Self-Consistent Simulation of CdTe Solar Cells with Active Defects
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We demonstrate a self-consistent numerical scheme for simulating an electronic device which contains active defects. As a specific case, we consider copper defects in Cadmium Telluride solar cells. The presence of copper has been shown experimentally to play a crucial role in predicting device performance. The primary source of this copper is migration away from the back contact during annealing, which likely occurs predominantly along grain boundaries. We introduce a mathematical scheme for simulating this effect in 2D and explain the numerical implementation of the system. Finally, we will give numerical results comparing our results to known 1D simulations to demonstrate the accuracy of the solver and then show results unique to the 2D case.

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I. INTRODUCTION

The push towards thin-film technology has been driven largely by predictions of future economic viability.1–4 Traditional single-crystal solar cells, such as Si and GaAs, demonstrate very high efficiencies (20 – 30%), but the production of crystalline material is expensive. The original reason thin-film materials were pursued was because they use much less material, which is directly related to the cost of production. Two of the leading thin-film materials are CdTe and Cu(In,Ga)Se2, chosen because their direct bandgaps require a smaller absorption length than Si (and thus require less thickness for optimum performance). CdTe is a nearly ideal material for terrestrial solar cell production, as its band gap of 1.45eV (room temperature) yields the maximum theoretical efficiency for a solar cell, of about 29%. The current record one-of-a-kind laboratory research cell was fabricated in 2015 by First Solar (FSLR) and has an efficiency of 21.5%.5

Despite overwhelming advances in thin-film CdTe technology in recent years, performance of thin-film CdTe devices are still subject to various metastable phenomena that could be characterized by temperature-dependent time constants (activation energies). Most of these metastable changes in CdTe are known to be reversible and require different recovery procedures; however, based on experimental and theoretical investigations at First Solar, metastabilities in CdTe device cannot be explained solely by electronic capture-emission phenomena assuming fixed distributions of point defects.

Many of the physical properties of crystalline solids are determined by the presence of native or foreign point defects. In pure compound crystals the native defects are atoms missing from lattice sites where, according to the crystal structure, atoms should be (vacancies); atoms present at sites where atoms should not be (interstitials); and atoms occupying sites normally occupied by other atoms. In addition, there may be defects in the electronic structure: quasi-free electrons in the conduction band or electrons missing from the valence band (holes). In impure or doped crystals there are also defects involving the foreign atoms. These may occupy normal lattice sites (substitutional foreign atoms) or interstitial sites (interstitial foreign atoms). In elemental crystals similar point defects occur, only misplaced atoms are missing.

In addition to point defects, the performance of CdTe solar cells is affected by the extended defects which include dislocations, stacking faults, grain boundaries (GBs) and inclusions of second phases. Dislocations and GBs are well known to attract impurities, and to promote diffusion.6 Such effects might be expected to lead to instability in devices, or to have an influence on the thermal processing conditions chosen to fabricate certain devices. An example is the inter-diffusion of CdTe and CdS in polycrystalline solar cells for which the grain boundary diffusion coefficient has been measured.7 Grain boundary segregation is well known in metals (e.g. Cu in Pb),8 the driving force being strain reduction at the boundary plane. Decoration of grain and twin boundaries in CdTe with Te inclusions is widely reported. Minor component impurities in CdTe have also been shown to segregate out to grain boundary regions9 and to dislocation arrays.10 The electrical states associated with grain boundaries and dislocations can have a number of adverse effects on the performance of CdTe solar cells. Firstly, the deep states associated with extended defects can promote undesirable recombination. Secondly, grain boundaries act as charge transport barriers. This is attributed to the grain boundary plane being a charged interface, causing it to present an electrical barrier to current transport. Such barriers have been observed directly for CdTe using the so-called remote electron beam induced current (EBIC) method11 and are considered responsible for lim-
iting effects in polycrystalline solar cells.\textsuperscript{12} Thirdly, grain boundaries and dislocations may act as conduits for current transport rather than barriers. The impact of the grain boundaries is likely to depend on their position in the layer; near surface grain boundaries are likely to be Te-rich (i.e. conducting) on account of the etching used to prepare contacts, whereas those remote from the free surface may nevertheless act as recombination centers.

In modern thin-film CdTe technology, Cu is the key dopant that defines major performance parameters such as open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$), and filling factor (FF) by affecting built-in potential of the junction, collection efficiency, and resistivity of the back contact.\textsuperscript{13} However, fast diffusion of Cu from the back contact toward the main junction is believed to contribute to degradation observed in long-term stability studies.\textsuperscript{14} It was determined that while modest amounts of Cu enhance cell performance, excessive amounts degrade device quality and reduce performance.\textsuperscript{15–17} Evolution of Cu-related point defects and complexes in CdTe grains and at grain boundaries (GBs) is expected to cause pronounced effect on device performance leading to observed metastable phenomena.\textsuperscript{18–20}

The paper is organized as follows. In Section II we discuss the drift-diffusion-Poisson system and the necessary extensions to the model for including active defects. The role of grain boundary transport and appropriate mathematical models for their inclusion are then elaborated. In Section III we introduce a self-consistent numerical scheme which allows for the efficient inclusion of any number of defects. We show that the use of an appropriate time-splitting scheme allows our simulation to scale linearly with the number of defects instead of the number of defects squared. Numerical results are presented in Section IV and include: (1) validation of the solver by comparison of 2D and 1D results (Section IV A) and (2) the role of grain boundary diffusion (Section IV B).

\section{MATHEMATICAL MODEL}

We begin with the standard semiconductor equations\textsuperscript{21}:

\begin{align}
-\nabla \cdot (\mathbf{e}_s \nabla V) &= q (p - n + C) \tag{1a}

\partial_t p - \nabla \cdot (D_p \nabla p + \mu_p p \nabla \phi) &= R_i(n, p) \tag{1b}

\partial_t n - \nabla \cdot (D_n \nabla n - \mu_n n \nabla \phi) &= R_i(n, p) \tag{1c}
\end{align}

where $V$ is the electric potential, $q$ is the fundamental charge, $p$ is the concentration of holes, $n$ is the concentration of electrons, $C$ is the net doping concentration, $D_{n/p}$ is the electron/hole diffusion constant, $\mu_{n/p}$ is the electron/hole mobility, and $R_i(n, p)$ is the recombination rate. In equilibrium, the electrochemical potential $\phi$ can be taken equal to the electric potential $V$, but in general it will include the quasi-fermi level potentials and contributions from heterojunctions and band offsets.\textsuperscript{22}

It is important to note here that the charge term on the right hand side of Poisson’s equation will no longer be constant, but will depend on the concentration of charged defects within the device. Each charged defect will have the ability to (a) diffuse, (b) drift under the electric field, and (c) react (either through ionization or with other defect types). Thus (using the quasi-fermi level representation) each defect, call it $X_i$, will obey a similar continuity equation as the electrons and holes\textsuperscript{23,24}:

$$\partial_t X_i - \nabla \cdot (D_i \nabla X_i + \mu_i \theta_i X_i \nabla \phi) = R_i(n, p, \bar{X}) \quad (2)$$

where the diffusion and mobility coefficients are defined analogously to the charge carrier case, $\theta_i$ is the charge of the $i^{th}$ defect, and $\bar{X}$ denotes the vector of concentrations for each of the $i$ defects. More details on how the diffusion rates will depend on the presence of grain boundaries are given in Section II B below.

Note also that the recombination rate may be unique for each defect and in general will depend on the concentrations of electrons and holes as well as the concentrations of all other defects (see Section II A).

\section{A. Reaction Rates}

For the typical reactions in semiconductors, including all applications in this paper, there are only two reaction prototypes, single molecule and bimolecular:

$$X_iX_j \leftrightarrow X_k \quad \text{and} \quad X_iX_j \leftrightarrow X_kX_l \quad (3)$$

which for convenience we will denote by their respective rates $R_{ij}^k$ and $R_{ij}^{kl}$, respectively. Although reactions between three defects simultaneously might be possible, they should be statistically unlikely to occur in usual device operation.\textsuperscript{25} The rate constants for these reactions in principle have to be calculated from first principle calculations, but for the sake of the current work they can be treated as being independent parameters.

Thus each concentration will have two types of loss mechanisms and two types of gain mechanisms. Assuming bimolecular recombination, for each species $X_k$ we may have both:

$$R_{ij}^{kl} = K_{ij}^{kl} (X_iX_j - X_kX_l) \quad \text{or} \quad R_{ij}^k = K_{ij}^k (X_iX_j - X_k). \quad (4)$$

The net rates $R_k(\cdot)$ above are then given as the sum of all of these individual reactions

$$R_k = \sum_{i,j<k, i\neq k} R_{i,j}^{k,l} - R_{k,l}^{i,j} + \sum_{i,j<i} R_{i,j}^k - \sum_{i,j\neq k} R_{i,k}^j. \quad (5)$$

In practice most of these combinations will not correspond to realistic reactions and will thus have a corresponding rate $R = 0$.

Note that the same reaction forms can be used for ionization reactions where species have multiple ionization states. If, for example, we assume that double ionization reactions occur in two states with an unstable intermediate ion then the reaction description will still fit into the above framework.
B. Grain Boundaries

One complication to the problem we aim to solve is that Cadmium Telluride when used for solar cell fabrication is generally not produced as a crystalline material. Under usual fabrication practices, the material is polycrystalline and will form grains which have a characteristic size of approximately 1µm.26 Because a typical cell will measure several centimeters in width, we expect a CdTe solar cell to have many different grains.27

To simplify the analysis in this work, we will not include effects which depend on the orientation of the grains. This is justified by findings in the literature, which suggest that crystal orientation has only a weak direct impact on device simulation parameters.28 However, these orientations result in grain boundaries which will have a large impact on the operation of the device. It has been experimentally shown that chlorine ions favor grain boundaries28 and Copper ions are also predicted to preferentially move along grain boundaries.29 In order to capture these effects we must have a 2D model and we have to specify a method for including the grain boundaries in the model. We note that some work has been done to create 2D device simulators while taking into account the effects of grain boundaries.31,32 However, in those cases the grain boundaries are treated in phenomenological fashion simply as locations where charge traps accumulate. Migration of defects is not considered.

1. Fisher Method

The most cited method for implementing grain boundary diffusion is the Fisher Method,33 in which grain boundaries of width δ at x = 0 (in 2D) are treated as one-dimensional lines:

\[ u_x = D_g u_{xx} + D_g u_{yy} \quad |x| \geq \delta/2 \]  
\[ u_x = \frac{2D_g}{s\delta} u_x + D_{gb} u_{yy} \quad |x| = \delta/2 \]  

where \( u \) is the diffusing concentration, \( D_g \) is the bulk diffusion in the grain, \( D_{gb} \) is the diffusion in the grain boundary, and \( s \) is the segregation factor.

For an isolated grain boundary, Fisher’s model is well understood in several regimes, including exact solutions.34–37 However, for more complicated geometries (such as intersecting grain boundaries) extensions to the method are required. The literature has several examples of extensions of the Fisher model based on symmetry,38,39 but both of these methods fail to describe realistic CdTe solar cell structures. In this work, we derive a new description starting from the original model from the Fisher’s derivation: Anisotropic diffusion.

2. Proposed Model

Our Anisotropic Diffusion Model for a single grain of width δ located at \( x = 0 \) is given by:

\[ \partial_t u = \partial_x (D_x(x)\partial_x u) + \partial_y (D_y(x)\partial_y u) \]  

where where

\[ D_x = \begin{cases} \frac{D_g}{s} & |x| < \delta/2 \\ D_g & |x| \geq \delta/2 \end{cases} \]  

and

\[ D_y = \begin{cases} D_{gb} & |x| < \delta/2 \\ D_g & |x| \geq \delta/2 \end{cases} \]

For a finite difference mesh with size \( h = \delta \) and a symmetric grain boundary, this model gives an identical discretization to the original Fisher model.40

The pure diffusion formulation has the advantage of being numerically more stable and leads to symmetric matrices which result in a more efficient unconditionally stable implicit numerical scheme.

The diffusion constants \( D_x \) and \( D_y \) above differ only in their values inside the grain boundary: \( D_g/s \) and \( D_{gb} \). We further claim (in support with numerical evidence) that for the case of Cu in Cadmium Telluride this difference is negligible at reasonable device temperatures. Let \( Q_{gb}/Q_g \) be the diffusion barrier in the grain and the grain boundary respectively and \( \Delta E \) be the difference in formation energy. Then

\[ \frac{D_g}{s} = D_0 e^{-\frac{Q_g}{k_B T}} = D_0 e^{-\frac{Q_g - \Delta E}{k_B T}} = D_0 e^{-\frac{Q_{gb} - Q_g + Q_g - \Delta E}{k_B T}} \]

\[ = D_0 e^{-\frac{Q_{gb}}{k_B T}} e^{\frac{\Delta Q - \Delta E}{k_B T}} = D_{gb} e^{-\frac{\Delta Q - \Delta E}{k_B T}} \]  

where \( \Delta Q = Q_g - Q_{gb} \). Our claim of isotropic diffusion then rests on showing that \( \Delta Q \approx \Delta E \).

Note that this is not the same as neglecting the temperature dependence of the segregation factor \( s \), rather, it assumes that the temperature dependence of \( s \) is the same as the temperature dependence of the ratio of the diffusions.

C. Slotboom Variables

Charges localized on the grain boundaries can create very strong electric fields in the device (see Section II.B). The convection terms in the drift-diffusion equations will thus cause large changes in the values of the defect concentrations. It is of utmost importance to use a scheme which can handle these large changes in concentration. In 1D, we could automatically account for these changes using a Scharfetter-Gummel discretization,41 however this method cannot
extend directly to higher dimensions on unstructured meshes. Instead, we can transform the system into Slotboom variables\textsuperscript{21}. We assume the Einstein relations: $D_i = U_T \mu_i$ are valid. Then:

\begin{equation}
-\nabla \cdot (\epsilon_s \nabla V) = q \left( p - n + \sum_i \theta_i X_i \right), \tag{10a}
\end{equation}

\begin{equation}
\partial_t p - \nabla \cdot (U_T \mu_p \nabla p + \mu_p p \nabla \phi) = R(n, p), \tag{10b}
\end{equation}

\begin{equation}
\partial_t n - \nabla \cdot (U_T \mu_n \nabla n - \mu_n n \nabla \phi) = R(n, p), \tag{10c}
\end{equation}

\begin{equation}
\partial_i X_i - \nabla \cdot (U_T \mu_i \nabla X_i + \mu_i \theta_i X_i \nabla \phi) = R_i(\bar{X}), \tag{10d}
\end{equation}

where $U_T$ is the thermal voltage.

1. Bulk equations

We use the following identity

\begin{equation}
e^{\frac{\phi}{U_T}} \nabla \left( X e^{\frac{\phi}{U_T}} \right) = e^{\frac{\phi}{U_T}} \left( \nabla X e^{\frac{\phi}{U_T}} \pm X \frac{1}{U_T} \nabla \phi \right) = \nabla X \pm \frac{1}{U_T} X \nabla \phi \tag{11}
\end{equation}

to rewrite the diffusion-reaction equations for the defects from

\begin{equation}
\partial_i X_i - \nabla \cdot (U_T \mu_i \nabla X_i + \mu_i \theta_i X_i \nabla \phi) = R_i(\bar{X}) \tag{12}
\end{equation}

to

\begin{equation}
\partial_i X_i - \nabla \cdot \left( \mu_i U_T e^{-\frac{\theta_i \phi}{U_T}} \nabla \left( X_i e^{\frac{\theta_i \phi}{U_T}} \right) \right) = R_i(\bar{X}) \tag{13}
\end{equation}

We define the variable $u_i = X_i e^{\frac{\theta_i \phi}{U_T}}$ and write:

\begin{equation}
\partial_i \left( e^{-\frac{\theta_i \phi}{U_T}} u_i \right) - \nabla \cdot \left( \mu_i U_T e^{-\frac{\theta_i \phi}{U_T}} \nabla u_i \right) = R_i(e^{-\frac{\phi}{U_T}} \bar{u}). \tag{14}
\end{equation}

With this manipulation of the equations, we have eliminated the convection term at the expense of a more complicated diffusion matrix and the addition of a coefficient for the time-dependent term.

2. Reformulation of the Problem

Using the Slotboom variables, we arrive at a set of equations for $V$, $n$, $p$, and the $u_i$. In fact, because $n$ and $p$ have the same form as the $X_i$ equations, we can define $\theta_n = -1$ and $\theta_p = 1$ so that

\begin{equation}
u_n = ne^{\frac{\phi}{U_T}} \quad u_p = pe^{\frac{\phi}{U_T}} \tag{15}
\end{equation}

Introducing the index set $I = \{n, p, 1, 2, \ldots, N\}$, where $N$ is the number of defects under consideration, we can write Poisson’s Equation as

\begin{equation}
-\nabla \cdot (\epsilon_s \nabla V) = q \sum_{i \in I} \theta_i u_i e^{-\frac{\theta_i \phi}{U_T}} \tag{16}
\end{equation}

and our $N + 2$ generalized diffusion-reaction equations as

\begin{equation}
\partial_t \left( e^{-\frac{\phi}{U_T}} u_i \right) - \nabla \cdot \left( \mu_i U_T e^{-\frac{\theta_i \phi}{U_T}} \nabla u_i \right) = R_i(e^{-\frac{\phi}{U_T}} \bar{u}). \tag{17}
\end{equation}

Note that we have added a subscript $i$ to $\phi_i$. This notation allows for asymmetric bands for electrons and holes and also allows us to modify the effects of a heterojunction on each defect independently.

It will also be convenient to use a mixed scheme with both $X_i$ and $u_i$ (especially for notational purposes). This gives the following system:

\begin{equation}
-\nabla \cdot (\epsilon_s \nabla V) = q \sum_{i \in I} \theta_i X_i \tag{18a}
\end{equation}

\begin{equation}
\partial_i X_i - \nabla \cdot \left( \mu_i U_T e^{-\frac{\theta_i \phi}{U_T}} \nabla u_i \right) = R_i(\bar{X}). \tag{18b}
\end{equation}

These equations are formally self-adjoint, but the coefficients depend exponentially on $\phi$ and thus have a large dynamic range. As we will show in the next section, this effect can be compensated numerically.

III. COMPUTATIONAL MODEL

We seek to numerically solve the system:

\begin{equation}
-\nabla \cdot (\epsilon_s \nabla V) = q \left( p - n + \sum_i \theta_i X_i \right) \tag{19a}
\end{equation}

\begin{equation}
\partial_t p - \nabla \cdot (D_p \nabla p + \mu_p p \nabla \phi) = R(n, p) \tag{19b}
\end{equation}

\begin{equation}
\partial_t n - \nabla \cdot (D_n \nabla n - \mu_n n \nabla \phi) = R(n, p) \tag{19c}
\end{equation}

\begin{equation}
\partial_i X_i - \nabla \cdot (D_i \nabla X_i + \mu_i \theta_i X_i \nabla \phi) = R_i(\bar{X}) \tag{19d}
\end{equation}

where $X_i$ is the concentration of the $i$th type of defect and $\theta_i$ is the charge of the $i$th type of defect. We also define $\phi = V + V_b$, where $V_b$ corresponds not only to the usual built-in-voltage, but also includes terms that account for heterojunctions and band offsets. In future analysis this term will include effects due to the change in chemical potentials for charge carriers in grain boundaries, to account for different materials, or both. (Note that for neutral particles ($\theta_i = 0$) this will require including a term in the fourth equation which is not proportional to $\theta$). We assume that $V_b$ is constant with respect to time and therefore does not require an additional partial differential equation.

Creating a numerical scheme for solving this system of $N + 3$ equations (where $N$ is the number of defects considered) requires consideration of several different characteristics of the system. In particular, we need to accurately discretize the system in the bulk, we need to implement suitable boundary conditions for each of the equations, and we need to define how the reaction rates will act.

The spatial discretization is the only portion which will depend on the dimension of the system, so we defer discussion of the grain boundaries to Section III.B.
A. Time Splitting

Leaving aside for a moment the issue of space discretization, we develop a time discretization scheme which allows us to decouple the equations. In particular, there are two types of coupling in Equations (18). The potential is the most involved of the couplings, with every (charged) defect appearing in Poisson’s equation and the potential appearing in each of the (charged) defect equations. This diffusion term involves only a single species of defect, but is nonlocal in space. The other coupling is through the \( R_i(\bar{X}) \) term, which couples all of the reaction-diffusion equations, but is local in space.

The usual first step is to use a Gummel-type iteration\(^42\), alternating between calculation of Poisson’s Equation and the reaction-diffusion equation. However, as we will see later, our scheme is significantly simplified if we first deal with the reaction term. Because the reaction terms are spatially independent, they can be solved as a nonlinear ODE. The remaining spatially-dependent diffusion problem will now be linear in \( X_i \) and decoupled from the other components of \( X \). These two stages are given by:

\[
\begin{align*}
\partial_t X_i - \nabla \cdot \left( \mu_i U_T e^{-\frac{\theta_i}{T_T}} \nabla u_i \right) &= 0 \quad (20a) \\
\partial_t X_i &= R_i(\bar{X}) \quad (20b)
\end{align*}
\]

We must still deal with Poisson’s equation, but since it too is linear in the \( X_i \), we can consider it in the same step as the diffusion equation for the \( X_i \), retaining the decoupled structure. The obvious benefit to this approach is that for \( N \) defects, the \( N \) drift-diffusion steps are decoupled, so instead of solving a large matrix including \( N \) times the number of spatial degrees of freedom, we can solve \( N \) significantly easier problems.

Note that we are left with significant freedom in the structure of the iteration. In particular, we note that the reaction equation does not a-priori respect the boundary conditions of the problem. For realistic final results, we should therefore choose to calculate the diffusion step last, or proceed by using a Strang-splitting method\(^43\).

B. Drift-Diffusion Implementation

Because we have decoupled each of the drift-diffusion equations from the larger problem, we only need to introduce an appropriate spatial discretization scheme to solve the following problem:

\[
\partial_t X_i - \nabla \cdot \left( \mu_i U_T e^{-\frac{\theta_i}{T_T}} \nabla u_i \right) = 0 \quad (21)
\]

This spatial discretization of the problem is to some degree flexible, since none of its properties are dictated by the time-splitting scheme discussed above. In 1D, the usual Scharfetter-Gummel\(^41\) is appropriate. The 1D version (obviously without grain boundaries) has already been demonstrated\(^44,45\).

In 2D, however, many of the schemes in the literature\(^46\) do not work as well as desired. Any scheme which relies upon a-priori knowledge information about the structure of the devices\(^47\) runs into significant difficulties when the doping can change throughout time. As we will show in Section IV, the doping at many points in the device will change from p-type to n-type over time. In particular, schemes which require edges perpendicular to the direction of the electric field will not deal well with the nonlinear wave-fronts associated with grain boundary diffusion, and schemes which require specialized meshes\(^48\) may not accommodate complicated grain boundary geometries. To handle these complicated geometries, we choose to use a finite element method (see Section III B 1). Instead of relying upon an elaborate grid scheme, we directly discretize the Slotboom variables\(^49\) (Section II C) and use the properties of the scheme to allow exponential fitting of the charge carriers and defects between nodes.

1. Spatial Discretization

In order to deal with the complicated geometries which arise from the grain boundaries, we seek to solve this equation using finite elements. In the usual way, we will triangulate our domain \( \Omega = \bigcup T_h \) with small triangles on the grain boundaries to handle large changes in the gradients. We then take the approximations \( u_i \in V_h \) of \( u_i \) which are piecewise linear on the triangles and continuous on the whole domain but still satisfy the boundary conditions.

Multiplying our equation by a test function \( v \) in the same space and integrating over the domain yields:

\[
\int_{\Omega} \partial_t X_i v dx = \int_{\Omega} \nabla \cdot \left( \mu_i U_T e^{-\frac{\theta_i}{T_T}} \nabla u_i \right) v dx. \quad (22)
\]

Integrating by parts and separating the terms allows us to calculate the stiffness and mass matrices:

\[
\begin{align*}
A_i &:= \sum_{K \in T_h} \mu_i U_T \int_K -e^{-\frac{\theta_i}{T_T}} \nabla \psi_j \cdot \nabla \psi_i dx \\
M_i &:= \sum_{K \in T_h} \int_K \psi_j \psi_i dx \quad (23)
\end{align*}
\]

Details can be found in a finite element method reference\(^50\).

Combining the previous results, we can reformulate our PDE by:

\[
\begin{align*}
\int_{\Omega} \partial_t X_i v dx &= \int_{\Omega} \nabla \cdot \left( \mu_i U_T e^{-\frac{\theta_i}{T_T}} \nabla u_i \right) v dx \quad (25a) \\
vM(\partial_t X_i) &= vA_i \forall v \in V_h \quad (25b)
\end{align*}
\]

In the usual manner for finite elements, we can assume that this relationship holds for all possible functions \( v \)
and write the equation as a function of $u$ and $X$ only. Inserting the definition of $u$ to close the equation yields:

$$M(\partial_t X_i) = A_i \left( X_i e^{\frac{\phi_i}{V_T}} \right)$$  \hspace{0.5cm} (26)

Note that for piecewise linear finite elements, the exponential inside the stiffness matrix $A$ will be evaluated at the barycenter of the finite elements. In contrast, the exponential on the left-hand side of Equation (26) must be evaluated at the grid points. For each entry of the stiffness matrix this will yield exponentials of the form:

$$e^{-\frac{\phi_i(r_k)}{V_T}} e^{-\frac{\phi_i(r_l)}{V_T}} = e^{\frac{\phi_i(r_k) - \phi_i(r_l)}{V_T}}.$$  \hspace{0.5cm} (27)

Note that this form bears great resemblance to the 1D Scharfetter-Gummel exponential.\(^{41}\) It plays a similar role in allowing a linear problem to approximate exponential fitting between nodes.

We can finish the solution by assuming implicit Euler for the time derivative:

$$M \frac{1}{\Delta t} (X_i^{k+1} - X_i^k) = A_i \left( X_i^{k+1} e^{\frac{\phi_i}{V_T}} \right)$$

$$\left( \frac{M}{\Delta t} - A_i \phi \right) X_i^{k+1} = \frac{M}{\Delta t} X_i^k$$  \hspace{0.5cm} (28)

where the matrix $\phi = \text{diag} \left( e^{\frac{\phi_i}{V_T}} \right)$.

Formally, our solution is given by:

$$X_i^{k+1} = \left( \frac{M}{\Delta t} - A_i \phi \right)^{-1} \frac{M}{\Delta t} X_i^k$$  \hspace{0.5cm} (29)

(but in practice we will use a numerical algorithm to solve the equation instead of actually inverting the matrix).

C. Reaction Step

The output from our drift-diffusion finite element step will be the values of $u$ at all of the finite element nodes. Because the reaction step is independent of the spatial variables, we may independently solve a reaction ODE at each node:

$$\partial_t X_i = R_i(\bar{X})$$  \hspace{0.5cm} (30)

This is not necessarily a simple ODE, however, since we have an arbitrary number of defects and an arbitrary number of reactions. However, as we saw in Section II A these reactions are all of two very specific forms, either the decay of a single defect or the bimolecular reaction of two defects.

For a single reaction, we can solve the reaction using the Implicit Euler method exactly. We consider the concrete case of four defects which can interact by either single molecular or bimolecular reactions and demonstrate the exact calculations. Note that these enumerate all possible reactions. Increasing the number of defects may increase the total number of possible reactions, but only 3 or 4 defects will be involved in any particular reaction.

There are two strategies for implementing individual reactions. Each direction can be implemented independently or simultaneously. However, we find that the latter case is vastly superior and does not present a significant computational issue because the reactions are local in space. As a simple test case, consider a reaction which is at equilibrium. There is no net reaction, but if there are large numbers of defects, then each direction will have a large number of reacting particles. This may create numerical instability in the iteration scheme depending on the order that we evaluate the reactions. In contrast, if the reaction is considered as a whole then we have a stable equilibrium for zero net reactions.

Note that the issue above does not apply in the case when we iterate any number of different reactions - See Section III C 3.

1. Dissociation Reaction

Let us consider the reaction given by rate $R_1^{2,3}$:

$$\partial_t X_1 = K_{1,2,3}^1 X_2 X_3 - K_{1,2,3}^1 X_1$$  \hspace{0.5cm} (31a)

$$\partial_t X_2 = K_{1,2,3}^2 X_1 - K_{1,2,3}^2 X_2 X_3$$  \hspace{0.5cm} (31b)

$$\partial_t X_3 = K_{1,2,3}^3 X_1 - K_{2,3}^3 X_2 X_3$$  \hspace{0.5cm} (31c)

This could, for instance, represent a knock-off reaction where interstitial Copper (Cu$_i$) replaces lattice Cadmium, resulting in Copper atom at a Cadmium site (Cu$_{Cd}$) and an interstitial Cadmium (Cd$_i$).

Note that the right hand sides are identical (up to sign) and that the quantities $(X_1 + X_2)$ and $(X_1 + X_3)$ are conserved (corresponding to conservation of copper and conservation of lattice sites in our example). In particular, if the superscript refers to the time-step, we have that $X_1^{k+1} + X_2^{k+1} = X_1^k + X_2^k$ and $X_1^{k+1} + X_3^{k+1} = X_1^k + X_3^k$. We will use these equations to decouple the ODEs. First, let us use the Implicit Euler method to write the first ODE for time step $k$ as an algebraic expression:

$$\frac{1}{\Delta t} (X_1^{k+1} - X_1^k) = K_{1,2,3}^{k+1} X_2^{k+1} X_3^{k+1} - K_{1,2,3}^{k+1} X_1^{k+1}$$  \hspace{0.5cm} (32)

Since $\Delta t$ should be small, we multiply it out to avoid numerically unstable division by a small number. Using our conservation laws, we can also write $X_2^{k+1}$ and $X_3^{k+1}$ in terms of $X_1^{k+1}$ and the known values of $X$ as time step $k$:

$$X_2^{k+1} = X_1^k + X_3^k - X_2^{k+1}$$  \hspace{0.5cm} (33a)

$$X_3^{k+1} = X_1^k + X_3^k - X_1^{k+1}$$  \hspace{0.5cm} (33b)

Substitution yields:
Discretizing the equation for $X_i^{k+1}$ yields

$$X_i^{k+1} = K_{2,3}^1 \Delta t \left( X_i^k + X_2^k - X_i^{k+1} \right) - K_{1,3}^2 \Delta t X_i^{k+1}$$

(34)

a quadratic equation for $X_i^{k+1}$ in the same manner as the previous section. The coefficients are:

$$A = \left( K_{3,4}^1 - K_{1,2}^3 \right) \Delta t$$

(35a)

$$B = -1 - K_{3,4}^1 \Delta t \left( 2X_2^k + X_3^k + X_4^k \right) - K_{1,2}^3 \Delta t \left( X_2^k - X_i^k \right)$$

(35b)

$$C = X_i^k + X_2^k \left( X_2^k + X_3^k \right) \left( X_2^k + X_3^k \right)$$

(35c)

and our solution is again given by (36).

3. Iteration by Reaction

Because every considered reaction is of one of the two above types, we can solve every reaction using just the explicit formulas given above. Simply iterating through all possible reactions in any order gives a first order unconditionally stable method for the reaction step. Experimental results demonstrate that changing this order has no significant impact on the results.

As we mentioned above, particular care needs to be taken to have a stable equilibrium. However, when any individual reaction is at equilibrium there is no net change. By the principle of detailed balance, we only expect general equilibrium when every individual reaction is at equilibrium. Because the steady-states are preserved, we can expect the time dependent case to converge stably regardless of order.

IV. NUMERICAL RESULTS

We will now demonstrate numerical results for a simple model system consisting of interstitial Copper ($Cu_i$), interstitial Cadmium ($Cd_i$), and Copper on Cadmium sites ($CuCd_i$). To verify the accuracy of the model we will first compare 2D results without grain boundaries with simulations results obtained with the 1D unified solver previously developed by the authors. Afterwards we will show how the introduction of grain boundaries changes the results.

A. Solver Validation

First, we demonstrate that our 2D finite element solver can replicate results from previously published 1D finite-difference work. We begin with a simulation of the migration of Copper in an anneal of the system for 220 seconds at a temperature of 200C. The results for the concentrations are given in Figure 1. The concentrations of $CuCd_i$ and $Cd_i$ are indistinguishable between the two cases. The concentrations of $Cu_i$...
are noticeably different near the back contact, but we observe that these concentrations are two orders of magnitude smaller than the corresponding values for $C_{\text{Cu}_{\text{Cd}}}$ and $C_{\text{Cd}}$. Note that we cannot expect exact matching, because we have not simply extended the 1D finite difference scheme to 2D, but introduced an entirely new finite element scheme. Thus numerical discretization errors are not expected to compensate perfectly. Furthermore, from an experimental perspective we can only really measure the total copper concentrations. The 1D and 2D simulations of this quantity, shown in Figure 2, are virtually indistinguishable.

B. Introducing Grain Boundaries

Having shown perfect agreement with corresponding 1D results, we next examine the role of the grain boundaries on the diffusion of interstitial Copper. For consistency and clarity, we use the same simulation parameters from Section IV A for all parameters in the bulk of the grain.

We use meshes with a single grain boundary at the center of the domain. The domain is symmetric and we use symmetric no-flux boundary conditions on the left and right boundaries. The width of the domain thus corresponds to the width of an average grain, although we center the domain on the grain boundary to better observe the dynamics nearby. A sample mesh is given in Figure 3. Sample results on the 2D mesh are shown in Figure 4.

To verify the artificial grain boundary width discussed in Section II B 2, we show numerical justification by using an artificially wide grain boundary corresponding to the results from the diffusion-only model. In Figure 5 we show the 1D total copper concentration crossections for grain boundaries with artificial widths ranging from 1.56nm to 100nm. These results are all extremely similar, but the number of degrees of freedom varies from 2595 to 13541. Using an even smaller .78nm grain boundary
as the base case, the percent error of the various approximations is shown in Figure 6.

C. Parameter Investigation

Having established the validity of the artificial grain boundary width, we next consider important characteristics associated with migration of copper along the grain boundary. The obvious parameter is the diffusivity of copper interstitial in the grain boundary, \( D_{gb} \). Figure 7 shows the results of changing the grain boundary diffusion coefficient over 3 orders of magnitude starting with twice the diffusivity in the grain. Indeed, by our assumptions in Section II B 2, this corresponds to changing the physical segregation coefficient \( s \) from .05 to \( 5 \times 10^{-5} \).

As expected, increasing the grain boundary diffusion increases the proliferation of copper into the device. However, we also note that the two largest grain boundary diffusion coefficients give very similar results. This is likely due to both saturation effects in the grain boundary and because the built-in potential (corresponding to the presence of a Cadmium Sulfide layer) repels the positively charged interstitial copper. For high diffusivities, the slope in the bulk region corresponds to the expected exponential decay dictated by convection dominated transport.

Because we plot the average copper concentration in a horizontal strip, the plots are strongly influenced by the “width” of the grain boundaries. From our simulation standpoint, this corresponds to the choice of boundary conditions on the side of the device. For simplicity, we have chosen symmetric no-flux conditions. This corresponds to either a device with insulating borders, or more realistically, to repeating grains with widths given by the
FIG. 7. Comparison of the calculated total copper concentration for segregation coefficients of different orders of magnitude. This corresponds to grain boundary diffusivities ranging from 20 to 20000 times the bulk diffusivity. Note that the plots essentially coincide in the first 200-300nm.

FIG. 8. Comparison of the calculated total copper concentration for CdTe grains which range from 2.6µm to 325nm in depth. These CdTe grains are all 2.6 µm long.

FIG. 9. Comparison of the calculated total copper concentration for different initial copper doses. Note the effects of the change in net doping near the back contact.

D. Simulation Capabilities

We can also investigate the results of changing the initial dose of copper in the system. Because the system is nonlinear, this does not serve to simply shift the averaged concentrations. In particular, near the back contact the energetically favorable Cu_Cd is negatively charged. When the concentration is high enough, this creates a small region where the electric field changes sign, which results in a local maximum for the total copper concentration (shown in Figure 9).

This demonstrates that our finite element system can correctly handle changes in doping and therefore changes in the direction of the electric field. We note that the change in doping does not occur at a pre-defined boundary, but rather dynamically as positively charged Cu_i moves throughout the device and reacts with Cadmium to form negatively charged Cu_Cd.

We can also simulate more complicated grain boundary
geometries. Because we give the grain boundaries artificial width, intersections are handled implicitly by the form of the drift-diffusion equations. This allows us to consider, for example, arbitrary asymmetric tri-junctions - See Figure 10.

![Sample finite element results for the total copper concentration in a domain with a forked grain boundary. Note the presence of copper along the grain boundary which quickly decays as we move into the bulk of the grains.](image)

**FIG. 10.** Sample finite element results for the total copper concentration in a domain with a forked grain boundary. Note the presence of copper along the grain boundary which quickly decays as we move into the bulk of the grains.

**V. CONCLUSIONS**

We have proposed, theoretically developed and implemented in MATLAB a consistent and efficient 2D numerical solver for modeling materials with grain boundaries. Our solver allows for efficient study of material systems with arbitrary number of defects described with arbitrary number of chemical reactions. The scheme scales linearly with the number of defects, resulting in a convenient tool that can be adapted for systems with a large number of defects. The main purpose of this scheme is, as already noted in the introduction part of this paper, to study metastabilities in CdTe solar cells due to, for example, annealing, short-circuit stress, open-circuit stress, etc., due to migration of Cu, Cl, S and O.

We also note that the capabilities of our new solver go significantly beyond earlier efforts to model defect migration in CdTe. As mentioned above, our previously published solver operated purely on a 1D domain and thus could not take into account the effects of grain boundaries. That 1D solver in turn represented an extension to simulation work that looked at the problem of defect migration almost exclusively in terms of diffusion, omitting self-consistent field effects and reaction terms. Simulation studies of defect diffusion along grain boundaries in 2D CdTe have previously been performed for the defect cases of Cu, Cl and P, using Fisher style models that were described in Section II B. These papers again omit the effects of reactions as well as self-consistent field effects.

At present, we have only studied Cu diffusion but inclusion of Cl, O, and S should allow us to mimic current experiments performed at First Solar and Colorado State University (our DOE PREDICTS partners). Nevertheless, predictive capabilities of the solver will depend on accurate first principle calculations of diffusion coefficients and reaction rates. We can also introduce formation energy differences related to the grain boundaries. This provides another mechanism for large concentrations on the grain boundaries and should give even more flexibility for matching experimental results.

We are now adding a standard solar cell device simulator to the existing tool. Using the already existing drift-diffusion framework this will allow us to calculate standard solar cell parameters such as open-circuit voltage, short-circuit current and the fill-factor. As such, this will represent a tool which can be used to motivate future efforts for improving the efficiency of CdTe solar cells.

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