Experimental and theoretical investigations of cadmium diffusion in vacancy-rich Cu(In, Ga)Se₂ material

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EXPERIMENTAL AND THEORETICAL INVESTIGATIONS
OF CADMIUM DIFFUSION IN
VACANCY-RICH CU(IN,Ga)SE₂ MATERIAL

by

Norbert J. Biderman

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Abstract

Copper indium gallium selenide (Cu(In,Ga)Se$_2$ or CIGS) has become a significant topic of research and development for photovoltaic application. CIGS photovoltaic devices have demonstrated record conversion efficiencies however are still below the maximum solar conversion efficiency. Losses in performance have been attributed structural defects including vacancies, doping, grain boundaries, and compositional non-uniformity that are poorly understood and controlled.

The cadmium sulfide (CdS) buffer layer plays a critical role in high-performance CIGS photovoltaic devices, serving as the n-type component of the p-n junction formed with the p-type CIGS absorber layer. Cadmium diffusion into the CIGS surface during CdS deposition creates a buried p-n homojunction in addition to the CIGS/CdS p-n heterojunction. CdS is believed to assist in reducing carrier recombination at the CIGS/CdS interface, an important attribute of high-efficiency solar cells. In the present work, cadmium diffusion mechanisms in CIGS are experimentally investigated via secondary ion mass spectroscopy (SIMS) and Auger electron spectroscopy (AES). Two cadmium diffusion profiles with distinct Arrhenius diffusion kinetics within a single depth profile of the CIGS thin film are observed with SIMS and AES: an intense first-stage diffusion profile directly below the CIGS/CdS interface and a long-range, second-stage diffusion profile that extends deep into the thin film. Cadmium grain boundary diffusion is also detected in fine-grain CIGS samples. These multiple diffusion processes are quantified in the present work, and the two-stage cadmium diffusion profiles suggest distinctive lattice diffusion mechanisms.

Calculations and modeling of general impurity diffusion via interstitial sites in CIGS are also conducted via numerical including cadmium, iron, and zinc. In the numerical simulations, the standard diffusion-reaction kinetics theory is extended to vacancy-rich materials like CIGS that contain 1 at. % copper vacancies. With rapid impurity interstitial diffusion in vacancy-rich materials, annihilation of vacancies in vacancy-rich materials occurs via the interstitial-vacancy recombination, introducing non-equilibrium vacancy concentration profiles. A semi-Fickian effective diffusion coefficient that is inversely proportional to the vacancy concentration is derived from the calculations despite the annihilation of excess vacancies. Additional simulations also show that semi-Fickian diffusion profiles can still be obtained even if impurity incorporation via the interstitial diffusion mechanism raises the vacancy concentration of the material, a behavior that may be relevant in CIGS-related materials.
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Chapter 1

Introduction

Worldwide energy consumption has unprecedentedly exploded over the last few centuries, largely due to the Industrial Revolution when methods were developed to harness abundant, cheap fossil fuels including coal and oil. The massive increase in energy consumption has brought prosperity and wealth to many nations in the world. Access to cheap energy revolutionized technologies in agriculture, medicine, and transportation, leading to a human population boom from less than one billion people in the centuries before the Industrial Revolution (circa 1700) to more than seven billion people in the 21st century [1].

However, to quote Paul R. Ehrlich et al., “… humanity has never been moving faster nor further from sustainability than it is now” [1]. Because Earth is essentially finite, unmitigated depletion of fossil fuels risks arresting the development of the human civilization. According to the U.S. Energy Information Administration, while renewable energy is currently in the upswing, fossil fuels still make up nearly 90% of the total energy consumption in the United States in early 2010s [2].

The increasing energy demand can only be met in the 21st century and beyond via a combination of renewable energy sources including but not limited to the following: wind, geothermal, and photovoltaics. Photovoltaics is a method of converting solar energy into direct current electricity using semiconducting materials exhibiting the photovoltaic effect. The photovoltaic effect occurs when the sunlight strikes a material and generates a voltage [3]. Photovoltaics is effective in addressing the world’s energy needs; in an hour, Earth receives enough energy from the sun to account for a single year of the world’s energy consumption at the current consumption rate [4].

To make photovoltaic devices (solar cells) economically competitive versus fossil fuels, solar cells need to exhibit high conversion efficiencies (from sunlight to electrical power) and low manufacturing cost. Currently, with its high laboratory conversion efficiency of ~25% (~16% for commercial systems) and relatively low cost, silicon based solar
cells largely control the photovoltaic market [5]. However, silicon has an indirect band gap which translates into a reduced absorption of the solar spectrum compared to semiconductors with a direct band gap. The indirect band gap forces a greater silicon film thickness on the order of several hundred micrometers to absorb the sunlight spectrum to support its high conversion efficiency.

Due to the energy intensiveness of the silicon solar cell manufacturing process as well as the relatively higher material costs of thick silicon solar cells, copper indium gallium selenide (Cu(In,Ga)Se\textsubscript{2} or CIGS) – a direct band gap semiconducting material – becomes an attractive candidate in challenging silicon’s grip on the solar cell market [4], [6], [7]. Semiconductors with a direct band gap have an inherent advantage: less material is required to collect the sunlight spectrum. In fact, CIGS solar cells with a conversion efficiency of 21.7% only require a CIGS absorber film thickness of \(\sim 2\ \mu m\) [6]. A significant material and processing cost saving can be realized with CIGS solar cells versus silicon solar cells.

While the performance of CIGS photovoltaic devices have vastly improved in recent years, the conversion efficiencies are still below their maximum theoretical Shockley-Queisser limit of approximately 30\% [8]. Losses in performance and subsequently device reliability can be attributed to CIGS structural defects (e.g. electronic doping, atomic vacancies, compositional inhomogeneity, interfaces, and grain boundaries) and the associated limited understanding [9]. Such a limited understanding is significant. For example, a complete CIGS photovoltaic device contains several different layers made of different materials. The presence of several layers alone means multiple interfaces to consider for performance losses and reliability.

Cadmium is an important element residing in the cadmium sulfide (CdS) layer that is deposited atop the CIGS layer in highly efficient CIGS solar cells. This doctoral dissertation focuses on cadmium diffusion into the CIGS layer. It is suspected that CdS exhibits a passivating behavior that minimizes losses in charge separation and electrical current collection at the CdS/CIGS interface. However, high-temperature movement of cadmium into the CIGS layer has been shown to induce performance degradation [10]. Properties of this performance degradation are poorly understood. Thus, an improved understanding of cadmium diffusion in CIGS is fundamental in improving the performance and reliability of CIGS photovoltaic devices. This work utilizes secondary ion mass spectroscopy (SIMS) and Auger electron spectroscopy (AES) to probe cadmium incorporation in solar-grade CIGS materials. Extensive numerical
simulations are also done in this doctoral dissertation to characterize cadmium as well as general impurity diffusion in vacancy-rich materials such as CIGS.

The outline of this thesis is as follows:

• Chapter 2 presents a summary of the Cu(In,Ga)Se₂ photovoltaic device. Topics discussed include the crystal structure, CIGS stoichiometry, and its role in electronic doping via intrinsic defects – especially copper vacancies. The critical CIGS/CdS p-n heterojunction and homojunction are also explored.

• Chapter 3 covers fundamental atomic diffusion theory and its application to the study of diffusion mechanisms in CIGS. Diffusion equations for anisotropic copper self-diffusion via the copper vacancy diffusion mechanism are derived, a key indicator for impurity diffusion via the copper vacancy diffusion mechanism. An overview of point-defect formation energy calculations for non-stoichiometric CIGS and related existing experimental results are also provided.

• Chapter 4 discusses the “semionic” nature of CIGS where both electronic and ionic conductivities are exhibited and the implications for diffusion studies. Early experimental attempts to control copper vacancy concentrations in CIGS for cadmium diffusion studies are elaborated upon in this chapter where negative bias is applied to a point electrode on the CIGS surface to promote ionic copper migration toward the surface and the subsequent precipitation of elemental copper. The experimental difficulty of controlling the precipitation of elemental copper out of CIGS is addressed.

• In Chapter 5, experimental methods to study cadmium diffusion in CIGS are developed using sample-preparation techniques and secondary ion mass spectroscopy (SIMS). Discussed are experiments revealing interesting cadmium diffusion properties in CIGS including high levels of cadmium incorporation in the near-surface region of CIGS (with respect to the CdS layer).

• Chapter 6 provides a specially developed background-signal correction method to confirm and accurately quantify cadmium incorporation in CIGS using Auger electron spectroscopy (AES). This chapter includes experimental considerations for utilizing complementary techniques of AES and SIMS for diffusion studies.
• In Chapter 7, two theoretical models are developed to characterize interstitial- and vacancy-based diffusion mechanisms of intrinsic and extrinsic point defects in vacancy-rich materials like CIGS. The models are derived from and built upon the standard diffusion-reaction theory that has been successfully applied to diffusion studies in traditional semiconductor materials.

• Chapter 8 summarizes the experimental and theoretical investigations of cadmium as well as general impurity diffusion in CIGS.
Chapter 2

Basics of Cu(In,Ga)Se$_2$ photovoltaic devices

2.1 Components of high-efficient Cu(In,Ga)Se$_2$ photovoltaic devices

Cu(In,Ga)Se$_2$ solar cells are made of several layers of different materials. The schematic in Figure 2.1 shows the structure of a typical CIGS solar cell with all layers. The fabrication sequence begins with the soda-lime glass substrate of three-millimeter in thickness. Soda-lime glass contains a significant amount of sodium oxide (Na$_2$O). A molybdenum layer – serving as the back electrical contact – of ~ 500 nm in thickness is deposited on the soda-lime glass substrate. Polycrystalline p-type CIGS is then deposited on the molybdenum layer. The function of the CIGS layer is to absorb and convert sunlight to electrical current. For this reason, the CIGS layer is also called the absorber layer. The thickness of the CIGS layer can vary but typically is 2 µm. Technologically important to CIGS solar cells, n-type cadmium sulfide (CdS) of 50 nm in thickness is deposited on the CIGS layer. CdS in high-efficient CIGS solar cells is typically deposited using chemical bath deposition (CBD). The Cu(In,Ga)Se$_2$ absorber and CdS layers are a central focus of this doctoral dissertation due to their special relationship in high-performance CIGS solar cells. To complete the n-type side of CIGS solar cells, two transparent conductive oxide (TCO) layers are then sputtered onto the CdS layer. The first TCO layer is typically an intrinsic zinc oxide (i-ZnO), highly resistive in nature, which inhibits shunts between underlying CIGS/CdS and top conductive TCO layer. Aluminum-doped zinc oxide (Al-ZnO) serves as the second TCO layer that acts as the transparent conductive window layer with a high band gap. The main function of the TCO layers is to allow the incoming sunlight to pass through to the CIGS layer without being absorbed by the TCO layers. The layers discussed thus far compose a complete p-n junction along with the back contact and a supporting substrate. To complete the CIGS solar cell device, front contacts are finally deposited on top of the ZnO, usually made of a nickel/aluminum grid. For a comprehensive review on the fabrication of Cu(In,Ga)Se$_2$ solar cells, the reader is encouraged to refer to [11].
2.2 Materials science of Cu(In,Ga)Se$_2$

2.2.1 Crystal structure

Copper indium gallium selenide (Cu(In,Ga)Se$_2$ or CIGS) is a I-III-VI$_2$ semiconductor, consisting of elements from periodic table group I (Cu), group III (In and Ga), and group VI (Se). CIGS is of the chalcopyrite crystal structure. The name is derived from the economically important, naturally occurring mineral ore chalcopyrite CuFeS$_2$. A vast
The majority of copper in the market is refined from CuFeS$_2$ [12]. Chalcopyrite crystallizes in the tetragonal system. The unit cell of the tetragonal crystal structure is a rectangular prism with a square base ($a \times a$) of length $a$ and height ($c$), where $c \neq a$. The crystal structure of chalcopyrite exists in many engineered forms: CuInSe$_2$, CuGaSe$_2$, CuInS$_2$, AgInSe$_2$, CuAlSe$_2$, etc. [13]. In fact, indium and gallium atoms share equivalent atomic sites in varying proportions in solar-grade CIGS materials. The chemical formula thus can be written as Cu(In$_{x}$Ga$_{1-x}$)$_2$Se$_2$. The reason for a mixture of indium and gallium in CIGS will be discussed in a following section.

The unit cell of the CIGS crystal structure is shown in Figure 2.2. Every copper atom is tetrahedrally coordinated by four selenium atoms. Likewise, every indium/gallium atom is coordinated by four selenium atoms tetrahedrally. Consequently, every selenium atom is coordinated by two copper and two indium/gallium atoms.

Because CIGS consists of four different elements, it provides for interesting chemical bonding properties. The bonding can be explained rather simply by the octet rule in the context of Linus Pauling’s electrostatic valency principle in ionic solids [13], [18]–[21]. Cu, In/Ga, and Se have one, three, and six valence electrons respectively. Selenium is more electronegative than copper, indium, and gallium, so selenium has an increased tendency to attract electrons [17]. Thus in the ionic solid model, copper, indium, and gallium give up electrons to selenium. To meet the octet rule, each copper atom provides a charge of $\frac{1}{4}+$ to its four Se neighbors. Each indium/gallium atom accordingly donates $\frac{3}{4}+$ to the four Se neighbors. In addition to the six valence electrons each Se atom already possesses, the contributions from neighboring copper and indium atoms brings the number to eight valence electrons, fulfilling the octet rule. Because of the two additional electrons, selenium in CIGS is assigned an oxidation state of 2-. Copper and indium/gallium have an oxidation state of 1+ and 3+ respectively. Due to their oxidation states, copper and indium/gallium atoms are called cations in CIGS whereas selenium atoms are anions. Bonding in CIGS is represented in the flattened two-dimensional schematic in Figure 2.3 that was deduced from the crystallographic structure of CIGS [18]. It can be seen in the figure that the octet rule of containing eight valence electrons is satisfied for all elements in CIGS. However, the reality of the bonding in CIGS is naturally more nuanced. Quantum mechanical calculations of local charge density in CIGS by Jaffe et al. suggest that Cu and Se bonding exhibits a weakly covalent character while the In/Ga and Se bond appears to be stronger and more ionic [19]. This causes a distortion in bond lengths [20].
2.2.2 Band theory of semiconductor Cu(In,Ga)Se$_2$

It was previously stated that Cu(In,Ga)Se$_2$ is a semiconductor material. This section elaborates upon such a distinction.

In terms of electronic properties, materials can be classified into three main categories: insulators, semiconductors, and conductors. Insulators do not transport electrons well while conductors – as the name suggests – are good conductors of electrons. Sandwiched in between insulators and conductors are semiconductors.

The electronic properties of materials are well described by the band theory of solids [21]–[23]. A qualitative construct of the band theory of solids begins with the consideration of a system of isolated atoms placed infinitely away from each other. Electrons in each isolated atom are confined in a potential energy well and occupy different energy levels. According to quantum mechanics, energy values electrons can assume while bounded to the atom are discrete. In other words, the discrete nature of the atomic energy levels dictates that the electrons cannot contain an arbitrary energy value that falls between any two given established energy levels. The energy levels of the electrons in two isolated atoms are represented in Figure 2.4 (a). When the two isolated atoms are brought closer together, the identical energy
levels of the two isolated atoms result in two slightly different energy sublevels. This is shown in Figure 2.4 (b). When a third atom is added to the system, we get three slightly different energy sublevels (Figure 2.4 (c)).

![Figure 2.4 - The potential wells of atomic cores. (a) Two atoms positioned far away from each other. (b) Two interacting atoms. (c) Three interacting atoms.](image)

As $N$ – the number of atoms in the ensemble – becomes very large (e.g. $N \approx 10^{23}$ in 1 cm$^3$ of copper), each of the originally discrete electron energy levels split into $N$ tightly spaced sublevels. The tightly spaced energy sublevels form energy bands as implied in Figure 2.4 (c) and evident in Figure 2.5. While the closely packed energy sublevels within each energy band are still discrete, they are treated as continuous. This can be understood beginning with considering an energy band width of 5 eV (a common figure). Dividing the energy band width by the number of energy states within the band gives us the following equation: $5 \text{ eV} / 10^{23} = 5 \times 10^{-23} \text{ eV}$ [22]. This indicates that the spacing between the discrete energy levels within an energy band is exceedingly small, thus an electron can assume virtually any value of energy within an energy band.

An unique discrete property manifests in the energy band structure of the solid of $N$ atoms. Note that at the equilibrium atomic spacing in Figure 2.5, there are several separate energy bands with continuous energy levels within each band and an absence of energy levels between the energy bands. The region of missing energy levels is commonly referred as the band gap. Energy band gaps are regions of forbidden electron energy values. This peculiar property of energy gaps – stemming from the wonderland of quantum mechanics – gives rise to a technologically important class of materials: semiconductors.

Typically, the only energy bands we concern ourselves are those near and in which the highest electron energy levels are occupied. In insulators and semiconductors, the energy band in which the highest electron energy level is occupied is the valence band. Beyond the band gap above the valence band is the conduction band. The energy level at the top
of the valence band is denoted as $E_V$ while the energy level at the bottom of the conduction band is $E_C$. At temperature $T = 0$ K, the valence band is completely full, and no electron has enough energy to be excited to a conduction-band energy state. Thus, no conduction can occur. At room temperature ($T = 300$ K), some electrons in semiconductors gain sufficient thermal energy to overcome the band gap and occupy energy states at the bottom the conduction band as illustrated in Figure 2.6. Recall that the electron energy levels are essentially continuous within energy bands, so thermally-agitated electrons at the bottom of the conduction band can be easily promoted upward to other energy states and conducted through the solid.

![Figure 2.5 – The electronic structure of an ensemble of many atoms. As atoms are brought together from infinity, their electronic energy levels interact with each other, forming bands of electronic states with band gaps in which no electronic state can exist. $a_0$ is the equilibrium interatomic spacing.](image)

When the valence-band electrons are promoted to the conduction band, they also leave behind “electron-holes” (or simply holes) as implied in Figure 2.6. Like conduction-band electrons, valence-band holes can contribute to overall conduction. In photovoltaic device operation, when an incoming photon strikes a semiconductor material with a sufficiently small band gap energy, an electron-hole pair is generated as a valence-band electron is excited to the conduction band.

Conductivity is a strong function of the magnitude of band gap energy. Semiconductors typically have band gap energies of less than 3 eV. Because insulators have particularly large band gaps, the number of valence-band electrons surpassing the band gap is negligible, hence their poor conducting nature. Conversely, the band structures of conductors
contain overlapping valence and conduction bands, leading to the absence of a band gap and allowing for strong conduction without significant energy input. The overlap of the conduction and valence bands in metals can be understood by considering that in such materials, the equilibrium interatomic spacing is shifted to the left in Figure 2.5 to the region of significant band overlap.

Figure 2.6 – Schematic of the formation of an electron-hole pair in a material with a band gap (e.g. a semiconducting material). At the temperature 0 K, no electron has sufficient energy to be excited to the conduction band. At a finite temperature, a certain number of electrons can be excited to the conduction band, leaving behind holes in the valence band.

It is emphasized that the model of electronic band structure – as well as electrons and holes – discussed above is qualitative and simplified. In the context of isolated atoms, the electrons are localized to their host atoms. In the assembly of N atoms, inner-core electrons still exhibit the localized property because they are tightly bound to the atomic nucleus and thus are less perturbed when N atoms are brought together. Their valence electrons, conversely, are not as strongly bound to the atomic nucleus. The valence energy states of an atom are more easily perturbed in the presence of neighboring atoms. Because of significant perturbation of those higher-energy valence states in the crystal of N atoms, the valence electrons become delocalized and belong to the entire crystal as a whole. The argument also applies to electron-holes; it is misleading to consider a hole belonging to a single atom. The principle of delocalization is responsible for the electrical conduction phenomenon seen in solids. A more rigorous treatment of the electronic band structure, electrons, and holes requires invoking the Schrödinger equation – a partial differential (or eigenvalue) equation describing the quantum state of a physical system – as well as Bloch’s theorem, a mathematical formulation for an electron in a periodic potential. References [16] and [17] provide an accessible discussion of the subject.

Here, it is sufficient to discuss the band gap of Cu(In,Ga)Se₂. CuInSe₂ has a band gap of 1.0 eV, and CuGaSe₂ has a band gap of 1.7 eV [24]. Because CuInSe₂ and CuGaSe₂ are I-III-VI₂ materials, different combinations of elements from groups I, III, and VI can be used to obtain chalcopyrite-based materials with different band gaps. All group I
elements indicated in the chemical formula in stoichiometric proportions—two group VI atoms for every pair of group I and group II atoms—occupy the same dedicated atomic sites. For example, Ag in AgInSe$_2$ and Al in CuAlSe$_2$ occupy the same atomic sites as Cu and In respectively in CuInSe$_2$.

Doping a pure ternary chalcogenide material (e.g. CuInSe$_2$ with gallium) allows for a tunable band gap energy $E_g$. A tunable band gap energy in a solar cell material allows for greater sensitivity and the range of sunlight to be collected [25]. To illustrate this point, refer to Figure 2.7 which is a schematic of internal quantum efficiency (IQE). Internal quantum efficiency is defined as the ratio of the number of charge carriers (electrons and holes) collected by the photovoltaic device to the number of photons with energy $E_\lambda$ that are absorbed by the device [26]. Lambda in $E_\lambda$ refers to the wavelength of a single photon that has the energy $E_\lambda$. Simply stated, internal quantum efficiency is a measure of how well the solar cell absorbs and converts a certain sunlight wavelength into electrical current.

![Figure 2.7 – Internal quantum efficiency spectrum. The more square the IQE curve, the more the irradiated photons are converted to electrical energy.](image)

In Figure 2.7, the dashed lines indicate the ideal internal quantum efficiency a solar cell where all photons through the entire spectrum are converted to electrical energy. Because of the inverse relationship between the wavelength and the corresponding energy of a photon [27], the dashed line ends at $\lambda_{E_g}$, the band gap energy-equivalent wavelength of the photon. If a photon does not have sufficient energy, it cannot surmount the band gap and generate an electron-hole pair. Due to inherent losses in the solar cell, the solid line in the figure represents a typical solar cell. A significant mechanism of loss in internal quantum efficiency is a low diffusion length $L_D$ of the charge carrier. When electron-
hole pairs are generated upon the incidence of photons, the generated electrons and holes must remain separated in order to contribute to electrical current. Solar cell performance is decreased if the recombination of electrons and holes occurs before they can be collected as electrical current.

Figure 2.8 – Left graph: the IQE curve of a CIGS photovoltaic device with a constant gallium ratio in the depth of the CIGS absorber layer. Right graph: the IQE curve of a CIGS photovoltaic device with an increasing (towards the CIGS/Mo interface) gallium ratio in the depth of the CIGS absorber layer. “Front” and “Back” refer to the side from which light is illuminated into the CIGS solar cell.

Not only gallium doping of CuInSe$_2$ enhances the internal quantum efficiency, but a spatially varying gallium doping – rather than an uniform distribution of gallium – leads to a more optimized internal quantum efficiency curve in CIGS solar cells. The left graph (a) in Figure 2.8 shows the IQE curve of a Cu(In,Ga)Se$_2$ material that was deposited at a constant gallium flux [28]. The right graph (b) is a sample deposited at a decreasing Ga/(In+Ga) flux. Ga/(In+Ga) is the amount of gallium with respect to the sum of indium and gallium components in CIGS. Stoichiometry ratios (e.g. Cu/(In+Ga), Ga/(In+Ga), etc.) is commonly used in discussion of controlling non-stoichiometry in CIGS. The “front” and “back” curves represent illumination from the front side and the back side of the CIGS layer respectively. The gallium-varying CIGS sample shows an increased internal quantum efficiency when illuminated from the back side compared to the constant-gallium sample, highlighting the benefit of tuning the band gap of CIGS solar cell materials. Figure 2.9 exhibits a recent improvement in the conversion efficiency of CIGS solar cells by creating a strong Ga/(In+Ga) gradient in CIGS where the ratio is ~ 0.2 at the minimum and ~ 0.45 at the maximum [6].
2.2.3 Electronic doping via intrinsic and extrinsic defects

Improving the sunlight absorption of the CuInSe$_2$ absorber layer via gallium doping layer was briefly introduced in section 2.2.2. At this point, it is useful to elaborate upon Cu(In,Ga)Se$_2$ doping to gain insight how electronic properties of CIGS can be further altered for increased performance. Two types of electronic doping exist – where the electronic properties of the material is modified: intrinsic and extrinsic doping. However, these doping types are defined differently compared to intrinsic and extrinsic semiconductors. An intrinsic semiconductor crystal is a perfect semiconductor crystal without impurities and is thus undoped. The intrinsic scenario correspond to the band diagrams in Figure 2.6 and Figure 2.10 (a). At $T = 0$ K, there are no charge carriers; at $T = 300$ K, the thermally generated electron-hole pairs make equal parts of holes in the valence band and electrons in the conduction band. (b) and (c) in Figure 2.10 is discussed after key concepts are introduced: the Fermi energy and the Fermi level.

Figure 2.10 – Impact of doping on the electronic properties of a semiconducting material depicted using the band diagram. (a) Intrinsic semiconductor (no doping). (b) P-type doped semiconductor. (c) N-type doped semiconductor.
$E_V$ is the energy level at the valence band maximum, and $E_C$ is the energy level at the conduction band minimum. $E_F$ is the Fermi level.

Figure 2.11 – The Fermi-Dirac distribution as a function of various temperatures.

The Fermi energy and Fermi level (both denoted as $E_F$) are important parameters describing the populations of electron and holes and thus deserve a discussion due to their roles in the analysis of defects and diffusion in section 3.7. The Fermi level is distinct from the Fermi energy which is sometimes used interchangeably in the scientific community, leading to confusion and inconsistent use [21], [29]–[31]. Using Hummel’s definition, at the temperature 0 K, the highest energy level filled with electrons is called the Fermi energy where the energy levels above (below) $E_F$ are entirely empty (full) (curve (a) in Figure 2.11) [21]. The solution to the Schrödinger equation for the one-dimensional infinite potential well (the particle in a box) problem with zero potential inside the well provides a simple analog for the concept of Fermi energy [21]. If the infinite potential well has multiple non-interacting electrons at 0 K, the electrons fill the energy levels, starting with the lowest level according to the Pauli exclusion principle where a given energy level can at the most hold two electrons. There is an abrupt cutoff of occupied energy levels at this Fermi energy where all energy levels above the Fermi energy are unoccupied. In the one-dimensional infinite potential well problem, all of the electron’s energy is kinetic at the Fermi energy if the electron’s potential energy is defined to be zero inside the well.
The Fermi energy definition becomes problematic at temperatures above 0 K. At a nonzero temperature, electrons have sufficient energy to excite into higher energy levels above the Fermi energy, leaving behind now unoccupied energy levels. There is no longer a single energy level that might correspond to the highest energy level occupied by an electron. The abrupt cutoff of filled energy levels now becomes smeared (curves (b)-(d) in Figure 2.11); there is a nonzero probability of an electron occupying an arbitrary energy level above the Fermi energy. Note that all curves in Figure 2.11 have a common pivot at energy level \( E_F \) where the occupancy probability is 50% according to Fermi-Dirac statistics [21]–[23]. Whether the material is a metal, a semiconductor, or an insulator, the occupation probability is still 50% at the Fermi level \( E_F \) at a finite \( T \). The Fermi level’s definition of having a 50% probability of being occupied by an electron makes it a convenient point of reference at various temperatures.

The Fermi energy and the Fermi level have been referred to as the chemical potential of electrons [29], [32]–[35]. In the context of the one-dimensional potential well problem at 0 K, the electron chemical potential \( \mu_e \) (Fermi energy \( E_F \)) can be seen as the change in energy \( \Delta E \) of the system of electrons when an electron is added to the system of \( N \) electrons with an initial total energy of \( E_N \) in the well (purely kinetic energy; no potential energy): \( \mu_e = E_F = \Delta E = E_{N+1} - E_N \) [34], [35]. Kasap also describes the Fermi level as a measure of the potential for an electron to do work [29].

Fermi level \( E_F \) is typically determined with respect to its distance from the valence band maximum. An important property of the Fermi-Dirac distribution is its symmetry about \( E_F \) at all temperatures. The probability of an energy state located \( \Delta E \) above \( E_F \) being occupied (by an electron) equals the probability of an energy state located \( \Delta E \) below \( E_F \) being empty (occupied by a hole) [23]. Because intrinsic semiconductors must have the same amount of electrons compared to holes at a temperature \( T \) above 0 K, \( E_F \) is required to be halfway between \( E_V \) and \( E_C \) in the band gap (Figure 2.10). To calculate the actual concentrations of electrons (holes) above \( E_C \) (below \( E_V \)), the density of available energy states must be known. While the Fermi-Dirac distribution is nonzero in the band gap between \( E_V \) and \( E_C \) at temperatures above 0 K, the lack of energy levels forbids electrons from occupying such energy levels. The intrinsic carrier concentration in CIGS at 300 K is \( 5 \times 10^9 \) cm\(^{-3} \), comparable to silicon’s \( 1.5 \times 10^{10} \) cm\(^{-3} \) [13], [23].

In many technological applications, impurities are added to intrinsic semiconductors to control the conductivity [23]. Such extrinsic doping changes the populations of electrons and holes by creating defect states close to the valence and
conduction band. Doping shifts the Fermi-Dirac probability distribution in Figure 2.11 to the left (right) for p-type (n-type) doping by lowering (raising) the electron chemical potential. The consequence is the shifting of the Fermi level — the point of 50% occupation probability — along the energy coordinate, populating the material with more electrons (holes) with a higher (lower) Fermi level (Figure 2.10 (b) and (c)).

Trace amounts of phosphorous (boron) is added to silicon to increase the electron (hole) population. Conversely, the carrier populations in solar-grade Cu(In,Ga)Se₂ materials are not primarily controlled by extrinsic doping. Rather, CIGS is intrinsically doped by controlling the stoichiometry of copper, indium, gallium, and selenium via the deposition rate of each element during fabrication. Intrinsic doping has similar effects compared to extrinsic doping with respect to the shift of the Fermi level in the band gap. Due to its quaternary nature, many intrinsic point defects exist in Cu(In,Ga)Se₂ materials:

- Vacancies: $V_{\text{Cu}}, V_{\text{In}}, V_{\text{Ga}}, V_{\text{Se}}$
- Self-interstitials: $\text{Cu}_i, \text{In}_i, \text{Ga}_i, \text{Se}_i$
- Antisite defects: $\text{Cu}_{\text{In}}, \text{Cu}_{\text{Ga}}, \text{In}_{\text{Cu}}, \text{In}_{\text{Ga}}, \text{Ga}_{\text{Cu}}, \text{Ga}_{\text{In}}$

The subscript refers to the atomic site in which the defect resides. Anion-cation antisite defects such as $\text{Cu}_{\text{Se}}$ and $\text{Se}_{\text{Cu}}$ are neglected due to their high estimated formation enthalpies ($\Delta H_f > 5 \text{ eV}$) stemming from extreme electrostatic repulsion [36], [37]. Consequently, their contribution to the electronic properties of CIGS is considered negligible.

Figure 2.12 – Two-dimensional (flattened) schematic of CuInSe₂ crystal structure, centered on the selenium atomic position, with a copper vacancy which acts as an acceptor defect.
Figure 2.12 shows the schematic of intrinsic “p-type” doping of CIGS via a copper vacancy. Recall that copper atoms have one valence electron and accordingly an oxidation state of 1+ in CIGS. When a single copper atom is removed from CIGS, it leaves behind one electron-hole. Such a vacancy defect is also referred to as an acceptor defect, meaning the vacancy can restore its octet rule by attracting an electron from the crystal. The hole then can be conducted through the crystal. According to Zhang et al., this process initiates relatively easily with $V_{\text{Cu}}^0 \rightarrow V_{\text{Cu}}^-$ requiring $\sim 0.03$ eV, comparable to the characteristic $kT$ of $\sim 0.03$ eV at room temperature (Figure 2.15) [38].

Alternately, a copper atom can occupy an interstitial site in the Cu(In,Ga)Se$_2$ crystal as illustrated in Figure 2.13. The interstitial copper atom can become ionized by donating its one valence electron, however the copper interstitial has a relatively deep donor defect level in the band gap, $\sim 0.20$ eV below the conduction band minimum. Because 0.20 eV is significantly higher than the $kT$ value of $\sim 0.03$ eV at room temperature, the population of Cu$_i$ with the oxidation state 1+ is expected to be smaller compared to neutral Cu$_i$ (Figure 2.15) [38]. However, copper self-interstitials may play an important role in the “semionic” conductivity of CIGS as discussed in Chapter 4.

Figure 2.13 – Two-dimensional (flattened) schematic of CuInSe$_2$ crystal structure, centered on the selenium atomic position, with a copper interstitial which may act as a donor defect.

Extrinsic doping is also critical to the performance of CIGS solar cells. High-efficiency CIGS solar cells involves depositing a cadmium sulfide (CdS) layer on top of the CIGS layer. Because the deposition takes place at a slightly elevated temperature in the range of 60-80 °C [39], some interdiffusion between the CIGS and CdS occurs [40]–[45]. Moderate interdiffusion of cadmium into CIGS has been suggested to be beneficial to the performance of CIGS solar cells due to its n-type doping of CIGS in the interface region. A schematic of substituting a copper atom with a cadmium atom (i.e. due to the interdiffusion of CdS and CIGS layers) is shown in Figure 2.14. Because cadmium has
two valence electrons, it has an oxidation state of 2+ [40]. One of the cadmium atom’s valence electrons is used to replace the copper atom’s bonds to its selenium neighbors to restore the octet rule. Cadmium has a donor defect level ~0.10 eV – slightly higher than $V_{Cu}$ ionization energy – below the conduction band maximum (Figure 2.15) [46]. Because such defects contribute extra electrons to the crystal, they are called donor defects. Creating donor defects to the crystal is termed as “n-type” doping.

Figure 2.14 – Two-dimensional (flattened) schematic of CuInSe$_2$ crystal structure, centered on the selenium atomic position, with a cadmium atom sitting in the copper sublattice which acts as a donor defect.

![Donor defect schematic](image)

Figure 2.15 – Defect transition energy levels for various intrinsic and extrinsic defects in CuInSe$_2$. Adapted from [38], [46].
2.2.4 Phase diagram and stoichiometry

Non-stoichiometric Cu(In,Ga)Se$_2$ generally contains copper content below the stoichiometric value of 25 atomic percent. Non-stoichiometric CIGS is remarkably stable. CuInSe$_2$ maintains its alpha phase even when it is copper-deficient on the order of several atomic percent as seen in the phase diagram in Figure 2.16 that was adapted from the Cu$_2$Se-In$_2$Se$_3$ pseudo-binary phase diagram [47]. This phase diagram discussion is limited to the temperature range between 500 °C and 600 °C due to the typical deposition temperature of copper in the solar-grade CIGS absorber layer [48]. The thermal-equilibrium phase diagrams aid the understanding the creation and stability of Cu(In,Ga)Se$_2$ defects especially during thin-film deposition, even though the deposition process itself may not necessarily be in thermal equilibrium [49] (elaborated in sections 3.7.3 and onward). When the copper content in CuInSe$_2$ is below ~ 22 atomic percent (Figure 2.16), an ordered vacancy compound (OVC) phase is formed – sometimes referred to as ordered defect compound (ODC) [50]. The exact nature of this phase is still a matter of debate; it may consist of a mixture of CuInSe$_2$ and copper-poor phases that include CuIn$_3$Se$_5$ and CuIn$_5$Se$_8$ [13], [38], [51], [52]. When the copper content exceeds 25 atomic percent, copper(I) selenide (Cu$_2$Se) precipitates form.

![Figure 2.16 – Pseudo-binary phase diagram between In$_2$Se$_3$ and Cu$_2$Se.](image)

Because of the metallic nature of copper selenide phases (Cu$_2$Se, Cu$_{2-x}$Se, etc.), they are detrimental to photovoltaic performance of CIGS solar cells [13]. The Cu(In,Ga)Se$_2$ layer in CIGS solar cells with high conversion efficiencies are made copper-poor. This is achieved by decreasing copper deposition rate relative to indium and gallium deposition rates. Copper-poor CIGS films. Noufi et al. characterized the carrier concentration in CuInSe$_2$ as a function of the Cu/In ratio [53]. Noufi et al. used stoichiometry ratios (e.g. Cu/(In+Ga), Ga/(In+Ga), etc.) – commonly used in the
discussion of controlling non-stoichiometry in CIGS – to study the relationship between stoichiometry and carrier concentration. The relationship is shown in Figure 2.17. Slightly copper-rich and copper-poor CIS films are p-type where the hole population is abundant compared to the electron population. However, when the film is significantly copper-poor below a Cu/In ratio of ~ 0.9, the carrier type is inverted to n-type.

![Figure 2.17 – CuInSe$_2$ stoichiometry versus carrier concentration. Adapted from [53].](image)

The inversion to n-type can be understood in the terms of In$_{Cu}$ antisite defects. As the film becomes richer in indium, indium atoms become more likely to occupy copper sites. With indium’s three valence electrons, one valence electron is used to replace the bonding between the copper site and its four selenium neighbors – to satisfy the octet rule. The two remaining valence electrons can be conducted through the crystal, but according to Figure 2.15, an energy significantly larger than the characteristic $kT$ of 0.03 eV at room temperature is required to excite one of the indium’s valence electrons to the conduction band. Hence, n-type doping of CuInSe$_2$ typically leads to a lower charge carrier population than that of p-type CuInSe$_2$ (Figure 2.17). When the CIS film contains excess copper relative to indium (Cu/In > 1), copper atoms are more likely to occupy indium sites. Because an indium atom – or equivalently the indium atomic site – uses its three valence electrons to meet the octet rule with its selenium neighbors, the Cu$_{In}$ antisite
defect effectively creates two holes. The CIGS absorber layer in high-efficiency CIGS solar cells has a carrier concentration on the order of $10^{16}$ cm$^{-3}$ and have a Cu/(In+Ga) ratio of $\sim 0.90$ [6], [54].

2.3 Cu(In,Ga)Se$_2$ photovoltaic device physics

The materials science of the Cu(In,Ga)Se$_2$ material – especially its electronic properties – was introduced in section 2.2. In order to understand the contribution of the CdS and Cu(In,Ga)Se$_2$ layers in high-efficiency CIGS photovoltaic devices, the discussion is extended to the physics of such CIGS solar cells.

2.3.1 The p-n homojunction

Arguably the most important element in semiconductor-based solar cells is the p-n junction. A simple p-n homojunction will be explored before the more complicated p-n junction seen in CIGS solar cells is discussed. A p-n homojunction refers to the junction that is formed between two similar semiconductors (e.g. joining a n-type silicon and a p-type silicon). A n-type semiconductor has a large population of electrons compared to holes. Conversely, p-type of the same semiconductor has a large hole population versus electrons. When a population of charge carriers dominate in number in a semiconductor, they are considered the majority charge carriers. The smaller charge carrier population is the minority carriers. When the two similar materials – but doped differently – are brought together into contact, a p-n homojunction is generated. The process of forming the junction is illustrated in Figure 2.18.

![Figure 2.18](image)

Figure 2.18 – Upper diagram: p- and n-type materials of the same band gap before they are joined. Lower diagram: the joined p- and n-type materials to form a p-n homojunction.
As seen in the figure, band-bending – of the band diagrams of the two originally isolated materials – occurs. In section 2.2.3, the Fermi level is defined as the total electron chemical potential. The n-type semiconductor has a higher Fermi level versus the p-type semiconductor as shown in Figure 2.18. Because particles in general have a tendency of moving from higher chemical potential to lower chemical potential, electrons in the n-type semiconductor will spontaneously flow to the p-type semiconductor upon contact. Similarly, a larger chemical potential of holes forms in the p-type semiconductor versus the n-type semiconductor. When put in contact, the holes flow from the p-type side to the n-type side.

However, the diffusion of electrons into the p-type side and holes into the n-type side is self-limiting. As the two-way diffusion proceeds, the Fermi levels in both materials at the interface region shift towards equilibrium, bending the joined band diagrams. The Fermi level in the n-type semiconductor at the interface is shifted downward due to a decreased population of electrons. Conversely, the Fermi level in the p-type material is increased due to the in-diffusion of electrons. The self-limiting case is reached when the n-type and p-type Fermi levels are equal at the near-interface region. The band-bending is confined to the near-interface region; the Fermi levels away from the p-n junction in both the n-type and p-type sides remain undisturbed.

The two-way diffusion leads to a positive charge build-up in the n-type side and negative charge build-up in the p-type side. Donor atoms in the n-type material become ionized when they lose electrons to the p-type side. Similarly, acceptor atoms in the p-type material are ionized when holes migrate to the n-type side. The charge build-up creates an internal electric field between the two semiconductors such that the direction and magnitude of the electric field repel further electrons from migrating to the p-type side. Further holes are also repelled from reaching the n-type side. The repulsion of electrons can be qualitatively seen in the figure as the difference in energy between the two conduction band minimums. Electrons would need to gain sufficient energy to overcome the potential barrier to enter the p-type semiconductor. Likewise, a potential energy barrier arises for the holes in the p-type side that attempt to diffuse into the n-type side – represented by the energy difference between the two valence band maximums. Because of the internal electric field between the two semiconductors as a result of the diffusion of charge carriers, the p-n junction becomes depleted of charge carriers. This area is commonly referred to as the depletion region or space charge region (SCR).
Two types of electronic current dominate p-n junctions: diffusion and drift currents. The diffusion current was discussed in the previous paragraph. It simply refers to the case of generating a current by the diffusion of the majority charge carriers from one side to the other side where they become the minority charge carrier electrons (holes) into the p-type (n-type side). Because electron-hole pairs are continuously thermally generated at a temperature $T$ above 0 K, the minority charge carriers that are thermally generated sufficiently close to the depletion region can be swept across the depletion region to the other side where they become the majority charge carriers. The thermally generated minority charge carriers that do not reach the edge of the depletion region recombine with the majority charge carriers. At thermal equilibrium, no net diffusion and drift currents across the junction exist.

The p-n junction has two main operating modes in a circuit: forward bias and reverse bias (Figure 2.19). Forward bias refers to the case where voltage is applied to the junction such that the internal electric field is reduced. The internal electric field is reduced because the direction of the applied voltage opposes the internal electric field. The lowered internal electric field increases the diffusion currents of electrons and holes into the p-type and n-type sides respectively. The non-equilibrium Fermi levels in forward bias in the diagram reflect the continuous diffusion current of electrons and holes. When the junction is reversed-biased, the applied voltage has the same polarity of the internal electric field, increasing the potential energy barriers for both the electrons and holes. As a result, the diffusion currents are severely diminished.

![Diagram of p-n junction](image)

Figure 2.19 – Applying bias to the p-n homojunction. $E_{F,FB}$ and $E_{F,RB}$ are the Fermi levels under forward and reverse biases respectively.
The graphical relationship between the applied voltage and current (IV curve) for the p-n junction is shown in Figure 2.20. Convention dictates positive applied voltage corresponding to forward bias, and negative applied voltage to reverse bias. Current exponentially rises with forward bias where current become negligibly small under reverse bias. The p-n junction is effectively a diode, allowing current to only flow in one direction. The p-n diode has important applications in the semiconductor industry other than in solar cells (e.g. transistors in computer chips).

![Image of IV curve](image-url)

Figure 2.20 – The current-voltage curve of the p-n junction.

### 2.3.2 The p-n heterojunction

![Image of band diagrams](image-url)

Figure 2.21 – The lined-up band diagrams of CuGaSe₂, CuInSe₂, and CdS.
Section 2.3.1 introduces a simple p-n homojunction. However, the p-n junction in Cu(In,Ga)Se$_2$ solar cells is more complicated. Figure 2.21 – as adapted from Harish Sankaranarayanan’s PhD thesis [55] – illustrates the band diagram lineup of CuGaSe$_2$, CuInSe$_2$ and CdS. Because CuInSe$_2$ and CdS have unequal band gaps (1.0 eV and 2.4 eV respectively), joining CuInSe$_2$ and CdS layers results in a p-n heterojunction, a p-n junction of dissimilar materials. Figure 2.22 – from Sebastian Schmidt’s PhD thesis [20] – shows the equilibrium band diagram of the CuInSe$_2$/CdS stack. Joining materials with dissimilar band gaps results in energy discontinuities both in the conduction and valence bands. The discontinuities are exemplified by the $\Delta E_C$ and $\Delta E_V$ spikes in Figure 2.22. The conduction-band and valence-band offsets can be approximated using Anderson’s rule [56]. The application of Anderson’s rule to the CuInSe$_2$/CdS dictates a positive conduction-band offset and a negative valence-band offset. A physical interpretation is as follows [55]: when a minority-carrier electron in the CuInSe$_2$ side reaches the depletion region edge and is swept towards the CdS side, the electron must have sufficient kinetic energy to overcome the potential energy spike barrier that is the positive conduction-band offset in order to enter CdS. At first glance, a positive $\Delta E_C$ value (spike) might suggest an increased carrier recombination at the CuInSe$_2$/CdS interface and thus a loss in solar cell efficiency, however theoretical studies done by Minemoto et al. [57] demonstrated that the short circuit current density $J_{SC}$ – a key performance parameter of solar cells along with open circuit voltage $V_{OC}$ – remains constant when $\Delta E_C$ is varied between -0.7 eV and 0.4 eV. When the value exceeds 0.4 eV, $J_{SC}$ decreases significantly. $V_{OC}$ is also unchanged above a conduction band offset of 0 eV. This has been explained in terms of the photoelectron losing its ability to surmount the potential energy barrier [55]. Niemeegers et al. showed similar results and proposed thermionic emission as a mechanism where photo-generated electrons gain enough thermal energy to bypass the potential barrier spike without loss in photo-generated current [58].
2.3.3 Operation of photovoltaic devices

Solar cells rely on the photovoltaic effect where a sunlight photon strikes a material with enough energy to excite an electron from the valence band to the conduction band, creating an electron-hole pair. This is illustrated in Figure 2.23. A properly functioning solar cell involves an efficient separation of the electron-hole pair. Because the Cu(In,Ga)Se$_2$ absorber layer in CIGS solar cells is made p-type, the minority charge carriers to be separated are electrons. For the efficient charge carrier collection, the photo-generated electrons must successfully diffuse to the CIGS depletion region edge and be swept away to the n-type CdS side. Without the separation of the charge carriers, the photo-generated electron-hole pair will recombine and not contribute to the power generation of the photovoltaic device.

Two main factors determine the likelihood of successful charge-carrier separation: 1) the minority carrier lifetime and 2) the minority carrier diffusion length. The former is defined as the average amount of time a minority carrier can spend in the excited state after being photo-generated before recombining with a majority carrier. The minority carrier diffusion length dictates the average length a minority carrier can travel after generation before recombining with a
majority carrier. These two parameters are related through the diffusion coefficient of the minority carrier. High values for those two important parameters lead to photovoltaic devices with high conversion efficiencies.

Because the CdS layer has a band gap of 2.4 eV – higher than the energies provided by the sunlight spectrum, little sunlight absorption occurs in the CdS layer. Nevertheless, there is a small probability of absorption and creation of electron-hole pairs in CdS. Their contribution to the power generation of the photovoltaic device, however, is negligible. The CdS layer tends to be heavily n-type doped, so photo-generated holes recombine with electrons before they reach the edge of the CdS depletion region.

The p-n junction in illuminated solar cells is forward-biased. To see why, two limiting cases are considered in the solar cell operation: the short circuit current $J_{SC}$ and the open circuit voltage $V_{OC}$. Under the short circuit current $J_{SC}$ condition, the solar cell (a p-n junction with an electrode on each side), the n-type and the p-type sides are directly connected to each other via an external, resistance-less wire (load). Under illumination, electron-hole pairs are generated in both sides of the junction, increasing the drift current. However, there is no build-up of charge carriers on either side of the junction because equilibrium can be restored rapidly with the light-generated electrons exiting through the external wire to recombine with holes. The lack of charge build-up means no potential difference is built up to be utilized for power generation. Power generation requires voltage as well as current.

The other limiting case – open circuit voltage $V_{OC}$ – occurs when the electrodes of the solar cell is connected to a load of infinite resistance, preventing current flow. The situation effectively becomes a broken circuit. With no current flow, the light-generated minority-carrier electrons and holes can separate into their majority-carrier sides and build up. The charge-build up opposes the existing internal electric field similar to the forward bias condition discussed in section 2.3.1. Further build-up is inhibited when the forward-bias current equals the light-generated current. The change in the voltage across the depletion region corresponds to the maximum possible voltage that can be used for power generation. This limiting case is also impractical; with maximum voltage obtainable from the solar cell, no current can flow.

A realistic operating solar cell has have finite resistance instead of zero (short circuit current) or infinite (open circuit voltage) resistance. An optimal balance between current and voltage provides the highest amount of power. When the IV curve of the solar cell is measured without illumination using an external power source, an IV curve similar to that
of Figure 2.20 is obtained. The IV curve a solar cell under illumination is shifted into the fourth quadrant of the graph and inverted about the voltage axis (Figure 2.24). The x-intercept of the IV curve is the open circuit voltage, and the y-intercept is the short circuit current. Even though practical solar cells do not operate at either condition, $J_{SC}$ and $V_{OC}$ are important parameters for the performance of the solar cell. Maximizing $J_{SC}$ and $V_{OC}$ translates to higher conversion efficiencies. Since the solar cell generates power rather than consuming it, convention has the IV curve inverted about the voltage axis (cf. Figure 2.20 and Figure 2.24). The voltage and current that correspond to the most power generation is the peak of the power curve, located towards the steep drop in current, requiring an optimal balance between current and voltage for the high performance of the photovoltaic device.

Figure 2.24 – The current-voltage curve of the illuminated photovoltaic device.
Chapter 3

Theoretical and experimental considerations of diffusion in Cu(In,Ga)Se$_2$

3.1 Fick’s first law of diffusion

If the concentration of an impurity – for example, cadmium – in a sample of homogeneous Cu(In,Ga)Se$_2$ is initially non-uniform, cadmium atoms in a region of higher concentration migrate to regions of lower concentration. The process of migration is commonly referred to as diffusion and proceeds until the concentration becomes uniform everywhere in the sample. Fick’s first and second laws of diffusion are the fundamental partial differential equations describing diffusion. A derivation of the laws is discussed and related to cadmium as well as general impurity diffusion in CIGS.

Figure 3.1 – On the left, a schematic of one-dimensional diffusion for atoms jumping from plane 1 across plane M to plane 2 with a concentration profile superimposed on the length. On the right, schematic of a typical one-dimensional diffusion experiment where a blanket of diffuser source is deposited on the host material.

Consider Figure 3.1 where diffusion can occur only in one dimension. This is equivalent to the situation where a thin layer of impurity diffuser source is deposited on the flat surface of a three-dimensional homogenous crystal. Because there will always be the same amount of impurity everywhere on a x-y plane parallel to the flat surface at any given z.
depth (Figure 3.1), the problem reduces to one dimension. The concentration of the impurity at atomic plane 1 is greater than that of atomic plane 2. Atoms at both planes jump randomly to the left and to the right. Because the jump can occur in two indistinguishable directions: \(-x\) and \(+x\). The probability of a jump in either direction is 50%.

As an example, suppose 100 impurity atoms are located at plane 1 and 20 impurity atoms at plane 2. After some time \(t\), 50 atoms will have moved to the left of plane 1 and 50 atoms to the right of plane 1 into plane 2. Similarly, 10 atoms will have moved from plane 2 to plane 1. The other 10 atoms moves to the right. There are more atoms crossing plane M to the right than to the left, hence there is a net diffusion in the direction of lower concentration.

With the initial number of atoms \(n_1\) and \(n_2\) (area concentration of atoms in cm\(^{-2}\)) planes 1 and 2 respectively, the diffusion flux – the number of atoms crossing plane M per unit time is expressed as

\[
J = \frac{1}{2} n_1 \Gamma_{tot} - \frac{1}{2} n_2 \Gamma_{tot}.
\]  

(3-1)

The factor \(\frac{1}{2}\) is due to the 50% probability of jumping across plane M. \(\Gamma_{tot}\) is the total atomic jump rate. \(n_1\) and \(n_2\) can be expressed in terms of volume concentrations \(c_1\) and \(c_2\) (cm\(^{-3}\)) through the relations \(n_1 = c_1 a\) and \(n_2 = c_2 a\) where \(a\) is the plane separation distance between planes 1 and 2, for example in a cubic lattice, where the spacing between host atoms of the matrix is the lattice parameter \(a\). Using the relations yields the following equation

\[
J = \frac{1}{2} \Gamma_{tot} a (c_1 - c_2).
\]  

(3-2)

If \(a\) is very small in the limit \(a \to 0\), \(c_1 - c_2\) can be written as the partial derivative \(-a \frac{\partial c}{\partial x}\). The negative sign is included to ensure that the diffusion current flows down the concentration gradient. Upon substitution, the \(J\) expression can then be written as

\[
J = -\frac{1}{2} \Gamma_{tot} a^2 \frac{\partial c}{\partial x}.
\]  

(3-3)

The term \(\frac{1}{2} \Gamma_{tot} a^2\) becomes the diffusion coefficient \(D\). However, the \(\frac{1}{2}\) factor in \(D\) should be substituted with \(\frac{1}{6}\). In a three-dimensional primitive cubic crystal, atoms can jump in six directions rather than just two \((-x, +x, -y, +y, -z, +z)\).
and \(+z\), thus jumping across plane \(M\) (Figure 3.1) in the \(x\) direction occurs only one-sixth of the time. Finally, the standard version of Fick’s first law reads as

\[
J = -D \frac{\partial c}{\partial x}.
\] (3.4)

where the diffusion coefficient is expressed as

\[
D = \frac{1}{6} \Gamma_{tot} a^2
\] (3.5)

in the case of the primitive cubic crystal system. The three-dimensional form of Eq. (3.4) is

\[
J = -D \nabla c
\] (3.6)

where

\[
\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}
\] (3.7)

if \(D\) is independent of direction. The following equation is obtained:

\[
J = -D \left( \frac{\partial c}{\partial x} + \frac{\partial c}{\partial y} + \frac{\partial c}{\partial z} \right)
\] (3.8)

Flux may vary with direction in anisotropic materials. This is addressed in section 3.5.

### 3.2 Fick’s second law of diffusion

Fick’s first law of diffusion relates flux to spatial distribution of concentration without the consideration for time. Thus, Fick’s first law can be treated as a steady-state treatment of diffusion. A steady-state diffusion scenario occurs when there is a diffuser source and sink in a region such that the concentration of diffuser does not vary.

However, most diffusion experiments are not well described by Fick’s first law. Most diffusion experiments result in an accumulation of the diffuser in a region of the sample over time. The accumulation of the diffuser is due to the diffusion flux not being equal everywhere (Figure 3.2). Thus, the time dependence of the accumulation must be
considered. Fick’s second law of diffusion describes the time evolution of concentration of the diffuser. Fick’s second law can be derived using the one-dimensional form of the continuity equation,

\[
\frac{\partial c}{\partial t} + \frac{\partial j}{\partial x} = 0.
\] (3.9)

Substituting in the diffusion flux \( j \) derived in section 3.1 gives

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right).
\] (3.10)

Eq. (3.10) is valid when \( D \) depends on concentration or position. Eq. (3.11) is the simplified version when \( D \) is assumed to be independent of concentration and position.

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}.
\] (3.11)

The three-dimensional form of Eq. (3.11) becomes

\[
\frac{\partial c}{\partial t} = D \nabla^2 c
\] (3.12)

where

\[
\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}
\] (3.13)

if \( D \) is once again assumed to not vary with direction. The following equation is then obtained:
\[
\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right). \tag{3-14}
\]

The case of varying \( D \) with direction is addressed in section 3.5.

### 3.3 The diffusion coefficient in random walk

![Random Walk Diagram](image)

Figure 3.3 – The randomly diffusing particle initially at position zero has an equal probability of jumping to position -1 and position 1.

In section 3.1, it was stated that atoms randomly jump to other lattice sites. As seen in the one-dimensional lattice in Figure 3.3, an atom begins at the lattice site \( x = 0 \). At every time length \( \frac{1}{f_{\text{rot}}} \) (the inverse of frequency \( \nu \) as introduced in section 3.1), the atom migrates to either of its two lattice neighbors (\( x = -1 \) or \( x = +1 \)). The migration is completely random. Either lattice site is equally likely. After the first migration, from \( x = 0 \) to either neighbor, the subsequent motions continue to be random. For example, the atom at \( x = +1 \) is equally likely to jump to \( x = +2 \) or back to \( x = 0 \).

To predict the position of the atom after \( n \) jumps, \( x_n \cdot x_n \) can be written as

\[
x_n = a_1 + a_2 + a_3 + \cdots + a_n. \tag{3-15}
\]

Each term in the right side of the above equation has a magnitude of \( a \), the lattice spacing, but may differ in sign. However, when the number of jumps \( n \) is very large, the number of positive steps (to the right) and the number of negative steps (to the left) are approximately the same. This is because jumping in either direction is equally probable.

The mean value of \( x_n \) is zero. However, the probability of finding the atom at some lattice site other than \( x = 0 \) is not zero. In other words, a net displacement of the atom is possible. Quantitatively, the net displacement can be conveniently described in terms of the mean square displacement of \( x_n \), and more importantly, by taking the root of the mean square displacement as discussed below. Instead of the single atom considered in the previous discussion, an ensemble of \( N \) atoms initially positioned at \( x = 0 \) is considered. If the mean displacement of the ensemble of \( N \) atoms is expressed as

\[
\langle x(n) \rangle = \frac{1}{N} \sum_{i=1}^{N} x_i(n) \tag{3-16}
\]
where \( x_i(n) \) is the position of the \( i \)-th atom after the \( n \)-th step, then averaging the square of the displacement yields a mean-square displacement expression:

\[
\langle x^2(n) \rangle = \frac{1}{N} \sum_{i=1}^{N} x_i^2(n). \tag{3-17}
\]

In these equations, \( x_i(n) \) is expressed as

\[
x_i(n) = x_i(n-1) \pm a. \tag{3-18}
\]

\( x_i^2(n) \) can then be written as

\[
x_i^2(n) = x_i^2(n-1) \pm 2a x_i(n-1) + a^2. \tag{3-19}
\]

Because the right side of the \( x_i(n) \) equation averages to zero in the ensemble of \( N \) atoms, the mean displacement of the atoms tends to zero. Likewise, the second term in the right side of the \( x_i^2(n) \) equation averages to zero in the ensemble of \( N \) atoms, so the mean-square displacement equation is reduced to

\[
\langle x^2(n) \rangle = \langle x^2(n-1) \rangle + a^2. \tag{3-20}
\]

According to the final \( \langle x^2(n) \rangle \) expression above, the mean-square displacement increases linearly with the number of jumps \( n \): \( \langle x^2(0) \rangle = 0, \langle x^2(1) \rangle = a^2, \langle x^2(2) \rangle = 2a^2, \langle x^2(3) \rangle = 3a^2 \), and so on.

The expression is compactly written as

\[
\langle x^2(n) \rangle = na^2. \tag{3-21}
\]

The total atomic jump frequency \( \Gamma_{tot} \) introduced in section 3.1 can be introduced into the average-square displacement equation by the relation \( n = \Gamma_{tot} t \) where \( t \) is the time interval:

\[
\langle x^2 \rangle = \Gamma_{tot} a^2 t. \tag{3-22}
\]
The $a^2$ term can be replaced with $\lambda^2$ for a jump of arbitrary length $\lambda$. Note that the right side of Eq. (3-22) is quite similar to the $\frac{1}{2} \Gamma_{tot} a^2$ term – the diffusion coefficient $D$ term – in the derivation of Fick’s first law in Eq. (3-3). To relate this treatment of the random walk problem to the Fick’s first law in terms of the diffusion coefficient, Eq. (3-22) can be rewritten as

$$\langle x^2 \rangle = 2Dt$$

(3-23)

where the factor 2 is added to ensure that Eq. (3-23) is consistent with Eq. (3-22) and Eq. (3-3). Atoms diffuse in all three dimensions in most cases rather than in just one dimension, so the generalized three-dimensional form of Eq. (3-21) is written as

$$\langle R^2 \rangle = n a^2 = \Gamma_{tot} a^2 t$$

(3-24)

where $\langle R^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$. When diffusion is assumed to be equivalent in all directions where $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$, the three-dimensional diffusion coefficient in Fick’s first law (Eq. (3-5)) can be incorporated in Eq. (3-24):

$$\langle R^2 \rangle = 6Dt$$

(3-25)

where $D = \frac{1}{6} \Gamma_{tot} a^2$ and the factor 6 is included to ensure consistency with Eq. (3-24). In fact, Albert Einstein showed that the average-square radial displacement of a group of randomly diffusing particles in three dimensions with diffusion coefficient $D$ after time $t$ can be written as Eq. (3-25) in generality [59]. Since $\Gamma_{tot}$ represents the total jump frequency from a particular atomic site, $\Gamma_{tot}$ can also be expressed in terms of the specific jump frequency to one of its $Z$ neighbors:

$$\Gamma_{tot} = \sum_{i=1}^{Z} \Gamma_i$$

(3-26)

Eq. (3-24) now reads as

$$\langle R^2 \rangle = Z \Gamma a^2 t$$

(3-27)
if the specific jump frequency to the all $Z$ neighbors is the same. This is justified for isotropic cubic crystals [60]. The anisotropic case of CIGS is discussed in section 3.5. Setting the right sides of Eq. (3-25) and Einstein’s general result Eq. (3-27) to equal to each other yields the following diffusion coefficient $D$ for isotropic cubic crystals with $Z$ equivalent nearest neighbors around an atomic position separated by jump distance $\lambda$:

$$D = \frac{1}{6} Z \Gamma \lambda^2. \quad (3-28)$$

A customary, simplified version of Eq. (3-28) for cubic crystals is expressed as [61]:

$$D = g \Gamma a^2 \quad (3-29)$$

where $g$ is denoted as the geometric factor if jump distance $\lambda$ is expressed in terms of unit cell spacing $a$. Note that a particular diffusion mechanism in a particular crystal structure has an unique $g$ value. For example, the vacancy diffusion mechanism in silicon (diamond cubic crystal structure) has a $g$ value of $1/8$ ($Z = 4$ and $\lambda^2 = \frac{3}{16} a^2$) [59], [60]. The $g$ values for the copper vacancy diffusion mechanism in Cu(In,Ga)Se$_2$ is derived in section 3.5.1.

An interesting property of Eq. (3-25) becomes apparent by first determining the mean-square displacement in one direction in the case of isotropic diffusion:

$$\langle x^2 \rangle = \frac{\langle R^2 \rangle}{3} = 2Dt, \quad (3-30)$$

then taking its square root:

$$\bar{x} = \sqrt{\langle x^2 \rangle} = \sqrt{2Dt}. \quad (3-31)$$

The characteristic diffusion length $\bar{x}$ is defined as $\sqrt{\langle x^2 \rangle}$. Plainly stated, due to the random-walk nature of diffusion, $\bar{x}$ is proportional to the square root of $2Dt$, a result also implied in the derivation of the mean-square displacement (Eq. (3-21)). In order for an atom to diffuse twice as far, it would take four times as long. A diffusion distance four times as far takes sixteen times as long, and so on.
Not only $\bar{x}$ is a convenient method to describing the spreading of the ensemble of $N$ atoms, it has another physical interpretation by considering the Gaussian distribution (Figure 3.4). At time $t = 0$, all $N$ atoms are located at $x = 0$. At some time $t$ after $t = 0$, the atoms spread away from the origin and continue to spread as time proceeds. The degree of spreading in the Gaussian distribution is described by the standard deviation. The standard deviation in the case of diffusion is defined as the root-mean-square displacement of Eq. (3-31). Physically, this means $\sim 68\%$ of the atoms in the ensemble can be found within one characteristic diffusion length (standard deviation) of the origin after some time $t$ has elapsed. The remaining $\sim 32\%$ of the atoms in the ensemble are found farther than one characteristic diffusion length [62]. Alternatively, in the terms of a single atom, the probability of finding the atom within one characteristic diffusion length of the origin after time $t$ is 0.68.

![Figure 3.4](image)

Figure 3.4 – On the left, the random spreading of an ensemble of $N$ atoms starting at position zero over time can be well-described by the Gaussian function. On the right, the random spreading of the ensemble of $N$ atoms is described by the root-mean-square displacement. For example, approximately 68% of the atoms are found within one characteristic diffusion length from the center. About 95% of the atoms are found within two characteristic lengths from the center.

### 3.4 Solutions of non-steady state diffusion

#### 3.4.1 Diffusion due to a limited diffuser source

If a sufficiently small amount of diffuser atoms (e.g. cadmium) is deposited on the flat surface of a material (e.g. Cu(In,Ga)Se$_2$), the situation results in a net migration of the diffuser atoms along the thickness of the material and a
depletion of the diffuser atoms at the surface as diffusion time elapses (Figure 3.4). To conserve the amount of limited quantity of diffuser atoms in the system, the following boundary condition applies to the one-dimensional form of the limited-source diffusion problem [60], [63]:

$$\int_{-\infty}^{+\infty} c(x, t) dx = M.$$  \hfill (3-32)

The one-dimensional form is relevant in practical diffusion experiments. $c(x, t)$ is the diffuser concentration at position $x$ and time $t$. $M$ represents the number of diffuser atoms per unit area on the surface (cm$^{-2}$). A second boundary condition ensures that the diffuser concentration $c$ attenuates to zero everywhere as time $t$ approaches infinity:

$$c(x, \infty) = 0.$$  \hfill (3-33)

An initial condition of this problem accounts for the absence of diffuser atoms everywhere at $t = 0$:

$$c(x, 0) = 0.$$  \hfill (3-34)

Satisfying the requirement of Eq. (3-33) implies a semi-infinite material where the material begins at $x = 0$ and ends at $x = \infty$. This is evidently impossible in a real material of a finite thickness as the diffuser atoms are simply redistributed in the material until they are homogenized everywhere. Nevertheless, materials used in diffusion experiments are typically sufficiently thick that the semi-infinite assumption holds without significant error. These boundary and initial conditions ensure that Fick’s second law (Eq. (3-11)) produces an analytical solution for the problem, in the form of a simple Gaussian function:

$$c(x, t) = \frac{M}{\sqrt{4\pi Dt}} \exp \left( - \frac{x^2}{4Dt} \right).$$  \hfill (3-35)

where $D$ is the diffusion coefficient. Figure 3.5 shows the time evolution of Eq. (3-35).
3.4.2 Diffusion due to an infinite diffuser source

Some diffusion experiments are better modelled with the solution to Fick’s second law that reflects a diffuser source that does not deplete over time, otherwise known as a constant-source diffuser source. The diffuser concentration at the surface is kept at \( c_s \). The appropriate initial and boundary conditions are

\[
c(x, 0) = 0, \tag{3-36}
\]
\[
c(0, t) = c_s, \tag{3-37}
\]
\[
c(\infty, t) = 0. \tag{3-38}
\]

With the initial and boundary conditions, the solution to Fick’s second law (Eq. (3-11)) becomes

\[
c(x, t) = c_s \text{ erfc} \left( \frac{x}{2\sqrt{Dt}} \right). \tag{3-39}
\]

Fig. 3.6 shows the time evolution of Eq. (3-39).
Figure 3.6 – The constant-source equation graphed with varying elapsed diffusion times ($t_1$, $t_2$, and $t_3$).

3.5 Anisotropic and directional diffusion in Cu(In,Ga)Se$_2$

3.5.1 Anisotropic diffusion of copper vacancies

An analysis of the CIGS crystal structure in Figure 3.7 shows that the copper vacancy diffusion – a likely cadmium diffusion vehicle – behaves anisotropically along one crystal axis compared to the other axes. The contention of copper vacancies rather than indium/gallium vacancies as a cadmium diffusion vehicle is justified in section 3.7.

Figure 3.7 (b) displays only the copper sublattice compared to the full CIGS crystal structure in (a) with indium/gallium and selenium atoms. The direct copper vacancy migration involves the jump of the copper atom at position 1 to neighboring position 2, 3, 4, or 5 shown in Figure 3.7 (b). If $c$ is taken to be exactly $2a$ – neglecting any deviations from the ideal $c/a$ ratio of 2 – the expression for the jump distance to a neighboring position is reduced to

$$\lambda = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{c}{4}\right)^2} \approx \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{2a}{4}\right)^2} = \frac{1}{\sqrt{2}}a \quad (3-53)$$

Eq. (3-53) and the geometric analysis of Figure 3.7 (a) show that jumps to positions 2, 3, 4, and 5 are energetically indistinguishable from each other. Therefore, the jump of the copper atom from position 1 to any of the nearest copper
neighbors where a vacancy might exist is equally probable. However, this does not mean that the diffusion coefficients in the $x$, $y$, and $z$ directions in a prescribed coordinate system are equal.

\[ D_x = D_1 = \frac{1}{2}Z\Gamma\lambda_x^2. \]  
\[ (3-54) \]

Figure 3.7 (b) reveals that there are two possible positions in the $x$ direction for the copper atom at position 1 to jump to (positions 3 and 4), so $Z = 2$. The $x$ component of the jump distance $\lambda$ denoted $\lambda_x$ is $\frac{a}{2}$. Eq. (3-54) becomes

\[ D_x = \frac{1}{4}\Gamma a^2. \]  
\[ (3-55) \]

The diffusion coefficient in the $y$ direction is written as

\[ D_y = \frac{1}{4}\Gamma a^2 \]  
\[ (3-56) \]

using the same argument ($Z = 2$ and $\lambda_y = \frac{a}{2}$). The diffusion coefficient in the $z$ direction is written as
\[ D_x = \frac{1}{2} \Gamma a^2 \]  

(3-57)

because \( Z = 4 \) and \( \lambda_x = \frac{a}{2} \). Looking at Figure 3.7 (b), the copper atom at position 1 indeed has access to four neighbors in the \( z \) direction. The geometric factor \( g \) value for the copper vacancy diffusion is \( \frac{1}{4} \) in the \( x \) (\( x_1 \)) and \( y \) (\( x_2 \)) directions. \( g = \frac{1}{2} \) for the \( z \) (\( x_3 \)) direction. These results are in conflict with the isotropic diffusion coefficient for copper vacancies derived by Pohl and Albe [65]. Their original isotropic diffusion coefficient equation reads as

\[ D = \frac{1}{6} Z v c_{V_{Cu}} d^2. \]  

(3-58)

\( c_{V_{Cu}} \) is the copper vacancy concentration. \( v \) is a jump rate-related parameter. \( v c_{V_{Cu}} \) in Pohl and Albe’s paper has the same meaning as \( \Gamma \) defined in the present thesis. The role of \( v \) and vacancy concentration in jump frequency \( \Gamma \) is explored in section 3.8. \( d \) also has the same meaning as \( \lambda \). Finally, \( d = \frac{1}{\sqrt{2}} a \) per Pohl and Albe’s \( c = 2a \) assumption, then the diffusion coefficient becomes

\[ D = \frac{1}{3} \Gamma a^2. \]  

(3-59)

This diffusion coefficient slightly differs from \( D_x = D_y = \frac{1}{4} \Gamma a^2 \) and \( D_z = \frac{1}{2} \Gamma a^2 \) as derived above. It is argued that the anisotropic diffusion coefficients derived in this thesis should be used instead of the isotropic diffusion coefficient in Eq. (3-59). A geometrical argument is presented below to justify the derivation of the anisotropic diffusion coefficients of copper vacancies in CIGS.

The anisotropic diffusion of copper vacancies in CIGS with respect to the \( x-y-z \) (\( x_1-x_2-x_3 \)) coordinate system – aligned with the CIGS crystal axes of symmetry – can be understood with Figure 3.8. Figure 3.8 (a) shows the diamond cubic crystal structure. Interestingly, the copper sublattice in CIGS is organized in a similar – but not exactly alike – structure as the diamond cubic crystal structure. This is shown with the partially drawn and labeled copper lattice in Figure 3.8 (a) that corresponds to the stand-alone copper sublattice in Figure 3.8 (b). It is emphasized that the traced copper sublattice structure in Figure 3.8 (a) is not an exact representation of the actual structure of the copper sublattice in CIGS; Figure 3.8 (a) is merely a visual aid for the following discussion.
Figure 3.8 – (a) The diamond cubic crystal structure with points A, B, C, and D traced from figure (b) on the right. (b) The copper sublattice of the CIGS crystal structures with the points A, B, C, and D. Adapted from University of Bristol PhD student Ben Mills’ illustrations of the CIGS and diamond crystal structures on Wikipedia.

The failure of the copper sublattice in CIGS to completely adhere to the diamond cubic crystal structure explains the anisotropic diffusion of the copper vacancy in CIGS. Defining line $\overline{AD}$ in Figure 3.8 (a) as the miller index direction [100] and line $\overline{AC}$ the direction [010], it can be shown that diffusion is isotropic in the diamond cubic crystal structure.

The atom at site $B$ can jump to one of its four neighbors, including sites $A$ and $D$ as pictured. If the lattice spacing of the diamond cubic crystal structure is $a$ – the length of line $\overline{CD}$ – then the projection of line $\overline{BD}$ onto line $\overline{AD}$ (in the [100] or x direction) is the x component of the jump distance $\lambda$, $\lambda_x$. The site $B$ has two neighboring positions in the x direction. With Eq. (3-54), $\lambda_x = \frac{a}{\sqrt{2}}$, $Z = 2$, the diffusion coefficient in the x direction is expressed in Eq. (3-60). In the y direction (line $\overline{AC}$, [010] direction), the diffusion coefficient is the same:

$$D_x = D_y = \frac{1}{8} \Gamma a^2.$$ (3-60)

The diffusion coefficient in the z direction becomes

$$D_z = \frac{1}{8} \Gamma a^2$$ (3-61)

with $\lambda_z = \frac{a}{4}$ and $Z = 4$. Thus, in a material with the diamond cubic crystal structure, $D_x = D_y = D_z$. While Figure 3.8 (a) can be visually deceiving, the copper sublattice in CIGS does not hold this isotropic diffusion property. Two equivalent forms of an argument are finally presented: the angle $\angle ABD$ in the diamond cubic crystal structure is
~109.5°, representative of the tetrahedral bonding in the diamond structure. However, the angle is 90° in the copper sublattice structure. Secondly, using the established coordinate system in Figs. 3.7 and 3.8 (a), the ratio \( \frac{\lambda_y}{\lambda_x} \) in the diamond cubic structure is \( \sqrt{2} \) and 1 in the copper sublattice structure. Thus, copper vacancy diffusion is not isotropic, contrary to what some workers in the literature have suggested. Cadmium diffusion in CIGS may also be anisotropic if copper vacancies mediate cadmium diffusion.

### 3.5.2 Anisotropic diffusion equations

The diffusion coefficient discussed in sections 3.1, 3.2, and 3.3 is for the simple case of isotropic materials where the diffusion coefficient is the same in all directions. The situation in CIGS is further complicated due to CIGS’ tetragonal crystal structure rather than simply a cubic crystal structure as shown in Figure 3.7 (a). The unit cell of the tetragonal crystal structure is a rectangular prism with a square base \((a \times a)\) of length \(a\) and height \(c\), where \(c \neq a\). Accordingly, certain diffusion mechanisms in CIGS may be anisotropic. In a general diffusion system, anisotropic diffusion is considered through the three-dimensional vector form of Fick’s first law [60], [66]:

\[
\mathbf{J} = -D \nabla c.
\] (3-40)

Fick’s second law in anisotropic materials is consequently expressed as

\[
\frac{\partial c}{\partial t} = -\nabla \mathbf{J}.
\] (3-41)

The diffusion coefficient is written as a second-rank tensor that accounts for diffusion in all possible directions:

\[
D = \begin{bmatrix}
D_{11} & D_{12} & D_{13} \\
D_{21} & D_{22} & D_{23} \\
D_{31} & D_{32} & D_{33}
\end{bmatrix}
\] (3-42)

The flux vector \( \mathbf{J} \) can be expressed in its directional components – that is, the fluxes along three orthogonal principal directions \(x_1, x_2, \) and \(x_3\) of a crystal system:

\[
J_i = -D_{1i} \frac{\partial c}{\partial x_1} - D_{2i} \frac{\partial c}{\partial x_2} - D_{3i} \frac{\partial c}{\partial x_3},
\] (3-43)
\[ J_2 = -D_{21} \frac{\partial c}{\partial x_1} - D_{22} \frac{\partial c}{\partial x_2} - D_{23} \frac{\partial c}{\partial x_3}, \quad (3-44) \]

\[ J_3 = -D_{31} \frac{\partial c}{\partial x_1} - D_{32} \frac{\partial c}{\partial x_2} - D_{33} \frac{\partial c}{\partial x_3}. \quad (3-45) \]

A \( D_{ij} \frac{\partial c}{\partial x_i} \) term can be interpreted as the contribution to the flux along principal axis \( x_i \) due to the concentration gradient along principal axis \( x_j \). If the \( x_1, x_2, \) and \( x_3 \) axes of the coordinate system are designated to be parallel to the orthonormal crystal axes of symmetry in the tetragonal crystal system (Figure 3.7), the non-diagonal diffusion coefficient terms (i.e. \( D_{ij} \) where \( i \neq j \)) vanish. The non-diagonal terms also disappear for cubic and orthorhombic crystals due to the crystal axes of symmetry being perpendicular to each other. With crystal structures of particularly low symmetry such as the triclinic crystal structure, the non-diagonal terms can be non-zero regardless of the chosen orientation of the coordinate system in the crystal. The diffusion tensor matrix for the CIGS’ tetragonal crystal structure reduces to

\[ \mathbf{D} = \begin{bmatrix} D_1 & 0 & 0 \\ 0 & D_1 & 0 \\ 0 & 0 & D_3 \end{bmatrix} \quad (3-46) \]

when the axes of the coordinate system are parallel to the crystal axes of symmetry. Note that \( D_{11} = D_1 = D_2 \) and \( D_{33} = D_3 \) for simplification.

The flux equations reduce to

\[ J_1 = -D_1 \frac{\partial c}{\partial x_1}, \quad (3-47) \]

\[ J_2 = -D_1 \frac{\partial c}{\partial x_2}, \quad (3-48) \]

\[ J_3 = -D_3 \frac{\partial c}{\partial x_3}. \quad (3-49) \]

The mean-square displacement in the \( x, y, \) and \( z \) directions – if they are alternatively taken as the \( x_1, x_2, \) and \( x_3 \) directions respectively – can then be written as [67]:
\[
\langle x^2 \rangle = 2D_1t, \quad (3-50)
\]
\[
\langle y^2 \rangle = 2D_1t, \quad (3-51)
\]
\[
\langle z^2 \rangle = 2D_3t. \quad (3-52)
\]

3.5.3 Directional diffusion in polycrystalline thin films

Figure 3.9 – On the left, a scanning electron microscopy image of the polished surface of polycrystalline CIGS thin film. On the right, the diffusion direction (bold arrow) as a function of crystallographic axes.

Photovoltaic-grade CIGS thin films are polycrystalline, meaning there are multiple single crystals of various sizes and crystallographic orientations making up a continuous thin film in the left image in Figure 3.9. Accordingly, diffusion may not always occur purely along a crystallographic axis as shown in Figure 3.9 on the right. This is especially important for practical experiments.

Experimental diffuser sources are often deposited on the flat surface of the material of interest such that the net diffusion occurs in one direction, perpendicular to the flat surface. A complete treatment of diffusion in a crystal of a particular orientation that differs from the crystal axes of symmetry requires the knowledge of the angles of the crystal axes with respect to the \( x_1, x_2, \) and \( x_3 \) axes of the coordinate system. Mathematically, the directional diffusion coefficient is completely described by the equation

\[
D(\alpha, \beta, \gamma) = D_1\cos^2\alpha + D_2\cos^2\beta + D_3\cos^2\gamma
\]  
(3-62)
where \( \alpha, \beta, \) and \( \gamma \) are the angles with respect to the principal axes \( x_1, x_2, \) and \( x_3 \) respectively [59]. \( D_1, D_2, \) and \( D_3 \) are the principal diffusion coefficients along their respective axes. In Cu(In,Ga)Se\(_2\), Eq. (3-62) for the copper vacancy diffusion mechanism is simplified to

\[
D(\alpha, \beta, \gamma) = D_1(\cos^2 \alpha + \cos^2 \beta) + D_3 \cos^2 \gamma. \tag{3-63}
\]

### 3.6 Dependence of diffusion on temperature

The diffusion coefficient in solids has been experimentally shown to be influenced by a myriad of factors including temperature, pressure, and atomic composition. The diffusion coefficient increases exponentially with temperature and is empirically described by the famous Arrhenius equation:

\[
D = D_0 \exp \left( \frac{-\Delta H}{k_B T} \right) \tag{3-64}
\]

where \( D_0 \) is the pre-exponential factor, \( \Delta H \) is the diffusion activation enthalpy, \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. The Arrhenius equation was originally a formula for the temperature dependence of chemical reaction rates [68], [69]. The Arrhenius equation has since been successfully applied to other thermally influenced processes and reactions such as atomic diffusion and the population of vacancies in a crystal. The logarithms of experimentally measured diffusion coefficients are typically plotted versus reciprocal temperature. Doing so usually yields a straight line, assuming a single dominant diffusion mechanism. The value of the diffusion activation enthalpy \( \Delta H \) can be extracted from the slope of the straight line:

\[
\Delta H = -k_B \frac{\partial \ln D}{\partial (1/T)}. \tag{3-65}
\]

The meaning of the parameters in Eq. (3-64) and the reasons for the temperature dependence of diffusion are elaborated in the following sections.
3.7 Formation of diffusion-mediating point defects in Cu(In,Ga)Se$_2$

3.7.1 Determining the formation energy of crystal point defects

Cu(In,Ga)Se$_2$ crystal point defects briefly introduced in section 2.2.3 play an important role in mediating the diffusion of cadmium, especially atomic vacancies. The vacancy diffusion vehicle requires a vacant lattice site for a neighboring atom to jump into. For the vacancy diffusion vehicle, diffusion is correlated to the number of vacancies; in other words, diffusion increases as the number of vacancies increases. The number of vacancies in a crystal depends on temperature as the vacancy creation process severs bonding between the atoms in the crystal structure. Breaking bonds cost energy. The energy used to create vacancies commonly come in the form of thermal energy, but vacancies can be generated by neutrons, ions, electrons, and gamma rays [59]. Generally, as the temperature of the material increases, more vacancies are created.

![Diagram of atomic vacancies](image.png)

**Figure 3.10** – Generating atomic vacancies in the lattice.

This can be quantitatively understood in the context of statistical thermodynamics for an one-element material (e.g. elemental copper). A perfect crystal at the absolute temperature of zero (0 K) has $N_0$ lattice sites occupied by $N_0$ atoms. However, at a finite $T$ above 0 K, the thermalized crystal has sufficient energy to eject a small number of atoms to the free surface (Figure 3.10), leaving $n_V$ empty lattice sites which are defined as vacancies. The total number of
lattice sites increase from $N_0$ sites at 0 K to $N_L(T) = N_0 + n_V$. The increase in vacancies at a temperature $T$ is due to the thermodynamic potential Gibbs energy (or Gibbs free energy) being lowered to $G_T$ from the Gibbs energy $G_0$ of the perfect crystal devoid of vacancies at 0 K [59]–[61]. This relationship can be written as

$$G_T = G_0 + \Delta G$$  \hspace{1cm} (3-66)

where

$$G = H - TS.$$  \hspace{1cm} (3-67)

$H, T, S$ in the right side of Eq. (3-67) are the enthalpy, temperature, and entropy terms respectively. The change in the Gibbs energy of the crystal $\Delta G$ can be expressed as Eq. (3-68) below. $\Delta G^F_V$ is the Gibbs energy of formation for a single vacancy, the energy that is required to remove an atom from its lattice site and place it at the free surface. $\Delta S_m$ is taken to be the entropy of mixing, that is, the increase in the number of ways the incorporated vacancies can be spatially arranged in the crystal.

$$\Delta G = n_V \Delta G^F_V - T \Delta S_m,$$  \hspace{1cm} (3-68)

where

$$\Delta G^F_V = \Delta H^F_V - T \Delta S^F_V.$$  \hspace{1cm} (3-69)

$\Delta H^F_V$ is the formation enthalpy of a single vacancy. $\Delta S^F_V$ is the change in vibrational entropy due to the creation of a single vacancy, resulting from the altered vibration in the neighboring atoms around the empty lattice site. The entropy of mixing is determined through the Boltzmann’s entropy formula:

$$\Delta S_m = k_B \ln(W_V)$$  \hspace{1cm} (3-70)

where $W_V$ is the number of possible ways to spatially distribute the vacancies in the crystal. Because $W_V$ is determined using the factorial equation

$$W_V = \frac{N_L!}{n_V!N_0!}$$  \hspace{1cm} (3-71)
the numerator and the denominator become very large and difficult to calculate for a real crystal (~ $10^{22} - 10^{23}$ atoms cm$^{-3}$). An approximation of the factorial equation is determined using Stirling’s formula which states that $\ln x! \approx x \ln x$:

$$\ln W_v \approx (N + n_v) \ln(N + n_v) - n_v \ln n_v - N \ln N.$$  \hspace{1cm} (3-72)

For a thermodynamic system to be at equilibrium at constant pressure and temperature, its Gibbs energy must be minimized. In other words, the number of vacancies $n_v$ reaches its equilibrium value when the partial derivative of $G_T$ with respect to $n_v$ is zero:

$$\left( \frac{\partial G_T}{\partial n_v} \right) = 0.$$  \hspace{1cm} (3-73)

Using Stirling’s formula and the equilibrium condition, differentiating $G_T$ with respect to $n_v$ yields

$$0 = \Delta H_v^F - T \Delta S_v^F + k_B T \ln \frac{n_v^{eq}}{N_0 + n_v^{eq}}$$  \hspace{1cm} (3-74)

where the subscript $eq$ denotes the respective quantities at equilibrium. The site fraction of vacancies is now defined as

$$C_v^{eq} = \frac{n_v^{eq}}{N_0 + n_v^{eq}}.$$  \hspace{1cm} (3-75)

The site fraction is the probability of having a vacancy at a given lattice site. The actual concentration of vacancies $\tilde{C}_v^{eq}$ can be found via the relation $\tilde{C}_v^{eq} = C_v^{eq} \rho_d$ where $\rho_d$ is the number density of atoms. For a real crystal, $\tilde{C}_v^{eq}$ becomes appreciably large.

The expression of $C_v^{eq}$ as a function of $\Delta H_v^F$, $\Delta S_v^F$, and $T$ involves taking the exponential of Eq. (3-74) after substituting in the site fraction from Eq. (3-75), yielding

$$C_v^{eq} = \exp \left( - \frac{\Delta G_v^{eq}}{k_B T} \right) = \exp \left( \frac{\Delta S_v^{eq}}{k_B} \right) \exp \left( - \frac{\Delta H_v^{eq}}{k_B T} \right).$$  \hspace{1cm} (3-76)
Eq. (3-76) shows that the population of vacancies increases with increasing temperature $T$ but decreases with increasing formation enthalpy $\Delta H^F_V$. A higher $\Delta H^F_V$ value costs more energy to form a vacancy, so the crystal can only accommodate a smaller vacancy population.

It is noted that the term formation enthalpy is specifically used rather than the term formation energy in this discussion. A different thermodynamic potential could be used to describe the formation energy of the vacancy, for example, the Helmholtz energy (or Helmholtz free energy). However, typical diffusion experiments take place at the atmospheric pressure. The atmospheric pressure does not change appreciably with volume change via the transfer of atoms to the surface and can thus be taken as constant. Enthalpy $H$ and the Gibbs energy $G = H - TS$ by extension – is defined for thermodynamic processes occurring at constant pressure and temperature [70]. Enthalpy is written as $H = U + pV$, the internal energy $U$ (in this case, the formation energy of the vacancy) plus the product of pressure $p$ and volume $V$ of the system. Through the $pV$ term, enthalpy conveniently incorporates the work done to push back the atmosphere while creating the vacancy and moving the displaced atom to the free surface. Thus, the consideration of the $pV$ term individually is removed.

The Helmholtz energy $A = U - TS$ is defined for thermodynamic processes at constant volume and temperature, hence it lacks a $pV$ term. While the Helmholtz energy is useful for diffusion experiments at high pressures where volume can be kept constant, most diffusion experiments are done at the atmospheric pressure. Using the Helmholtz energy may lead to a small error in the measurement of the formation energy $\Delta U$, or $\Delta E$ as commonly used. For example, the creation of one mol of vacancies with a molar volume of 10 cubic centimeters at the atmospheric pressure would require $p\Delta V = 0.0001$ eV of work to be done against the atmosphere compared to the typical $\Delta H^F_V$ values of 1-3 eV [71]. Despite the very small error in $\Delta E$, the formation enthalpy $\Delta H$ and the formation energy $\Delta E$ are nevertheless used interchangeably in the literature [59].

The quantification of other point defects at thermal equilibrium such as self-interstitials is done using the same statistical thermodynamics approach. The population of defect $D$ is described using the equation

$$C_D^{eq} = \exp \left( -\frac{\Delta G^F_D}{k_B T} \right) = \exp \left( \frac{\Delta S^F_D}{k_B} \right) \exp \left( -\frac{\Delta H^F_D}{k_B T} \right)$$

(3-77)
where $\Delta G_D^F$, $\Delta H_D^F$, and $\Delta S_D^F$ are the defect’s Gibbs energy of formation, enthalpy of formation, and entropy of formation respectively.

### 3.7.2 Point defects in compound semiconductors

In the discussion of vacancies in section 3.7.1, electrically charged vacancies – and other electrically charged point defects by extension – were neglected. In metals, conduction electrons are extremely populous [71]. The number of conduction electrons in a crystal of a monovalent metal (e.g. copper) is the same as the number of atoms in the host crystal ($\sim 10^{23}$ atoms in 1 cm$^3$ copper) [22]. The high concentration of copper conduction electrons overwhelms the room-temperature concentration of copper vacancies of $\sim 10^8$ cm$^{-3}$ ($\Delta H_V^F = 0.9$ eV, 300 K) [72]. Every lattice site in the copper crystal, including the vacancies, is populated by one electron on average. The populous conduction electrons in metals lead to efficient charge-screening of vacancies [59]. Therefore, the average copper vacancy can be treated as electrically neutral.

Compound semiconductors – CIGS in particular – contain significantly lower charge carrier populations than metals and subsequently require special consideration. As discussed in section 2.2.3, copper vacancies in CIGS are considered acceptor defects such that they supply electronic holes to the valence band at temperatures above 0 K. Because the copper vacancy is populated by the hole in CIGS at 0 K – as well as under heavy p-type doping, the copper vacancy is considered electrically neutral. However, at temperatures above 0 K, the hole is thermalized away from the vacancy, ionizing the vacancy. In solar-grade CIGS, the carrier concentration of holes is $\sim 10^{16}$ cm$^{-3}$ [54], corresponding to approximately one conduction hole for every million atoms in a cubic-centimeter CIGS crystal of $\sim 10^{22}$ atoms. Accordingly, the average copper vacancy is negatively charged.

According to [59], the site fractions of point defect populations in semiconductors can then be written as the sum of various charge species:

$$
C_{X_x}^{eq} = C_{X_x}^{eq_0} + C_{X_x}^{eq_1+} + C_{X_x}^{eq_1-} + C_{X_x}^{eq_2+} + C_{X_x}^{eq_2-} + \cdots
$$

(3-78)

where $X$ denotes a specific type of defect. However, the exact configuration of charged point defects can be notoriously difficult to identify in elemental semiconductors with germanium being the exception [59]. Doping in germanium has
been shown to influence the germanium self-diffusion coefficient where n-type (p-type) doping increases (decreases) the self-diffusion coefficient [73]. Because germanium vacancies can exist as acceptor defects and mediate self-diffusion, enhanced self-diffusion has been attributed to an increase in negatively charged vacancies. For semiconductors in general, the position of the Fermi level in the energy band gap influences charged defect populations.

3.7.3 Theoretical formation energies of point defects

It was deductively shown in section 3.7.1 and 3.7.2 that 1) semiconductors contain neutral and charged point defects and 2) the charged defects are influenced by the Fermi level in the band gap. Cu(In,Ga)Se₂ is no exception. However, because of the quaternary nature of CIGS, the study of defects in CIGS becomes difficult. For example, the vacancy formation energy and concentration calculations do not follow the same method discussed for single-element materials.

First-principles studies based on computational quantum mechanics – using the density functional theory (DFT) – have been conducted to understand defects in difficult materials like CuInSe₂ and CuGaSe₂. [74], [75]. The quantum mechanical calculations are done by inserting defects in an artificially large unit cell of Cu, In/Ga, and Se atoms called a “supercell” [38], [76]. In such calculations, the defect formation energy \( \Delta H^F_{D,q} \) of defect type \( D \) and charge \( q \) \((q > 0 \text{ if the defect is an electron donor and } q < 0 \text{ if the defect is an electron acceptor})\) is governed by the electron chemical potential as well as the atomic chemical potential [77]:

\[
\Delta H^F_{D,q}(E_F, \mu) = (E_{D,q} - E_0) + q(E_V + E_F) + \sum_\alpha n_\alpha (\Delta \mu_\alpha + \mu^0_\alpha) .
\] (3-79)

The \((E_{D,q} - E_0)\) term is the change in total energy of the crystal due to the insertion of the defect \( D \) with charge \( q \) into the defect-free crystal. For charged defects \((q \neq 0)\), the second term on the right side of Eq. (3-79) accounts for the cost of adding a charge \( q \) to the “electron reservoir”. The final term is a summation of the energy required to move \( n \) atoms of element \( \alpha \) involved in the formation of defect \( D \) to the “atomic reservoir” where the reservoir chemical potential for element \( \alpha \) is \( \mu_\alpha \). Because the concepts of atomic and electron reservoirs can be challenging, their meaning is elucidated in the following discussion.
Figure 3.11 – Schematic of copper, indium, and selenium atomic reservoirs and the CuInSe$_2$ material system used in first-principles calculations.

Studying defect properties of CuInSe$_2$ and CuGaSe$_2$ using computational methods involves removing (adding) an atom from (to) the supercell. However, barring the creation of the universe, atoms cannot simply disappear or come into existence from nothingness. For example, when an atom is removed from the calculation supercell, it must go somewhere. The atomic reservoir is a convenient point of reference: atoms are added to and removed from the calculation supercell using the reservoir. The concept of an atomic reservoir is illustrated in Figure 3.11 as adapted from [78]. For simplicity, CuInSe$_2$ will be considered rather than Cu(In,Ga)Se$_2$. The interaction between the reservoir and the supercell requires energy exchange. This energy exchange is quantified using chemical potentials [79]. The chemical potential $\mu_i$ is defined as the partial derivative

$$
\mu_i = \mu_i(T, P, N_1, N_2, \ldots N_s) = \left( \frac{\partial G}{\partial N_i} \right)_{T, P, N_j (j \neq i)} \tag{3-80}
$$

for a system with a fixed number of particles $N_s$ of the $s$-th type – except for particles of type $i$ – at constant temperature $T$ and pressure $P$. The chemical potential is also known as the partial molar Gibbs free energy. The meaning of partial molar Gibbs free energy is how much the system’s Gibbs free energy changes when a particle of type $i$ is added to (or removed from) the system with everything else kept constant.

It should be noted that inconsistent terminology and notation plague the computational materials science community. In several first-principles works, $\Delta H^F_{D,q}$ in Eq. (3-79) is denoted as $\Delta G^F_{D,q}$, alluding to the thermodynamic parameters enthalpy $H$ and the Gibbs energy $G$ respectively as discussed toward the end of section 3.7.1 [38], [46], [65], [80], [81]. In thermodynamic equilibrium of a compound-semiconductor system with its atomic and electron reservoirs, the concentration of a defect – copper vacancies in CuInSe$_2$ for example – is still determined by the Boltzmann distribution
in Eq. (3-77) [80]. Eq. (3-77) is derived from Eq. (3-68) which states that $\Delta G = n_v \Delta G_v^\text{F} - T \Delta S_m$. $\Delta G$ includes enthalpy of formation $\Delta H_v^\text{F}$ as well as configurational entropy $\Delta S_m$, and vibrational entropy $\Delta S_v^\text{F}$. Configurational entropy is already intrinsically embedded into the defect concentration expression in Eq. (3-77) via the Boltzmann approach according to the derivation in section 3.7.1. The only entropy parameter to be calculated via first principles is vibrational entropy $\Delta S_v^\text{F}$. However, in some first-principles works, $\Delta S_v^\text{F}$ is implicitly or explicitly ignored [38], [81]. Thus, without $\Delta S_v^\text{F}$, defect concentration calculations using the Boltzmann expression in Eq. (3-77) are not complete.

The chemical potential $\mu_{\alpha}$ of element $\alpha$ in the atomic reservoir is expressed with respect to the chemical potential of the respective element in its standard state $\mu_{\alpha}^0$. In the case of copper, the solid form of copper acts as the atomic reservoir for copper in the computational CuInSe$_2$/CuGaSe$_2$ supercell. $\mu_{\alpha}$ is related to $\mu_{\alpha}^0$ through the delta term $\Delta \mu_{\alpha}$ [82]. In the case of copper, the delta term is expressed as

$$\Delta \mu_{\text{Cu}} = \mu_{\text{Cu}} - \mu_{\text{Cu}}^0.$$  \hspace{1cm} (3-81)

In such calculations, the reference chemical potential of a metallic element is usually taken to be the negative of the cohesive energy of the metal in its solid phase – the energy per atom required to pull the atoms in a bulk solid apart into isolated atoms [38]:

$$\mu_{\alpha}^0 = -\Delta E_{\alpha}^\text{cohesive}$$ \hspace{1cm} (3-82)

Where $\Delta E_{\alpha}^\text{cohesive}$ is the cohesive energy of the element $\alpha$ in its bulk phase. For example, the cohesive energy of solid copper was calculated as 3.49 eV [33]. Hence, the chemical potential of copper is -3.49 eV. Preventing the precipitation of elemental copper requires the chemical potential of the atomic reservoir to be equal to or less than the chemical potential of elemental copper:

$$\Delta \mu_{\text{Cu}} \leq 0.$$ \hspace{1cm} (3-83)

Indium, gallium, and selenium follow the same convention. In practice, the chemical potentials of Cu, In, Ga, and Se in the atomic reservoir correspond to their respective gaseous partial pressures in the deposition chamber [83]. For example, an increasing partial pressure (chemical potential) of copper tends to add Cu$_i$ and/or remove V$_{\text{Cu}}$ defects.
Eq. (3-83) is also true for indium, gallium, and selenium. Additionally, for the system of the CuInSe$_2$ crystal and the atomic reservoirs to be in equilibrium, chemical potential must be the same everywhere. In terms of the Gibbs phase rule, maintaining a stable CuInSe$_2$ phase requires an equilibrium condition, namely the sum of chemical potentials $\mu_{\text{Cu}}$, $\mu_{\text{In}}$, and $\mu_{\text{Se}}$ must equal the chemical potential of the bulk CuInSe$_2$ $\mu_{\text{CuInSe}_2}$ [84]:

$$\mu_{\text{Cu}} + \mu_{\text{In}} + 2\mu_{\text{Se}} = \mu_{\text{CuInSe}_2}. \quad (3-84)$$

Independently assigning values to two of the elemental chemical potentials (e.g. $\mu_{\text{Cu}}$ and $\mu_{\text{In}}$) forces a specific value for the third elemental chemical potential (e.g. $\mu_{\text{Se}}$). $\mu_{\text{CuInSe}_2}$ is related to the standard enthalpy of formation $\Delta H_f^0$ of CuInSe$_2$. Following the spirit of the derivation in [85], the $\Delta H_f^0$ of the reactants and products of the Eq. (3-85) reaction in Eq. (3-86) can be shown to be equivalent to the sum of $\Delta \mu_{\text{Cu}}$, $\Delta \mu_{\text{In}}$, and $\Delta \mu_{\text{Se}}$ using Eq. (3-84), yielding Eq. (3-87).

$$\text{Cu}(s) + \text{In}(s) + 2\text{Se}(s) \leftrightarrow \text{CuInSe}_2, \quad (3-85)$$

$$\Delta H_f^0(\text{CuInSe}_2) = \mu_{\text{CuInSe}_2} - (\mu_{\text{Cu}}^0 + \mu_{\text{In}}^0 + 2\mu_{\text{Se}}^0). \quad (3-86)$$

$$\Delta H_f^0(\text{CuInSe}_2) = \Delta \mu_{\text{Cu}} + \Delta \mu_{\text{In}} + 2\Delta \mu_{\text{Se}}. \quad (3-87)$$

Thus, Eq. (3-87) is simply the equilibrium condition of Eq. (3-84) in the terms of the standard enthalpy of formation $\Delta H_f^0$ which can be experimentally determined. In other words, Eq. (3-87) imposes thermodynamical limits on the range of chemical potentials for a stable CuInSe$_2$ phase. For example, when $\Delta \mu_{\text{In}} = 0$, $\Delta \mu_{\text{Cu}}$ cannot be arbitrarily small, otherwise a competing phase precipitates. Literature values of $\Delta H_f^0$ for CuInSe$_2$ range from -2.0 eV to -4.0 eV [38], [46], [86], [87].

Using $\Delta H_f^0(\text{CuInSe}_2) = -2.0 \text{ eV}$ in Zhang and Zunger’s works [38], [76], Eqs. (3-83) and (3-87) can be graphically visualized in the phase stability triangle projected to the ($\Delta \mu_{\text{Cu}}$, $\Delta \mu_{\text{In}}$) space (Figure 3.12) [38]. At point A, $\Delta \mu_{\text{Se}} = -1 \text{ eV}, \Delta \mu_{\text{In}} = 0 \text{ eV}$ on all points on line BC. Lines parallel to line BC in the phase stability triangle denote a constant $\Delta \mu_{\text{Se}}$. As suggested by the phase stability triangle, the chemical potentials have to be further restricted due to competing phases such as In$_2$Se$_3$ and Cu$_2$Se. To prevent the precipitation of phases $A_aB_b$, $A_aB_bC_c$, etc., the sum of the atomic chemical potentials must be smaller than the formation enthalpy of their respective phase:
\[ a \Delta \mu_A + b \Delta \mu_B \leq \Delta H^0_f (A_a B_b). \]  
(3-88)

\[ a \Delta \mu_A + b \Delta \mu_B + c \Delta \mu_C \leq \Delta H^0_f (A_a B_b C_c). \]  
(3-89)

Figure 3.12 – The stability triangle of the Cu-In-Se system. Points A, B, and C represent respective deposition conditions (e.g. copper-rich, indium-rich, and selenium-poor). Area D represents photovoltaic-grade CuInSe\(_2\) material. Adapted from [38].

To illustrate the significance of chemical potentials and its role in the stoichiometry of a deposited CuInSe\(_2\) film via coevaporation, consider creating one neutral copper vacancy in CuInSe\(_2\). Eq. (3-79) can then be reduced to

\[ \Delta H^F_{Cu} (\mu) = (E_{CIS:V_{Cu}} - E_{CIS}) + (\Delta \mu_{Cu} + \mu^0_{Cu}) \]  
(3-90)

where \(E_{CIS:V_{Cu}}\) is the crystal energy with the neutral copper vacancy and \(E_{CIS}\) the crystal energy without the neutral copper vacancy. \(\mu_{Cu}\) is the chemical potential of copper in the atomic reservoir. The \(n_a\) term reduces to \(n_{Cu}\) because only one copper atom is involved in the process of creating the copper vacancy. The value of \(n_{Cu}\) is +1 when a single copper is removed from the crystal and added to the atomic reservoir. This is explicitly seen in Eq. (3-90) where an increasing copper chemical potential up to 0 eV increases the formation energy of the neutral copper vacancy, making it more difficult to generate a copper vacancy. When the chemical potential \(\mu_{Cu}\) in the atomic reservoir becomes equal to \(\mu^0_{Cu}\), the neutral copper vacancy formation energy equation reduces further to
\[ \Delta H^E_{\text{Cu}}(\mu) = (E_{\text{GISE}_{\text{Cu}}} - E_{\text{GIS}}) + \mu^0_{\text{Cu}}. \] (3-91)

The \( \Delta \mu_{\text{Cu}} \) term vanishes and only the \( \mu^0_{\text{Cu}} \) term is left. Under this copper-rich condition, the \( (E_{\text{GISE}_{\text{Cu}}} - E_{\text{GIS}}) \) term, the change in the total energy of the defect supercell, must be greater than \( -\mu^0_{\text{Cu}} \) to maintain a stable CuInSe\(_2\) phase. Additional energy must be supplied for the vacancy creation. Otherwise, copper vacancies would spontaneously form, destabilizing the CuInSe\(_2\) phase. Physically, when the cohesive energy in the atomic reservoir becomes higher, the atoms in its elemental form (elemental copper) have an increased tendency to 1) stay together and 2) pull an atom (copper atom) of the same type from the system (CuInSe\(_2\)) to create a vacancy (copper vacancy in CuInSe\(_2\)). Consequently, less additional energy is required to complete the vacancy creation process which might come in the form of thermal energy.

Decreasing the copper chemical potential relative to the indium chemical potential sufficiently to point B (the Cu-poor; In-rich diagram in the middle of Figure 3.12) causes the \( V_{\text{Cu}} \) defect formation energy to become negative. Copper vacancies would spontaneously form and destabilize the CuInSe\(_2\) phase. According to the location of B in the stability triangle in Figure 3.12, the In\(_2\)Se\(_3\) compound would be the equilibrium phase instead of CuInSe\(_2\) under this particular Cu-poor, In-rich condition. Likewise, when the crystal is sufficiently indium-poor relative to copper, the Cu\(_2\)Se phase is most stable, denoted by point C. Point D represents chemical potentials seen in photovoltaic-grade CIGS based on the hole concentration of \( \sim 10^{16} \text{ cm}^{-3} \) [88], [89].

While CuInSe\(_2\) contains two cations – copper and indium – in addition to the selenium anion, altering the chemical potential of the atomic reservoir of the respective cation type does not necessarily change the atomic reservoir chemical potential of the other cation in the first-principles calculations according to Eq. (3-84). If the difference in the chemical potentials of two cation atomic reservoirs \( \mu_{\text{CA}} - \mu_{\text{CB}} \) at constant anion chemical potential is instead used, one obtains a relationship between the richness of a cation type and its respective vacancy and self-interstitial formation energies (Figure 3.13). As a material is made richer in a cation type, more (less) energy is required to create a vacancy (self-interstitial) of the same cation type. At the same time, the vacancy (self-interstitial) formation energy of the other cation type decreases (increases).
Figure 3.13 – Defect formation energy as a function of varying cation chemical potentials in a $C_A$-$C_B$-$A$ compound via the chemical potential difference $\mu_A - \mu_B$. For example, CuInSe$_2$ where copper and indium are the cations ($C_X$ or $CX$ where $X$ is cation A or B). The anion chemical potential is kept constant. Adapted from [38], [90]. $CX_i$ is the self-interstitial $CX$ atom.

A similar relationship exists in terms of difference in the chemical potentials of the anion and cation atomic reservoirs as shown in Figure 3.14. Anion and cation vacancies are harder to create in anion- and cation-rich materials respectively.

The electron reservoir controls the formation energy of a charged defect. The electron chemical potential in the electron reservoir is determined by an arbitrary Fermi level representing a doping level of the CuInSe$_2$ crystal. The reservoir electron chemical potential term ($E_V + E_F$) in Eq. (3-79) can be written as $\mu_e$:

$$\mu_e = E_V + E_F$$  \hspace{1cm} (3-92)

where $E_F$ is referenced with respect to the calculated valence band maximum [91]. Because the Fermi level lies in the band gap between the valence and conduction bands in non-degenerate semiconductors, the value of $E_F$ in the electron reservoir is constrained between the valence and conduction bands. Thus, $E_F$ can at the minimum be zero and at the most equal to the band gap energy $E_g$ [92]:

$$0 \leq E_F \leq E_g.$$  \hspace{1cm} (3-93)
The sum $E_V + E_F$ signifies the absolute electron chemical potential in the reservoir in first-principles defect calculations [93]. Recall that the Fermi level is defined as the total electron chemical potential in section 2.2.3. The higher (lower) electron chemical potential in the reservoir, the more difficult it is to ionize a donor (acceptor) defect.

In the case of the copper vacancy according to Zhang et al., the formation energy for the neutral copper vacancy is lower than that of an ionized (negatively charged) copper vacancy when the electron reservoir energy is between $E_V$ and $E_F = 0.03$ eV. Above $E_F = 0.03$ eV, the formation energy of the charged copper vacancy becomes lower than that of the neutral copper vacancy [38]. To illustrate this point, consider the versions of Eq. (3-79) for the neutral and negatively charged copper vacancies as similarly demonstrated in [91]. Setting their formation energies to equal each other, the equality

$$\Delta H^F_{V_{Cu}^0} = \Delta H^F_{V_{Cu}^-}$$  \hspace{1cm} (3-94)

reduces to

$$E_F = E_{CIS:V_{Cu}^0} - E_{CIS:V_{Cu}^0} - E_V$$  \hspace{1cm} (3-95)
after some algebra. Eq. (3.95) is valid when the Fermi level $E_F$ equals the ionization level $E_{V_{Cu}^{(0/-)}}$ for the singly, negatively charged copper vacancy:

$$E_F = E_{V_{Cu}^{(0/-)}} = E_{CIS:\cdot V_{Cu}} - E_{CIS:\cdot V_{Cu}^0} - E_V. \quad (3.96)$$

The ionization level is defined as the Fermi level $E_F$ where the formation energy is the same for two charge states. As stated above, $E_{V_{Cu}^{(0/-)}} = 0.03$ eV. $E_{V_{Cu}^{(0/-)}}$ can also be interpreted as the energy difference between a system with the negatively charged copper vacancy and a system with a neutral copper vacancy and an electron at the valence band maximum. Thus, in the calculations by Zhang et al., an energy of 0.03 eV is required to excite the electron from the valence band maximum to the copper vacancy defect level [38]. It is noteworthy to mention that other first-principles workers have calculated the ionization level of the copper vacancy in CuInSe$_2$ and CuGaSe$_2$ to be below the valence band maximum, so the question of the actual ionization level remains open [89]. However, assuming that the ionization level occurs within the band gap, the generalized form of Eq. (3.96) for the ionization level $E_A$ of a singly charged acceptor defect in CuInSe$_2$ can be written as

$$E_{A^{(0/-)}} = (E_{CIS:A^-}) - (E_{CIS:A^0}) - E_V$$

where $E_{CIS:A^-}$ is the energy of the CuInSe$_2$ system with the negatively charged acceptor defect. $E_{CIS:A^0}$ is the system energy with the neutral acceptor defect. The ionization level $E_D$ for a singly charged donor defect is also written as

$$E_{D^{(+/-)}} = (E_{CIS:D^0}) - (E_{CIS:D^+}) - E_V.$$  

$E_{CIS:D^+}$ represents the energy of the CuInSe$_2$ system with the positively charged donor.

The influence of the Fermi level on defect formation energies in CuInSe$_2$ is graphically shown in Figure 3.15 (adapted from [38], [76]) as a function three selected pairs of chemical potentials of copper and indium. It is seen that the defect formation energies in CuInSe$_2$ strongly depend on the Fermi level. Acceptor defects like $V_{Cu}^-$ and $Cu_{In}^{2+}$ are more easily formed in n-type CuInSe$_2$ while donor defects like $In_{Cu}^2$ form easily in p-type CuInSe$_2$. For a given species, its various charge states exist simultaneously but differ in concentrations due to different formation energies that depend on the Fermi energy. Balanced deposition conditions are needed to create a stable copper-poor CuInSe$_2$ phase as well its
copper-poor CuIn$_3$Se$_5$ and CuIn$_5$Se$_8$ phases typically seen at the surface of solar-grade CuInSe$_2$/Cu(In,Ga)Se$_2$ thin films.

Figure 3.15 – Formation energies of charged and neutral defects in compound semiconductors as a function of the Fermi energy (with respect to the valence band maximum). Bold lines are the defect species with the lowest formation energy. Dotted lines are the higher formation energies for the defect species. Adapted from [38], [90].

As seen in Figs. 3.13, 3.14, and 3.15, the defect formation energies $\Delta H_{D,q}^{F}$ is a strong function of both the chemical potentials of the atomic components and the Fermi level, varying by several electronvolts (eV). Consequently, it is somewhat involved to identify general defect properties of CuInSe$_2$ and ultimately Cu(In,Ga)Se$_2$ thin films. An analysis of the tendency of defect formation independently of chemical potential and Fermi level can be done by using the terms in Eq. (3-79) that are independent of such parameters: the $(E_{D,q} - E_0)$, $qE_V$, and $n_\alpha \mu_\alpha^0$ terms. After defining a new parameter to represent the independent parameters [76],

$$\Delta \tilde{H}_{D,q}^{F} = (E_{D,q} - E_0) + qE_V + n_\alpha \mu_\alpha^0,$$  \hspace{1cm} (3-97)

various defects in CuInSe$_2$ and CuGaSe$_2$ can be compared without considering the varying atomic chemical potential or the Fermi level. Qualitatively, $\Delta \tilde{H}_{D,q}^{F}$ can be thought as the formation energy for a defect $D$ with charge $q$ when the system is in equilibrium with the solid phase of the respective element ($\mu_\alpha = \mu_\alpha^0$) and the Fermi level $E_F$ is as low as possible, equal to the valence band maximum $E_V$. 

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Figure 3.16 – The $\Delta H_{D,q}^F$ parameter for various charged defects in CuInSe$_2$ derived from the literature: (a) Zhang et al. [38]; (b) Bekaert et al. [89]; (c) Persson et al. [46]; (d) Pohl et al. [65], hybrid functional calculations; (e) Pohl et al. [65], generalized gradient approximation (GGA) calculations; (f) Oikkonen et al. [94]. $\Delta H_{D,q}^F$ is the formation energy for defect $D$ with charge $q$ when the CuInSe$_2$ system is in equilibrium with the solid phase of the respective element in the atomic reservoir ($\mu_\alpha = \mu_\alpha^0$) and the Fermi energy $E_F$ equal to the valence band maximum.

Figure 3.17 – The $\Delta H_{D,q}^F$ parameter for various charged defects in CuGaSe$_2$ derived from the literature: (a) Zunger et al. [76]; (b) Bekaert et al. [89]; (c) Persson et al. [46]; (d) Pohl et al. [65], hybrid functional calculations; (e) Pohl et al. [65], generalized gradient approximation (GGA) calculations. $\Delta H_{D,q}^F$ is the formation energy for defect $D$ with charge $q$ when the CuGaSe$_2$ system is in equilibrium with the solid phase of the respective element in the atomic reservoir ($\mu_\alpha = \mu_\alpha^0$) and the Fermi energy $E_F$ equal to the valence band maximum.
Figs. 3.16 and 3.17 show the $\Delta H^F_0$ parameters for various defects in CuInSe$_2$ and CuGaSe$_2$ respectively derived from [38], [46], [65], [76], [89], [94]. As indicated in the plots, only charged defects are shown rather than their neutral states. The plotting choice is due to the calculations by Bekaert et al. as well as those by Oikkonen et al. that suggest the transition to the neutral charge state for the acceptor (donor) defects takes place at an energy level below (above) $E_V$ ($E_C$) [89], [94]. The effect in Figure 3.15 is a shift of the defect formation energy curves in such that the transition to the neutral charge state does not happen within the band gap. As a note, not all first-principles workers suggest the same behavior. In fact, Zhang et al. as well as other workers finds that the transition to the neutral charge state for $V_{\text{Cu}}$ occurs at 0.03 eV above $E_V$ [38], [46], [76]. Fundamental difficulties of first-principles calculations are responsible for the discrepancy as discussed below.

Nevertheless, the dominating defect in CuInSe$_2$ and CuGaSe$_2$ appears to be the negatively charged copper vacancy. $V_{\text{Cu}}^-$ has low formation energies in both materials with most values below 1 eV (Figs. 3.16 and 3.17). Using just the enthalpy term in Eq. (3-76), the equilibrium concentration of copper vacancies equation reduces to

$$
C_{V_{\text{Cu}}}^{\text{eq}} \propto \exp\left(-\frac{\Delta H^F_0}{k_BT}\right).
$$

An assumed copper vacancy formation energy of 0.60 eV and a deposition temperature of 500 °C (773 K) in CuInSe$_2$ with $\sim 1 \times 10^{22}$ copper lattice sites per cubic centimeter corresponds to a vacancy concentration on the order of $10^{18}$ cm$^{-3}$ with the Fermi level at the valence band maximum $E_V$. Achieving a copper vacancy concentration of 1 at. % ($\sim 10^{20}$ cm$^{-3}$) at 773 K requires a formation energy of $\sim 0.3$ eV. A slightly copper-poor, p-type ($\sim 10^{16}$ holes cm$^{-3}$) deposition condition where the Fermi level is shifted appreciably above $E_V$ can easily achieve such a low $V_{\text{Cu}}^-$ formation energy.

Figs. 3.16 and 3.17 also show that the next most likely defects in CuInSe$_2$ and CuGaSe$_2$ are $\text{Cu}_{\text{In/Ga}}^{2-}$ and $\text{In/Ga}_{\text{Cu}}^{2+}$. Interestingly, the $\text{In/Ga}_{\text{Cu}}^{2+}$ formation energies are the source of significant discrepancy between several first-principles works. For example, Zhang et al. suggest a $\text{In}_{\text{Cu}}^{2+}$ formation energy of $\sim 2$ eV while Bekaert et al. and Persson et al. calculate a formation energy of $\sim -2$ eV and $-0.5$ eV respectively. [38], [46], [89]. The negative values of the $\text{In}_{\text{Cu}}^{3+}$ defect formation energy is not implausible; section 3.7.5 discuss the exothermic ordering of defect pairs such as $2V_{\text{Cu}}^- + \text{In}_{\text{Cu}}^{3+}$. However, the unresolved differences in formation energies have enormous implications in explaining
the defect properties of CuInSe$_2$ and CuGaSe$_2$ and their conductivities as well as tailoring the deposition method for high-efficiency photovoltaic devices.

A common, serious problem with the implementation of the density functional theory for the first-principles calculations is the tendency to underestimate the band gap size. As a common practice in density functional theory to correct this underestimation, the conduction energy band is shifted by a constant value to match the experimentally measured band gap. In the work of Zhang et al. [38], the shift is +0.87 eV from the calculated band gap of 0.17 eV to the CuInSe$_2$’s experimental value of 1.04 eV. Domain et al. added +1 eV to the calculated band gap of < 30 meV in their work [95]. Using the screened-exchange hybrid density functional theory to address the band gap underestimation instead of simply shifting the conduction band, Pohl et al. showed that $\Delta \tilde{H}^F_{\text{Cu}}$ in CuInSe$_2$ becomes 0.92 eV [65], compared to 0.63 eV as calculated by Zhang et al. [38] and 0.90 eV by Persson et al. [46].

Kosyak et al. discuss two additional challenges of the first-principles calculations for compound semiconductors [80]. First, calculating the equilibrium defect concentration requires the knowledge of the actual Gibbs free energy for defect formation at a finite temperature while the electronic structure of the compound-semiconductor material is calculated in first principles at $T = 0$ K using the Born-Oppenheimer approximation. Data extracted from first-principles may then be a better representation of $T = 0$ K than a finite temperature [96]. Second, the Gibbs free energy of formation for a phase has a temperature dependence because of the temperature dependence of the specific heats of the phase formation reactants and products. Specifically, severely non-stoichiometric CuInSe$_2$ might have a different Gibbs free energy of formation compared to a stoichiometric CuInSe$_2$. These issues must be considered while interpreting the defect formation energies from first-principles calculations.

Nevertheless, for cadmium to diffuse through the cation sublattice in Cu(In,Ga)Se$_2$ via the vacancy mechanism, cation vacancies other than the copper vacancies should be ignored. The high formation energies for indium (gallium) vacancies mean vacancy concentrations that are several orders of magnitude smaller than that of the copper vacancies. If vacancies are a cadmium diffusion vehicle in CIGS, the extremely abundant copper vacancies would likely be responsible rather than the indium/gallium vacancies.
3.7.4 Experimental formation energies of point defects

Some experimental data on formation energies of defects in CuInSe₂ exist. Copper vacancy formation energies have been experimentally studied by measuring chemical potentials via cyclic voltammetry. Stoichiometric CuInSe₂ samples yielded copper chemical potential in CIGS $\mu_{\text{Cu}_{\text{CIGS}}}$ measurements between -0.3 eV and -0.4 eV while selenium-rich (copper-poor) CuInSe₂ samples had values between -0.45 eV and -0.50 eV. $\mu_{\text{Cu}_{\text{CIGS}}}$ of photovoltaic-grade Cu(In,Ga)Se₂ samples was measured to be -0.55 eV [87], [97], [98].

Following Guillemoles’ physical argument: the negative of the calculated or measured value of the lowest copper chemical potential $\mu_{\text{Cu}_{\text{CIGS}}}$ possible for a stable CuInSe₂ phase provides the lower bound for the standard free energy of copper vacancy formation in CIGS [87]:

$$\Delta H^F_{\text{Cu}} > -\mu_{\text{Cu}_{\text{CIGS}}}.$$  \hspace{1cm} (3-99)

The standard free energy of formation is the free energy of formation at 25 °C and 100 kPa. The chemical potential of copper in its standard state $\mu_{\text{Cu}}^0$ (solid copper) is sometimes taken to be 0 eV rather than the -3.49 eV value as previously given. Note that differences in chemical potentials are used rather than absolute chemical potentials because the chosen reference potential is arbitrary. The reaction

$$\text{Cu}_{\text{CIGS}} \rightarrow \text{Cu}^0 + V_{\text{Cu}}$$ \hspace{1cm} (3-100)

must have a positive standard free energy of formation. If the free energy of formation is negative, copper vacancies would form spontaneously and the free energy would not be at a minimum, decomposing CIGS. In the case of Zhang’s first principles work, the limiting chemical potential $\mu_{\text{Cu}_{\text{CIGS}}}$ for stable CuInSe₂ equals to approximately -0.335 eV [38]. Creating a copper vacancy – by moving a neutral copper atom to the atomic reservoir where chemical potential is taken to be 0 eV, that is, equal to the chemical potential of solid copper in its standard state – requires a calculated value 0.6 eV. Referring to Eq. (3-91) for neutral copper vacancies, the chemical potential is not the only criterion for the vacancy formation energy; the term $(E_{\text{CIS}V_{\text{c}}} - E_{\text{CIS}})$ must be included. Thus, the formation energy of the copper vacancy must be greater than the negative of the copper chemical potential in CuInSe₂, satisfying the condition in Eq. (3-99).
Figure 3.18 – On the left, schematic of the copper chemical potential in CIGS in equilibrium with the external atomic reservoir. On the right, copper-poor CIGS has a smaller copper chemical potential than elemental copper.

The argument can be graphically extended and understood with Figure 3.18. The chemical potential of copper in CIGS $\mu_{\text{Cu,CIGS}}$ is equal to the chemical potential of copper in the atomic reservoir $\mu_{\text{Cu}}$ under the equilibrium crystal growth condition (the left diagram in Figure 3.18). Recall that one of the equilibrium conditions is ensuring that $\mu_{\text{Cu}}$ holds a negative value in the atomic reservoir to avoid the precipitation of solid copper. This condition is easily fulfilled under the copper-poor crystal growth condition. Consequently, $\mu_{\text{Cu,CIGS}}$ is also negative and equal to $\mu_{\text{Cu}}$ at equilibrium.

Now, solid copper is placed in contact with CIGS following deposition. Moving a neutral copper atom to the reservoir of solid copper requires an amount of energy greater than the negative of $\mu_{\text{Cu,CIGS}}$ (the right diagram in Figure 3.18). This situation might correspond to plating solid copper out of CIGS and onto the CIGS surface via electrical bias which has actually been experimentally observed (see Chapter 4). The $\mu_{\text{Cu,CIGS}} = -0.55$ eV value stated above indicates that the standard copper vacancy formation energy must be at least 0.55 eV. Through the important inequality statement of Eq. (3-99), the experimental $\mu_{\text{Cu,CIGS}}$ values offer the most direct evidence supporting the low copper vacancy formation energies seen in the first principles works.

### 3.7.5 Defect pairs

Up to this point, the lack of metal-like conductivity in Cu(In,Ga)Se$_2$ materials with a significant amount of point defects on the order of 1 at.% has not been conspicuously addressed. In section 3.7.2, the charge carrier populations in CIGS and metallic copper were compared, with the former containing $\sim 10^{16}$ cm$^{-3}$ and the latter $\sim 10^{23}$ cm$^{-3}$. The large defect population in CIGS implies a charge carrier population greater than $10^{20}$ cm$^{-3}$ if a CIGS crystal is assumed to contain 1 at.% of copper vacancies that generate one conduction hole for every copper vacancy, however it is clearly not the case. CIGS maintains semiconducting properties in face of large defect populations.
The defect pairs \((2V_{\text{Cu}}^- + \text{In}_{\text{Cu}}^2^+)\) and \((\text{Cu}_{\text{In}}^{2^-} + \text{In}_{\text{Cu}}^{2^+})\) has been suspected to be responsible for the electrically neutralizing behavior seen in CulnSe\(_2\)-related materials. Point defects such as \(V_{\text{Cu}}\) and \(\text{In}_{\text{Cu}}^2^+\) can interact and rearrange crystallographically to further minimize the formation energies of the said point defects. According to [38] and [93], the general expression for the formation energy of a defect pair is written as

\[
\Delta H_f(\alpha + \beta) = \Delta H_{\text{non}} + \delta H_{\text{int}} + \delta H_{\text{ord}}
\]

(3-101)

where

\[
\Delta H_{\text{non}} = \Delta H_f(\alpha) + \Delta H_f(\beta).
\]

(3-102)

The \(\Delta H_{\text{non}}\) term is the sum of the formation energies of non-interacting, neutral defects of type \(\alpha\) and \(\beta\). For a \((2V_{\text{Cu}}^- + \text{In}_{\text{Cu}}^2^+)\) defect pair, \(\Delta H_{\text{non}} = 2\Delta H_f(V_{\text{Cu}}^0) + \Delta H_f(\text{In}_{\text{Cu}}^0) = 4.54\) eV which corresponds to the \(\Delta H_{\text{non}}\) at the chemical potentials of point \(A\) in Figure 3.12 [38]. \(\delta H_{\text{int}}\) is the change in energy when the defects \(\alpha\) and \(\beta\) are next to each other such that they interact electrostatically. With the \((2V_{\text{Cu}}^0 + \text{In}_{\text{Cu}}^0)\) defect pair, \(\delta H_{\text{int}} = 4.21\) eV, indicating that the electrostatic interaction is attractive. This leads to the ionization of the defect complex from \((2V_{\text{Cu}}^0 + \text{In}_{\text{Cu}}^0)\) to \((2V_{\text{Cu}}^- + \text{In}_{\text{Cu}}^2^+)\). Forming the \((2V_{\text{Cu}}^- + \text{In}_{\text{Cu}}^2^+)\) complex eliminates a deep \(\text{In}_{\text{Cu}}\) donor level along with a shallow \(V_{\text{Cu}}^\text{a}\) acceptor level. In effect, interacting copper vacancies and the In-on-Cu antisite defects electrically inactivate each other.

Defect pairs can also form an ordered defect array in the crystal structure to further lower the formation energies, represented by \(\delta H_{\text{ord}}\). For the \((2V_{\text{Cu}}^- + \text{In}_{\text{Cu}}^2^+)\) pair, \(\delta H_{\text{ord}} = -0.43\) eV. In the case of the \((2V_{\text{Cu}}^0 + \text{In}_{\text{Cu}}^0)\) defect pair, the sum of \(\delta H_{\text{int}} + \delta H_{\text{ord}}\) is -4.64 eV, outweighs the formation energy of the respective non-interacting defects \(\Delta H_{\text{non}}\), leading to the spontaneous formation of electrically neutralized, crystallographically arrayed defect pairs even in CulnSe\(_2\) systems with high \(\mu_{\text{Cu}}\) and \(\mu_{\text{In}}\) chemical potentials. Under low \(\mu_{\text{Cu}}\) conditions (e.g. the copper-poor point \(C\) in Figure 3.12), the defect pair formation energies become even more strongly exothermic. The formation energy of the \((\text{Cu}_{\text{In}}^{2^-} + \text{In}_{\text{Cu}}^{2^+})\) defect pair is similarly low. The low \(\text{In}_{\text{Cu}}\) formation energies are also confirmed by Bekaert et al. and Persson et al. (section 3.7.3) [46], [89]. Ultimately, the spontaneous formation of electrically neutralizing defect pairs may assist in maintaining the semiconducting nature of CulnSe\(_2\) and CIGS materials despite the high defect concentration that otherwise suggests a metallic conductivity.
3.7.6 Equilibrium defect concentrations

With the considerations explored in the previous sections, the expression for defect concentrations in Cu(In,Ga)Se$_2$ materials in equilibrium with the respective reservoirs can be written using the chemical potential $\mu_\alpha$ and Fermi level $E_F$ dependencies of the defect formation energy (Eq. (3-79)) [46]:

$$C_{D,q}(E_F, \mu_\alpha, T) = N \exp \left( - \frac{\Delta H_{D,q}^F (E_F, \mu_\alpha)}{k_B T} \right)$$  \hspace{1cm} (3-103)

where $N$ is the concentration of lattice sites (e.g. the number of copper sites in CIGS), $\mu_\alpha$ corresponds to the chemical potential of element $\alpha$, and $T$ is the temperature at which the equilibrium concentration of defect $D$ with charge $q$ occurs. Note that in elemental semiconductors like silicon and germanium, $C_{D,q}(E_F, \mu_\alpha, T)$ reduces to $C_{D,q}(E_F, T)$ due to the lack of chemical potential dependence [99]. The expression is further reduced to $C_D(T)$ for metals due to the vanished dependence on $E_F$ (see the copper example in section 3.7.2).

The first-principles calculations discussed above in the present section are valid for the thermodynamic equilibrium between the system (e.g. CuInSe$_2$) and its atomic reservoirs (e.g. Cu, In, and Se) where the elements are kept at constant chemical potentials as well as the electron reservoir. In first-principles works, it is common to see Eq. (3-103) as the expression to estimate the concentration of a given defect species [46], [89]. In practical terms, the defect properties of a given CIGS thin film are reflective of the deposition parameters $E_F$, $\mu_\alpha$, and $T$. It is assumed that the CIGS thin film is cooled down to room temperature sufficiently rapidly that the defects become “frozen in” due to kinetic barriers even if such defects become thermodynamically unfavorable at room temperature. Calculating of the thermodynamic equilibrium defect concentrations of a closed CuInSe$_2$ system without external atomic reservoirs (i.e. fixed CIGS stoichiometry) at various temperatures are complicated. Refs. [49], [64], [100] provide discussions of such approaches.

3.8 Atomic diffusion processes in Cu(In,Ga)Se$_2$

3.8.1 Atomic jump frequency $\Gamma$

It was shown in the preceding sections that the anisotropic diffusion coefficients in Cu(In,Ga)Se$_2$ can be generalized as
\[ D_x = \frac{1}{2} Z \Gamma \lambda^2_x, \quad D_y = \frac{1}{2} Z \Gamma \lambda^2_y, \quad D_z = \frac{1}{2} Z \Gamma \lambda^2_z. \]  

(3-104)

In section 3.5.1, it was said that the jump frequency \( \Gamma \) is influenced by the vacancy concentration in the case of copper vacancy diffusion mechanism. More precisely, for a general diffusion process with a mediating defect in thermal equilibrium (e.g. with an equilibrium vacancy concentration), the jump frequency is defined in terms of the number of available sites \( C^\text{eq}_N \) to jump to and the frequency \( \nu \) of the vibrating atom hitting the energy barrier with an amount of energy equal to or greater than the barrier energy:

\[ \Gamma = \nu C^\text{eq}_N. \]  

(3-105)

The process of the diffuser atom migrating to an available site in the case of an interstitial atom in a two-dimensional square lattice is schematically shown in Figure 3.19. For the diffuser atom to successfully jump from interstitial site \( A \) to \( C \), it must squeeze past two lattice atoms at \( B \) which provide resistance to the process. The migration barrier energy is equal to the difference between the Gibbs free energies at positions \( A \) and \( B \):

\[ \Delta G^M = G_B - G_A \]  

(3-106)

\[ \Delta G^M = \Delta H^M - T \Delta S^M. \]  

(3-107)

Figure 3.19 – The Gibbs free energy landscape of atomic migration via interstitial sites in a two-dimensional lattice.

As usual, \( \Delta G^M \) can be decomposed into its enthalpy and entropy terms:
\( \nu \) can also be decomposed into the following:

\[
\nu = \nu_0 \exp \left( -\frac{\Delta G^M}{k_B T} \right)
\]

(3-108)

or

\[
\nu = \nu_0 \exp \left( -\frac{\Delta H^M}{k_B T} \right) \exp \left( \frac{\Delta S^M}{k_B} \right).
\]

(3-109)

\( \nu_0 \) is the frequency of the oscillation of the atom around its atomic position (e.g. an atom at position \( A \) in Figure 3.19). This frequency is sometimes known as the Debye frequency (between \( 10^{12} \) and \( 10^{13} \) s\(^{-1} \)) [59]. The exponential term represents the probability of the vibrating atom gaining an amount of energy equal to \( \Delta G^M \). Assuming \( \nu_0 = 10^{12} \) s\(^{-1} \) and \( \Delta G^M = 1 \) eV, the vibrating atom gains 1 eV and hits the energy barrier of 1 eV approximately once per day at the room temperature (300 K). However, \( \nu \) has to be multiplied by \( C_N^{eq} \) to determine the probability of a successful jump per unit time. For interstitial diffusion – a diffuser atom jumping from one interstitial site to another, the probability of having an available interstitial site to jump to in a dilute solid solution approaches unity. For the vacancy diffusion mechanism, the probability of a successful jump becomes limited by the probability of having an available vacancy next to the vibrating atom as expressed by \( C_V^{eq} \).

### 3.8.2 Correlation effects in diffusion

The random walk approach to diffusion contains an implicit assumption: the jump probability of the diffuser atom is independent of its previous jump; that the diffusion of the diffuser atom is purely random. In reality, diffusion may not always proceed randomly. Consider a two-dimensional square lattice of identical atoms with a single vacancy and a “tracer” atom in Figure 3.20. The tracer atom is indistinguishable from the other atoms; the only difference is that the tracer atom is tagged.

Figure 3.20 (a) shows that before the vacancy exchanges position with the tracer atom, the probabilities of the vacancy jumping to positions 1-9 are all equal. From the vacancy’s perspective, its diffusion is completely random. After the vacancy makes an exchange with the tracer atom at position 8, its motion continues to be random (Figure 3.20 (b)). However, from the tracer atom’s perspective, there is a greater chance of reverting back to position 8 after jumping to
position 5 due to the lack of other vacancies around position 5. As a result, the tracer atom has a smaller root mean square displacement than as suggested by purely random walk.

An extreme case of correlation manifests in the one-dimensional chain of atoms with a vacancy and a tracer atom in Figure 3.21. The vacancy may move wildly between the two ends, but the tracer atom will only be able to move back and forth between two positions, resulting in no net motion in either direction. In this case, the correlation factor becomes zero. Correlation effects must be considered as vacancies are typically not directly observed in diffusion experiments. Studying self-diffusion in a material often involves diffusing radioactively tagged atoms of the same type into the material via annealing (e.g. $^{64}$Cu in CuInSe$_2$ in [101]). Impurity diffusion is also used to study vacancies. Nickel, cobalt, and copper have been correlated to vacancy properties in germanium [102], [96].

To account for correlation effects in diffusion, correlation factor $f$ is included in the Cu(In,Ga)Se$_2$ diffusion equations (Eq. (3-104)):

$$D_x = \frac{1}{2} f_x Z T \lambda_x^2, \quad D_y = \frac{1}{2} f_y Z T \lambda_y^2, \quad D_z = \frac{1}{2} f_z Z T \lambda_z^2.$$  

(3-110)

The correlation factor is always greater than zero and can be unity at the most:

$$0 < f \leq 1.$$  

(3-111)
\( f = 0 \) represents the case where no net diffusion can occur which is satisfied by the one-dimensional chain in Figure 3.21 for example. The correlation factor calculation and measurement for a given diffusion mechanism and crystal structure can be difficult but can be approximated [59]:

\[
f \approx 1 - 2 \frac{1}{Z}.
\]  

(3-112)

\( Z \) is the number of neighbors. \( f = 1 \) for pure interstitial diffusion when the number of interstitial atoms is very low such that virtually all interstitial neighbors are unoccupied. \( f < 1 \) for vacancy-based diffusion mechanisms, and in the case of copper vacancy diffusion, \( f \approx 0.5 \) since \( Z = 4 \).

### 3.8.3 Impurity diffusion

When foreign impurity atoms are substitutionally incorporated in a host material as solutes in a solid solution (e.g. cadmium atoms occupying copper vacancies in Cu(In,Ga)Se\(_2\)), the Gibbs free energy of vacancy formation of solvent atoms around the impurity atom may be altered due to interaction:

\[
\Delta G^F_V \neq \Delta G^F_{V-I}
\]  

(3-113)

where \( \Delta G^F_V \) represents the Gibbs free energy of vacancy formation of the lattice sites (e.g. Cu sites in CIGS) around a host material atom (e.g. Cu site in CIGS). \( \Delta G^F_{V-I} \) is the Gibbs free energy of vacancy formation of the lattice sites (e.g. Cu sites in CIGS) surrounding the substitutional impurity atom (e.g. Cd\(_{Cu}\) in CIGS). To determine the effect of an altered vacancy formation energy on diffusion of the impurity atoms, an interaction term is introduced [59]:

\[
\Delta G^B_V = \Delta G^F_V - \Delta G^F_{V-I}.
\]  

(3-114)

\( \Delta G^B_V \) denotes the binding energy of the vacancy-impurity interaction. Eq. (3-115)’s convention dictates an increase in vacancies surrounding an impurity atom when the binding energy is positive. Assuming a dilute concentration of the impurity atoms, the vacancy population in the material with the impurity now is

\[
C^eq_{V-I} = \exp \left( -\frac{\Delta G^F_V}{k_B T} \right) \exp \left( \frac{\Delta G^B_V}{k_B T} \right).
\]  

(3-115)
Alternatively, the altered vacancy population can be written with the enthalpy and entropy terms:

\[ C_{V}^{eq} = \exp \left( - \frac{\Delta H_{V}^{F} - \Delta H_{B}^{F}}{k_{B}T} \right) \exp \left( \frac{\Delta S_{V}^{F} - \Delta S_{B}^{F}}{k_{B}T} \right). \] (3-116)

Eqs. (3-115) and (3-116) are sometimes written as

\[ p = C_{V}^{eq} \exp \left( \frac{\Delta G_{V}^{F}}{k_{B}T} \right). \] (3-117)

where \( p \) – called the Lomer expression – represents the probability of finding a vacancy at a lattice site that neighbors an incorporated impurity atom [59].

### 3.8.4 CIGS diffusion equations

With the considerations in the preceding sections, final forms of diffusion equations for various species in CIGS can now be derived.

The copper tracer self-diffusion coefficient via the copper vacancy diffusion mechanism is written as

\[ D_{xCu} = \frac{1}{4} f_{x} \Gamma_{Cu} a^{2}, \quad D_{yCu} = \frac{1}{4} f_{y} \Gamma_{Cu} a^{2}, \quad D_{zCu} = \frac{1}{2} f_{z} \Gamma_{Cu} a^{2}. \] (3-118)

where

\[ \Gamma_{Cu} = v_{Cu} C_{eq}^{Cu}. \] (3-119)

The intrinsic copper vacancy diffusion coefficient can be expressed as

\[ D_{xV_{Cu}} = \frac{1}{4} \Gamma_{V_{Cu}} a^{2}, \quad D_{yV_{Cu}} = \frac{1}{4} \Gamma_{V_{Cu}} a^{2}, \quad D_{zV_{Cu}} = \frac{1}{2} \Gamma_{V_{Cu}} a^{2}. \] (3-120)

where

\[ \Gamma_{V_{Cu}} = v_{Cu} C_{eq}^{Cu} = v_{Cu}. \] (3-121)
\( C_{\text{Cu}}^{eq} \) – the probability of having a neighboring Cu site in the Cu sublattice – equals to unity. The copper vacancy is less constrained to diffuse through the crystal than the tracer copper atom. The latter species depends on an available neighboring vacancy to diffuse. Correlation factor \( f \) equals to unity and thus absent from the equation because the diffusion of the copper vacancy is completely uncorrelated (purely random walk).

The equation for the cadmium tracer diffusion coefficient via the copper vacancy diffusion mechanism is a modified version of Eq. (3-118):

\[
D_{x \text{CdCu}} = \frac{1}{4} f_x \Gamma_{\text{CdCu}} a^2, \quad D_{y \text{CdCu}} = \frac{1}{4} f_y \Gamma_{\text{CdCu}} a^2, \quad D_{z \text{CdCu}} = \frac{1}{2} f_z \Gamma_{\text{CdCu}} a^2, \tag{3-122}
\]

where

\[
\Gamma_{\text{CdCu}} = \nu_{\text{CdCu}} C_{\text{Cu}}^{eq} \exp \left( \frac{\Delta G_{\text{Cu}}^{\text{v}}}{kT} \right). \tag{3-123}
\]

The \( \text{CdCu} \) subscript denotes the diffusion of cadmium via the copper vacancy diffusion mechanism. Copper vacancies may not be the only defect type that mediates cadmium diffusion. Direct cadmium interstitial transport is also considered. The cadmium interstitial diffusion coefficient equation can be written as

\[
D_{\text{Cd}i} = g \Gamma_{\text{Cd}i} a^2 \tag{3-124}
\]

where

\[
\Gamma_{\text{Cd}i} = \nu_{\text{Cd}i}. \tag{3-125}
\]

Once again, the correlation factor vanishes due the uncorrelated diffusion of direct interstitials. In a CIGS solution with a dilute amount of interstitials, the probability of a neighboring interstitial site being empty for the cadmium interstitial to jump to approaches unity. \( g \) is a parameter that depends on the geometry of the interstitial diffusion. The diffusion expressions developed in this section are revisited in Chapter 7 to model impurity diffusion in vacancy-rich CIGS.
Chapter 4

Investigating cadmium diffusion via copper depletion of Cu(In,Ga)Se$_2$ materials

4.1 Electronic and ionic conductivity of Cu(In,Ga)Se$_2$ materials

Literature works show that copper has remarkably high diffusion coefficients in CIGS [65], [88], [101], [103]. This is in part due to the high concentration of copper vacancies. In solar-grade CIGS materials, copper vacancies have concentrations on the order of several atomic percent, significantly higher than metals and traditional semiconductors like silicon at a given temperature. The effect of vacancy concentration on the diffusion coefficient – assuming vacancy diffusion – is apparent in Eqs. (3-118) and (3-119). The copper self-diffusion coefficient via the vacancy mechanism $D_{\text{Cu}}$ is proportional to the copper vacancy concentration $C_{\text{Cu}}^{eq}$. The contribution of $C_{\text{Cu}}^{eq}$ is significant in CIGS compared to the counterpart in silicon (i.e. $C_{\text{Si}}^{eq}$) [59].

The high copper self-diffusion coefficients have also been explained in the terms of low copper self-interstitial energies. In a related study, Pohl et al. suggest that copper self-interstitial formation (migration) energy may be as low as 0.17 eV (0.22 eV) [88]. In a separate work, Oikkonen et al. calculated the formation (migration) energy of the copper self-interstitial to be as low as 0.30 eV (0.20 eV) [104]. The variation in the formation energy is due to the varying chemical potentials as discussed in section 3.7.3 as well as the choice of the first-principles calculation method. The copper self-interstitial formation increases as the copper chemical potential is lowered from the copper-rich condition towards the copper-poor condition. In the copper-poor condition, the copper self-interstitial formation energy can be as high as 1.09 eV [104].
The relatively low formation and migration energies of copper vacancies and self-interstitials lead to an interesting property for CuInSe₂-related materials: solid-solution ionic conductivity occurring at the room temperature. Ionic conductivity – rather than electronic conductivity – is traditionally seen in alkali and silver halides (i.e. NaCl, LiF, and AgBr) at high temperatures [59]. Such halides are ionic compounds in which the cations (+) and anions (-) are held together by ionic bonding. Because of this ionic bonding, electrons are not available for conductivity and only the movement (diffusion) of the ions themselves contributes to the conductivity of ionic compounds. At room temperature, the diffusion of ions in alkali halides is negligible but significant at temperatures close to their melting points. Traditional semiconductors like silicon and germanium exhibit covalent bonding, so no ionic conductivity occurs. On the other hand, IB-III-VI₂ – referring to the columns in the periodic table such as CuInSe₂ and AgInSe₂ – semiconductors have been observed to conduct IB ions at room temperature fairly easily [103], [105]. For this reason, CuInSe₂-related semiconductor materials have sometimes been called semionics where they exhibit electronic and ionic conductivity simultaneously.

One of the original objectives of the dissertation research into cadmium diffusion mechanisms in Cu(In,Ga)Se₂ included controlling the copper content of post-deposition CIGS thin films. Because cadmium diffusion in Cu(In,Ga)Se₂ relies on native point defects, it was thought that decreasing copper content would provide insights into cadmium diffusion mechanisms. As-deposited CIGS thin films would provide the baseline cadmium diffusion profiles, and copper-modified CIGS thin films would give altered cadmium diffusion profiles. The primary means of decreasing copper content of CIGS would occur via applying a negative electrical bias to the point electrode in contact with the surface of the CIGS thin film.

4.2 Experimental evidence of copper depletion of Cu(In,Ga)Se₂ thin films

The aforementioned copper depletion of Cu(In,Ga)Se₂ has been experimentally observed by precipitating – also known as plating out or solid-state anodization – copper onto the CIGS surface via electrical bias [101], [103], [105]–[107] at low temperatures and applied bias. Dagan et al. shows solid copper precipitation on the surface of millimeter-thick CuInSe₂ thin film, next to a platinum point electrode after applying -5 V at 50 °C for 30 min via a scanning electron
microscopy (SEM) image. Energy dispersive x-ray spectroscopy (EDS) and wavelength dispersive x-ray spectroscopy (WDS) were used for quantification [103].

<table>
<thead>
<tr>
<th></th>
<th>Cu (at.%)</th>
<th>In (at.%)</th>
<th>Se (at.%)</th>
<th>Cu/In Ratio</th>
<th>Cu/Se Ratio</th>
<th>In/Se Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Before</strong></td>
<td>25.1</td>
<td>24.1</td>
<td>50.8</td>
<td>1.04</td>
<td>0.49</td>
<td>0.47</td>
</tr>
<tr>
<td><strong>After</strong></td>
<td>23.9</td>
<td>24.4</td>
<td>51.7</td>
<td>0.98</td>
<td>0.46</td>
<td>0.47</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td><strong>-0.06</strong></td>
<td><strong>-0.03</strong></td>
<td><strong>0.00</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4-1 – CuInSe₂ stoichiometry before and after Dagan’s depletion experiment in [103].

Table 4-1 shows the change in the bulk composition of Dagan’s CuInSe₂ material due to the application of negative electrical bias [103]. The Cu/Se and In/Se ratios calculated for the present thesis work demonstrate that CuInSe₂ is preferentially depleted of copper while leaving indium and selenium contents unchanged.

<table>
<thead>
<tr>
<th></th>
<th>Cu (at.%)</th>
<th>In (at.%)</th>
<th>Ga (at.%)</th>
<th>Se (at.%)</th>
<th>Cu/(In+Ga) Ratio</th>
<th>Cu/Se Ratio</th>
<th>(In+Ga)/Se Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24.1</td>
<td>18.5</td>
<td>4.5</td>
<td>53.0</td>
<td>1.05</td>
<td>0.45</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Table 4-2 – Atomic composition of the CIGS sample for the depletion experiment in present work.

Dagan’s results are replicated on two-micrometer Cu(In,Ga)Se₂ thin films – of the composition presented in Table 4-2 – in the present dissertation work versus the millimeter-thick CuInSe₂ samples in the former case. Because of the lack of access to advanced microprobe equipment similar to Dagan’s experimental set-up, a small piece of indium – tens of micrometers in diameter – was attached to the tip of a conductive sewing needle. The apparatus containing the indium piece and the needle was connected to a constant-voltage power supply using an alligator clip and an electrical wire. The electrical wire was suspended – to minimize force and subsequently the contact area of the indium piece on the CIGS surface – by taping parts of it to a makeshift structure designed for the purpose. The electronic circuit was completed via a contact with the metallic molybdenum layer. A schematic of this set-up is shown in Figure 4.1.

A potential difference of -1 V (with respect to the molybdenum layer) was applied to the indium tip for 45 min while the CIGS sample was on a 100⁰ C hot plate. The effect is the attraction of Cu⁺ ions to the negatively biased tip according to the CIGS form of the reductive decomposition equation suggested by Chernyak et al. [105]:
\[ \text{Cu}_{\text{CIGS}}^+ + e^- \rightarrow \text{Cu}^0 \]  

Figure 4.1 – Copper depletion experimental set-up.

Figure 4.2 – Current-time plot of copper depletion experiment with an applied voltage of -1 V at the point electrode at the CIGS surface on a 100°C hot plate.

The electron necessary to precipitate copper onto the CIGS surface is supplied by the negatively biased indium point electrode. Chernyak et al. argue that copper precipitation occurs because copper ions in bulk CuInSe2 are ejected from their original lattice sites and migrate under the strong electric field generated by the point electrode, on the order of \(10^5-10^6\) V/cm. Copper precipitation would not occur at the larger back contact (i.e. the Mo back contact) as the voltage drop is significantly smaller for a planar contact [105].
The time evolution of the current is shown in Figure 4.2. The resistance is also displayed. The current increases rapidly in the first few minutes, then the increase slows albeit at a steady pace. After about 40 min, the current appears to have peaked. The power supply was immediately shut down to avoid damaging the sample as had previously occurred with other samples. The continuous increase in current has been explained in terms of the increase in effective contact area of the point electrode as copper is plated out of CIGS and form physical contact with the point electrode [103]. Copper precipitation on the CIGS surface is shown in Figure 4.3 as a 150 µm × 70 µm oval outlined by smaller-sized clusters of solid copper.

Figure 4.4 displays the EDS map of the oval in Figure 4.3 where the Cu Kα signal was collected. The EDS map verifies that the oval is made of copper clusters. Figure 4.5 also shows an overlay of the Cu, In, Ga, and Se EDS signals of a single copper cluster that had approximate dimensions of 10 µm × 5 µm × 5 µm. Gallium and selenium appear to be absent from the copper cluster. The cluster also contains indium. However, that should not be interpreted as indium being plated out of CIGS. Recall that as the copper precipitation proceeds, the plated-out copper attaches to the indium point electrode contact, increasing the effective contact area of the electrode. Because 1) the registered direct current was over several hundred microamperes, 2) the sample was on a 100 °C hot plate, and 3) indium’s melting point is 156.6 °C, sufficient joule heating may have occurred in the indium point electrode, allowing some small areas on the indium point electrode to fuse with the precipitated copper. When the point electrode was withdrawn from the CIGS surface, the fused copper/indium contacts were broken, leaving behind indium residue. The copper and indium EDS maps in Figure 4.5 are consistent with this argument as the indium signal appears to be coming mostly from the top of the precipitated copper cluster.

EDS quantification of areas inside the oval as well as areas outside the oval showed no significant difference in copper content due to copper precipitation. This suggests that the precipitated copper may have been extracted from areas far away from the point electrode, with a depletion radius of several hundred micrometers.
Figure 4.3 – Precipitation of elemental copper on the CIGS due to negatively applied bias point electrode on the CIGS surface.

Figure 4.4 – Energy dispersive spectroscopy (EDS) image of the precipitated copper on the CIGS surface due to negatively applied bias point electrode on the CIGS surface.
4.3 Failure of copper depletion experiments

While there have been isolated cases of successfully copper-depleted Cu(In,Ga)Se$_2$ thin films as discussed in section 4.2, copper depletion was not consistent nor sufficient in the change of the copper content in CIGS thin films. Out of multiple types of CIGS samples, only those coming from the 10 cm $\times$ 10 cm pallet (with the composition listed in Table 4-2) showed copper precipitation on the surface after applied electrical bias. The amount of precipitated copper was minimal according to bulk analysis of the CIGS thin film surrounding the area of copper precipitation using EDS.

Geula Dagan’s PhD thesis shows that the minimum voltage to plate out copper onto the CuInSe$_2$ surface varies between -0.3 V and < -8.0 V [108]. Dagan suggests that the required “decomposition” voltage depends on the bulk and surface quality of the CuInSe$_2$ materials. CuInSe$_2$ materials with better crystalline quality require higher voltages for copper precipitation. The nearly stoichiometric CuInSe$_2$ sample A (25.1 at. % Cu, 25.0 at. % In, and 49.9 at. % Se) in Dagan’s thesis had many voids and scratches. Subsequently, copper began to precipitate at -0.6 V at room temperature.

Nearly stoichiometric CIGS thin films (24.9 at. % Cu, 24.8 at. % In+Ga, and 50.3 at. % Se) of thickness of 6 µm were also investigated in the present thesis work for copper depletion experiments. Applied electrical bias as low as -10 V did not result in copper precipitation even when a 100 $^\circ$C hot plate was used. A cross sectional analysis was conducted with focused ion beam (FIB) and 45$^\circ$-tilt SEM imaging (Figure 4.6). Figure 4.6 shows that the fabricated stoichiometric CIGS thin films had many large voids in addition to a rough surface (root mean square $R_{RMS}$ of $\sim$ 200-
500 nm). The rough surface and the presence of voids may explain the inability to precipitate copper on the CIGS surface. Rough surface may mean a higher contact resistance due to the reduced contact area between the point electrode and the CIGS thin film. The effect is a decreased intrinsic voltage drop (applied electric field) in the CIGS thin film. Without a sufficiently strong electric field, copper ions are not able to migrate. The internal voids may act as a barrier to copper diffusion, inhibiting the transport of copper ions to the surface. Additionally, the difficulty of generating a sufficient electric field may stem from the indium point electrode’s radius of curvature relative to the film thickness of the CIGS thin film. If the radius of curvature is not sufficiently small, the point electrode may behave like a parallel conductor plate – rather than a point electrode that can generate high electric fields due to its small radius of curvature – to the CIGS thin film of thickness of 2 µm. Consequently, the behavior of copper depletion with micrometer-thick CIGS films may be significantly different from that of millimeter-thick CIS films as seen with Dagan’s work.

Figure 4.6 – Focused ion beam (FIB) milled cross-section image of a CIGS thin film to investigate the challenges of copper depletion in thin-film CIGS. The image was taken with scanning electron microscopy (SEM) at 45⁰ angle with respect to the electron beam and the plane forming the top surface of the CIGS thin film. Note the voids in the cross section.
Chapter 5

Cadmium diffusion profiles in thin-film Cu(In,Ga)Se$_2$ materials

5.1 Secondary ion mass spectroscopy (SIMS)

5.1.1 Physical fundamentals

Secondary ion mass spectroscopy (SIMS) is a powerful tool to characterize diffusion in materials [109]. SIMS is the technique of identifying ionized atoms that are ejected from the surface after bombardment with high-energy primary ions. The bombardment process is called sputtering [110]. The term “primary” relates to the “secondary” ions that are created due to bombardment where the former are the incident ions generated from an ion source. SIMS should be viewed as a technique with the combination of sputtering and spectroscopy as sputtering is the only method that dissociates atoms from the host material [111]. As sputtering gradually erodes the surface, a depth profile can be produced from the resulting crater where the signal of a respective secondary-ion species are recorded versus depth. SIMS then becomes an attractive candidate for diffusion studies [59], [109].

A schematic of the sputtering process is shown in Figure 5.1. The process begins with irradiating the target surface with primary ion beam energies in the range of 250 eV and 30 keV [111]. Typical primary ions include Cs$^+$, O$_2^+$, and Ar$^+$ [111]. As a primary ion enters the surface, it collides with a series of host-material atoms in its trajectory (dashed line in Figure 5.1). Each collision between the primary ion and the host-material atom generates a collision cascade – dubbed the moving sea of particles – where energy is transferred to the host-material atom such that the energetic host-material atom collides with more atoms in varying directions [112]. The collision cascades lead to atomic intermixing as the host-material atoms are knocked out of their original atomic positions and mixed with other atoms. The ejection of an atom from its position can only occur when the sum of phonon and collisional energies are greater than a threshold value [59].
The irradiated surface then becomes amorphized and implanted with primary ions. The thickness of the amorphized layer is on the order of the vertical distance from the surface to the implanted primary ion at rest (Figure 5.1) which is typically called the implant depth $I_D$ [112]. Range is the distance the primary ion travels once it enters the target surface before it comes to a stop. Because range is geometrically defined with respect to the longitudinal axis of the primary ion beam, it is independent of the angle of incidence of the primary beam with respect to the surface normal. Denoting the longitudinal range as $R_L$, the implant depth $I_D$ is written to a first approximation [111], [113]:

$$I_D (\text{nm}) = R_L \cos(\theta)$$

(5-1)

where

$$R_L (\text{nm}) \approx E (\text{keV}).$$

(5-2)

$\theta$ is the angle of incidence with respect to the surface normal and $E$ is the energy of the primary ion (in keV). Both $I_D$ and $R_L$ are written in terms of nanometers (nm). With a 1 keV Cs$^+$ beam (typical value in the present work) at 45° incidence, the implant depth $I_D$ is approximately 0.7 nm. A more empirical form of Eq. (5-2) exists as $R_L (\text{nm}) = CE^n (\text{keV})$ for real primary ions and target materials where constants $C$ and $n$ are extracted from experimental data and assume values on the order of unity [113]. $I_D$ is a key parameter that indicates the approximate depth resolution.
for a given SIMS analysis. Increasing $\theta$ and decreasing $E$ reduces the implant depth and improves the depth resolution but often at the expense of signal.

Some of the host-material atoms absorb sufficient energy to eject from the material. The thickness of the sputtered layer is noted in Figure 5.1. Not all ejected atoms are ionized; some will be ejected as neutral ions and others as negative and positive ions. The liberated secondary ions are collected by applying an electrical bias on the order of several kilovolts (kV) between the sample and the extraction electrode located above the sample. The collected secondary ions ejected from the surfaces travel to the mass spectrometer via a series of electrostatic and magnetic lenses. Mass spectrometers common to SIMS instruments include the quadrupole mass spectrometer, the magnetic sector mass spectrometer, and the time-of-flight (TOF) mass spectrometer [111].

### 5.1.2 SIMS equations and quantification

The following equations are inspired from D.S. McPhail’s review paper on the SIMS analytical technique [111]. The number $N$ of impurity atoms of type $A$ that are ejected and ionized with a positive charge is written as

$$N_{A^+} = P_{A^+} \rho_A V$$  \hspace{1cm} (5-3)

where $V = a z$, the volume of the sputtered section with area $a$ and depth $z$. $P_{A^+}$ is the ionization probability for impurity species $A^+$. No mass spectrometer is perfect and will induce losses in the secondary ions optics and the detector. Transmission coefficient $T$ accounts for such losses; denoting $N'_{A^+}$ as the ions that are actually detected:

$$N'_{A^+} = T_{A^+} P_{A^+} \rho_A V.$$  \hspace{1cm} (5-4)

In the SIMS community, the parameter useful ion yield $Y_{A^+}$ is used in the place of the product $T_{A^+} P_{A^+}$ due to difficulty in independently measuring the parameters inside the product:

$$N'_{A^+} = Y_{A^+} \rho_A V.$$  \hspace{1cm} (5-5)
$Y_{A^+}$ has a simple physical interpretation: the ratio of the number of detected $A^+$ ions to the total number of sputtered atoms $A$. Sputter yield – the total number of host material atoms removed per incident primary ion – is typically between 0.1 and 10 atoms per primary ion and can be written as

$$S = \frac{\rho_H V}{(\frac{I_p}{q})t}$$  \hspace{1cm} (5-6)

with host material density $\rho_H$, primary ion beam current $I_p$, elapsed time $t$, and elementary charge $q$. SIMS quantification involves converting the detected secondary ion count to atomic concentration (e.g. cm$^{-3}$). By rearranging Eq. (5-5), the atomic concentration for an impurity in a matrix material can be written as

$$\rho_A = \frac{N_{A^+}^V}{Y_{A^+}V}.$$  \hspace{1cm} (5-7)

A practical perspective – especially in terms of quantification – begins with defining the rate of sputtering $r_s$ as the derivative of depth $z$ with respect to time $t$:

$$r_s = \frac{dz}{dt}.$$  \hspace{1cm} (5-8)

Rewriting Eq. (5-6) in terms of the analytical area $a$ and depth $z$ ($V = az$) and take the derivative of depth $z$ with respect to time $t$, the following expression is obtained:

$$\frac{dz}{dt} = \frac{SI_p}{qa\rho_H}$$  \hspace{1cm} (5-9)

which is equivalent to Eq. (5-8). If Eq. (5-5) is also rewritten in terms of $a$ and $z$ and $z$ is redefined as the sputtering rate $r_s$, the new $N_{A^+}^r$ expression is $N_{A^+}^{r_\text{s}}$ (the number of $A^+$ ions detected per unit time). The impurity concentration equation finally becomes

$$\rho_A = \frac{N_{A^+}^{r_\text{s}}}{Y_{A^+}ar_s}.$$  \hspace{1cm} (5-10)

A significant obstacle to the ease of quantification with SIMS is the ionization probability $P_{A^+}$ (enclosed in the useful ion yield $Y_{A^+}$ parameter above) [111]. $P_{A^+}$ is a function of many things: the element of interest $A$, the host matrix $H$,
the primary ion beam type (e.g. cesium), the primary ion beam energy $E$, and the angle of incidence with respect to the surface normal $\theta$. It is more convenient to utilize the relative sensitivity factor (RSF):

$$\frac{I_R}{C_R} = RSF_E \frac{I_E}{C_E}$$

(5-11)

$I$ is secondary ion intensity where $C$ is the atomic concentration (e.g. cm$^{-3}$). The subscripts $E$ and $R$ refer to the element of interest for quantification and the reference element respectively. A major (or the only) matrix element is chosen as the reference element. The relative sensitivity factor for the element of interest $RSF_E$ is different for different host matrices for the reasons discussed above. For a given host matrix, the relative sensitivity factor can be compacted into

$$RSF = C_R RSF_E,$$

(5-12)

simplifying the calculation for the concentration of the trace element of interest:

$$C_E = RSF \frac{I_E}{I_M}.$$

(5-13)

### 5.1.3 Static versus dynamic secondary ion mass spectroscopy

It is useful to distinguish between static and dynamic SIMS, the two main modes in SIMS [111], [114]. The static condition – by definition – occurs when a low primary ion dose is used to probe the specimen surface on the order of 1 nA cm$^{-2}$ (or equivalently $6.242 \times 10^9$ ion cm$^{-2}$s$^{-1}$ in terms of the number of singly charged primary ions) or less. Probing a silicon specimen means the surface of the silicon material has approximately $10^{15}$ cm$^{-2}$ silicon atoms. With an one-second pulse of 1 nA probing an area of 1 mm$^2$, a dose of $6.242 \times 10^{11}$ cm$^{-2}$ is obtained, giving a probability of 0.06% for a primary ion hitting the same point on the silicon surface more than once. Because the static limit is defined as $~10^{12}$ cm$^{-2}$, the surface can only be probed for $\sim 1.6$ seconds before the limit is reached. The obtained spectrometric information due to such a low dose is then characteristic of the surface chemistry. Calculations suggest that each primary ion strike excites an area of 10 nm$^2$ by transferring energy to atoms and molecules from this area, causing emission of such species from the surface. Relatively low primary ion beam energies between 0.1 and 5 keV are typically used in the static SIMS mode. With such low beam energies, the static SIMS technique allows for
chemical analysis of the uppermost atomic/molecular layers of the material, enabling applications in many fields of study from pharmaceuticals to biomaterials to semiconductors to metallurgy.

Despite static SIMS’ ability of the analysis of surfaces and the associated chemistry, the technique becomes impractical for diffusion studies which often require depth-profiling, the process of measuring the composition of the material as a function of depth. The sputtering rate of a fraction of a monolayer per hour typically obtained with static SIMS is problematic for thin films of several micrometers in thickness like Cu(In,Ga)Se₂, so the primary ion beam current is raised to 100 nA or higher. The entire thin film of several micrometers in thickness can be sputtered in less than an hour using a relatively small sputtering area (~ 0.25 mm²) with a primary ion beam current of 100 nA (or ~ 10¹⁵ ions cm⁻² s⁻¹). The dose of primary ions in the surface becomes ~ 10¹⁶ (10¹⁷) ions cm⁻² after 10 (100) seconds [111], [114].

A steady state of sputtering rate and surface chemistry is created after a threshold dose level in the surface has been reached where the dose no longer changes significantly (typically > 10¹⁶ cm⁻²) [111], [114]. Accurate quantification of elements in the depth can then be possible. However, up to this point, information on the original surface chemical environment is entirely lost. Dose is the differentiating factor between static and dynamic SIMS: in static SIMS, low dose is used to minimize the destruction of the surface to maximize obtainable information on the chemical environment of the surface while dynamic SIMS requires a “dynamic equilibrium” during sputtering to maximize quantification of the elements in the depth. The dynamic equilibrium in dynamic SIMS occurs under high dose conditions. For dose regimes between the static and dynamic limits, quantification becomes practically impossible due to the continuously changing surface chemistry, sputtering rate, and ion yields. The part of the depth profile where the dose is increasing to its threshold value before steady state is typically called the pre-equilibrium region.

5.1.4 Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) depth profiling

Some SIMS instruments can operate in both the static and dynamic modes. The IONTOF TOF-SIMS⁵ is a versatile high-end SIMS instrument capable of both modes. Compared to conventional dynamic SIMS instruments where primary-ion sputtering and secondary-ion analysis are done concurrently, the dynamic mode of IONTOF TOF-SIMS⁵ utilizes a dual-beam setup: Cs⁺ and Bi⁺ ion beams as schematically shown in Figure 5.2. The sample is alternately
sputtered with Cs$^+$ primary ions and analyzed with Bi$^+$ analytical ions. The purpose of Bi$^+$ analytical ions is to liberate ion species in the Cs$^+$-implanted/sputtered surface to be detected by the time-of-flight detector. The sample surface is irradiated with Bi$^+$ analytical ions only for several nanoseconds to minimize sputtering due to Bi$^+$ ions. The detected species including single M$^+$ ions representing the matrix species and CsM$^+$ compound ions. The main advantage of the time-of-flight detector is that in a given analytical cycle, the entire mass spectrum can be recorded – for example from hydrogen ions to heavy cesium-based compound ions. The time-of-flight detector operates on the principle that all liberated and collected ion species of the same charge begin with the same kinetic energy at the bottom of the long time-of-flight column (Figure 5.2). Lighter ions of the same charge reach the detector before heavier ions of the same charge due to their different masses yet same kinetic energy that dictate their speed. However, ions with different charges have different potential energies in an electric field ($E = qV$ where $E$ is the potential energy of an ion with charge $q$ traveling under electric potential difference $V$), so they have different kinetic energies. The time-of-flight detector is especially useful for monitoring all species of the matrix of the thin film at the same depth.

![Diagram of the dual-beam time-of-flight secondary ion mass spectroscopy (TOF-SIMS) system.](image)

Dynamic SIMS does not have this advantage of all ion species being detected simultaneously at the same depth into the sample; analyzing one (quadrupole mass spectrometer) or several ion species (magnetic sector mass spectrometer) at a given time in dynamic SIMS means all other species are rejected. The requirement of alternating pulses of primary
and analytical ions in the case of the time-of-flight detector is a minor drawback and results in a slower sputtering rate compared to the dynamic SIMS counterpart.

The IONTOF TOF-SIMS is typically equipped with Cs⁺ and O₂⁺ primary ion sources that can bombard the sample surface with beam energies up to 10 keV and can have beam current on the order of 100 nA. The Bi⁺ analytical ions are accelerated to 25 keV with 20 nA of current. The analytical area the Bi⁺ ion beam scans – the area from which the secondary ions are collected and quantified – is significantly smaller than the sputtering area in TOF-SIMS. The TOF-SIMS experiments in the present work typically have a Cs⁺ sputtering area of 1 mm × 1 mm and a Bi⁺ analysis area of 200 µm × 200 µm. The Bi⁺ analysis area is divided into a two-dimensional square array of pixels. The pixel size ranges from 1 × 1 to 128 × 128 to 2048 × 2048. During the Bi⁺ analysis portion of the TOF-SIMS depth-profiling, each pixel can be set to be shot with the analytical gun more than once to improve counting statistics. When the pixel is shot with Bi⁺ analytical ions, the liberated secondary ions are extracted into the time-of-flight column.

![Image](Figure 5.3 – Two analytical-sputtering modes of time-of-flight secondary ion mass spectroscopy (TOF-SIMS): interlaced and non-interlaced modes.)

The two main modes of alternating primary and analytical ion bombardment of the surface in TOF-SIMS are illustrated in Figure 5.3 with an example of two pixels for the sake of illustration. The interlaced mode refers to the case where sputtering begins while the secondary ions travel up the time-of-flight column to the detector. However, sputtering cannot begin until the last pixel of the square array is reached, represented by the second analytical gun bar from the left in the interlaced mode image. The travel time for the secondary ions from the bottom to the top of the column is on the order of tens of microseconds. Thus, the sputtering gun is only turned on for tens of microseconds. The sputtering is paused prior to the next raster scan of the newly sputtered layer as represented by the end of the first sputtering cycle in the interlaced mode image.
In the non-interlaced mode, the sputtering part of the TOF-SIMS depth-profiling does not overlap with the time-of-flight portion of the depth-profiling as shown in the non-interlaced mode image in Figure 5.3. The advantage with the non-interlaced mode is an increased control over the sputtering time and other adjustable instrumental parameters including the amount of time the surface is flooded with electrons to control charging which can be problematic with insulating materials. The choice of either mode depends on experimental parameters especially on pixel array sizes (e.g. a square array of 1024 × 1024 pixels takes 64 times longer to scan compared to 128 × 128 pixels).

5.1.5 Challenges of SIMS studies of Cu(In,Ga)Se₂

Figure 5.4 – Cross-section scanning electron microscopy (SEM) image of unpolished CIGS sample (~ 2 µm in CIGS layer thickness). Note the rough surface.

Figure 5.5 - Scanning electron microscopy (SEM) image of unpolished CIGS sample, taken at an angle of 45⁰ versus the surface, rendering both the CIGS cross-section and the surface visible. Note the rough surface.

Polycrystalline Cu(In,Ga)Se₂ thin films are a challenging material from the analytical perspective due to the rough as-deposited surface as shown in Figure 5.4 and Figure 5.5. A common parameter quantifying the surface roughness is the root-mean-square roughness $R_{RMS}$ which is given as
\[ R_{RMS} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} z_i^2} \]  

(5-14)

where \( n \) is the number of measurements and \( z \) is the vertical distance from an arbitrarily defined centerline that travels through the surface valleys and peaks to the surface height for the \( i \)-th measurement. \( R_{RMS} \approx 150\text{-}200 \text{ nm} \) for typical as-deposited CIGS thin film of 2 \( \mu \text{m} \) in thickness. For the experiments discussed in section 5.2, thinner CIGS thin films were deposited – 700 nm in thickness – which results in smaller \( R_{RMS} \) values of \( \sim 20 \text{ nm} \). Rough surfaces lead to a loss in depth resolution, the ability to accurately locate the concentration measurement of a material species in the depth. A significant amount of effort was put in mechanically polishing the CIGS surface using an alumina slurry. The procedure is elaborated in section 5.3.2. Here, it suffices to show the scanning electron microscopy (SEM) cross-section and surface images of polished CIGS samples (Figs. 5.6 – 5.8).

Figure 5.6 - Cross-section scanning electron microscopy (SEM) image of polished CIGS sample. Note the smooth surface due to polishing with alumina slurry.

Figure 5.7 - Cross-section scanning electron microscopy (SEM) image of polished CIGS sample. Note the smooth surface due to polishing with alumina slurry.
Figure 5.8 – Top-down scanning electron microscopy (SEM) image of polished CIGS sample after polishing with alumina slurry. The image was taken with 1 keV incident electrons and the in-lens detector. Note the visible grain structures with different orientations on the smooth surface as a consequence of CIGS deposition process. Also note the nanoscale-sized surface scratches from the erosion of polishing particles.

Figure 5.9 – Mechanical profilometry of polished CIGS surface. The CIGS surface was scanned with a profilometry tip radius of 12.5 µm.
Figure 5.9 contains mechanical profilometry results of the polished surface. The results reveal that the surface is extremely smooth with a $R_{RMS}$ value of ~2.6 nm across a surface distance of 50 µm.

Section 5.1.3 introduces the pre-equilibrium regime of the SIMS analysis – between the static and dynamic limits – where continuously changing surface chemistry, sputtering rate, and ion yields distort the true depth profile as shown for a polished Cu(In,Ga)Se$_2$ sample in Figure 5.10. Steady state is not reached until approximately 70 nm below the surface where the Cs$_2^+$ ion cluster counts begin to stabilize. CIGS thin films are typically deposited with a homogenous composition with respect to the depth for copper and selenium except but not for gallium and indium as gallium (indium) increases (decreases) in concentration versus depth (section 2.2.2). Figure 5.10 however shows varying secondary ion intensities of CsCu$^+$, CsIn$^+$, CsGa$^+$, and CsSe$^+$ in the pre-equilibrium region. The variance is likely artificial – due to the mostly uniform composition during deposition – and characteristic of the evolving pre-equilibrium region as the dose of primary ions reaches the threshold level in the surface. Accurate quantification of cadmium – especially for Figure 5.10’s associated cadmium diffusion profiles in section 5.3.4 – in the region up to ~70 nm below the surface is thus difficult and can only offer semi-quantitative information at the most.

Figure 5.10 – TOF-SIMS depth profile of CIGS thin film. Note the pre-equilibrium region up to ~60 nm in the depth.
5.1.6 Depth resolution

Figure 5.11 – Illustration of two depth resolution parameters: the decay length \( \lambda_d \) and the decay slope \( A_d \).

Depth resolution is the ability to determine the location of a concentration measurement in the depth as a result of ion beam sputter as well as the ability to discern between two features at different depths [114]. A thorough discussion of depth resolution involves utilizing advanced statistics concepts, thus it suffices to discuss two common parameters used for depth resolution in the SIMS community: the decay length \( \lambda_d \) and the decay slope \( A_d \) (Figure 5.11). Both parameters are used in the idealized case of a deposited monolayer of impurity on a perfectly flat thin film surface prior to sputtering. The monolayer can then be modeled as a delta function that exponentially decays as the impurity atoms become mixed and knocked into the host matrix over the course of sputtering as discussed in section 5.1.1. The decay length \( \lambda_d \) is defined in terms of the impurity concentration \( C \) at depth \( x \) where \( A \) is a constant:

\[
C(x) = A \exp \left( -\frac{x}{\lambda_d} \right)
\]  

(5-15)

The physical significance of \( \lambda_d \) becomes apparent when \( x \) is set to equal \( \lambda_d \): at depth \( \lambda_d \), the concentration will have attenuated to 36.8% of its original intensity. The decay slope \( A_d \) is a slightly more conservative depth resolution parameter, defined as the distance that the concentration drops by a factor of ten [114].

As discussed in section 5.2, a Cu(In,Ga)Se\(_2\) thin film of 700 nm thickness was used to study cadmium diffusion in CIGS without polishing. The 700 nm CIGS film was deposited with a cadmium sulfide (CdS) layer using a standard
chemical bath deposition (CBD) procedure where the CIGS thin film was immersed in the bath – containing ammonium hydroxide, cadmium sulfate, and thiourea – for 10 minutes at 60 °C [115]. Figure 5.15 shows a scanning electron microscopy (SEM) cross-section image of the CIGS/CdS stack with both the CIGS and CdS layers visible. The root \( R_{\text{RMS}} \) of the CIGS surface under the CdS layer was estimated from the SEM image by measuring the CIGS film thickness (with respect to the Mo layer) at several points to be \( \sim 25 \) nm.

In the subsequent cadmium diffusion experiments of varying annealing temperatures and durations, the CdS layer in one of the samples was immediately etched off via a 38% hydrochloric acid solution (HCl) without annealing to obtain a baseline cadmium signal in the sample for SIMS and AES analysis. Because CdS is deposited on CIGS at a slightly elevated temperature of 60 °C in a bath for 10 minutes, elevated cadmium diffusion into the near-surface region in the CIGS layer occurs as experimentally observed by several workers [40], [41], [116]. Cojocaru-Mirédin shows that due to CBD at 65 °C for 10 minutes, the majority of indiffused cadmium resides in a layer of \( \sim 2 \) nm in thickness in the CuInSe\(_2\) surface [40], [41].

Figure 5.12 shows the cadmium depth profile of the unpolished, nominally unannealed 700 nm CIGS sample where the CdS layer was etched off prior to SIMS analysis. Concerning the 700 nm CIGS thin film, because 1) the thickness of cadmium-doped CIGS layer in CIGS due to CBD is greater than the thickness of an ideal cadmium monolayer based on its atomic diameter (\( \sim 2 \) nm vs. \( \sim 0.3 \) nm) and 2) the thin layer of indiffused cadmium atoms conforms to the rough topography at the CIGS surface (where \( R_{\text{RMS}} \approx 25 \) nm), the original definition of depth resolution must be amended. The decay slope \( A_d \) is then redefined as an effective depth resolution parameter chiefly controlled by the initial surface roughness rather than by the relatively thick cadmium “monolayer” at the surface. This is because the initial \( R_{\text{RMS}} \) is comparable to the decay slope \( A_d \) measured from the 700 nm CIGS depth profile in Figure 5.12 while the thickness of the section of the CIGS film that is doped with cadmium is significantly smaller).

The drop in cadmium signal intensity by a factor of ten at the depth of \( \approx 17 \) nm is close to the measured \( R_{\text{RMS}} \) of \( \approx 25 \) nm for the CIGS surface. The poor depth resolution is due to the as-deposited surface roughness of the 700 nm CIGS thin film rather than enhanced cadmium indiffusion due to CBD. Thus, for the SIMS analysis of unpolished, CdS-etched 700 nm CIGS specimens in section 5.2 has a depth resolution \( A_d \approx 17 \) nm.
Figure 5.12 – Measured depth resolutions of two different CIGS samples. $A_{d,P}$ ($A_{d,700}$) is the depth resolution parameter for the polished sample (as-deposited 700 nm CIGS thin film).

Figure 5.13 – Sputtered crater of a CIGS thin film. Note the smooth bottom in the analytical area.

As for the polished samples, one polished, unannealed CIGS sample was used for estimating the depth resolution. 2 M aqueous cadmium chloride (CdCl$_2$) was dripped onto the mirror-like CIGS surface using a pipette. Drying was done using an infrared lamp for an hour. For the depth resolution measurement, the CdCl$_2$-dripped CIGS sample was dipped in 38% hydrochloric acid (HCl) to remove the CdCl$_2$ residue. SIMS analysis (Figure 5.12) reveal sufficient
cadmium signal remaining on the surface to be used for depth resolution approximation where $A_d \approx 0.8$ nm. The polishing procedure is elaborated in sections 5.1.5 and 5.3. Polishing led to a significant improvement in surface roughness over the unpolished 700-nm CIGS thin-film. $R_{RMS}$ for the polished samples in the Bi+ analytical area after depth-profiling was measured to be $\sim 2.0$ nm which is smaller than the $R_{RMS}$ measured prior to depth-profiling (Figure 5.9). An overall improvement in depth resolution after sputtering begins is improbable because the sputtering process fundamentally induces ion-beam mixing and knock-on damage over the course of the depth-profiling (section 5.1.1). The depth resolution at the bottom of the sputtering crater at the analytical area is likely to be worse than suggested by $R_{RMS} \approx 2$ nm. However, the sputtering-induced loss in depth resolution appears to be greatly minimized in the polished samples.

5.2 Experimental evidence of multiple diffusion processes in thin-film Cu(In,Ga)Se$_2$

5.2.1 Rationale and sample preparation

Using a relatively thin CIGS material to study cadmium diffusion in CIGS was deemed necessary. A thinner CIGS film led to a smoother as-deposited surface rather than the rougher surface of the standard 2 µm CIGS thin film. Analysis difficulties because of undesirable effects of smoothing CIGS material of the standard thickness via polishing or chemical etching (e.g. embedded polishing particles, surface scratches, uneven film thickness, preferential etching, etc.) are avoided. A typical SIMS depth profile of the 700 nm CIGS sample is shown in Figure 5.14. SEM imaging also revealed very few pinholes in the CIGS surface (Figure 5.15).

700 nm CIGS was deposited on Mo-coated soda lime glass at CNSE’s Solar Energy Development Center (PVME) using a three-stage coevaporation process. Depositions were performed in a R&D-scale thermal evaporation system using resistive boat sources at a minimum $4 \times 10^{-6}$ Torr base pressure. Metals rates were controlled using electron impact emission spectroscopy (EIES). Selenium rate was controlled using a quartz crystal microbalance (QCM). Following deposition, the Ga/(Ga+In) and Cu/(Ga+In) ratios of the samples were measured via inductively coupled plasma atomic emission spectroscopy (ICP) and x-ray fluorescence (XRF) to be 0.27 and 0.90 respectively.
Figure 5.14 – TOF-SIMS depth profile of a 700-nm CIGS sample.

Figure 5.15 – SEM cross-sectional image of a 700-nm CIGS sample. Note the visible molybdenum, CIGS, and CdS layers.

A CdS layer thickness of 50 nm was deposited using a standard chemical bath deposition (CBD) process at 60 °C for 12 minutes. The samples were annealed in a thermocouple-regulated vacuum tube in nitrogen gas. The thinner 700 nm CIGS thin film meant limiting the range of annealing temperatures and durations for the 700 nm CIGS samples compared to a wider range possible with a 2 µm CIGS film.
The 700 nm CIGS samples were annealed in the following experiments: 250 °C for 20 minutes, 275 °C for 20 minutes, and 300 °C for 5 minutes. The 700 nm CIGS samples were immersed in 38% hydrochloric acid for two minutes to remove the CdS layer to avoid the interference of the CdS layer during ion-beam sputtering. An unannealed 700 nm CIGS/CdS sample was also etched with hydrochloric acid to obtain a baseline cadmium signal in SIMS for reference.

5.2.2 Diffusion profile measurement

Secondary ion mass spectroscopy is an ideal choice for diffusion studies due to its excellent ability of detecting trace impurities as elaborated in section 5.1. TOF-SIMS parameters such as sputtering energy and raster size were optimized for optimal signal acquisition of the ionic cluster that represents cadmium, CsCd+. Using Cd+ directly would be difficult as Cd+ has a lower ion yield than CsCd+. The Cs+ sputtering ions were accelerated to 1 keV with a current of 70 nA with a rasterizing area of 1 mm × 1 mm. The Bi+ ions were accelerated to 25 keV at 20 nA, scanning an area of 200 µm × 200 µm (1024 pixels × 1024 pixels) inside the 1 mm × 1 mm sputtering crater. The CsCd+ signal was significantly increased compared to the standard operating parameters (128 pixels × 128 pixels on 50 µm × 50 µm analytical area in 300 µm × 300 µm sputtering area). However, analysis time the background CsCd+ signal level increased as a result. The analysis time increased from ten minutes per profile to several hours per profile. The CsCd+ background level rose from ~10⁰ to ~10² per data point. A mechanical profilometer was used to measure the depth of the sputtered crater, then the measured depth is incorporated into the diffusion profiles.

5.2.3 Results and Discussion

Figure 5.16 shows the cadmium diffusion profiles [117]. All profiles show at least two apparent simultaneous diffusion processes. Only the 275 °C curve (curve (c) in Figure 5.16) exhibits three concurrent diffusion processes. The first two diffusion processes – likely two different lattice diffusion mechanisms – are referred to as first- and second-stage profiles respectively. The third diffusion process is believed to be grain boundary diffusion.

The two stages in each diffusion profile – except for the second stage of the 300 °C profile – were analyzed using the constant diffuser source equation (section 3.4). At the end of the curves (b), (c), and (d) in Figure 5.16, tails with slopes above the background signal level in curve (a) are visible. Grain boundary diffusion is responsible for these
tails, that is, the diffusion of cadmium from grain boundaries into the CIGS grains. Grain boundary diffusion is described by the empirical equation [59]:

\[ C(x, t) = C_0 e^{-Gx^{6/5}}. \]  \hspace{1cm} (5-16)

\( G \) is the absolute value of the fitted slope of the grain boundary tail and contains the grain boundary diffusion coefficient [59].

Figure 5.16 – Cadmium diffusion profiles of the HCl-etched 700-nm CIGS samples. (d) 300 °C, 5 min; (c) 275 °C, 20 min; (b) 250 °C, 20 min; and (a) nominally unannealed (60 °C, 12 min chemical bath deposition). Inset: double-logarithmic representation of the curves. The solid lines represent least-squares fitting using the constant- and limited-source equations.

Because the diffusion profiles contain several diffusion processes, a least squares fitting approach – using Microsoft Excel’s built-in Solver capability – was used: the fitted \( C_F \) curves are simply the superposition of the components within a given diffusion profile, the first lattice diffusion component \( C_1 \), the second lattice diffusion component \( C_2 \), and the grain boundary tail \( C_{GB} \):

\[ C_F(x, t) = C_1(x, t) + C_2(x, t) + C_{GB}(x, t). \]  \hspace{1cm} (5-17)
The 250 °C and 275 °C profiles show that the middle region – 0 nm to 100 nm for the 250 °C curve and 25 nm to 150 nm for the 275 °C curve – are best fitted with the constant diffuser source equation (section 3.4). The 300 °C curve is best fit with the limited source model in the region between ~ 25 nm and the end of the depth profile.

The as-deposited 50 nm CdS layer is sufficiently thick for the constant diffuser source equation, the experiments suggest that the CdS film thickness may not be the only condition that differentiates between constant and limited sources. At lower annealing temperatures and shorter durations, the CdS layer may be considered a constant source but as a limited source at higher temperatures and durations.

Cadmium diffusion into CIGS from the CdS layer may be accompanied by copper outdiffusion from the CIGS layer to the CdS layer [10], [40]. It is possible that cadmium vacancies in the CdS layer absorb copper atoms during anneal, inhibiting cadmium self-diffusion in CdS, reducing further incorporation of cadmium in CIGS and generating a diffusion profile based on the limited-source equation (section 3.4).

The unannealed CsCd+ surface signal is similar to the surface signal of the 250 °C curve. CdS via chemical bath deposition at an elevated temperature is likely the culprit for the non-negligible signal of cadmium at the surface in the unannealed sample. The data-point tail in the unannealed curve – while fitted using the grain boundary diffusion model – reflects the background level of CsCd+ rather than grain boundary diffusion. The divergence seen in the end of the 250 °C profile where the CsCd+ background level is approached supports the argument. Surface roughness is likely responsible for the CSCd+ signal in the corner area of the unannealed curve.

In polycrystalline materials, there are three classified grain boundary diffusion regimes that may occur: types A, B, and C kinetics. The prevailing regime determines the appropriate diffusion model for analysis [59]. Type A happens when the annealing time is sufficiently long or the grain size sufficiently small that the grain boundary and volume diffusion fields overlap each other. Type C kinetics applies with relatively short annealing times and/or the volume diffusion coefficient becomes small such that diffusion is confined to the grain boundaries. Type B kinetics dominates in the intermediate range between types A and C. Type A diffusion profiles can be analyzed with either the constant- or limited-source equations. The apparent diffusion coefficient tends to be larger the intrinsic lattice diffusion due to significant contribution from grain boundaries. The constant- and limited- source equations can also be used with type
C kinetics as long as the majority of diffusion is confined to the grain boundaries. The conditions under which types A (Eq. (5-18)) and B (Eq. (5-19)) kinetics occur are defined as:

\[(D_L t)^{1/2} \geq d/0.8,\]  \hspace{1cm} (5-18)

\[s\delta \ll (D_L t)^{1/2} \ll d.\]  \hspace{1cm} (5-19)

\(D_L\) is the lattice diffusivity, \(s\) is the grain boundary segregation factor, \(\delta\) is the grain boundary width, typically assumed to be 0.5 nm, and \(d\) is the distance between neighboring grain boundaries, that is, the grain size.

The 250 °C, 275 °C, and nominally unannealed diffusion profiles contain a tail at greater depths. The nominally unannealed sample profile in Figure 5.16 reveals a CsCd\(^+\) signal reducing to the background level of \(\sim 10^2\) counts. The attenuated signal is unlikely to represent grain boundary diffusion. Ignoring the unannealed grain boundary diffusion data, an Arrhenius analysis of the 250 °C and 275 °C grain boundary diffusion curves shows a cadmium grain boundary diffusion activation energy of 2.9 eV, significantly higher than the calculated lattice diffusion activation energy in this work and previous studies [118].

The unsatisfactory measurements in grain boundary diffusion may be due to three reasons. First, based on the grain size of 100 nm, the conditions for type B kinetics are not sufficiently satisfied according to the inequality in Eq. (5-19). The \(\sqrt{Dt}\) values for the 250 °C and 275 °C experiments (36 nm and 65 nm) are somewhat close to the upper limit in Eq. (5-19). Second, CsCd\(^+\) signal in the tail region of the profiles is close to background signal level of \(\sim 10^2\) counts as suggested in the SIMS depth profile of the unannealed, HCl-etched 700 nm sample. Third, the depth resolution may have gotten worsen due to ion beam-induced sputtering.

The \(\sqrt{Dt}\) value of 160 nm meets the condition for type A kinetics for the 300 °C experiment. Thus, the diffusion coefficient is an effective diffusion coefficient with a non-negligible grain boundary diffusion contribution.

Diffusion coefficients were obtained from all experimental data and plotted in an Arrhenius plot as shown in Figure 5.17. Despite the scatter in data, the temperature-dependent second-stage diffusivities of cadmium in CIGS are in general agreement with those reported by Hiepko et al. [118]. For comparison, Hiepko’s Arrhenius equation is represented by the dashed line in Figure 5.17 with an activation energy of 1.04 eV and a preexponential factor of 4.8
× 10⁻⁴ cm² s⁻¹. CuInSe₂-based diffusion studies with elemental cadmium report higher volume diffusion activation energies values of 1.19 eV [119] and 1.25 eV [120] with an outlier value of 0.47 eV [121]. The activation energies from the first stage and the grain boundary diffusivities cannot be reliably determined with just two data points for each diffusion process (Figure 5.17). Several orders of magnitude separate the three diffusion processes.

5.3 Analyzing two-stage cadmium diffusion profiles in Cu(In,Ga)Se₂

5.3.1 Rationale and sample preparation

The smaller grain size in the 700 nm films means the contribution of grain boundary diffusion to either stage in the diffusion profiles could not be ruled out. A chemical reaction between the CdS and CIGS layers in the previous creating the first stage may also have occurred. Enabled by advances in surface polishing techniques, it was sought to address these two issues in order to better quantify the first-stage cadmium diffusion in CIGS thin films. CIGS thin films with larger grain sizes with cadmium chloride (CdCl₂) instead of CdS as the cadmium source were used.
Soda lime glass (SLG)/Mo/CIGS structures were made at CNSE's Solar Energy Development Center (SEDC-PVMC) via a three-stage coevaporation process. 1.9 µm CIGS films were grown on Mo-coated glass substrates in a thermal evaporation system using resistive boat sources at a $5 \times 10^{-3}$ Pa base pressure. The deposition of copper, indium, and gallium were regulated using electron impact emission spectroscopy (EIES). The selenium deposition rate was controlled using a quartz crystal microbalance (QCM). Inductively coupled plasma atomic emission spectroscopy (ICP) measurements of the as-deposited CIGS films showed a Cu/(In+Ga) ratio of 0.88, a Ga/(In+Ga) ratio of 0.32, and a Se/(Cu+In+Ga) ratio of 0.93.

### 5.3.2 Thin film Cu(In,Ga)Se$_2$ polishing technique

The as-deposited surface of the 1.9 µm thick CIGS films were rough (root mean square roughness $R_{RMS}$ of 200 nm), thus the decreased depth resolution due to the initial and sputtering-induced surface roughness were a concern. To minimize the loss in depth resolution, 2 cm $\times$ 2 cm SLG/Mo/CIGS samples were polished by hand to obtain smooth surfaces. Polishing was conducted using a 50-nm alumina ($\text{Al}_2\text{O}_3$) slurry on a nylon cloth on a mechanical rotating polishing machine. Polishing was done at two-minute intervals at the end of which the square samples were rotated by 90 degrees. The slurry-polished samples were subsequently held down against a deionized water-immersed nylon cloth on the mechanical rotating polishing tool to mechanically remove embedded alumina particles.

Final CIGS film thicknesses after polishing were not consistent because of the variable force exerted by hand but was at least 1 µm. ICP measurements of the polished CIGS films showed a Cu/(In+Ga) ratio of 0.84, a Ga/(In+Ga) ratio of 0.35, and a Se/(Cu+In+Ga) ratio of 1.01.

Isopropyl alcohol-dipped clothes were used to wipe the water-polished CIGS samples. The samples were subsequently immersed in 38% hydrochloric acid (HCl) for two minutes to remove the oxidized film surface [122]. 2 M aqueous cadmium chloride (CdCl$_2$) was dripped onto the clean, mirror-like CIGS surfaces using a pipette. Drying was done using an infrared lamp for an hour. The samples were then annealed in ambient atmosphere in a thermocouple-controlled quartz tube in the temperature range between 275 °C and 425 °C for between 10 and 80 minutes. The temperature in the quartz tube was confirmed using an external thermometer. After annealing, the annealed samples were immersed in a 38% HCl solution for two minutes to dissolve remaining CdCl$_2$. 

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The samples were wiped once again with isopropyl alcohol before analysis to remove water spots and other impurities as well as reduce dust-related particles that can interfere with the SIMS measurement. The $R_{RMS}$ of the polished surface was measured with a mechanical profilometer to be 2-5 nm. Scanning electron microscopy (SEM) analysis revealed grain sizes of $2 \pm 1 \mu m$. SEM images also showed minor surface damage; scratches with a width on the order of tens of nanometers were observed. Cross-section SEM analysis showed that the scratches were shallow, on the order of the measured surface roughness. Such minor surface effects do not have a significant impact on the interpretation of the data.

5.3.3 Diffusion profile measurement

To obtain cadmium diffusion profiles with a high depth resolution, time-of-flight secondary ion mass spectroscopy (TOF-SIMS) was utilized [109]. Using the ION-TOF TOF.SIMS$^5$ equipment, the Cs$^+$ sputtering ions were accelerated to 1 keV at a current of 25 nA while the Bi$^+$ analytical ions were accelerated to 25 keV at 20 nA. Out of six samples, only two samples were successfully depth-profiled for several hours. Depth-profiling in the other four samples was terminated after ~ 100 nm due to beam stability issues. The depths of the sputtered craters were measured with a mechanical profilometer and incorporated into the diffusion profiles.

5.3.4 Results

TOF-SIMS counts of the characteristic compound cesium cadmium (CsCd$^+$) were normalized to the maximum CsCd$^+$ intensity within each first-stage curve in Figure 5.18. The diffusion profiles were subjected to non-linear least squares fitting using Microsoft Excel’s built-in Solver capability. The last data point was fitted such that last theoretical data point could fall on the last experimental data point. Figure 5.18 (d) was best fitted with the limited source model while the others were better fitted with the constant source model (section 3.4). The apparent cadmium diffusion increases with annealing temperature and time. The divergence towards the end of the curves may be a transition between diffusion mechanisms.

The two full, non-normalized diffusion profiles in Figure 5.19 suggests two different diffusion mechanisms. The two stages can be fitted using the limited source model. The fitted second-stage curve in Figure 5.19 (b) has a diffusion coefficient of $2 \times 10^{-12} \text{ cm}^2\text{s}^{-1}$, close to $4 \times 10^{-12} \text{ cm}^2\text{s}^{-1}$ that was calculated with the Arrhenius equation obtained by
Figure 5.18 – Near-surface (i.e., first-stage) cadmium diffusion profiles at various annealing temperatures and durations: (a) unannealed; (b) 275 °C, 80 min; (c) 325 °C, 40 min; (d) 375 °C, 15 min; (e) 425 °C, 15 min). The solid lines represent fits using the constant-source equation ((b), (c), and (e)) and the limited-source equation (d).

Figure 5.19 – Two full cadmium diffusion profiles at different annealing temperatures and durations: (a) 360 °C, 10 min and (b) 375 °C, 15 min (sample #2, procured for verification, using the same sample preparation process). Two separate diffusion stages in each profile are shown. The solid lines represent fits of both diffusion stages using the limited source model. Five-point adjacent data-point averaging was applied. Due to data-point crowding, selected data points are shown.
For comparison, the first stage’s $2 \times 10^{-16}$ cm$^2$s$^{-1}$ (Figure 5.19 (b)) is several orders of magnitude lower than the second-stage counterpart (cf. Figure 5.20). The first stage shows significantly higher CsCd$^+$ signals, suggesting different levels of cadmium incorporation in the lattice that may depend on diffusion mechanisms.

![Figure 5.20 – Cadmium diffusion coefficients in CIGS as a function of reciprocal temperature. The open circles and triangles (d) represent experimental first-stage diffusion data points from Figs. 5.18 and 5.19 respectively. The red line (d) is the least squares fit of the experimental data. The blue line (c) is the copper vacancy diffusion coefficient curve as derived by Pohl et al. [65]. The open triangles (a) are the experimental second-stage diffusion coefficients from Fig. 5.19. The black line (a) is the cadmium diffusion coefficient curve by Hiepko et al. The first-stage diffusion coefficients in this work display a temperature dependence that can be quantified using the following Arrhenius equation (Figure 5.20, curve (d)):

$$D_1 = 3.0 \times 10^{-4} \exp \left( -\frac{1.53 \text{ eV}}{k_B T} \right) \text{cm}^2\text{s}^{-1}. \quad (5-20a)$$

$k_B$ is the Boltzmann constant and $T$ is the annealing temperature. The standard error of the activation energy ($\Delta E = 1.53$ eV) is 0.05 eV, and the standard error in the pre-exponential factor ($D_0 = 3.0 \times 10^{-4}$ cm$^2$s$^{-1}$) results in an uncertainty factor of 2.5.

For reference, Hiepko et al. obtained the second-stage cadmium diffusion equation of

$$D_2 = 4.8 \times 10^{-4} \exp \left( -\frac{1.04 \text{ eV}}{k_B T} \right) \text{cm}^2\text{s}^{-1} \quad (5-20b)$$
as discussed in Ref. [118]. The second-stage cadmium diffusion coefficients obtained from the two samples in the present work (Figure 5.19) closely match the cadmium diffusion coefficient equation by Hiepko et al. (solid line (a) in Figure 5.20 and Eq. (5-20b)). Cadmium atoms are believed to preferentially occupy copper vacancies in CIGS, so the temperature dependence of copper self-diffusion in CIGS by the copper vacancy mechanism as calculated by Pohl et al. is included, curve (c) in Figure 5.20 [65]. Pohl’s Arrhenius equation can be written as the following:

\[ D_{Cu} = 4.6 \times 10^{-4} \exp \left( \frac{-1.26 \text{eV}}{k_B T} \right) \text{cm}^2\text{s}^{-1}. \]  

(5-21)

5.4 Underlying diffusion mechanisms of the two-stage cadmium diffusion profiles

A discrepancy between this work’s first-stage cadmium diffusion coefficients and the copper self-diffusion coefficients that represent the copper vacancies themselves is visible in Figure 5.20 and Eq. (5-21). To derive the copper self-diffusion equation, Pohl assumed that the copper vacancy concentration was due to off-stoichiometry – set to 4% of copper vacancies on the copper sublattice or a total vacancy concentration of 1 at. %. Subsequently, copper self-diffusion as a function of temperature is significantly influenced by Pohl’s calculated migration barrier \( \Delta H_m \) of 1.26 eV. In a separate first-principles work, Oikkonen et al. suggests a lower copper vacancy migration barrier of 1.09 eV along with copper vacancy formation energy \( \Delta H_f \) being influenced by the Fermi level in the band gap and the CIGS stoichiometry (e.g. copper-poor versus copper-rich) [104].

If it is assumed that the first stage represents substitutional-vacancy diffusion (and interstitial-based diffusion in the second stage), the temperature-independent vacancy concentration assumption may not hold in the present work. The first-stage diffusion activation energy 1.53 eV is higher than suggested by Pohl and Oikkonen. Thus, contributions from the vacancy formation energy \( \Delta H_f \) and the binding energy of the impurity-vacancy interaction \( \Delta H_B \) may be included (i.e. 1.53 eV = \( \Delta H_f + \Delta H_m + \Delta H_B \)). \( \Delta H_B \) represents the altered vacancy population around an incorporated impurity (cadmium) atom [59].

The copper vacancy concentration assuming a temperature dependence in CIGS – despite the as-deposited copper vacancies on the order of several atomic percent – can be reconciled in the terms of low copper self-interstitial energies
In a related study, Pohl et al. suggest that copper self-interstitial formation (migration) energy may be as low as 0.17 eV (0.22 eV) [88].

With such low formation and migration energies, additional copper vacancies may be generated by the ejection of copper atoms to interstitial sites during annealing. The newly created copper interstitials in the near-surface region in CIGS then diffuse to the surface while cadmium atoms move into CIGS. Because copper self-interstitial formation energies decrease with decreasing copper vacancies, a domino effect may occur, where more copper atoms to form self-interstitials as cadmium atoms diffuse into CIGS and occupy copper vacancies [90]. Cadmium incorporation promoting further copper depletion of CIGS is not new; Kiss et al. suggest a similar behavior in a CuInSe₂-related material [9].

An alternative model might involve cadmium substitutional-vacancy diffusion in the second stage. The substitutional-vacancy diffusion mechanism is defined as the exchange between cadmium atom in the substitutional configuration (Cd₃Cu) and a copper vacancy (V₃Cu). The pre-exponential factor $D_0$ in Eq. (5-21) for Pohl’s equation for copper self-diffusion via the vacancy mechanism is close to the pre-exponential factor as obtained by Hiepko et al. If Oikkonen’s migration activation energy of 1.09 eV is used instead of Pohl’s 1.26 eV, Eq. (5-21) becomes very similar to the Hiepko’s second-stage cadmium diffusion equation [65], [104], [118]. The copper self-diffusion equation with Oikkonen’s $V₃Cu$ migration energy is written as

$$D_{Cu} = 4.6 \times 10^{-4} \exp \left(-\frac{1.09 \text{ eV}}{k_B T}\right) \text{cm}^2\text{s}^{-1}. \quad (5-22)$$

The first-stage cadmium diffusion may then represent a secondary diffusion mechanism in CIGS or diffusion in a newly formed copper-poor CuIn₃Se₅/CuIn₅Se₈ phase at the surface due to copper depletion as suggested. In fact, Kiss et al. show through first principles calculations that the kick-out diffusion mechanism for cadmium is relatively energetically favorable in CuIn₃Se₈ with an activation energy of ~ 1.5 eV, comparable to ~ 1.5 eV that was obtained from the first-stage cadmium diffusion profile in the present dissertation. The cadmium kick-out mechanism in CuIn₃Se₈ is described by Kiss et al. to operate when a substitutionally incorporated cadmium (Cd₃Cu) knocks a copper atom out of its lattice position to an empty interstitial site, a process requiring ~ 1 eV. The cadmium atom then jumps to the now-empty copper atomic site with a migration energy barrier of ~ 0.5 eV [124]. The two processes result in a
total diffusion activation energy of 1.5 eV. Thus, the first-stage cadmium diffusion profile may be representative of cadmium diffusion in a copper-poor phase of CIGS.
Chapter 6

Auger peaks deconvolution and background correction as applied to cadmium in Cu(In,Ga)Se₂

6.1 Introduction

This section concerns confirming the TOF-SIMS first-stage cadmium diffusion profile Cu(In,Ga)Se₂ seen in Chapter 5 using a complementing analytical technique, the Auger electron spectroscopy (AES). The main cadmium Auger peaks happen to sit on a peak shoulder in the indium MNN peak series where standard background-correction methods were found unsuitable, complicating the analysis of cadmium incorporation in CIGS. In this chapter, an algorithm is developed to correct for the background signal in the Auger spectrum under the cadmium Auger peaks.

6.2 Auger electron spectroscopy (AES)

TOF-SIMS data suggests multiple cadmium diffusion processes within a single depth profile in sections 5.2 and 5.3. However, quantification of the first-stage cadmium diffusion profiles is very difficult because they occur in the SIMS’ characteristic pre-equilibrium region, early in the sputtering process where the ion yields are continually evolving (section 5.1.3). Thus, it was necessary to confirm that the first-stage cadmium diffusion profiles are not a SIMS artifact. Auger electron spectroscopy (AES) is a common technique for diffusion studies [125]–[127]. AES is typically unsuitable for diffusion studies of impurities in trace amounts (e.g. parts per million) because of its detection limit of 0.1-1 at. % [128]. However, with the significant absorption of cadmium in CIGS (~ 3 at. %), AES becomes a suitable technique to study the first-stage cadmium diffusion profiles [40], [118].

The characteristic CsCd⁺ peak in TOF-SIMS analysis – representing the presence of cadmium in CIGS – at ~ 246.8 amu in the time-of-flight mass spectrum (Figure 6.1) has a linear background intensity profile that can be accounted
for by simply drawing a straight line between the sides of the peak as illustrated. Analyzing Cd\(^{+}\) directly would be difficult as it has a lower ion yield than CsCd\(^{+}\).

![Graph showing TOF-SIMS mass spectrum centered on the CsCd\(^{+}\) peak on the right with an illustrated straight line for background signal correction. The minor peak on the left shoulder of the main CsCd\(^{+}\) peak is suspected to be the Cs\(^{113}\)InH\(^{+}\) compound.]

The analysis of the Auger data was more involved. Due to software limitations, each sputtering cycle consisted of five separate scans. Each scan formed an Auger spectrum by averaging the intensities of 100 sweeps at each Auger kinetic energy channel. Consequently, there were five Auger spectrums to process per sputtering cycle. After applying the proposed background correction method to all five spectrums per sputter cycle, the five background-corrected intensity curves were individually integrated and added together to provide the final background-corrected intensity curve at a given sputtering depth.

### 6.3 Sample preparation and AES experiment

The experiment consisted of studying two separate 700 nm CIGS samples. Cadmium was diffused into one of the CIGS samples from a solutionally-deposited CdS capping layer by annealing at 300 °C for 5 min (the same sample as curve (d) in Figure 5.16). The other CIGS sample was not annealed and had the existing CdS capping layer etched off using hydrochloric acid. The cadmium-free as-deposited CIGS sample was used to collect the “background” intensity
in the Auger spectrum in the energy range where the cadmium Auger lines are located, on the shoulder of an indium plasmon peak. Sample preparation is further discussed in section 5.2.1.

Analysis was performed using the Phi 680 Field Emission Scanning Auger Nanoprobe instrument with an electron beam current of 10 nA at 10 keV. An unrasterized electron beam was used to minimize the analysis area and avoid defective areas on the sample surface such as voids and pinholes. Depth profiling was done with a 2 keV Ar⁺ ion sputtering gun rasterizing an area of 2 mm × 2 mm. The depth of the AES crater was measured to be 490 nm using a mechanical profilometer. The Auger depth profile’s sputtering time was converted to spatial depth using the known depth of the crater.

6.4 Background signal correction

To obtain the hidden background intensity curves under the intense cadmium Auger peaks, a separate CIGS sample without cadmium was analyzed. The background intensity in the energy spectrum in the vicinity of the cadmium Auger lines was observed to contain a distinct curving function that has been determined to be the left shoulder (the side of lower Auger kinetic energy) indium plasmon peak. It was recognized that constructing a background intensity profile in the analysis spectrum of a cadmium-diffused CIGS sample in the presence of prominent cadmium peaks would require a method to apply the shape of the background intensity curve (i.e. the shape of the indium peak shoulder) without violating the boundary conditions. The calculated intensity of the background curve must not exceed or fall below the experimental intensity exactly at the chosen start and end points away from the peaks of interest. The imposed boundary conditions are critical: due to instrumental reasons, every cadmium spectrum collected has a varying overall intensity. Consequently, the background intensity curve of the cadmium-free CIGS spectrum cannot be simply directly subtracted from a cadmium-diffused CIGS spectrum.

The AES spectrum of the cadmium-free CIGS sample between kinetic energies of 365 eV and 395 eV – totaling 300 energy-versus-intensity data points at the 0.1 eV step size – was subjected to the 25-point Savitzky-Golay smoothing filter as specified in Figure 6.2.

In order to easily subtract the modeled background from acquired spectrum, a straight line was drawn between two energy points on the smoothed curve (Figure 6.3). The straight line is used to derive a “fractional change” constant
Figure 6.2 – 25-point Savitzky-Golay smoothing filter applied to the AES spectrum in the cadmium-free CIGS sample.

Figure 6.3 – Illustration depicting the fractional change constant derived using the smoothed background curve from the cadmium-free CIGS sample.

for every scanned kinetic energy which represents the difference between the measured background intensity curve and the value of the straight line at a given kinetic energy $E$. The fractional change $\Delta$ is subsequently applied to cadmium-diffused spectrums to determine the background intensity curve under the intense cadmium peaks using another straight line.
The two points on the straight line in the cadmium-free spectrum are chosen such that they are sufficiently far away from the known locations of cadmium peaks to give a reproducible fit to the background. For every measured background intensity at their respective kinetic energy, the fractional change between the measured background intensity $I_B$ and the value of the straight line $I_S$ at the kinetic energy $E$ was calculated as the following:

$$\Delta(E) = \frac{I_B(E) - I_S(E)}{I_S(E)} \quad (6-1)$$

As Figure 6.3 implies, the fractional change $\Delta(E)$ gradually changes throughout the spectrum according to the magnitude of difference in intensity between the measured curve and the straight line. Also shown are three points of intersection of the straight line with the measured background intensity curve where the sign of $\Delta(E)$ changes.

Once $\Delta$ is calculated for all kinetic energies that are scanned with the cadmium-free sample, another straight line is constructed, in each spectrum from the cadmium-diffused sample throughout all sputtering cycles with the same start and end kinetic energies. The background intensity curve for the cadmium-diffused CIGS spectrum is then determined through the following equation where $I_{cab}(E)$ is the background intensity at kinetic energy $E$ and $I_{cas}(E)$ is the calculated straight-line value at kinetic energy $E$ of the cadmium-diffused CIGS spectrum:

$$I_{cab}(E) = I_{cas}(E)[1 + \Delta(E)]. \quad (6-2)$$

Finally, we have the background-subtracted curve where $I_{bc}(E)$ is the intensity after background correction and $I_{cd}(E)$ is the measured intensity at their respective kinetic energy $E$ in the cadmium-diffused spectrum:

$$I_{bc}(E) = I_{cd}(E) - I_{cab}(E). \quad (6-3)$$

The fractional change approach ensures two main effects: 1) the background intensity curve under the intense cadmium peaks maintains the same shape as the curve measured in the cadmium-free CIGS sample and 2) the constructed background intensity at a given kinetic energy $E$ is proportional to the overall intensity of the spectrum. Accordingly, the effect of varying overall intensity across different spectrums throughout sputter depth is accounted for.
6.5 Spectral correction of the proposed algorithm versus other methods

Figure 6.4 – Cadmium AES spectrum of the cadmium-diffused CIGS sample at the surface with the proposed background correction method. Cadmium AES spectrum of the cadmium-diffused CIGS sample at the sputtering depth of 500 nm with the proposed background correction method.

Figure 6.4 shows the “background” correction approaches applied to Savitzky-Golay smoothed cadmium Auger peaks at the sample surface and at the depth of ~ 490 nm into the cadmium-diffused sample. When the cadmium Auger peaks are intense, the proposed method replicates the background curve well. The proposed algorithm shows its strength when the cadmium Auger peaks become increasingly faint (the right graph in Figure 6.4) as it heavily depends on prior knowledge of the background level of the trace-element cadmium.

For comparison, a background correction technique standard to AES and XPS were also applied in Figure 6.4 to analyze the cadmium Auger peaks, but it was not as successful as the proposed method. Shirley’s background correction method operates on the assumption that the background signal intensity at energy $E$ is proportional to the signal intensity integrated from a convenient point $E_{min}$ on the side with the lower measured background intensity with the integral ending at energy $E$ [129]. For the first few depth scans, Shirley’s method was adequate in correcting for the “background” intensity that is the indium plasmon peaks. However, as the cadmium Auger peaks attenuate to the background level, the use of Shirley’s method results in an overcorrection of the background signal, leading to difficulty in quantifying cadmium in CIGS. The application of Shirley’s nonphysical method here could be deemed
not completely appropriate as the cadmium Auger peaks do not sit on a broad, slow-varying electron energy loss background but on a sloped shoulder of an indium plasmon peak.

Clearly, methods exist that could be utilized to deconvolute the indium and cadmium peaks. However, this peak-fitting approach would introduce a non-trivial step in the analysis in addition to background subtraction. The proposed background correction/peak deconvolution method in this paper eliminates the need for peak-fitting as long as the peak of interest belongs to an element that is not a major component of the material’s matrix.

### 6.6 AES and TOF-SIMS diffusion profiles of cadmium

![Graph showing AES and TOF-SIMS diffusion profiles of cadmium in CIGS after annealing for five minutes at 300 °C](image)

Figure 6.5 – AES and SIMS diffusion profiles of cadmium in CIGS after annealing for five minutes at 300 °C (cf. Figure 5.16).

Figure 6.5 compares two cadmium diffusion profiles analyzed on the same CIGS sample annealed at 300 °C for five minutes. One determined using TOF-SIMS and the other by AES. The AES diffusion profile was obtained using the proposed background correction method. While TOF-SIMS is clearly a more sensitive technique for detecting cadmium, the proposed background correction method improves detectability of the small signal of cadmium in CIGS using AES.
6.7 Possible sources of error in application of the algorithm

While the good correspondence between the AES and TOF-SIMS diffusion profiles indicates a lack of a systematic flaw of the proposed algorithm, several minor inconsistencies need to be addressed. The AES data points can be seen oscillating about the curve that is made up by the TOF-SIMS data points. Because the AES depth profile experiment consisted of high-resolution scans totaling 500 measurements per kinetic energy $E$ per sputtering depth, a significant uncertainty in measurement is unlikely. In addition, the oscillating AES data points are unlikely to represent the true depth profile of cadmium in CIGS. It was observed that over the course of the depth profiling, there was a slight lateral drifting of the electron beam on the surface of the CIGS sample. The CIGS surface was relatively rough (root mean square roughness $R_{RMS}$ of 20 nm) with an average grain size of 100 nm. These values are on the order of the size of the electron beam in the Phi 680 Field Emission Scanning Auger Nanoprobe instrument. Therefore, the movement of the beam on the sample surface may have skewed the measurement due to variable surface topography.

Background-corrected cadmium Auger spectrums at several selected sputtering depths (Figure 6.6) show that the proposed algorithm is adequate in removing the background level. However, a closer inspection shows that with increasing sputtering depth, the right side of the cadmium peak complex tends to overestimate the background intensity between kinetic energies of 383 eV to 388 eV, causing that kinetic energy range to assume mostly negative corrected intensities. This could explain the underreporting of cadmium intensity in the diffusion profile at larger depths (cf. Figure 6.6).

A minor disadvantage of the proposed background correction method is the lack of consideration of the cadmium Auger electrons’ contribution to the intensity of the region housing the indium plasmon peak under the baseline level of the indium plasmon peak once the obvious cadmium peaks vanish. As indicated, peak-fitting can play a role in discerning the cadmium Auger electrons’ contribution to the indium plasmon peaks. However, peak-fitting requires further assumptions, adding complexity to the entire procedure and may become impractical.

If cadmium Auger electrons have a significant contribution to the indium plasmon peak – possibly altering the background intensity – the linear slopes calculated for the spectrums in cadmium-diffused sample may be significantly different from the linear slope calculated in the cadmium-free sample. This would suggest that the “fractional change”
constants calculated from the cadmium-free spectrum using the enclosed straight line should be different in the cadmium-diffused spectrums, negating the applicability of the constants for all spectrums.

Figure 6.6 – Selected cadmium Auger spectrums at various sputtering depths using the proposed background correction method: (A) 21 nm, (B) 63 nm, (C) 83 nm, (D) 188 nm, (E) 271 nm (F) 313 nm, (G) 438 nm, (H) 490 nm.

To check for this possibility, the slopes of the derived straight lines in all cadmium-diffused spectrums were calculated. The result of the calculation is shown in Figure 6.7 with the average value of the slope and the minimum and maximum values as the error bars for the five 100-sweep scans at each sputtering cycle. If the first two points – representing two surface scans before sputtering began – are ignored, it can be seen that the slopes of the derived straight lines remains virtually constant throughout all spectrums in the cadmium-diffused sample.

The disagreement of the first two slope data points compared to the rest can be reconciled with the data from literature showing that the CIGS surface can have a radically different atomic composition compared to the bulk depending on type of chemical treatment of the surface used in fabrication process [122]. The hydrochloric acid treatment used in the CdS/CIGS sample preparation could explain the disagreement. A different surface composition up to several nanometers in depth certainly could have altered the diffusivity of cadmium due to copper depletion during cadmium source deposition via chemical bath deposition (CBD) (Chapter 4 and section 5.4), promoting greater incorporation near the surface. The relatively constant slope in the rest of the sputtering cycles confirms the validity of using the “fractional change” constants in cadmium-diffused spectrums that were derived from the cadmium-free spectrum.
Figure 6.7 – Average slopes of the constructed straight lines between the start and end kinetic energy points as a function of analytical cycle in the cadmium-diffused sample.

6.8 Conditions for practical diffusion studies using AES and SIMS

For diffusion studies, AES and SIMS offer different advantages, influencing the optimal choice for a given diffusion study. SIMS has been demonstrated to detect trace elements on the order of parts per million while AES trace element detection is approximately parts per ten thousand [130], [131]. However, a strength of AES over SIMS is the lateral resolution offered by the smaller diameter of the electron beam versus SIMS’ larger analysis area [132]. The high-end lateral resolution of 5-10 nm in scanning Auger microscopies and 100 nm in SIMS instruments have been cited [133]. In most practical cases, the lateral resolutions for AES and SIMS are greater than these values. Despite SIMS’ superior detection limit, focusing the Bi⁺ ion beam in TOF-SIMS to a smaller diameter would reduce the beam current, resulting in a lower count rate. An ion beam diameter in the micrometer range is typically used in practical SIMS work.

Physical processes occurring in the SIMS instrument also impose a lower limit on the chosen analytical area size inside the sputtering crater. Not all atoms of the impurity of interest that are sputtered by primary ions will be ionized. Based on the configured charge polarity of SIMS instrument, unlike-charge secondary ions representing the element of interest will be pulled in the generated electric field towards the SIMS optics and detector system, and like-charge ions will be repulsed. Further secondary ion losses occur in the secondary ion optical system before the remaining
secondary ions finally reach the detector. Calculations suggest that an analytical area of less than one square micrometer – assuming a sputtering depth of 1 nm in a given analytical cycle – will physically not emit enough detectable secondary ions unless the ion yield of the impurity is extraordinarily high [111].

However, low ion yields – which are a significant function of the material being analyzed – can still become a concern in larger SIMS analytical areas. In prior TOF-SIMS experiments with the same type of samples, the CsCd+ ion was barely detectable with a lateral scan of 128 pixels × 128 pixels in an analytical area of 50 µm × 50 µm (<10² counts per sputtering cycle). Increasing the lateral scan parameter to 1024 pixels × 1024 pixels in an analytical area of 200 µm × 200 µm increased the CsCd+ count to ~ 10³ per sputtering cycle. Despite the non-marginal increase in count, the analysis time increased from ten minutes to several hours. With the proposed background correction algorithm, AES became an attractive candidate to study trace amounts of cadmium in CIGS.

The ability of AES to analyze areas smaller than SIMS’ physical lower limit of one square micrometer is advantageous for the analysis of small concentrations of impurities in grains and other features in the nanoscale range. Because SIMS usually requires a relatively large analysis area on the sample, the resulting diffusion profile of an impurity will be distorted if the surface is sufficiently rough or contains voids. Such considerations can be minimized using AES and the proposed background correction method. The point on the sample surface from which Auger electrons are emitted and detected is on the order of the size of the unrasterized electron beam. Thus, the apparent surface roughness across the small electron beam is significantly smaller versus the roughness seen with the larger SIMS analysis area.

A background correction algorithm for the detection of trace elements in a material using Auger electron spectroscopy was proposed. The proposed algorithm comprised of using a CIGS sample that contained no cadmium to derive a fractional change constant at every scanned kinetic energy $E$. The fractional change constants were defined in terms of the difference between the background intensity curve and a drawn linear line that connected the start and end points in the analyzed kinetic energy range. Once the constants were derived, they were applied to spectrums obtained from a CIGS sample containing cadmium where cadmium Auger peaks were intense. Another linear line was drawn between the same start and end kinetic energies in the spectrums. The fractional change constants were applied to the second linear line to construct the “hidden” background intensity curve under the intense cadmium Auger peaks that was not originally obvious. This proposed method allowed for a precise quantification of cadmium in CIGS. To test
the validity of the proposed method, cadmium was diffused into a separate CIGS sample via thermal annealing and analyzed with both Auger electron spectroscopy and time-of-flight secondary ion mass spectroscopy – a sensitive technique for trace element detection – to obtain a cadmium diffusion profile. The SIMS cadmium diffusion profile revealed that the AES analysis showed a similar diffusion profile, validating the use of the proposed AES background correction method.
Chapter 7

Numerical simulations of multiple cadmium diffusion mechanisms in Cu(In,Ga)Se$_2$

7.1 Analyzing diffusion in open Cu(In,Ga)Se$_2$ crystal structure

The crystal structures of many semiconductor materials are considered open, including Cu(In,Ga)Se$_2$. Referring to Table 7-1, metals like copper and iron crystallize in the face-centered cubic (FCC) and the body-centered cubic (BCC) structures respectively. The atomic packing factor is defined as the volume that is occupied by the atoms divided by the total volume of the unit cell of the crystal, including the empty space. The atomic packing factor can be considered a measure of the openness of the crystal structure [134], [135]. Many metals crystallize in the body-centered cubic (BCC) and face-centered cubic (FCC) systems where their crystal structures are packed closely together. Semiconductor materials like silicon, germanium, and Cu(In,Ga)Se$_2$ crystallize in crystal structures of lower atomic packing factors, resulting in smaller densities.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Atomic packing factor</th>
<th>Density at room temperature (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Face-centered cubic (FCC)</td>
<td>Example: copper</td>
<td>0.74</td>
</tr>
<tr>
<td>Body-centered cubic (BCC)</td>
<td>Example: iron</td>
<td>0.68</td>
</tr>
<tr>
<td>Diamond cubic</td>
<td>Example: silicon</td>
<td>0.34</td>
</tr>
<tr>
<td>Cu(In,Ga)Se$_2$ (tetragonal)</td>
<td></td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 7-1 – Atomic packing factor of crystal structure and density of the respective material.

The openness – or the atomic packing factor – of the crystal structure has significant implications for the relative equilibrium concentrations of point defects (and impurities) as well as the migration barrier energies for diffusion.
Wollenberger shows that the formation enthalpy of self-interstitials in metals is about two or three times higher than the formation enthalpy of vacancies [59], [136]. Using Eq. (3-76), doubling or tripling the formation enthalpy in the exponential term means the vacancy concentration is significantly greater than the self-interstitial concentration by several orders of magnitude at thermal equilibrium. Thus, it is hardly surprising that vacancies are the dominant diffusion mechanism in metals for both the host atoms and impurity atoms of a similar size.

More open crystal structures generally allow for greater interstitial incorporation of host and impurity atoms compared to closely packed metals. Because CIGS is considered an open structure (Table 7-1), the consideration of different possible diffusion mechanisms becomes more relevant (e.g. via vacancies and interstitials). However, experimental data on diffusion in CIGS is sparse compared to experimental diffusion data in silicon. Thus, silicon is briefly discussed to gain insight. The activation energies in the “flow products” of vacancies $C^e_q D_V$ and self-interstitials $C^e_I D_I$ in silicon have been shown to be similar [137], [138]:

$$C^e_I D_I = 0.298 \exp \left( \frac{-4.95 \text{eV}}{k_B T} \right) \text{m}^2\text{s}^{-1},$$  \hspace{1cm} (7-1)

$$C^e_q D_V = 0.92 \times 10^{-4} \exp \left( \frac{-4.14 \text{eV}}{k_B T} \right) \text{m}^2\text{s}^{-1}. \hspace{1cm} (7-2)$$

The meaning of the flow product – $C^e_q D_V$ for example – is the same as Eq. (3-118) when correlation factor $f$ is added to the former expression: $f_V C^e_q D_V$ where $f_V$ is the correlation factor of the vacancy diffusion mechanism. Traditional experimental techniques for vacancy concentration measurement that have worked for metals fail for elemental semiconductors like silicon and germanium due to the extremely low vacancy concentrations. While it is beyond the capabilities of such direct techniques, the equilibrium vacancy concentrations in these materials are believed to be as low as one part per million close to the melting point [59]. The typical radiotracer diffusion experiment yields a diffusion profile with some fitted diffusion coefficient $D^*$. If only the vacancy diffusion mechanism exists, then the diffusion profile due to the self-diffusion of tracer atoms (e.g. tracer atoms of type $A$ in the matrix made of only $A$ atoms) has the experimentally measured diffusion coefficient of

$$D^* = f_V C^e_q D_V. \hspace{1cm} (7-3)$$
Without the direct knowledge of the intrinsic defect populations, it is sometimes more convenient to consider experimental tracer self-diffusion profiles of semiconductor materials in terms of $D^*$ or the flow product $C_{X}^{\text{eq}} D_X$ for intrinsic defect $X$ than $C_X^{\text{eq}}$ and $D_X$ separately [59]. In contrast to metals, Eqs. (7-1) and (7-2) show that the difference between the silicon vacancy and self-interstitial flow products is sufficiently small that both diffusion mechanisms significantly contribute to silicon self-diffusion at most temperatures. Therefore, the experimentally measured diffusion coefficient for silicon tracer self-diffusion can be written as $D^* = f_V C_{V}^{\text{eq}} + f_I C_{I}^{\text{eq}} D_I$ [137], [138]

Because metals have large intrinsic defect populations compared to semiconductors (e.g. $\Delta H^F_V = 0.9$ eV in copper and $\Delta H^F_F \approx 2$ eV in silicon assuming $\Delta H^F_F$ makes up half of the 4.14 eV figure in Eq. (7-2)), self-diffusion is generally a slower process in semiconductors versus metals [72]. The difference in intrinsic defect populations between metals (more populous) and elemental semiconductors (less populous) stems from the contrasting properties of the metallic and covalent bonding as the latter is typically stronger than the former [59].

Cu(In,Ga)Se$_2$ is an interesting exception to the rule of small intrinsic defect populations for semiconductors as elaborated in sections 2.2 and 3.7. The expression for defect populations in non-stoichiometric materials like CIGS is

$$C_{D,q}(E_F, \mu_\alpha, T) = N \exp(-\Delta H^F_{D,q}(E_F, \mu_\alpha)/k_B T).$$

(7-4)

$N$ is the concentration of lattice sites (e.g. the number of copper sites in CIGS), $\mu_\alpha$ corresponds to the chemical potential of element $\alpha$, $T$ is the temperature at which the equilibrium concentration of defect $D$ with charge $q$ occurs, and $E_F$ refers to the Fermi level position in the band gap (see section 3.7.6) [46]. Using the highest calculated $V_{\text{Cu}}$ formation energy via first principles of $\sim 0.6$ eV by Zhang et al. which might represent a stoichiometric CuInSe$_2$ thin film, a deposition temperature of $500 \,^\circ C (773 \, K)$ in CuInSe$_2$, and $\sim 1 \times 10^{22}$ cm$^{-3}$ copper lattice sites, a copper vacancy concentration on the order of $10^{18}$ cm$^{-3}$ (0.01 at. %) is obtained [38]. Achieving a copper vacancy concentration of 1 at. % ($\sim 10^{20}$ cm$^{-3}$) at 773 K requires a formation energy of $\sim 0.3$ eV. Neutron diffraction confirms suggest that copper-poor, chalcopyrite-phase CuInSe$_2$ (Cu/In = 0.84-0.95) can contain copper vacancy concentrations as high as 3 at. % [123]. Thus, experimental knowledge of $C_V$ is straightforward. However, $C_V^{\text{eq}}$ component of the vacancy transport product $C_V^{\text{eq}} D_V$ is not as well-defined as single-element materials due to the dependence on stoichiometry for equilibrium defect concentrations in non-stoichiometric materials as explored in sections 3.7.3 and 3.7.6.
7.2 Modeling impurity diffusion and reaction in a host matrix

This chapter concerns the dissociative diffusion mechanism (alternatively known as the Frank-Turnbull mechanism) – where an impurity atom rapidly travels through interstitial sites before reacting with a vacancy – in vacancy-rich materials [139]. Two cases are studied where 1) the impurity interstitial diffusion is sufficiently rapid that vacancies are practically immobile, and 2) impurity interstitial diffusion becomes exceedingly fast that the concentration of impurity atoms in interstitial sites are maintained at the equilibrium value everywhere at all times, leading to the case where vacancy diffusion is the slowest process. We begin with a discussion of the traditional model [59], [140] The reaction between a foreign interstitial atom $i$ and a vacancy in the host material $V$ to become a substitutional impurity atom $S$ is modelled as a reaction equation:

$$i + V \leftrightarrow S. \quad (7-5)$$

Both forward and reverse reactions are possible according to Eq. (7-5). The forward and reverse rate constants seen in the net reaction rate $\delta$ equation of Eq. (7-6) and the equilibrium concentrations $C_i^{eq}$, $C_V^{eq}$, and $C_S^{eq}$ are related through the law of mass action in Eq. (7-7) assuming the $i$-$V$ reaction is elementary (single step):

$$\delta = k_F C_i C_V - k_R C_S, \quad (7-6)$$

$$\frac{k_F}{k_R} = \frac{C_S^{eq}}{C_i^{eq} C_V^{eq}}. \quad (7-7)$$

The ratios in Eq. (7-7) are constants dependent upon temperature and can but not always display an Arrhenius behavior [59]. To describe the $i$-$V$ reaction component of the dissociative diffusion mechanism, Eq. (7-6) is incorporated into each species’ Fick’s second law partial differential equation:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - \delta, \quad (7-8)$$

$$\frac{\partial C_V}{\partial t} = D_V \frac{\partial^2 C_V}{\partial x^2} - \delta. \quad (7-9)$$
\[
\frac{\partial C_S}{\partial t} = D_s \frac{\partial^2 C_S}{\partial x^2} + \delta.
\]  

(7-10)

As discussed in section 3.8.4, the diffusion coefficients \( D_i \) and \( D_V \) have a correlation factor \( f \) of 1 because assuming dilute concentrations of the species (< 1 at. %), the probability of having an empty (occupied) interstitial (copper lattice) site for the impurity atom (vacancy) to migrate to is nearly unity. Alternatively stated, the diffusion of vacancies and interstitial impurity atoms are completely random. Eq. (3-120) applies for the case of intrinsic copper vacancy diffusion in CIGS, and Eq. (3-124) is used for the intrinsic cadmium interstitial diffusion in CIGS. Conversely, substitutional diffusion – \( D_S \), defined for the diffusion mechanism where the impurity atom in the substitutional configuration exchanges position with a neighboring vacancy – is controlled by the probability of having a vacancy a neighboring lattice site. Additionally, the tracer diffusion of an impurity via the vacancy mechanism is correlated as discussed in section 3.8.2. If the Cd\(_{\text{Cu}}\)–V\(_{\text{Cu}}\) exchange in CIGS is considered, then Eq. (3-122) – including the \( C_{V_{\text{Cu}}} \) and correlation factor \( f \) dependencies – becomes valid.

Because of the dependence on each other, the three coupled diffusion-reaction differential equations above do not have analytical solutions in full generality. Several specific-case analytical solutions can be derived starting with assuming local equilibrium between the three species [59]:

\[
\frac{C_S}{C_i C_V} = \frac{C_S^{eq}}{C_i^{eq} C_V^{eq}}.
\]  

(7-11)

Eq. (7-11) is a statement of extremely fast reaction rates at any position and time step; the three species will always maintain the ratio given by their respective equilibrium concentrations on the right side of the equation. This assumption can be made for long diffusion times [59], [140]. Other versions of the equations above include source/sink terms (e.g. dislocations) and extra diffusion-reaction differential equations for other diffusing species (e.g. self-interstitials) [138]. The method in this chapter is only for the dissociative diffusion mechanism, so such additional terms are ignored.

Impurity diffusion in elemental semiconductors – Si:(Au and Zn), Ge:(Co, Cu, Ag, and Au) has been successfully studied with the diffusion-reaction form of the Fick’s second law [59], [96], [138]–[142]. Before discussing the results
of the simulation results of variable vacancy concentration under the dissociative diffusion theory, two pertinent analytical solutions to the set of Eqs. (7-6) through (7-11) are reviewed [59].

### 7.2.1 Standard interstitial-limited dissociative diffusion model

For nearly zero substitutional diffusion via vacancies (or direct substitutional exchange) as expressed by

\[ D_S = 0, \]  

Eq. (7-10) reduces to

\[ \frac{\partial C_S}{\partial t} = \delta. \]  

When the concentration of vacancies is assumed to be maintained at the equilibrium concentration everywhere at all times:

\[ C_V = C_V^{eq}. \]  

With Eqs. (7-11) and (7-14), rearranging Eqs. (7-8), (7-9), and (7-13) yields the following diffusion equation

\[ \frac{\partial C_S}{\partial t} = D_{eff}^i \frac{\partial^2 C_S}{\partial x^2} \]  

where the effective (i.e. experimentally measured) diffusion coefficient \( D_{eff}^i \) becomes

\[ D_{eff}^i = \frac{C_i^{eq} D_i}{C_i^{eq} + C_S^{eq}}. \]

\( D_{eff}^i \) denotes a diffusion coefficient that is controlled by the foreign interstitials because the foreign interstitial diffusion is the limiting process. \( D_{eff}^i \) depends on the foreign-interstitial diffusion coefficient \( D_i \), the equilibrium concentrations of foreign interstitials \( C_i^{eq} \) and substitutionals \( C_S^{eq} \).
Standard diffusion theory dictates two analytical solutions to Fick’s second law after applying the appropriate boundary conditions for tracer diffusion from a constant (non-depletable) source or a source of a limited quantity of tracer atoms. The analytical solutions yield erfc- and Gaussian-shaped diffusion profiles respectively [59].

\[ C(x, t) = C_0 \text{erfc} \left( \frac{x}{2\sqrt{D t}} \right), \] (7-17)

\[ C(x, t) = \frac{\phi}{\sqrt{4\pi D t}} \exp \left( -\frac{x^2}{4D t} \right). \] (7-18)

\( C(x, t) \) is the concentration at position \( x \) after time \( t \). \( C_0 \) for the constant-source equation denotes the fixed concentration imposed by the boundary condition at \( x = 0 \) at any given time \( t \). In the limited-source case, \( Q \) is the limited quantity of the tracer atoms at the surface at \( t = 0 \). \( D \) is the apparent diffusion coefficient of the profile. Eq. (7-15) is a form of Fick’s second law and yields an analytical solution, thus \( D_{eff} \) can be substituted into the constant- and limited-source equations.

### 7.2.2 Standard vacancy-limited dissociative diffusion model

Conversely, when the diffusion of vacancies becomes the limiting process such that the equilibrium concentration of foreign interstitials is rapidly established everywhere and the intrinsic vacancy diffusion is the slowest process:

\[ C_i = C_i^{eq}, \] (7-19)

Eqs. (7-8), (7-9), (7-11), (7-13), (7-19) now produce a diffusion equation with a vacancy-controlled diffusion coefficient:

\[ \frac{\partial C_S}{\partial t} = D_{eff}^V \frac{\partial^2 C_S}{\partial x^2}, \] (7-20)

where

\[ D_{eff}^V = \frac{c_S^{eq} D_V}{c_V^{eq} + c_S^{eq}}. \] (7-21)
$D_{eff}^V$ is controlled by the intrinsic vacancy diffusion coefficient $D_V$, the equilibrium concentrations of vacancies $C_{eq}^V$ and foreign substitutionals $C_{eq}^S$. Eq. (7-20) is also a form of Fick’s second law and leads to an analytical solution. For vacancy-limited dissociative diffusion using a constant or limited tracer-atom source, $D_{eff}^V$ is substituted into the constant- and limited-source equations.

7.3 Simulation approach

The following sections are based on the published *AIP Advances* paper entitled “Dissociative diffusion mechanism in vacancy-rich materials according to mass action kinetics” [143]. The one-dimensional form of the finite difference method (FDM) is used where the concentration $C$ of a species at a given pair of discrete position $p$ and time step $j$ is determined using the forward difference for the temporal derivative $\partial c / \partial t$ and the second-order central difference for the spatial derivative $\partial^2 c / \partial x^2$ [144]. The generalized version of the algorithm is expressed as

$$\frac{C_p^{j+1} - C_p^j}{\Delta t} = D \frac{C_p^{j+1} - 2C_p^j + C_p^{j-1}}{\Delta x^2} \pm \delta$$

(7-22)

where $C_p^j$ is the concentration of a given species at position point $p$ at time point $t$. $\Delta t$ is the temporal difference between two time points, and $\Delta x$ is the spatial difference between two position points. The sign of the reaction term $\delta$ depends on the species the concentration is being calculated for. The diffusion coefficient $D$ also depends on the species. During the calculation, $C_p^{j+1}$ – the concentration of the species at a given position point at the next time point in the future – is solved for where all other variables are previously defined. For the algorithm to be numerically stable and convergent, $\Delta x$ and $\Delta t$ must be sufficiently small while maintaining sufficiently large $k_F$ and $k_R$ reaction rate constants for Eq. (7-11) to be satisfied virtually at all positions and time steps. The algorithm was implemented using the Maplesoft Maple™ software. The source code is a heavily modified version of Maple™ code written by Professor Junping Shi for his course titled “Math 490: Partial Differential Equations and Mathematical Biology.” The original Maple™ code is provided on Prof. Shi’s course website. The modified source code is attached in Appendices A and B. All simulation parameters discussed in the following sections are listed in Appendix C.
7.4 Simulation results

7.4.1 Dissociative diffusion with immobile vacancies

The standard dissociative diffusion model via mass action kinetics is extended to materials with high vacancy concentrations. Three main insights are discussed through the simulations: First, material conditions in vacancy-rich materials largely determine the concentration and the shape of the impurity diffusion profile. Second, semi-Fickian impurity diffusion profiles – based on Eqs. (7-15) and (7-16) – can be obtained even though the assumption $C_V = C_V^{eq}$ no longer holds. Third, the apparent diffusion coefficient is a function of the initial vacancy concentration $C_V^{ini}$.

All species except for the foreign interstitials are immobile in the simulations, so the intrinsic vacancy diffusion coefficient is zero:

$$D_V = 0.$$  
(7-23)

With Eq. (7-23), Eq. (7-9) becomes

$$\frac{\partial C_V}{\partial t} = -\delta.$$  
(7-24)

The initial vacancy concentration $C_V^{ini}$ is arbitrarily set to a value as high as unity that is the same at all position points. The equilibrium vacancy concentration $C_V^{eq}$ is also set to varying values as high as unity in the simulations which can be equal to $C_V^{ini}$. It also will be shown that the absolute magnitude of $C_V^{eq}$ numerically matters less than the ratio $C_S^{eq}/C_V^{eq}$, $C_i^{eq}$ and $C_S^{eq}$ are also arbitrarily set to 0.01 arb. unit and 1 arb. unit respectively ($C_S^{eq}/C_i^{eq}$ ratio of 100) as the substitutional solubility may be greater than the interstitial solubility [59]. $D_i$ is set to $10^3$ nm$^2$s$^{-1}$ ($1 \times 10^{-11}$ cm$^2$s$^{-1}$). The unitless $C_V^{ini}$, $C_V^{eq}$, $C_S^{eq}$, and $C_i^{eq}$ values defined above may mean equivalence to 1 at. %, 1 at. %, 1 at. %, and 0.01 at. % respectively or smaller concentrations in the same proportions. Relative differences in the unitless concentrations of the species are enough to draw conclusions from the simulations. The insights of the simulations are also still valid for different $D_i$ values. $C_V^{eq}$ in this set of simulations contains an assumption: $C_V^{eq}$ is set prior to the impurity diffusion and does not account for the possibility of being altered by the impurity atoms due to interaction which is addressed in section 7.4.3.
The ratio of $k_F$ to $k_R$ is determined by Eq. (7-7) and the rate constants themselves are set sufficiently large that the law of mass action is virtually fulfilled everywhere at all times. It should be pointed out that if the law of mass action is strictly fulfilled, $\delta$ becomes zero which is physically impossible. A small deviation from the equilibrium in Eq. (7-11) is always required for a net $i-V$ reaction to proceed [59], [140]. The Dirichlet (fixed) boundary condition is used at the first position point for the foreign interstitials at $C_i^{eq}$. The Neumann (reflecting) boundary condition is applied to the first position point of substitutionals and vacancies in addition to the last position point for all species [144]. It is emphasized that due to the dictated boundary conditions in the simulations, interstitial sites at position $x = 0$ are the only entry points for impurity atoms.

![Simulated foreign substitutional $C_S$ diffusion profiles](image)

**Figure 7.1** – Simulated foreign substitutional $C_S$ diffusion profiles (circles) with $C_S^{eq}/C_V^{eq} = 1$ at various diffusion durations and their limited-source equation fits (solid lines): (a) 250 s; (b) 500 s; (c) 1,000 s; (d) 2,000 s. The profiles are due to the dissociative diffusion mechanism in a material with initial condition of $C_V = 1$ arb. unit, $D_i = 10^9 \text{nm}^2 \text{s}^{-1}$ $(1 \times 10^{11} \text{cm}^2 \text{s}^{-1})$, and constant surface foreign interstitial concentration $C_i^{eq} = 0.01$ arb. unit (not shown).

Shaded circles in Figure 7.1 show the simulated foreign substitutional concentration $C_S$ as a function of depth into a thin film as typically seen with radiotracer diffusion experiments, with four different diffusion durations between 250 seconds and 2,000 seconds in the depth of hundreds of nanometers. The four curves (solid lines) are fitted with the same $D_{eff}^i$ ($\sim 9.9 \text{nm}^2 \text{s}^{-1}$ or $9.9 \times 10^{-14} \text{cm}^2 \text{s}^{-1}$) via the limited-source equation (Eqs. (7-16) and (7-18)) reasonably well, despite the non-equilibrium vacancy concentration that otherwise suggests non-Fickian profiles. Further simulations reveal that Eq. (7-16) is not the proper expression for the dissociative diffusion under a non-equilibrium vacancy
concentration profile. A modified $D_{eff}^{ini}$ expression incorporating the initial vacancy concentration $C_{V}^{ini}$ is found to be valid:

$$D_{eff}^{ini} \approx \frac{c_{i}^{eq} D_{i}}{c_{i}^{eq} + c_{S}^{eq} \left(\frac{C_{V}^{ini}}{C_{V}^{eq}}\right)}$$  \hspace{1cm} (7-25)

Varying values of $C_{i}^{eq}$, $C_{S}^{eq}$, $C_{V}^{eq}$, $C_{V}^{ini}$, and $D_{i}$ does not change the validity of $D_{eff}^{ini}$. Eq. (7-25) still generates semi-Fickian diffusion profiles with different values of $C_{V}^{ini}$ as long as the $C_{S}^{eq} / C_{V}^{eq}$ ratio remains close to or less than unity.

Figure 7.2 – Simulated concentration profiles for all three different species: vacancies $C_{V}$, foreign substitutionals $C_{S}$, and foreign interstitials $C_{i}$ for curve (d) in Figure 7.1. The inset figure shows the same plot with a non-logarithmic y-axis.

Because of the Dirichlet boundary condition (constant source) of foreign interstitials at the surface, the traditional dissociative diffusion-reaction theory demands a constant-source $C_{S}$ profile described by the $D_{eff}^{i}$ in Eq. (7-16) rather than a limited-source profile [59]. The deviation from the constant-source diffusion profile shape is due to the violation of Eq. (7-14). The simulated $C_{V}$ profile in Figure 7.2 at the diffusion duration of 2,000 seconds (cf. curve (d) in Figure 7.1) shows a non-equilibrium vacancy profile. The vacancy concentration decreases close to the surface to accommodate the arriving interstitials. Vacancy depletion decreases with increasing depth. The $C_{i}$ diffusion profile is
weakly representative of the constant source fixed at $C_{i}^{eq}$ at the first position point and can be approximated with Eqs. (7-17) and (7-25).

To study how varying $C_{S}^{eq}$ under constant $C_{i}^{eq}$ (0.01 arb. unit) and $C_{V}^{eq}$ (1 arb. unit) impacts the shape of the $C_{S}$ profile, normalized $C_{S}$-depth diffusion profiles with different $C_{S}^{eq}/C_{V}^{eq}$ ratios are generated from the simulations (Figure 7.3). The depth is normalized to the point where $C_{S}$ drops by three orders of magnitude. $C_{S}$ is normalized to the maximum $C_{S}$ at the surface. This normalization method is chosen for two reasons. First, changing $C_{S}^{eq}$ perturbs the apparent diffusion coefficient (Eq. (7-25)) and thus spatially distorts the diffusion profiles away from each other. Second, varying $C_{S}^{eq}$ changes the maximum apparent concentration at the surface. The dual-normalization allows for a pure analysis of the diffusion profile shape. Figure 7.4 shows some of the non-normalized analogs of the curves in Figure 7.3.

![Normalized simulated $C_{S}$-depth diffusion profiles with different equilibrium substitutional concentration to equilibrium vacancy concentration ratios ($C_{S}^{eq}/C_{V}^{eq}$) and their impact on the dissociative diffusion mechanism-induced $C_{S}$ profiles in a material with initial condition of $C_{V}^{eq}$ = 1 arb. unit.](image)

Figure 7.3 – Normalized simulated $C_{S}$-depth diffusion profiles with different equilibrium substitutional concentration to equilibrium vacancy concentration ratios ($C_{S}^{eq}/C_{V}^{eq}$) and their impact on the dissociative diffusion mechanism-induced $C_{S}$ profiles in a material with initial condition of $C_{V}^{eq}$ = 1 arb. unit.

The standard constant- and limited-source diffusion profiles are included in Figure 7.3 for reference. The $C_{S}$ profile shape seen in Figure 7.1 curve (d) and Figure 7.2 correspond to the curve (e) in Figure 7.3. The simulated $C_{S}$ profile has an adequate fitting with the limited-source profile. Departure from the fitting occurs close to the surface where the limited-source equation predicts a higher $C_{S}$ than the simulated $C_{S}^{eq}/C_{V}^{eq}$ = 1 profile. Decreasing $C_{S}^{eq}$ with respect to
$C_{V}^{eq}$ shifts the $C_S$ profile shape into an intermediate region of a blend between the constant- and limited-source profile shapes (curves (b) and (c) in Figure 7.3). The constant-source profile shape (curve (a) in Figure 7.3) becomes the lower limit for further decreases in the ratio. Large increases of the ratio above unity causes non-negligible divergence from the constant- and limited-source profile shapes.

![Graph of $C_{S}^{eq}/C_{V}^{eq}$ ratio vs. Depth (nm)](image)

Figure 7.4 – Selected non-normalized simulated $C_S$-depth diffusion profiles from Fig. 7.3; after diffusion time of 500 s with $D_i = 10^3$ nm$^2$s$^{-1}$ ($1 \times 10^{-11}$ cm$^2$s$^{-1}$) using the same initial condition $C_{V}^{ini} = 1$ arb. unit.

The simulation results of Figure 7.3 can be generalized to any concentration in the numerator and denominator of the $C_{S}^{eq}/C_{V}^{eq}$ ratio, independent of the actual value of $C_{i}^{eq}$. For example – assuming instant fulfillment of the law of mass action – the set of $C_{S}^{eq} = 0.1$ arb. unit and $C_{V}^{eq} = 0.1$ arb. unit produces the same curve shape and concentration compared to $C_{S}^{eq} = 1$ arb. unit and $C_{V}^{eq} = 1$ arb. unit (curve (c) in Figure 7.3) for any given set of $C_{i}^{eq}$ and $C_{V}^{ini}$ (Eq. (7-25)). This can be understood by referring to Eq. (7-7). When $C_{S}^{eq}/C_{V}^{eq}$ equals unity, they cancel each other in the ratio in Eq. (7-7), so varying the actual magnitude in the numerator and the denominator while maintaining a ratio of unity yields the same numerical result.

Interpreting the actual magnitudes of the numerator and denominator in the $C_{S}^{eq}/C_{V}^{eq}$ ratio must be taken with care. The imposed local equilibrium condition in Eq. (7-11) can lead to $S$ incorporation in the depth exceeding the equilibrium concentration of substitutionals $C_{S}^{eq}$ in the material. Per the definition of $C_{S}^{eq}$, the $C_S$ concentration in the
depth should not exceed $C_S^{eq}$, otherwise a tendency for a net $S$ outdiffusion and/or a secondary phase nucleation is created.

![Diagram](image)

Figure 7.5 – Simulated $C_S$-depth diffusion profiles with different initial vacancy concentration $C_V^{ini}$ values; after diffusion time of 250 s with $D_i = 10^3 \text{nm}^2\text{s}^{-1}$ ($1 \times 10^{-11} \text{cm}^2\text{s}^{-1}$). All curves have the same $C_S^{eq}/C_V^{eq}$ ratio (1 arb. unit / 1 arb. unit) = 1, thus they all have the same shape as curve (b) in Figure 7.4.

Next, the initial vacancy concentration $C_V^{ini}$ is allowed to vary while $C_S^{eq}$, $C_V^{eq}$, and $C_i^{eq}$ are fixed at 1 arb. unit, 1 arb. unit, and 0.01 arb. unit respectively. The $C_V^{ini}$-varying simulation results are shown in Figure 7.5. As the initial concentration of vacancies decrease, the apparent diffusion coefficient increases. The physical interpretation is that with fewer vacancies, the more likely the foreign interstitials atoms will travel farther before finding a vacancy to recombine with. The vacancies might be viewed as traps for the foreign interstitials. As long as the diffusion profiles are reasonably Fickian – that is, $C_S^{eq}/C_V^{eq}$ does not significantly exceed unity – the apparent diffusion coefficient is described by Eq. (7-25) which has a $C_V^{ini}$ dependency. Note that when $C_V^{ini}$ approaches $C_V^{eq}$, Eq. (7-25) becomes

$$D_{eff}^{ini} = \frac{C_i^{eq} D_i}{C_i^{eq} + C_V^{eq} \left( \frac{C_S^{eq}}{C_V^{eq}} \right)}$$  \hspace{1cm} (7-26)

which is exactly the traditional interstitial-limited dissociative diffusion model where $C_V = C_V^{eq}$ is maintained everywhere at all times.
Figure 7.6 – Plot of $D_{\text{eff}}^{\text{ini}}$ of Eq. (7-25) as a function of $C_{\text{V}}^{\text{ini}}$ and $C_{\text{eq}}^{\text{eq}}$. $D_{\text{eff}}^{\text{ini}}$ of Eq. (7-25) is only valid for $C_{\text{eq}}^{\text{eq}}/C_{\text{V}}^{\text{eq}}$ ratios up to unity such that the $C_{\text{V}}^{\text{ini}}$-dependent diffusion profiles are sufficiently Fickian.

Figure 7.6 shows $D_{\text{eff}}^{\text{ini}}$ as a function of $C_{\text{V}}^{\text{ini}}$ and $C_{eq}^{eq}$ using Eq. (7-25). $D_l$ is set to 1 arb. unit and represents the maximum observable diffusion coefficient when $C_{\text{V}}^{\text{ini}}$ equals zero. As $C_{\text{V}}^{\text{ini}}$ increases for a given arbitrary $C_{eq}^{eq}$ value, the apparent $D_{\text{eff}}^{\text{ini}}$ decreases. The $D_{\text{eff}}^{\text{ini}}$ decrease can be significant under certain material conditions. For example, Figure 7.6 curve (a) shows that $D_{\text{eff}}^{\text{ini}}$ is suppressed by two orders of magnitude when $C_{\text{V}}^{\text{ini}}$ is increased by two orders of magnitude from $10^0$ arb. unit to $10^2$ arb. unit. The plots also reveal that $C_{eq}^{eq}$ and $C_{\text{V}}^{\text{ini}}$ must be in certain proportions for the change in $D_{\text{eff}}^{\text{ini}}$ to be observable: with $C_{eq}^{eq} = 10^2$ arb. unit, the change in $D_{\text{eff}}^{\text{ini}}$ may not be observed at $C_{\text{V}}^{\text{ini}}$ values below $10^0$ arb. unit.

7.4.2 Equilibrium vacancy concentration considerations

$C_{\text{V}}^{eq}$ is typically very low in elemental semiconductors on the order of parts per million close to the melting point ($\leq 0.0001$ at. %) [59]. Such physical $C_{\text{V}}^{eq}$ values compared to $C_{\text{eq}}^{eq}$ values tend to be smaller than suggested by the simulations in this paper. The $C_{\text{V}}^{eq}$ values as high as unity are used in the simulations, equal to the equilibrium substitutional concentration $C_{\text{s}}^{eq}$ of unity. They might correspond to 1 at. % and 1 at. % respectively (or 0.1 at. % and 0.1 at. %; 0.01 at. % and 0.01 at. %; etc.). While the $C_{\text{s}}^{eq}/C_{\text{V}}^{eq}$ ratio of unity at low concentrations are more reasonable, the ratio of unity for $C_{\text{s}}^{eq}/C_{\text{V}}^{eq}$ in the case of high $C_{\text{s}}^{eq}$ means that the material thermodynamically dictates a high
equilibrium vacancy concentration. In the following calculation, it’s shown that a thermodynamically high vacancy concentration may be possible. According to Persson et al., the defect concentration in CuInSe$_2$ is determined by the formation energy $\Delta H$ for defect $D$ of charge $q$, $N$ which is the concentration of lattice sites that are substituted by the defect, and temperature $T$ [46]:

$$C_{D,q} (E_F, \mu_\alpha, T) = N \exp\left( - \frac{\Delta H_{D,q}(E_F, \mu_\alpha)}{k_B T} \right)$$  \hspace{1cm} (7-27)

The formation energy $\Delta H$ depends on the Fermi level $E_F$ and the chemical potential $\mu_\alpha$ of atom $\alpha$ dictated by the growth condition (e.g. copper-poor or copper-rich) due to CIGS’ unique tolerance toward significant non-stoichiometry. $k_B$ is the Boltzmann constant. The following values are used for the copper vacancy $V_{Cu}$ concentration calculation: highest calculated $V_{Cu}$ formation energy via first principles of $\sim 0.6$ eV by Zhang et al., which might represent a stoichiometric CuInSe$_2$ thin film, $N = 1 \times 10^{22}$ cm$^{-3}$ – the concentration of copper lattice sites in CuInSe$_2$, and a diffusion temperature $T$ of $500 \, ^0\text{C} \, (\sim 773 \, \text{K})$ [38], [104]. The $V_{Cu}$ concentration then become $\sim 1 \times 10^{18}$ cm$^{-3}$, equivalent to $\sim 0.01$ at. %. If $T$ is raised to $1250 \, ^0\text{C}$ – close to the melting point of CuInSe$_2$, the $V_{Cu}$ concentration increases to 0.1 at. %, three orders of magnitude greater than elemental semiconductors (0.0001 at. %). Thus, a high $C_{V}^{eq}$ may be thermodynamically possible. However, Eq. (7-27) is only valid when CuInSe$_2$ is in equilibrium with its atomic and electron reservoirs as suggested in sections 3.7.3 and 3.7.6. Disconnecting CuInSe$_2$ from the reservoirs means a dependence on stoichiometry for equilibrium defect concentrations in non-stoichiometric materials rather than a dependence on the reservoirs. Thus, two competing effects should be recognized in a diffusion experiment via where impurity atoms are indiffused into a host matrix from the surface via high-temperature annealing (e.g. Zn in CIGS): 1) the redistribution of intrinsic defect concentrations in non-stoichiometric CIGS (e.g. $V_{Cu}$) due to the disconnected reservoirs and 2) the effect of the impurity (e.g. Zn) on the intrinsic defect concentrations. Elucidating these effects is unfortunately no trivial task.

The measured zinc concentration of $\sim 0.2$ at. % and the corresponding zinc diffusion profiles also suggest that the $C_{V}^{eq}$ levels in CIGS might be unusually high in the case of impurity incorporation based on the zinc’s Fickian-like humps in the profiles protruding from both the front and back sides of the thin film. The CIGS:Zn diffusion profiles are striking because zinc diffuser source was deposited on only the front side [145], [146]. The double-hump diffusion profiles have been traditionally attributed to the indiffusion of new vacancies from each of the front and back sides of
the material that react with the awaiting foreign interstitials – the vacancy-limited diffusion condition in Eq. (7-21) [96]. The concentration decrease in copper vacancies because of recombination with some foreign interstitials may be energetically unfavorable as suggested for zinc [145]. $c_{v}^{eq}$ and $c_{s}^{eq}$ at high and low values respectively to represent the energetically unfavorable Zn$_{i}$-V$_{Cu}$ recombination in the $C_{v}^{ini}$ model may not be unreasonable.

Impurity indiffusion in CIGS-related materials promotes further copper depletion – raising the $V_{Cu}$ concentration – has been suggested for CIGS-related materials and may be relevant for the case of CIGS:Zn. Kiss et al. conducted density functional theory (DFT) studies on cadmium in CuIn$_5$Se$_8$, a copper-poor phase of CuInSe$_2$ to study cadmium’s behavior in high-efficient CIGS photovoltaic devices. CuIn$_5$Se$_8$ is believed to form at the CIGS surface, between the p-type CIGS absorber layer and the n-type CdS layer under the copper-poor deposition condition [9]. CuIn$_5$Se$_8$ is sometimes called an ordered defect compound (ODC) or ordered vacancy compound (OVC) due to the periodic rearrangement of atoms and vacancies in the structure. According to the calculations done by Kiss et al., removing two copper atoms (producing two copper vacancies) and inserting one cadmium atom (producing a Cd$_{Cu}$ defect) is energetically favorable compared to removing one copper atom to make one $V_{Cu}$ ($\Delta E \approx 0.35$ eV versus $\Delta E = 0.93$ eV respectively). The number of atoms in the calculation supercell is then decreased to 503 ($504 - 2 + 1$) which means cadmium accounts for ~ 0.2 at. % in the calculation supercell. The cadmium intake of CuIn$_5$Se$_8$ makes additional $V_{Cu}$ energetically favorable at low cadmium concentrations, suggesting that $c_{v}^{eq}$ may be increased.

7.4.3 Dissociative diffusion due to impurity-induced increase in vacancy concentration

To investigate the impact of increasing $c_{v}^{eq}$ due to impurity incorporation in the material – for example, CuIn$_5$Se$_8$ – on the apparent diffusion profile, another model was developed. A straightforward approach involves making $c_{v}^{eq}$ a function of the concentration of substitutionals $C_{s}$ (e.g. the Cd$_{Cu}$ defect):

$$c_{v}^{eq} = c_{v}^{0} + X C_{s}. \quad (7-28)$$

$c_{v}^{0}$ is the equilibrium vacancy concentration of the system without impurity. $X$ is the vacancy enhancement factor and ranges from zero to 1/1,000 to 100,000 in the simulations. A factor $X$ of zero means no change to $c_{v}^{eq}$. A factor $X$ of 1/1,000 physically dictates a $c_{v}^{eq}$ increase by one vacancy for every thousand of incorporated impurity atoms. A factor
of unity corresponds to one additional vacancy for every impurity atom. While a factor of 100,000 is unphysical, it is utilized in the simulations for insight.

This approach is called the $D_{\text{eff}}^X$ model and contains two particular assumptions. First, when an impurity atom is substitutionally incorporated in the material via the $i$-$V$ reaction, the only way the material can restore its original $C_V^0$ value (or higher if $X$ is nonzero and positive according to Eq. (7-28)) in the depth is the indiffusion of vacancies from the front surface. Other mechanisms of generating a vacancy – including ejecting a host material atom from its site to an interstitial site to form a self-interstitial in addition to a vacancy – are not included. Second, $C_V^0$ is significantly smaller than $C_S^{eq}$, in line with the traditional dissociative diffusion theory. Diffusion then becomes vacancy-limited. Every position in the simulation depth may hold its own $C_V^{eq}$ value due to the $C_S$ dependence.

Before discussing the $D_{\text{eff}}^X$ parameters in the simulations, the purpose of the $D_{\text{eff}}^X$ model is elaborated upon. While CuIn$_5$Se$_8$ is considered a copper-poor phase related to CuInSe$_2$, it is stoichiometric in its own respect. CuInSe$_2$ and CuIn$_5$Se$_8$ have similar copper atomic positions. CuIn$_5$Se$_8$ contains fewer intrinsic copper sites while the rest of the copper atomic positions in the CuInSe$_2$ phase become empty interstitial sites in CuIn$_5$Se$_8$ as shown in the crystal structure diagram in Fig. 1 in Ref. [9] (Kiss et al.). The $D_{\text{eff}}^X$ model is for the case where the initially stoichiometric material with a relatively low vacancy population absorbs substitutional impurity atoms – using interstitial sites as the pathway – and increases the vacancy intake due to impurity incorporation as discussed with CuIn$_5$Se$_8$. As explored in section 7.5 below, the $D_{\text{eff}}^X$ model may be inappropriate for CIGS:Zn where the $V_{cu}$ concentration is initially high on the order of 1 at. %.

Eq. (7-19) is set to be valid everywhere in the depth at all time steps. Consequently, the specific diffusion coefficient for $D_l$ becomes irrelevant as the concentration of foreign interstitials is maintained at $C_l^{eq}$ (1 × 10$^{-3}$ arb. unit) at all time steps. The initial vacancy concentration $C_V^{init}$ is also set to 1 × 10$^{-3}$ arb. unit at all positions. $D_V$ is set to 10 nm$^2$s$^{-1}$ (1 × 10$^{-13}$ cm$^2$s$^{-1}$), rendering a vacancy-limited diffusion condition. Because $D_V$ is nonzero – contrary to the $C_V^{init}$ model – the intrinsic vacancy diffusion and reaction follows Eq. (7-9) instead of Eq. (7-23). $C_S^{eq}$ is set at unity. $C_V^{eq}$ at the surface is controlled by Eq. (7-28). $C_V^{eq}$ becomes completely saturated once $C_S$ reaches $C_S^{eq}$. The saturation occurs instantaneously according to the fulfillment of the mass action law everywhere at all times in Eq. (7-11). Eq. (7-7) and
subsequently Eq. (7-6) are recalculated at all positions at every time step because of the spatial dependence of \( C_{V}^{eq} \) in Eq. (7-7).Interstitial sites at position \( x = 0 \) are again the only entry points for impurity atoms.

The data points in Figure 7.7 show the simulated foreign substitutional diffusion profiles after various diffusion durations under the vacancy-limited case with a vacancy enhancement factor \( X = 1 \). The double-logarithmic representation is used to emphasize the near-surface properties of this vacancy-limited dissociative diffusion with the dependence of \( C_{V}^{eq} \) on \( C_{S} \). The vacancy enhancement factor \( X = 1 \) is the case of intake of one cadmium atom in CuIn\(_5\)Se\(_8\) that increases \( C_{V}^{eq} \) by one vacancy per unit concentration. The solid lines are the fit of the simulated data points of a given diffusion duration using the limited-source equation (Eq. (7-18)). As stated above, the equilibrium vacancy concentration at the surface is quickly established where \( C_{V}^{eq} \approx C_{S}^{eq} \) because \( X = 1 \) and \( C_{V}^{0} \) is small. The limited-source equation provides the best fit despite the constant impurity diffuser source at \( x = 0 \). The fitting becomes poorer at greater depths where the limited-source profiles overshoot the simulated \( C_{S} \) profiles. The fitted curves using the limited-source equation all give the same apparent diffusion coefficient \( D_{a} \) of \( \sim 4 \text{ nm}^2\text{s}^{-1} \) using non-linear least squares fitting.

Figure 7.7 – Simulated foreign substitutional \( C_{S} \) diffusion profiles (circles) with \( X = 1 \) at various diffusion durations and their limited-source equation fits (solid lines): (a) 250 s; (b) 500 s; (c) 1,000 s; (d) 2,000 s. The profiles are due to the vacancy-limited dissociative diffusion mechanism with \( D_{V} = 10 \text{ nm}^2\text{s}^{-1} (1 \times 10^{-13} \text{ cm}^2\text{s}^{-1}) \), initial \( C_{V}^{0} = 1 \times 10^{-3} \text{ arb. unit everywhere, and } C_{V}^{eq} = 1 \times 10^{-3} \text{ arb. unit everywhere at all time steps.} \)
The simulated $C_i$, $C_V$, and $C_S$ profiles in Figure 7.8 at the diffusion duration of 500 seconds (cf. curve (b) in Figure 7.7) show features not seen in Figure 7.7. First, the $C_V$ profile is also non-Fickian. Second, $C_S \approx C_V^0$ at depths larger than 150 nm because the instant conversion of most of the vacancies to substitutionals undersaturate the material of vacancies. New vacancies from the front surface is the only mechanism that reestablishes (and exceeds if $X$ is nonzero and positive) the original equilibrium vacancy concentration.

Figure 7.8 – Simulated concentration profiles for all three different species: vacancies $C_V$, foreign substitutionals $C_S$, and foreign interstitials $C_i$ for curve (b) in Figure 7.7.

Next, the simulations are extended to various vacancy enhancement factor values $X$ with everything else kept constant (Figure 7.9 and Figure 7.10). Curve-fitting is done in Figure 7.9 for selected simulated data points from Figure 7.10. Only the intermediate $X$ values – curves (d), (e), and (f) in Figure 7.9 – are fitted using the limited-source equation. Using the constant-source equation gives an even poorer fit. Curves (b) and (d) are better fitted with the constant-source equation. Curve (a) in Figure 7.9 and Figure 7.10 is the limiting case of Eq. (7-21) where the impurity incorporation does not change the original equilibrium vacancy concentration. The apparent diffusion profile then perfectly reflects the constant diffuser source, and the yielded diffusion coefficient $D_{eff}^V$ is exclusively controlled by $D_V$, $C_S^{eq}$, and $C_V^0$. $D_{eff}^V \approx 0.1 \text{ nm}^2\text{s}^{-1} (1 \times 10^{-15} \text{ cm}^2\text{s}^{-1})$. At small $X$ values (e.g. 1/1000), only a small deviation from $D_{eff}^V$ occurs (curve (b) in Figure 7.10). Interestingly, an additional vacancy even for every 10 or 100 incorporated impurity atoms results in a noticeable change in the $C_S$ diffusion profile (curves (c) and (d)) compared to the intrinsic
Figure 7.9 – Simulated foreign substitutional $C_S$ diffusion profiles (circles) at 500 s at various vacancy enhancement factor $X$ and their constant- or limited-source equation fits (solid lines): (a) 0; (b) 1/1,000; (c) 1/100; (d) 1/10; (e) 1; (f) 10; (g) 100,000. The profiles are due to the vacancy-limited dissociative diffusion mechanism with $D_V = 10 \text{ nm}^2\text{s}^{-1}$ ($1 \times 10^{-13} \text{ cm}^2\text{s}^{-1}$), initial $C_V^0 = 1 \times 10^{-3}$ arb. unit, and $C_i^{eq} = 1 \times 10^{-3}$ arb. unit everywhere at all time steps.

Figure 7.10 – Extension of Figure 7.9, simulated foreign substitutional $C_S$ diffusion profiles at 500 s at various vacancy enhancement factor values $X$: (a) 0; (b) 1/1,000; (c) 1/100; (d) 1/10; (e) 1/2; (f) 1; (g) 2; (h) 5; (i) 10; (j) 25; (k) 50; (l) 100; (m) 250; (n) 100,000.

case where $C_V^{eq}$ is not perturbed (curve (a)). Inspecting the curves from (a) to (n) in Figure 7.10, a given curve can be seen to be better fitted using the constant-source equation at low $X$ values, the limited-source equation at moderate $X$
values, and again the constant-source equation at large $X$ values. When $X$ becomes extraordinarily high, the $C_S$ profile converges to the constant-source equation with an apparent diffusion coefficient of $\sim 20 \text{ nm}^2\text{s}^{-1} (2 \times 10^{-13} \text{ cm}^2\text{s}^{-1})$ (cf. curve (g) in Figure 7.9).

If $C_{V}^{eq}$ in Eq. (7-21) is replaced by the $C_{V}^{eq}$ of Eq. (7-28) and $C_S$ is changed to $C_S^{eq}$, a new effective diffusion coefficient is obtained:

$$D_{eff}^X \approx \frac{D_V (C_V^0 + XC_S^{eq})}{(C_V^0 + XC_S^{eq})C_S^{eq}}$$

(7-29)

$D_{eff}^X$ represents the vacancy-limited diffusion coefficient of the dissociative diffusion mechanism containing a $X$ dependence. $D_{eff}^X$ gives comparable diffusion coefficients versus the apparent diffusion coefficients $D_a$ through the standard constant- and limited-source equation fits (solid lines) of the simulation data points (circles) in Figure 7.9. For example, with $X = 1$, the $D_{eff}^X$ model predicts a diffusion coefficient of $5 \text{ nm}^2\text{s}^{-1}$ while the fitted limited-source curve gives $D_a \approx 4 \text{ nm}^2\text{s}^{-1}$. The table of $D_a$ and $D_{eff}^X$ parameters for Figure 7.9 is shown in Appendix C. Negative $X$ values – reduced $C_V^{eq}$ due to impurity incorporation – inhibit the $C_S$ diffusion profile.

7.5 Evaluation of experimental data of impurity diffusion in Cu(In,Ga)Se$_2$

The $D_{eff}^{ini}$ and $D_{eff}^X$ models operate under the assumption of the exceedingly rapid reaction of an $i$-$V$ pair, excluding any possible reaction barrier. The lack of a reaction barrier results in both $V$ annihilation and $S$ incorporation in large amounts. Such behavior might not be realistic as discussed for the $C_S^{eq}/C_V^{eq}$ ratio in the $C_{V}^{ini}$ model. The same concentration profile is generated for a given $C_S^{eq}/C_V^{eq}$ ratio regardless of the actual magnitude in the numerator and denominator. If $C_{V}^{ini}$ is set to a large value as seen in CIGS (e.g. 1 at. %), along with a smaller $C_V^{eq}$ that might reflect thermal equilibrium, $C_S^{eq}$ is forced to be on the same order of magnitude as $C_V^{eq}$ at the most in order to make a semi-Fickian diffusion profile. Even with a smaller $C_S^{eq}$ on the order of the thermal-equilibrium $C_V^{eq} (C_S^{eq}/C_V^{eq} \approx 1)$, a large $S$ concentration profile is still obtained that exceeds $C_S^{eq}$.
The simulations are compared to existing data on zinc, iron, and cadmium diffusion in CIGS [117], [145]–[149]. CIGS:Zn diffusion profiles have two prominent features: 1) the double Fickian-like humps at the front and back sides, and 2) a zinc signal plateau in the middle region. As discussed in section 7.4.2, zinc diffusion may operate under the vacancy-limited dissociative diffusion mechanism in the hump regions. Note that Figure 7.9 shows that at intermediate $X$ factors, the limited-source equation consistently predicts larger $C_S$ in the tail of the diffusion profile versus the $D_{eff}^X$ model (curves (d) and (e)). Several experimental CIGS:Zn diffusion profiles show that the limited-source equation fits slightly overestimate the experimental profiles at relatively low annealing temperatures and durations [145], [146]. The initial surface roughness of the as-deposited CIGS thin film and ion beam-induced sputtering during depth-profiling skew the “true” diffusion profile. Numerical simulations of the impact of surface roughness done by Eschen et al. show that a finite surface roughness broadens the diffusion profile compared to the case of a flat surface [146]. A perfectly flat surface is assumed in the simulations in the present dissertation.

If diffusion-profile broadening due to the finite CIGS surface roughness (root mean square roughness $R_{RMS} \approx 150$ nm) is considered in the CIGS:Zn diffusion experiments, the “true” CIGS:Zn diffusion profiles may actually be reduced in the tail region, further overestimating the limited-source equation. The two humps in the zinc diffusion profiles may be modelled by the $D_{eff}^X$ model if it is assumed that the vacancy concentration increases due to zinc incorporation. A more appropriate $D_{eff}^X$ model would consider the high initial $V_{Cu}$ concentration seen in CIGS. Additionally, Bastek et al. suggest that the copper divacancy may in fact be the mediating defect for zinc diffusion in CIGS since $Zn_{Cu-V_{Cu}}$ is suspected to be the most stable configuration [145]. Divacancy dependence would then need to be incorporated into the model.

The middle region in the CIGS:Zn diffusion profile may be a candidate for study of the $C_{V}^{ini}$ model. The flat zinc signal is believed to be interstitially saturated zinc atoms ($Zn_i$) as discussed by Stolwijk et al. for cobalt in germanium in the middle region of the Ge:Co diffusion profile [96]. Otherwise, it might be the limited incorporation of zinc atoms in copper vacancies ($Zn_{Cu}$) due to the $Zn_i$-$V_{Cu}$ reaction [145], [146]. The $C_{V}^{ini}$ model may be used in either case; the $Zn_{Cu}$ profile might be described through Eq. (7-25) if the plateau region is controlled by $Zn_{Cu}$. Eq. (7-25) is also used for the $Zn_i$ profile if $Zn_i$ dominates. With a thick CIGS film (tens or hundreds of micrometers), a transition from the plateau to a constant- or limited-source diffusion profile occurs. If $c_{S}^{eq}/C_{V}^{eq} \leq 1$ in this region due to the energetically
unfavorable Zn\textsubscript{i}-V\textsubscript{Cu} recombination ($C^\text{eq}_s$ represents the maximum Zn\textsubscript{Cu} incorporation before new vacancies diffuse from the front and back surfaces, and $C^\text{eq}_v$ estimates the thermodynamically preferred V\textsubscript{Cu} concentration in the presence of Zn), the proposed $C^\text{ini}_v$ model may be used by altering the as-deposited V\textsubscript{Cu} concentration. The double-hump zinc profiles – along with the plateau in the middle – were found copper-poor CIGS samples (Cu/(In+Ga) = 0.85) by Bastek et al [145]. If their samples had V\textsubscript{Cu} on the order of 1 at. % as seen via a neutron diffraction study, the experimentally measured zinc diffusion coefficient should increase in a more stoichiometric CIS/CIGS thin film according to the $C^\text{ini}_v$ model in this chapter [123].

Altering the initial copper vacancy concentration and can be done via two methods to study the $C^\text{ini}_v$ model. First, because of the low vacancy formation energies, copper atoms can be pulled out of CIGS onto the CIGS surface to form elemental copper precipitation via electrical bias through a point electrode applied on the surface as shown in Chapter 4. Second, a thin layer of elemental copper can be deposited onto a copper-poor CIGS film to be diffused into the bulk film via annealing to fill the copper vacancies. The impurity indiffusion would be performed after etching the elemental copper off the CIGS surface in the first method and any elemental copper residue in the second method.

The $C^\text{ini}_v$ model might be inappropriate for some impurities in vacancy-rich materials such as iron and cadmium diffusion in CIGS. Steel foils – containing iron – are being used as a flexible supporting substrate in the CIGS roll-to-roll manufacturing process. Iron diffuses through the Mo layer into the CIGS layer during deposition, damaging the photovoltaic performance. Iron is a fast diffuser compared to zinc under a wide temperature range by a factor of ten and displays step function-like diffusion profiles in certain cases [145], [147]. The CIGS:Fe diffusion profiles may be attributed to the $C^\text{ini}_v$ model with a high $C^\text{eq}_s/C^\text{eq}_v$ ratio where $C^\text{eq}_v \gg 1$ at. %. The concentration of iron in CIGS is ~ 1 at. %. The step function-like CIGS:Fe diffusion profiles may actually be due to ion-beam sputtering through the CIGS/Mo interface instead of the $C^\text{ini}_v$ model. The Fe and Mo signals in another paper by the same research group show CIGS depth profiles where the CIGS/Mo interface is sputtered.

As discussed in the preceding chapters, CIGS:Cd diffusion profiles contain two Fickian-like diffusion stages within a single depth profile, a high-signal stage near the surface and a low-signal stage in the depth. The first-stage diffusion coefficients are four orders of magnitude smaller than the second-stage diffusion coefficients. The nature of the two-stage cadmium diffusion profile in CIGS is still unclear. The second stage cadmium diffusion profiles show that
Cadmium has similar Arrhenius diffusion equation as iron in CIGS, suggesting a similar diffusion mechanism [117], [118], [149].

Cadmium was indiffused into a copper-poor CIGS thin film from an elemental source at a high temperature/duration, resulting in a virtually homogenous cadmium distribution of ~ 3 at. % [118]. If 3 at. % is taken to be $C_S^{eq}$ in the $C_V^{ini}$ model and representative of the second-stage cadmium diffusion profile in CIGS, $C_V^{eq}$ must be at least on the same order of magnitude so that $C_S^{eq}/C_V^{eq} \approx 1$ to get a semi-Fickian diffusion profile. A high $C_V^{eq}$ value (1 at. %) due to cadmium incorporation is unlikely. Even applying a smaller $C_V^{eq}$ value as predicted by Eq. (7-27) to the $D_{eff}^{ini}$ model with a high $C_S^{eq}$ would produce non-Fickian profiles, in direct conflict with the published Fickian cadmium diffusion profiles. The vacancy diffusion mechanism – where an impurity atom in the substitutional configuration exchanges position with a neighboring vacancy – may in fact govern for CIGS: Cd and CIGS: Fe instead of an interstitial-based mechanism. According to some first principles works, the CIGS: Cd and CIGS: Fe diffusion equations match that of the copper self-diffusion via the vacancy mechanism [38], [104], [117], [149].

The match between copper and cadmium diffusion coefficients and the dominance of the copper vacancy mechanism for the latter are somewhat unsurprising as the ionic radii of Cu$^+$ and Cd$^{2+}$ are similar (0.096 nm versus 0.097 nm) [40]. It is even less surprising that an interstitial mechanism is more likely to dominate for zinc than for cadmium in CIGS considering the Zn$^{2+}$ ionic radius is ~ 20% smaller than that of Cd$^{2+}$ (0.074 nm versus 0.097 nm) [150].
The goal of the present work was to identify the cadmium diffusion mechanism(s) in Cu(In,Ga)Se$_2$ (CIGS) via experimental and theoretical methods including secondary ion mass spectroscopy (SIMS), Auger electron spectroscopy (AES), and numerical methods extended from the standard diffusion-reaction kinetics theory. Figure 8.1 provides a summary of known experimental (lattice) diffusion data for various impurities in CIGS (cadmium, iron,
sodium, and zinc). Existing grain boundary diffusion data is not included; lattice diffusion is the primary focus of the present work. One of the contributions of the present dissertation is the characterization of the first-stage cadmium diffusion profiles in CIGS (curve (a)).

It is striking that the majority of diffusion curves lie in the close vicinity of the theoretically determined copper self-diffusion curve (via the copper vacancy diffusion mechanism, based on Eq. (5-22)). The curves suggest that the copper vacancy may be the dominating diffusion vehicle for these impurities in copper-poor CIGS materials thanks to the 1 at. % copper vacancies typically seen in the CIGS absorber layer in photovoltaic-grade CIGS photovoltaic devices. Sodium, however, appears to operate via a different diffusion mechanism based on its location in the Arrhenius plot in Figure 8.1 [151]. The nature of this mechanism may be interstitial-based if the copper vacancy mediates second-stage cadmium, iron, and first-stage zinc diffusion.

The naming of the first-stage zinc diffusion coefficients is derived from the Fickian-like humps in the CIGS:Zn diffusion profiles [145], [146]. The flat plateau of zinc signal in the middle region of the CIGS depth profile is tentatively denoted as the second-stage zinc diffusion as it may represent rapid zinc interstitial diffusion. This second-stage zinc diffusion profile may be utilized for future studies. The first- and second-stage zinc diffusion profiles may have completely different properties versus those of the first- and second-stage cadmium diffusion profiles that were explored in this dissertation.

Like the sodium data, the first-stage cadmium data has its own position in the Arrhenius plot in Figure 8.1, possibly reflecting an unique diffusion mechanism. There is a significant disagreement between the first-stage cadmium diffusion and the copper self-diffusion curves ((a) versus (c)). As discussed in sections 5.4 and 7.4.2, due to the energetically favorable diffusion kinetics suggested by first-principles calculations by Kiss et al., it is suspected that over the course of cadmium indiffusion from the diffuser source, the near-surface region of CIGS thin film is transformed to a copper-poor CIGS phase due to copper outdiffusion. In this copper-poor phase, another diffusion mechanism may then dominate – for example, the kick-out mechanism as investigated by Kiss et al. [124].

The \( C_{i}^{\text{int}} \) model developed in Chapter 7 reveal that if the interstitial diffusion of an impurity is sufficiently rapid in vacancy-rich materials like CIGS, the concentration profile of an impurity – due to the non-equilibrium annihilation of vacancies via the interstitial-vacancy recombination that generates impurity substitutionals – may be modeled by
an effective diffusion coefficient that is inversely proportional to the initial vacancy concentration. The $D_{eff}^X$ model in the second part of the simulations in Chapter 7 suggests semi-Fickian diffusion profiles can still be obtained even if impurity incorporation raises the equilibrium vacancy concentration of the material, a behavior that may be relevant in CIGS-related materials.
Appendix A

Maple source code: dissociative diffusion with immobile vacancies

clear internal memory
> restart:

load the plot package
> with(plots):

length L of diffusion space (nm) and spatial step h (nm)
> L := 400: h := 20:

diffusion time T (s) and time step k (s)
> T := 250: k := 0.00008:

vacancy, substitutional, and interstitial diffusion coefficients (um^2/s)
> Dv := (1e-1000)*((10^-7)*2):
> Ds := (1e-1000)*((10^-7)*2):
> Di := (1e-11)*((10^-7)*2):

equilibrium vacancy, substitutional, and interstitial concentrations (arb. unit)
> VEq := 1:
> SEq := 1:
> IEq := 0.91:

vacancy concentration initial condition (arb. unit)
> Vini := 1:

equilibrium constant of interstitial-vacancy reaction
> equil-cons := SEq/(VEq*IEq):

speed of interstitial-vacancy reaction
> speed := 10:

rate constants for forward and reverse interstitial-vacancy reactions
> kF := equil-cons*speed:
> kR := speed:

iteration formula constant
> 0 := k/k^2:
> cl := c/Di:

total number of spatial grids
> n := floor(L/h) + 1: x := [seq(0+(i-1)*h, i=1..n)]:

total number of time grids
> n := floor(T/k) + 1: t := [seq(0+(j-1)*k, j=1..n)]:

initialize vacancy, substitutional, and interstitial solution matrices by zero
> cv := matrix(n, m, [seq(seq(0.0, j=1..2), i=1..n))):
> cs := matrix(n, m, [seq(seq(0.0, j=1..2), i=1..n))):
> ci := matrix(n, m, [seq(seq(0.0, j=1..2), i=1..n))):
initial vacancy, substitutional, and interstitial conditions
> for i from 1 to n do
>  c[i][1] = kEq;
>  cv[i][1] = Vini;
>  cs[i][1] = 0;
> end;

> for i from 2 to n do
>  cv[i][1] = Vini;
>  cs[i][1] = 0;
> end;

iteration interval for if then else statement for plot animation memory storage
> q = 1:
> q1 = 500:
> q2 = 1:
> qe = 500:

first set of plots
> A[2] = plot([seq([x[i], cv[i][1]], i = 1..n)], color = "Red");
> B[2] = plot([seq([x[i], cv[i][1]], i = 1..n)], color = "Blue");
> C[2] = plot([seq([x[i], cl[i][1]], i = 1..n)], color = "Black");

> q1 = q1 + q;
> q = q1 + 1:
> q2 = q2 + 1:

time march
> for i from 1 to n-1 do
>   Dvp := (1/2)*(Dv[i] + Dv[i-1]);
>   Dvm := (1/2)*(Dv[i] + Dv[i+1]);
>   Dpr := (1/2)*(Dp[i] + Dp[i-1]);
>   Dmr := (1/2)*(Dp[i] + Dp[i+1]);
> #Dirichlet boundary conditions
> #cv[1,2] = VEq;
> #cs[1,2] = SEq;
> cl[1,2] = lEq;

#Neumann boundary conditions

#Dirichlet boundary conditions
> cv[n,2] := VEq;
> cs[n,2] := SEq;
> cl[n,2] := lEq;

#Neumann boundary conditions
for i from 1 to n-1 do
Dvp := (1/2)*(Dv[i] + Dv[i-1]);
Dvm := (1/2)*(Dv[i] + Dv[i+1]);
Dpr := (1/2)*(Dp[i] + Dp[i-1]);
Dmr := (1/2)*(Dp[i] + Dp[i+1]);
#Dirichlet boundary conditions
#cv[1,2] = VEq;
#cs[1,2] = SEq;
#cl[1,2] = lEq;
#Neumann boundary conditions
for i from 2 to n-1 do
Dvp := (1/2)*(Dv[i] + Dv[i-1]);
Dvm := (1/2)*(Dv[i] + Dv[i+1]);
Dpr := (1/2)*(Dp[i] + Dp[i-1]);
Dmr := (1/2)*(Dp[i] + Dp[i+1]);
#Dirichlet boundary conditions
#cv[1,2] = VEq;
#cs[1,2] = SEq;
#cl[1,2] = lEq;

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# Neumann boundary conditions

c[i, 2] = c[i, 1] * (c[i, 1] + 1) + (c[i, 1] + 1) * c[i, 1] + c[i, 1] + 1

c[i, 2] = c[i, 1] * (c[i, 1] + 1) + (c[i, 1] + 1) * c[i, 1] + c[i, 1] + 1

c[i, 2] = c[i, 1] * (c[i, 1] + 1) + (c[i, 1] + 1) * c[i, 1] + c[i, 1] + 1

c[i, 2] = c[i, 1] * (c[i, 1] + 1) + (c[i, 1] + 1) * c[i, 1] + c[i, 1] + 1

end do

if q = q0
    then
        A(q2) = plot(seq(x[i], i ∈ 1..n), color = "Blue");
        B(q2) = plot(seq(x[i], i ∈ 1..n), color = "Red");
        C(q2) = plot(seq(x[i], i ∈ 1..n), color = "Black");
        q1 = q0 + q;
        q = q+1;
    else
        q = q + 1
    end if;

for i from 1 to n do
    c[i, 1] = c[i, 2];
end do;

display plots for last time step

> display(A(q2 = 1), B(q2 = 1), C(q2 = 1));

animated plots

> d1 = display(seq(A(q2), q2 ∈ 1..(q2-1)), insequence = true);
> d2 = display(seq(B(q2), q2 ∈ 1..(q2-1)), insequence = true);
> d3 = display(seq(C(q2), q2 ∈ 1..(q2-1)), insequence = true);
> display(d1, d2, d3);
Appendix B

Maple source code: dissociative diffusion due to impurity-induced vacancy concentration increase

```maple
# clears internal memory
> restart;

# loads the plot package
> with(plots):

# length L of diffusion space (nm) and spatial step h (nm)
> L := 160; h := 10;

# diffusion time T (s) and time step k (s)
> T := 500; x := 0.004;

# vacancy, substitutional, and interstitial diffusion coefficients (nm^2/s)
> Dv := (1e-13)*(10^(-7))^2;  # vacancy concentration increase
> Ds := (1e-1600)*(10^(-7))^2;  # substitutional concentration increase
> Di := (1e-11)*(10^(-7))^2;   # interstitial concentration increase

# equilibrium vacancy, substitutional, and interstitial concentrations (arb. unit)
> VbEq0 := 0.001;
> CbEq0 := 1;
> CiEq0 := 0.001;

# vacancy concentration initial condition (arb. unit)
> V0 := VbEq0;

# speed of interstitial-vacancy reaction
> speed := 1;

# iteration formula constant
> c := k/h^2;
> cl := c/Di;

# total number of spatial grids
> n := floor(L/h)+1:
> x := [seq(0+(i-1)*h, i=1..n)];

# total number of time grids
> m := floor(T/k)+1:
> t := [seq(0+(j-1)*k, j=1..m)];

# initialize vacancy, substitutional, and interstitial solution matrices by zero
> uv := matrix(n, m, [seq([seq(0.0, j=1..m)], i=1..n)));
> us := matrix(n, m, [seq([seq(0.0, j=1..m)], i=1..n)));
> ui := matrix(n, m, [seq([seq(0.0, j=1..m)], i=1..n)));

# initial vacancy, substitutional, and interstitial conditions
> for i from 1 to n do
    uv[i, 1] := V0;
    us[i, 1] := C0;
    ui[i, 1] := C0;
end;

> for i from 2 to n do
    ui[i, 1] := 0;
    uv[i, 1] := V0;
    us[i, 1] := C0;
end;
```

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iteration values for if then else statement for plot animation memory storage

q := 1;
q1 := 200;
q2 := 1;
q3 := 200;

first set of plots

U[2] := plot(seq([u[i][1], w[i][1]], i = 1..n), color = "Blue");
V[2] := plot(seq([u[i][1], w[i][1]], i = 1..n), color = "Red");
M[2] := plot(seq([u[i][1], w[i][1]], i = 1..n), color = "Black");
R[2] := plot(seq([u[i][1], (0)], i = 1..n), color = "Green");
qu := q1 + q2;
qu := q3 + q1;
qu := q1 + 1;

time march

for j from 1 to n-1 do
    Dvp := (1/2) * (Dv + (Dv));
    Dvm := (1/2) * (Dv + (Dv));
    Ddp := (1/2) * (Dv * Dv) + (Dv * Dv));
    Ddm := (1/2) * (Dv * Dv) + (Dv * Dv));
    Dli := (1/2) * (Di + (Di));
    Dln := (1/2) * (Di + (Di));
    #Dirichlet boundary conditions
    u[1, 2] := VcuEqr + 1 * u[1, 1];
    w[1, 2] := VcuEqr;
    u[1, 2] := CduEq;
    #Neumann boundary conditions
    VcuEqr := VcuEqr + 1 * u[1, 1];
    equil_cone := CduEq / (VcuEqr * CduEq);
    kpl := equil_cone / speed;
    knl := speed;
    #uv[1, 2] := c * (u[1, 2] * u[1, 1] + (Dv * (Dv + (Dv))) + (Dv * (Dv + (Dv))));
    uv[1, 2] := c * (u[1, 2] * u[1, 1] + (Dv * (Dv + (Dv))) + (Dv * (Dv + (Dv))));
    #uv[1, 2] := c * (u[1, 2] * u[1, 1] + (Dv * (Dv + (Dv))) + (Dv * (Dv + (Dv))));
    #uv[1, 2] := c * (u[1, 2] * u[1, 1] + (Dv * (Dv + (Dv))) + (Dv * (Dv + (Dv))));
    #uv[1, 2] := c * (u[1, 2] * u[1, 1] + (Dv * (Dv + (Dv))) + (Dv * (Dv + (Dv))));
    #uv[1, 2] := c * (u[1, 2] * u[1, 1] + (Dv * (Dv + (Dv))) + (Dv * (Dv + (Dv))));
    #uv[1, 2] := c * (u[1, 2] * u[1, 1] + (Dv * (Dv + (Dv))) + (Dv * (Dv + (Dv))));
    #uv[1, 2] := c * (u[1, 2] * u[1, 1] + (Dv * (Dv + (Dv))) + (Dv * (Dv + (Dv))));
    for j from 1 to n-1 do
        Dvp := (1/2) * (Dv + (Dv));
        Dvm := (1/2) * (Dv + (Dv));
        Ddp := (1/2) * (Dv * Dv) + (Dv * Dv));
        Ddm := (1/2) * (Dv * Dv) + (Dv * Dv));
        Dli := (1/2) * (Di + (Di));
        Dln := (1/2) * (Di + (Di));
        #Dirichlet boundary conditions
        u[n, 2] := VcuEqr;
        w[n, 2] := CduEq;
        u[n, 2] := CduEq / (VcuEqr * CduEq);
        kpl := equil_cone / speed;
        knl := speed;
        #uv[n, 2] := c * (u[n, 2] * u[n-1, 1] + (Dv * u[n-1, 1]) + (Dv * u[n-1, 1]));
        uv[n, 2] := c * (u[n, 2] * u[n-1, 1] + (Dv * u[n-1, 1]) + (Dv * u[n-1, 1]));
        #uv[n, 2] := c * (u[n, 2] * u[n-1, 1] + (Dv * u[n-1, 1]) + (Dv * u[n-1, 1]));
        #uv[n, 2] := c * (u[n, 2] * u[n-1, 1] + (Dv * u[n-1, 1]) + (Dv * u[n-1, 1]));
        #uv[n, 2] := c * (u[n, 2] * u[n-1, 1] + (Dv * u[n-1, 1]) + (Dv * u[n-1, 1]));
        #uv[n, 2] := c * (u[n, 2] * u[n-1, 1] + (Dv * u[n-1, 1]) + (Dv * u[n-1, 1]));
        #uv[n, 2] := c * (u[n, 2] * u[n-1, 1] + (Dv * u[n-1, 1]) + (Dv * u[n-1, 1]));
        for j from 1 to n-1 do
            Dvp := (1/2) * (Dv + (Dv));
            Dvm := (1/2) * (Dv + (Dv));
            Ddp := (1/2) * (Dv * Dv) + (Dv * Dv));
            Ddm := (1/2) * (Dv * Dv) + (Dv * Dv));
            Dli := (1/2) * (Di + (Di));
            Dln := (1/2) * (Di + (Di));
            #Dirichlet boundary conditions
            u[1, 2] := VcuEqr;
            w[1, 2] := CduEq;
            u[1, 2] := CduEq;
Neumann boundary conditions
VeqK = VeqK0 + 1 * us[1, 1];
equilibrium = C0*VeqK/(VeqK + C0*Eq);
kpl = equilibrium * speed;
Kn1 = speed;

uv[1, 2] = (c*(Dvp*uv[1, 1]) + (Dvm*uv[1, 0]) + (uv[1, 1] - (c*(Dvp + Dvm))) + kpl*Kn1*us[1, 1]*ksp*us[1, 1]*uv[1, 1];
us[1, 2] = (c*(Dvp*us[1, 1]) + (Dvm*us[1, 0]) + (us[1, 1] - (c*(Dvp + Dvm))) + kpl*uv[1, 1]*us[1, 1]*ksp*us[1, 1]*us[1, 1];

if q = q1 then
    U[Q[i]] = plot([seq(x[i], us[i, j], i = 1 .. n)], color = "Blue");
    V[Q[i]] = plot([seq(x[i], uv[i, j], i = 1 .. n)], color = "Red");
    W[Q[i]] = plot([seq(x[i], us[i, j], i = 1 .. n)], color = "Black");
    if us[1, 1]*uv[1, 1] = 0 then
        M[Q[i]] = plot([seq(x[i], ksp*us[1, 1]*us[1, 1]*uv[1, 1], i = 1 .. n)], color = "Green");
    else
        M[Q[i]] = plot([seq(x[i], ksp*us[1, 1]*us[1, 1]*uv[1, 1], i = 1 .. n)], color = "Green");
    end if:
else
    q := q + 1:
end if:
for i from 1 to n do
    u[i, 1] := u[i, 2];
    u[i, 2] := 0;
    uv[i, 1] := uv[i, 2];
    uv[i, 2] := 0;
    us[i, 1] := us[i, 2];
    us[i, 2] := 0;
end do;
end do;
generate plots
> for i from 1 to 1 do
    Us[i] := plot([seq(x[i], us[i, j], i = 1 .. n)], color = "Blue");
end do:
for i from 1 to 1 do
    U[i] := plot([seq(x[i], uv[i, j], i = 1 .. n)], color = "Red");
end do:
for i from 1 to 1 do
    Us[i] := plot([seq(x[i], us[i, j], i = 1 .. n)], color = "Black");
end do:
display plots for last time step
> display(U[1], Uv[1], U[1]);

animated plots
> d1 := display([seq(U[i], q = 1 .. (Q2 - 1))]), insequence = true; 
> d2 := display([seq(V[i], q = 1 .. (Q2 - 1))]), insequence = true; 
> d3 := display([seq(W[i], q = 1 .. (Q2 - 1))]), insequence = true; 
> d4 := display([seq(M[i], q = 1 .. (Q2 - 1))]), insequence = true; 
> display(d1, d2, d3);
Appendix C

Tabulated diffusion-reaction simulation parameters

<table>
<thead>
<tr>
<th>Figure</th>
<th>$C_i^{eq}$ (arb. unit)</th>
<th>$C_V^{eq}$ (arb. unit)</th>
<th>$C_S^{eq}$ (arb. unit)</th>
<th>$C_V^{ini}$ (arb. unit)</th>
<th>$C_V^0$ (arb. unit)</th>
<th>$D_i$ (nm$^2$s$^{-1}$)</th>
<th>$D_V$ (nm$^2$s$^{-1}$)</th>
<th>$X$ (arb. unit)</th>
</tr>
</thead>
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<td>7.1</td>
<td>0.01</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>N/A</td>
<td>1,000</td>
<td>0</td>
<td>N/A</td>
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<tr>
<td>7.2</td>
<td>0.01</td>
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<td>1</td>
<td>1</td>
<td>N/A</td>
<td>1,000</td>
<td>0</td>
<td>N/A</td>
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<td>N/A</td>
<td>1,000</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
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<td>0</td>
<td>N/A</td>
</tr>
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<td>7.5</td>
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<td>1</td>
<td>Varied</td>
<td>N/A</td>
<td>1000</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>7.6</td>
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<td>Varied</td>
<td>Varied</td>
<td>Varied</td>
<td>N/A</td>
<td>$\frac{1}{m}$ (arb. unit)</td>
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<td>N/A</td>
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<td>1</td>
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<tr>
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<td>$\infty$</td>
<td>10</td>
<td>Varied</td>
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</tbody>
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Table A. Simulation parameters of all figures in Chapter 7.
<table>
<thead>
<tr>
<th>Curve</th>
<th>( X ) (arb. unit)</th>
<th>Diffuser-source curve fitting equation (solid line)</th>
<th>( D_a ) (nm²s⁻¹)</th>
<th>( D_{eff}^X ) (nm²s⁻¹)</th>
</tr>
</thead>
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<td>(a)</td>
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<td>N/A</td>
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<td>(c)</td>
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<td>Constant</td>
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<td>0.99</td>
</tr>
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<td>5</td>
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<tr>
<td>(f)</td>
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<td>Limited</td>
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Table B. Simulation parameters of each curve in Figure 7.9 in section 7.4.3.
Bibliography


