



Numerical reactive diffusion modeling of stacked elemental layer rapid thermal annealed chalcopyrite absorber layer formation



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ABSTRACT

The diffusion processes during chalcopyrite (CuInSe_2) layer formation by rapid thermal annealing (RTA) of stacked elemental layers are still not completely understood. We present a one-dimensional kinetic model, which describes the diffusive reaction kinetics for layers of partial miscible systems to describe the RTA process. The model was applied to a layer stack of elemental Se between the metallic layers Cu and In. First, some binary phases occur. After the Se layer is consumed, CuInSe_2 is observed between the binary compounds Cu_2Se and In_2Se_3 .

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1. Introduction

Thin film solar cells with chalcopyrite absorber have low production costs and are less material consuming compared with the classical Si-based solar cells. Usually, the elements Cu, In, Ga, Se and S are incorporated, which leads to the highest module efficiencies. One route of production is the stacked elemental layer and subsequent rapid thermal annealing (SEL-RTA), which up to now allows the highest efficiency chalcopyrite-based solar cells for large area production up to 16.6% by AVANCIS [1]: First, the Mo backside contact and metallic layers (Cu, In, Ga) are usually sputtered on a glass substrate followed by vapor deposition of Se and S. This so-called precursor is annealed, where reactive diffusion takes place, and several intermediate phases form, which finally react to form the chalcopyrite absorber [2]. However, the mechanisms during the reactive diffusion are still not completely understood. Another not completely solved problem is the occurrence of inhomogeneities in the chalcopyrite absorber, which decrease the efficiency of the solar cells. There have been earlier studies on the growth kinetics of the chalcopyrite absorber formation of the SEL-RTA by fitting dynamic calorimetric measurement curves [3] and recent approaches to model parts of absorber formation process by first principle method [4].

In this paper, we present a numerical tool with the aim to completely model the RTA-step. It will allow a prediction of the phases occurring during the annealing in the future. The initial state is described by a sequence of layers, which can be either elements such as Cu, In, and Se or also intermetallic compounds. It is capable of describing the occurrence of new phases by seed formation and diffusion of species in the layers by

implementing a multi-phase and multi-component diffusion model. Although the model has been developed for 3D simulation, we will focus on the 1D case to demonstrate the simulation capabilities in this work.

While the computer code presented in this work is already fully developed in terms of thermal budget, diffusion of elements and reaction kinetics to form CuInSe_2 via intermediate binary compounds, the chemical and physical boundary conditions applied to the modeling exhibit a number of assumptions. Most of them are related to the lack of material parameters.

2. Calculation

The absorbers vertical cross section of the layer is represented by a bar, which is divided into cubic cells. A cellular automata is defined on it with the following rules:

1. Each cell has a phase as a state.
2. Cells with different phases must not be located next to each other. A special grain boundary cell must be located between the two cells.
3. A grain boundary is characterized that it belongs to two grains and therefore has two phases as states.

A similar approach has earlier been used by Jacot et al. to simulate the microstructure evolution in Fe-C-alloys [5].

For each cell, the concentrations c_i of the $i = 1 \dots n - 1$ atomic species i are stored, where n is the number of the atomic species in the system. The dependent species n can be calculated from the other concentrations because $\sum c_i = 1$. c_{gbp1} and c_{gbp2} are the concentration boundary conditions at the grain boundary, in which values are close to the ideal concentrations c_{id} of the phases (e.g., for In_2Se_3 $c_{\text{id}}(\text{Cu}) = 0$, $c_{\text{id}}(\text{In}) = 0.4$ and $c_{\text{id}}(\text{Se}) = 0.6$): To calculate c_{gbp1} , the ideal

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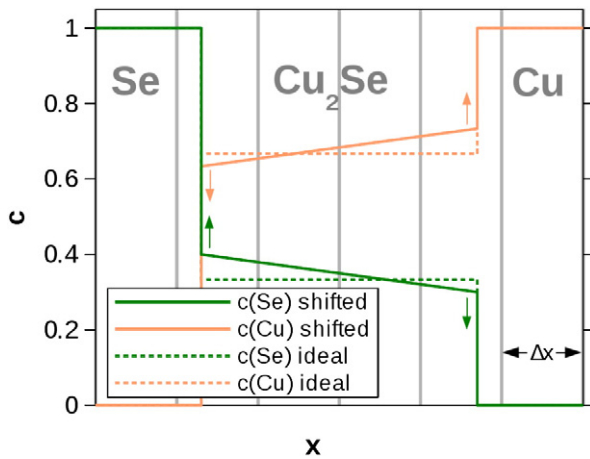


Fig. 1. Shifting of c_{gb} for Cu_2Se between Se and Cu (shown exaggeratedly).

concentration of the phase c_{id1} is slightly increased or decreased in dependence of the ideal concentration of the neighbor phase c_{id2} by

$$c_{gbp1} = c_{id1} + (c_{id2} - c_{id1}) \times 0.005 \quad (1)$$

which is also illustrated by Fig. 1.

This is necessary to create the concentration gradient which is the driving force for the diffusion of the species. There is one exception of this rule: Concentrations of species which are not involved in the formation of a phase are always zero (i.e., impurities are neglected and therefore no impurity diffusion is respected). From c_{gbp1} and c_{gbp2} , the exact position of the grain boundary inside the cell is determined: This is done via the phase contents of the two phases f_1 and f_2 , which are separated by the grain boundary. For each grain boundary cell with the concentration c and two involved elements, the following equations hold

$$f_1 = \frac{c - c_{gbp2}}{c_{gbp1} - c_{gbp2}} \quad (2a)$$

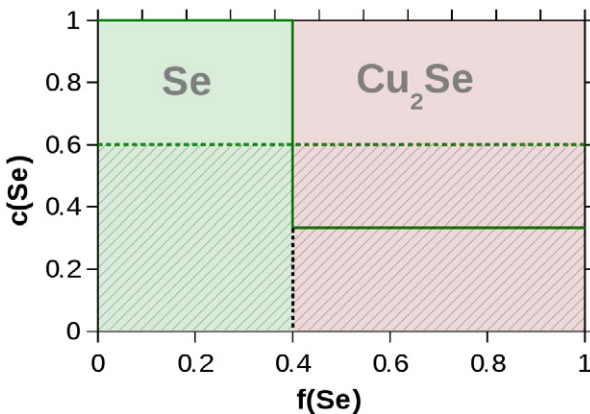


Fig. 2. Illustration of a grain boundary cell with the phases Se and Cu_2Se with $c(\text{Se}) = 0.6$ (dashed horizontal line). This is equivalent with $f(\text{Se}) = 0.4$ and $f(\text{Cu}_2\text{Se}) = 0.6$, which means that the grain boundary is located at $f(\text{Se}) = 0.4$, i.e., the left part of the cell belongs to the Se grain and the right part to the Cu_2Se grain. The concentration in the grain can also be understood as the continuous line, with a jump at the grain boundary. The shifting of c_{gb} at the grain boundary is neglected here.

$$f_2 = \frac{c - c_{gbp1}}{c_{gbp2} - c_{gbp1}} \quad (2b)$$

As long as the concentration is between c_{gbp1} and c_{gbp2} , the values of f_1 and f_2 define the position of the grain boundary in the grain boundary cell because $f_1 + f_2 = 1$ and $0 <= f <= 1$, as also illustrated in Fig. 2.

However, this calculation does not necessarily hold if more than two elements are involved. In this case, it is most likely that some part of the concentrations remain as elements solved in the grain boundary. As an example, a grain boundary cell of the model with the phases CuSe_2 and InSe has the concentrations $c(\text{Cu}) = 0.2$, $c(\text{In}) = 0.28$ and $c(\text{Se}) = 0.52$. Because of Se deficiency in the cell first, as much $f(\text{InSe}) = 0.56$ as possible is formed because it has the more exothermal formation enthalpy, which consumes all In in the cell. From the remaining concentrations, $f(\text{CuSe}_2) = 0.36$ is formed and $c(\text{Cu}) = 0.08$ solutes in the grain boundary.

Using the definition of f_1 and f_2 , the state transition functions of the cellular automata are defined as follows:

1. If f_1 or f_2 is zero the grain boundary is moved into the neighbor cell, which is adjacent to the phase with $f = 0$.
2. If rule 1 is applied and the neighbor cell contains a grain boundary the grain in between is eliminated.
3. If a seed reaches a phase content of $f_s = 0.9$, a new grain boundary is inserted into the neighbor cell the seed grows into and a new grain is created. Thus, a new grain always forms at a grain boundary, which is also the most likely case from thermodynamic point of view.

Applying one of these rules, i.e., a grain boundary movement or a seed formation process always implies an exchange of concentrations, because $f = 0$ (plus a remaining concentration) usually means, that the grain boundary has already moved out of the previous cell.

The concentration changes, which trigger the movement of the boundaries, are driven by chemical diffusion. A comprehensive model for calculation of such problems has been developed by Ågren et al. [6,7]. They described the system as a kinetic part (the mobilities) and a thermodynamic part (which are respected by the thermodynamic factors). Later, they extended their model to multi-phase problems as well [8]. Because exact thermodynamic data are missing to calculate the thermodynamic factors, the model is simplified by calculating the tracer diffusion. Also kinetic data (i.e., diffusion constants), which are necessary to perform the tracer diffusion calculation, are only partially known for the phases which are occurring during CuInSe_2 formation. In the model, the diffusion constant of each phase is set the same for all atomic species.

The diffusion calculation is performed by implementing the finite volume method. The differential equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \quad (3)$$

is integrated piecewise on both sides over each volume defined by the cellular automata. Thus, for each cell an equation is created, which describes the change of concentration from c_C^0 to c_C in dependence of the neighbor cells c_N and c_S

$$(c_C - c_C^0) \cdot \Delta x = D \frac{c_N - c_C}{\Delta x} \Delta t + D \frac{c_S - c_C}{\Delta x} \Delta t \quad (4)$$

where Δt is the distance between two time steps and Δx is the cell size. This has to be done for each atom species except for the dependent one.

The domain boundaries are modeled as zero flux von Neumann boundary conditions to keep the overall concentrations inside the domain constant.

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