDIX D**

**RELATIONSHIP BETWEEN TRANSITION LEVEL AND FORMATION ENTHALPY FOR DEFECTS**

Suppose the formation enthalpies and transition levels of a defect are as shown in Fig. 11. Then, it is clear that
\[
\Delta H_f^+ = \Delta H_f^- + (+1) (E_{+}^{/0} - 0)
\]
\[
\Delta H_f^0 = \Delta H_f^0 + (+1) (E_{+}^{/0} - E_{2+/+})
\]
\[
\Delta H_f^{2+/+} = \Delta H_f^- + (+2) (E_{2+/+} - 0)
\]
\[
\Delta H_f^- = \Delta H_f^0 - (-1) (E_{0/-0})
\]
(69)
by simple rules of coordinate geometry for straight lines with slopes. For further details please see [10].

**APPENDIX E**

**TIME EVOLUTION OF THERMALLY GENERATED CARRIERS**

The reaction representing thermally generated carriers is given in (12). The differential equation for this system is (43).

Choosing charge neutrality for the initial condition we have
\[
n(0) = p(0), \quad n(t) = p(t)
\]
(70)
where \(n(t)\) and \(p(t)\) represent the concentration of electrons and hole at time \(t\). Thus, the differential equation to be solved is given as follows:
\[
\frac{dp}{dt} = \frac{dn}{dt} = K_b (n_i^2 - n^2)
\]
(71)
which is a Ricatti equation with the constant value \(n(t) = n_i\) as one particular solution. Obviously, this solution cannot be the physically correct solution to our system. The other solution can be found by writing the solution as follows:
\[
n(t) = n_i + \frac{1}{z(t)}
\]
(72)
Substituting this into (71) and simplifying we obtain
\[
-\frac{1}{z^2} \frac{dz}{dt} = K_b \left( n_i^2 - \left( n_i + \frac{1}{z} \right)^2 \right)
\]
\[
\Rightarrow \frac{1}{z^2} \frac{dz}{dt} = K_b \left( \frac{2n_i}{z} + 1 \right)
\]
\[
\Rightarrow \frac{dz}{dt} - 2K_b n_i z - K_b = 0
\]
\[
\Rightarrow \frac{d}{dt} \left( ze^{-2K_b n_i t} \right) = K_b e^{-2K_b n_i t}
\]
\[
\Rightarrow z(t) e^{-2K_b n_i t} - z(0) e^0 = K_b \frac{e^{0} - e^{-2K_b n_i t}}{2K_b n_i}
\]
\[
\Rightarrow z(t) = z(0) e^{2K_b n_i t} + \frac{e^{2K_b n_i t} - 1}{2n_i}
\]
(73)
The value of \(z(0)\) can be found as follows:
\[
n(0) = n_i + \frac{1}{z(0)}
\]
\[
\Rightarrow z(0) = \frac{1}{n(0) - n_i}
\]
(74)
Hence, the final solution can be given as follows:

\[
n(t) = n_i + \frac{1}{z(t)} = n_i + \left(\frac{1}{n(0) - n_i} + \frac{1}{n_i} \right) e^{2K_{in}n_i t} - \frac{1}{n_i} = n_i + \frac{2}{n(0) - n_i} e^{2K_{in}n_i t} - \frac{1}{n_i},
\]

(75)

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REFERENCES


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