# DIFFUSION OF SODIUM IN

# COPPER INDIUM GALLIUM DISELENIDE BASED MATERIALS

by

Robert V. Forest

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

Summer 2015

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# DIFFUSION OF SODIUM IN COPPER INDIUM GALLIUM DISELENIDE BASED MATERIALS

by

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# TABLE OF CONTENTS

LI LI A	LIST OF TABLESxiLIST OF FIGURESxiiABSTRACTxvi					
C	hapto	er				
1	INT	RODU	UCTION	1		
	1.1	Photo	voltaic Energy	1		
		$1.1.1 \\ 1.1.2$	Basics of Solar Cell Operation	$3 \\ 6$		
	1.2	CIGS	Solar Cells	8		
		$1.2.1 \\ 1.2.2 \\ 1.2.3 \\ 1.2.4 \\ 1.2.5$	Substrates for CIGS devices	8 9 10 11 11		
	1.3	Sodiu	m in CIGS Solar Cells	11		
		$1.3.1 \\ 1.3.2$	Incorporation of Sodium	12 13		
	$\begin{array}{c} 1.4 \\ 1.5 \end{array}$	Impac Scope	et of Chemical Engineering Fundamentals	$\begin{array}{c} 15\\ 15\end{array}$		
<b>2</b>	EX	PERIN	MENTAL METHODS	17		
	2.1	Introd	luction	17		

	2.2	Thin	Film Deposition	17
		2.2.1 2.2.2 2.2.3 2.2.4 2.2.5	Magnetron Sputtering of Molybdenum	17 18 20 20 21
	2.3	Mater	ial Characterization	21
		2.3.1 2.3.2 2.3.3	Energy-dispersive X-ray Spectroscopy (EDS) and X-ray Fluorescence Spectroscopy (XRF)	21 23 25
	2.4	Electr	onic Characterization	27
3	SOI	2.4.1 2.4.2 2.4.3	Conductivity	27 28 29 <b>32</b>
	$3.1 \\ 3.2$	Introc Measu	luction	32 32
		3.2.1	Donth Drofling Techniques	ച
		3.2.2	Surface Accumulation Techniques	$\frac{33}{34}$
	$3.3 \\ 3.4$	3.2.2 Mecha Diffus	Depth Froming Techniques	33 34 34 36
	3.3 3.4	3.2.2 Mecha Diffus 3.4.1 3.4.2 3.4.3	Depth Froming Techniques	33 34 36 37 37 39
	3.3 3.4 3.5	3.2.2 Mecha Diffus 3.4.1 3.4.2 3.4.3 Chem	Depth Froming Techniques	<ul> <li>33</li> <li>34</li> <li>34</li> <li>36</li> <li>37</li> <li>37</li> <li>39</li> <li>39</li> </ul>

4	SODIUM DIFFUSION THROUGH THE MOLYBDENUM BACK CONTACT LAYER		
	4.1	Introduction	43
	4.2	Sodium Diffusion through Molybdenum Thin Films	45
	4.3	Results and Discussion	46
		4.3.1 Characterization of Mo Films	46
		4.3.2 Controlling Surface Oxygen on Mo	48
		4.3.3 Relationship of Surface Oxygen to Na Segregation	52
		4.3.4 Diffusion Modeling	54
	4.4	Conclusions	62
5	DIF SOI	FUSION IN CuInSe <sub>2</sub> SINGLE CRYSTALS: ROLE OF DIUM IN THE GRAIN INTERIOR	64
	5.1	Introduction	64
	5.2	Sodium Incorporation into $CuInSe_2$ Single Crystal	67
		5.2.1 Preparation of Single Crystals	67
		5.2.2 Characterization of Crystals	67
		5.2.3 Sodium Treatment of Single Crystals	68
	5.3	Results and Discussion	70
		5.3.1 Analysis of Diffusion Profile	70
		5.3.2 Analysis of the Extended Defect Structure	72
		5.3.3 Diffusion Kinetics at Dislocations	74
		5.3.4 Mechanism for Lattice Diffusion of Sodium in $CuInSe_2$	77
	5.4	Conclusions	80
6	RE OF	VERSIBILITY OF ELECTRICAL PROPERTIES: ROLE SODIUM AT GRAIN BOUNDARIES	81
	6.1	Introduction	81

	6.2	Measuring Electrical Properties as a Function of Sodium Content	83			
		6.2.1Sample Deposition6.2.2Control of Na Concentration Within Films6.2.3Electrical Measurements	83 84 86			
	6.3	Results and Discussion	86			
		<ul><li>6.3.1 Conductivity and Seebeck Effect</li></ul>	86 90			
	6.4	Conclusions	91			
7	UN FRO	DERSTANDING THE EFFECT OF Na IN $Cu(In,Ga)Se_2$ OM A SOLID-STATE DIFFUSION PERSPECTIVE	93			
	$7.1 \\ 7.2 \\ 7.3$	Introduction	93 94 98			
		7.3.1Na at CIGS Grain Boundaries	98 103			
	7.4	Opportunities and Challenges	104			
		7.4.1Atomic Defects Related to Na7.4.2Na at the CIGS/CdS Junction	105 108			
	7.5	Concluding Remarks	112			
8	CO FU	CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK				
	8.1	Summary of Results	113			
		8.1.1Na Diffusion Through Mo	113 114			

	8.1.3	Na in CIGS Grain Boundaries	116
8.2	Recon	amendations for Future Work	118
	8.2.1	Extended Single Crystal Diffusion Study	118
	8.2.2	Effect of Na at the CdS Junction	119
	8.2.3	Effect of Na Migration on Long-Term Device Stability	120
	8.2.4	Effects of Other Alkali Elements	122
REFE	RENC	ES	125
Appen	dix		
PE	RMISS	SION LETTERS	142

# LIST OF TABLES

4.1	List of parameters used in the diffusion model along with approximated values	58
4.2	Optimized values of $D_b$ and $s'$ for various temperatures and surface oxygen concentrations	59
5.1	Atomic composition for Bridgman and melt-grown crystals as measured by XRF	68
5.2	Diffusion coefficients and solubility limits obtained from best fit to SIMS depth profiles of sodium in CIS.	73
7.1	JV characteristics and average Na concentrations of the devices presented in Figure 7.2.	99

# LIST OF FIGURES

1.1	Map of the U.S. depicting average solar irradiance. The area needed to meet current U.S. energy demands with current PV technology is shaded in green	2
1.2	Schematic of a p-n junction. Diffusion of majority carriers across the junction leads to annihilation exposing ionized dopants that create an electric field.	4
1.3	(a) Cross section illustration of a p-n diode used as a solar cell. (b) Energy band diagram of a p-n junction depicting the creation and separation of charge carriers	6
1.4	Comparison of absorption vs. thickness between a crystalline silicon cell and CIGS thin film cell.	7
1.5	CIGS unit cell. Cu atoms are red, In/Ga are blue, and Se are yellow	9
1.6	(a) Cross-section illustration of a complete solar cell and (b) scanning electron micrograph of CIGS on Mo coated SLG	10
1.7	APT measurement of CIGS depicting the segregation of Na at grain boundaries and small amounts of Na at grain interiors	14
2.1	Schematic of bell jar chamber used for CIGS co-evaporation	19
2.2	Illustration of X-ray emission process	22
2.3	Illustration of (a) the photoelectron and (b) Auger processes	23
2.4	Illustration of SIMS at an atomic scale	26
2.5	Schematic of a Kelvin probe measurement	27

2.6	Schematic of the apparatus used for measuring the Seebeck coefficient.	29
2.7	Diagram of a typical JV curve	30
3.1	(a) Vacancy mechanism with diffusing atom in transition state. (b) Energy vs. position of diffusing atom showing the activation energy of a lattice jump	36
3.2	Typical concentration profiles in polycrystalline materials for (a) type A, (b) type B, and (c) type C diffusion kinetics. $\ldots$	37
3.3	(a) Concentration profile for type B diffusion in a thin film. (b) Depth profile from Gilmer and Farrel for diffusion in a thin film.	38
4.1	<ul> <li>(a) Cross-section SEM image of sputter deposited Mo on SLG.</li> <li>(b) Enlarged schematic of seven Mo grains with arrows denoting the diffusion path of Na.</li> <li>(c) Schematic depicting two adjacent Mo grains with their shared grain boundary. Dimensions used for diffusion modeling are depicted and are not shown to scale.</li> </ul>	47
4.2	(a) XPS spectrum of Mo 3d region for as-deposited Mo surface with peaks for oxide and metallic species. (b) XPS spectrum of Na 1s region for SLG/Mo sample after heating at 400 °C for 10 min.	49
4.3	(a) XPS and (b) SIMS depth profile through surface of Mo coated SLG	50
4.4	Surface oxygen content of Mo on SLG as measured by XPS for samples (a) heated in ambient air at 200 °C and (b) sputtered in vacuum.	51
4.5	Na concentration on Mo surface as measured by XPS as a function of heating time at 400 °C for samples with a high amount of surface oxygen (red diamonds) and low amount of surface oxygen (blue squares)	52

4.6	The saturation concentration of Na as a function of initial surface oxygen on the Mo film after heating in vacuum at 400 °C (blue squares) or 500 °C (red diamonds). Surface oxygen was varied from as-deposited films by either sputter etching or heating in air at 200 °C.	53
4.7	The Hwang-Balluffi model (solid line) fit to experimental data (circles) for as-deposited SLG/Mo samples after diffusion at 400 °C, $350$ °C, and 300 °C. Dashed lines denote the model with $\pm 25\%$ of the optimized grain boundary diffusion coefficient.	59
4.8	Arrhenius plot for the grain boundary diffusion coefficient	61
4.9	Ellingham diagram depicting Gibbs free energy of formation for $Na_2O$ , $MoO_2$ , and $MoO_3$ .	62
5.1	Laue photographs of (a) Bridgman grown and (b) melt-grown CIS.	69
5.2	SIMS Na depth profiles in the NaF-coated areas of the (a) Bridgman grown CIS and (b) melt-grown CIS after heating at 420 °C (orange) and 480 °C (red) along with best fit line (black). The Na profile on the masked uncoated area of the Bridgman crystal is shown in blue.	71
5.3	Electron diffraction pattern for the Bridgman crystal	74
5.4	A series of BF and DF TEM images of the Bridgman crystal taken under a $g = [224]^*$ two-beam condition. (a) A multi-beam BF image with no apparent contrast of dislocations. (b) and (c) are a pair of BF and DF images from the same region with dislocations circled	75
5.5	A series of BF and DF TEM images of the melt grown crystal taken under a $g = [112]^*$ two-beam condition. (a) A multi-beam BF image showing two isolated grains embedded in the CIS matrix, and (b) a BF image with dislocations circled	76
5.6	Illustration of a hybrid interstitial-substitutional diffusion mechanism for an arbitrary solute/solvent system	79

6.1	Schematic of Mo pattern used with ACIGS samples on alumina substrates for conductivity and Seebeck measurements	84
6.2	Flow diagram depicting material deposition, Na removal, and electrical measurements.	85
6.3	(a) Room temperature ACIGS conductivity and (b) Seebeck coefficient as a function of heating time at 200 °C for the Na-free control (open circles), after the 1 <sup>st</sup> NaF treatment (orange diamonds), and after the 2 <sup>nd</sup> NaF treatment (red triangles)	88
6.4	Seebeck coefficient (dashed red line) and conductivity (solid black line) as a function of majority carrier concentration for an arbitrary semiconductor with $p >> n$ from Equations 6.3 to 6.4.	90
6.5	Schematic of the passivation of $\mathrm{In}_{\mathrm{Cu}}$ defects with Na	91
7.1	ACIGS $V_{OC}$ (a) and efficiency (b) vs. age of Mo before ACIGS deposition. Red lines are displayed to serve as a visual aid. Data provided by Chris Thompson	96
7.2	(a) Na SIMS depth profiles through CIGS for an as-deposited film and after Na removal. (b) JV curves for CIGS devices with standard Na (solid) and with Na removal (dashed)	99
7.3	Band diagram of the region near a grain boundary in CIGS. A positively charged grain boundary (a) repels holes creating a depletion region and attracts electrons increasing recombination. Na can passivate donor defects at grain boundaries (b) eliminating the depletion region, possibly creating accumulation regions (dotted lines) and lowering electron recombination.	101
7.4	(a) Na 1s spectra measured with XPS of CIGS after rinsing (blue) then after 16 hours exposure to room air at 25 °C. (b) Na accumulation on the surface of CIGS measured with XPS as a function of time exposed to room air.	109
7.5	SIMS depth profiles on a CIGS/CdS for (a) the entire film and (b) near the CdS heterojunction. The dashed line denotes the nominal CdS interface.	111

# ABSTRACT

Cu(In,Ga)Se<sub>2</sub> (CIGS) thin film photovoltaic technology is in the early stage of commercialization with an annual manufacturing capacity over 1 GW and has demonstrated the highest module efficiency of any of the thin film technologies. However there still is a lack of fundamental understanding of the relationship between the materials properties and solar cell device operation. It is well known that the incorporation of a small amount of Na into the CIGS film during processing is essential for high efficiency devices. However, there are conflicting explanations for how Na behaves at the atomic scale. This dissertation investigates how Na is incorporated into the CIGS device structure and evaluates the diffusion of Na into CIGS grain boundaries and bulk crystallites.

Most commercially available CIGS modules are fabricated on soda-lime glass coated with Mo as the back electric contact, and Na in the glass diffuses through the Mo layer into the CIGS during film growth. The transport of Na through Mo was evaluated using a combination of X-ray photoelectron surface accumulation measurements along with diffusion modeling to obtain diffusion coefficients at several temperatures. It was determined that Na diffusion in Mo only occurs along grain boundaries and that oxygen provides an additional driving force to enhance Na transport. Device data revealed that older Mo substrates with a greater amount of surface oxide resulted in slightly higher efficiencies due to enhanced Na incorporation caused by the oxide. This finding shows that Mo substrates could potentially undergo an oxidation treatment prior to CIGS deposition to optimize the incorporation of Na.

While it is known that Na segregates at CIGS grain boundaries, debate remains whether Na diffusion into grain interiors is significant enough to affect device performance. Single crystal  $CuInSe_2$  was used as a model system to represent the grain interiors of CIGS, and crystals of different composition and dislocation density were evaluated. Diffusion coefficients and solubility were obtained for each crystal at two temperatures using concentration depth profiles measured after Na diffusion with secondary ion mass spectrometry. Characterization of extended defects with transmission electron microscopy confirmed that the dislocation density was too low to significantly impact the effective diffusion coefficient. The Cu-poor crystal had a higher solubility suggesting that Na diffusion is mediated by Cu-vacancies, but this was not accompanied by an expected increase in diffusion coefficient. The activation energy for diffusion was similar to values expected for interstitial diffusion, but the large size of Na<sup>+</sup> ions should result in a solubility that is much lower than what was experimentally measured. To resolve this contradiction, a hybrid interstitialsubstitutional mechanism is proposed that combines the fast diffusion of interstitial atoms with the high solubility common for substitutional impurities. Lattice diffusion of Na proceeds fast enough that CIGS grain interiors should have Na concentrations near the solubility of  $10^{18} \,\mathrm{cm}^{-3}$  limit when manufactured under standard conditions.

To determine if Na in grain interiors affects device performance, Na was selectively removed from only grain boundaries using a series of heat treatments in air at 200 °C to drive Na out of grain boundaries onto the CIGS surface followed by rinsing in water to dissolve accumulated Na. Due to the low temperature of this heat treatment, Na at grain boundaries remained mobile while diffusion within bulk grains was too slow for significant removal. Changes in electrical properties were evaluated by measuring conductivity and Seebeck coefficient and both were found to decrease as Na was removed reaching a value similar to Na-free films. This simultaneous decrease in both properties can be explained by the compensation of donor defects causing an increase in the free carrier concentration. Devices also showed a decrease in efficiency and open-circuit voltage after Na removal confirming that the beneficial effects of Na must be due to its presence at grain boundaries and not associated with Na within the grains. The findings of this dissertation potentially could provide guidance for rational optimization of Na incorporation procedures in the manufacturing of CIGS solar cells.

# Chapter 1 INTRODUCTION

#### 1.1 Photovoltaic Energy

The rising demand for energy and growing environmental concerns have led to a large effort in developing technologies that harness clean, renewable sources of energy. Photovoltaics (PV), the direct conversion of sunlight into electricity, remains one of the most promising clean energy technologies. Sunlight is the most abundant energy source making PV ideal for widespread use. The maximum potential energy generation rate of solar energy after taking into account limitations such as land use restrictions and conversion efficiencies is larger than 1500 exajoules per year [1]. This is several times larger than the current world-wide energy demand and much larger than other alternative energy sources, with wind energy having a maximum technical potential of 640 EJ/year and biomass 276 EJ/year [2]. Solar abundance is so great that the current U.S. electricity demand could be met with PV covering an area of less than 40000 square miles, which is much smaller than the total land mass of the U.S. as shown in Figure 1.1.

There are still several technical hurdles that must be overcome for widespread adoption of PV energy, and there is considerable research into lowering costs and increasing efficiencies of solar cells. Silicon is the most established PV materials today, but thin film materials such as Cu(In,Ga)Se<sub>2</sub> (CIGS) have significant potential to provide low-cost energy. In CIGS solar cells, efficiency can be greatly improved



Figure 1.1: Map of the U.S. depicting average solar irradiance. The area needed to meet current U.S. energy demands with current PV technology is shaded in green. This map was created by the National Renewable Energy Laboratory for the U.S. Department of Energy. by incorporating  $\sim 0.1$  at% Na, but the cause of this effect is not well understood. This dissertation investigates the diffusion of Na in CIGS and related materials to expand the current understanding of how Na benefits device performance.

#### 1.1.1 Basics of Solar Cell Operation

Photovoltaic electricity is the result of extracting electrons that have been excited by sunlight to create a usable electric current. Semiconductors are an ideal PV material since they (1) can effectively absorb incident light to create excited charge carriers, and (2) can extract these excited charge carriers before they return to their non-excited states. Charge carriers in semiconductors consist of either electrons excited to the conduction band (CB) or electron vacancies left behind in the valence band (VB). These VB vacancies are commonly referred to as holes ( $h^+$ ) and for convenience can be treated as positively charged particles.

Semiconductors can be made so they have an excess of either charge carrier at room temperature. Semiconductors with an excess of holes are referred to as p-type, and semiconductors with an excess of electrons are n-type. An excess of either charge carrier is achieved by the incorporation of impurities known as dopants. Dopants are atoms which easily give up electrons to the CB (donors) or accept electrons from the VB (acceptors). A semiconductor with both acceptors and donors is known as a compensated material, which is usually undesirable because competing carriers annihilate one another causing an overall decrease in carrier concentration. A pure semiconductor without dopants is known as an intrinsic semiconductor, and charge carriers in these materials are created by thermal excitation of electrons across the band gap so that the concentration of electrons equals the concentration of hole.



Figure 1.2: Schematic of a p-n junction. Diffusion of majority carriers across the junction leads to annihilation exposing ionized dopants that create an electric field.

When light strikes a semiconductor, it can excite an electron to the CB leaving behind a hole in the VB. The energy of the light must exceed the difference between the CB minimum and the VB maximum, referred to as the band gap  $(E_g)$ , otherwise the light passes unabsorbed. Without a driving force for separation, the electron and hole eventually recombine and the absorbed energy is dissipated as heat. The presence of an electric field will cause the electron and hole to drift in opposite directions so that they can be extracted as an electric current.

An electric field is created in a semiconductor by stacking n and p-type materials forming a diode as shown in Figure 1.2. When a p-type material is in contact with an n-type material, holes from the p-type layer diffuse into the n-type layer where they are annihilated by the excess of electrons. The reverse happens for electrons in the n-type layer. After annihilation only immobilized charged dopant atoms remain in a region known as the space charge region or depletion region. The charged dopants create an electric field that opposes diffusion of majority carriers creating an equilibrium that limits the width of the space charge region. The exact width of the space charge region is a function of doping densities in both the n-type and p-type layers. While the built-in electric field created by the diode opposes the diffusion of majority carriers, it aids in the transport of minority carriers across the junction allowing for separation of photogenerated charge carriers. Figure 1.3 shows the process of carrier photo-excitation and separation. When a minority carrier is excited within the space charge region the electric field quickly sweeps it across the junction. If charge carriers are excited outside the electric field, they must first diffuse to the space charge region before they can be extracted. Therefore, the total collection length of a p-n solar cell is the sum of the depletion region width and the average length a minority carrier diffuses before it recombines. Any process which causes excited carriers to recombine before they are extracted will result in a decreased device performance. The process of charge separation can also be illustrated through the use of energy band diagrams (Figure 1.3b), which depict band energy vs. position. The electric field is denoted by curvature in the bands, known as band bending.

Typically one of the layers, known as the absorber, is much thicker and is responsible for absorbing most incident light. The other layer, known as the buffer layer, has a much higher doping concentration so that the space charge region extends deep into the absorber. A p-n junction where the absorber and buffer layers consist of the same material with opposite dopants is known as a homojunction while one that consists of different materials is known as a heterojunction. Traditional silicon solar cells usually have homojunctions while most thin film cells have heterojunctions.



**Figure 1.3:** (a) Cross section illustration of a p-n diode used as a solar cell. (b) Energy band diagram of a p-n junction depicting the creation and separation of charge carriers.

#### 1.1.2 Thin Film Photovoltaics

Thin film PV encompasses a class of materials that absorb light very effectively. Due to their high absorption coefficients, these materials absorb 100% of light with a thickness that is typically two orders of magnitude thinner than silicon as depicted in Figure 1.4.

Thin-film solar cells often are often as thin as 1 µm to 5 µm, allowing for a significant reduction in materials costs. The thinness of these materials allows them to be deposited on flexible substrates without any significant loss in performance. Flexible substrates allow for continuous roll-to-roll processing which can significantly lower manufacturing compared to batch processing. Flexible solar cells can also be used in a range of applications not possible for rigid silicon cells. The downside of thin-film materials is that they are less efficient than single crystal Si producing less power per area and research often focuses on improving thin film efficiency.

Thin film research originally began in the 1970s with the development of  $Cu_2Se$  solar cells, though research into this material was eventually abandoned



Figure 1.4: Comparison of absorption vs. thickness between a crystalline silicon cell and CIGS thin film cell.

due to stability problems. Today thin film solar cells have reached the low costs and high efficiencies needed to compete with traditional Si-based technologies. Thin film solar cells are in the early stages of commercialization with a current global manufacturing capacity of approximately 5 GW,<sup>†</sup> and production capacity is expected to double by the end of 2018.<sup>‡</sup> The two most prevalent thin-film materials today are CdTe and CIGS. Historically, CdTe has dominated commercial thin film manufacturing although recently CIGS manufacturing capacity has been catching up. Also, CIGS has consistently demonstrated higher champion efficiencies than CdTe.

 $<sup>^\</sup>dagger\,$  Based on 2015 manufacturing capacities of the following companies: Solar Frontier—1.1 GW, Hanergy—2.2 GW, First Solar—1.9 GW

<sup>&</sup>lt;sup>‡</sup> Based on planned expansions for the following companies: Hanergy—Additional 3 GW by 2016, First Solar—Additional 1.6 GW by 2018

#### 1.2 CIGS Solar Cells

CIGS is a highly studied p-type thin film material that has the highest record efficiencies of all thin-film technologies with champion cell efficiencies that regularly exceed 20% [3–9]. CIGS is a solid-solution of CuInSe<sub>2</sub> and CuGaSe<sub>2</sub> and has a chalcopyrite lattice structure as shown in Figure 1.6. Its chemical formula is most accurately described by CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub>. The Ga content can vary from x = 0 to 1 giving direct control of the band gap, which varies from 1.0 eV to 1.6 eV. Cells with a Ga content in the range of x = 0.3 to 0.4 typically give the best performance.

The Cu content of the film can greatly deviate from stoichiometry, and high efficiency CIGS devices have been made with Cu / (In + Ga) ratios ranging from 0.7 to 1.0. This high tolerance to deviations from stoichiometry has been attributed to the formation of neutral  $2 V_{Cu}$  + In<sub>Cu</sub> defect complexes [10]. This notation is commonly used to describe crystalline point defects where the subscript denotes the lattice site, the normal text denotes the atom that has substituted on to that lattice site, and V denotes a vacancy [11].

CIGS is does not require external doping and instead its native defects act as dopants. Device quality CIGS is p-type due to the large concentration of copper vacancies [12] which act as acceptor defects. CIGS is a highly compensated material due to the low formation energies of  $In_{Cu}$  and  $V_{Se}$  donor defects, and CIGS can even be made n-type if grown Se-poor [11].

#### 1.2.1 Substrates for CIGS devices

A completed CIGS device consists of several layers as depicted in Figure 1.6, and because these layers are so thin, they must be supported on a substrate. The most important factors for a substrate are it must have a coefficient of thermal



Figure 1.5: CIGS unit cell. Cu atoms are red, In/Ga are blue, and Se are yellow [13].

expansion that matches CIGS and it must not introduce impurities that are harmful to the device performance [14]. A mismatched coefficient of thermal expansion can lead to strain that harms device performance, and at its worst can cause severe adhesion problems. The substrate sits at the back of the cell and therefore can be opaque since light does not have to pass through it. Commonly used substrates include soda-lime glass, metal foils [15–18], and polyimide films [19–23].

#### **1.2.2** Back Electric Contact

The first layer deposited on the substrate is a thin 1 µm metallic layer that serves as the back electric contact for the solar cell. Any resistive losses from the electrical contacts will result in loss of efficiency, so this layer is optimized to have a high conductivity. Molybdenum is almost always used because it provides adequate conductivity without reacting with CIGS or introducing any detrimental impurities. Often a thin layer of  $Mo_2Se$  forms at the Mo surface during CIGS deposition, which promotes the creation of an ohmic contact [24–26].



Figure 1.6: (a) Cross-section illustration of a complete solar cell and (b) scanning electron micrograph of CIGS on Mo coated SLG.

## 1.2.3 Absorber Layer

The absorber layer is comprised of CIGS and is deposited directly on Mo. This layer is responsible for absorbing light and creating excited charge carriers. CIGS is usually deposited using either physical vapor deposition (PVD) of the constituent elements (discussed in Section 2.2.2) or by chemical vapor deposition (CVD) with a precursor film of metallic Cu, In, and Ga. PVD deposition involves evaporating elemental precursors onto a heated substrate where they condense and react to form CIGS. CVD deposition involves the reaction of Cu, In, and Ga metal precursor layers with either Se vapor or H<sub>2</sub>Se. The absorber layer is usually 2  $\mu$ m to 3  $\mu$ m since most incident light is absorbed in this distance, however, there is current research that investigates ultra-thin absorber layers with thicknesses less than 500 nm [27].

#### 1.2.4 Buffer Layer

To complete the diode needed for charge separation, a thin buffer layer of n-type CdS is deposited on CIGS. This layer is usually only 50 nm thick to reduce electrical and optical losses while still creating an electric field for charge separation. It is speculated that Cd can diffuse into CIGS creating  $Cd_{Cu}$  donor defects, and at high enough concentration the near the interface becomes n-type creating a buried homojunction that improves device quality [28].

#### 1.2.5 Front Electric Contact

A front electric contact is deposited directly on the CdS layer. The front contact must be both transparent to light and electrically conductive so transparent conductive oxides are used for this layer. To further enhance conductivity of the front contact a thin metallic grid is deposited on the transparent conducting oxide layer. The size of this grid optimizes the trade-off between enhanced conductivity and the amount of light blocked.

#### 1.3 Sodium in CIGS Solar Cells

A crucial aspect in the manufacturing of CIGS solar cells is the introduction of a small amount of Na into the CIGS absorber layer. It is well known that a Na concentration on the order of  $1 \times 10^{19}$  atoms/cm<sup>3</sup> will increase both device open circuit voltage (V<sub>OC</sub>) and fill factor (FF) [22, 29–32] (for a description of these parameters, see Section 2.4.3). Incorporation of Na can lead to a relative increase in efficiency as high as 60% [33] and is necessary for manufacture of high efficiency and cost-effective modules.

#### **1.3.1** Incorporation of Sodium

Na can be incorporated using a wide variety of techniques. The simplest and most widely used method is to use a soda-lime glass (SLG) substrate as a Na source. SLG contains ~14 wt% Na<sub>2</sub>O, and during the high temperatures used during the CIGS deposition Na become mobile and diffuses though the Mo layer into the growing CIGS film. This incorporation method is simple and inexpensive, but some studies report that it can result in a non-uniform Na concentration [34].

An external source of Na from various Na compounds can be used instead of relying on Na from the substrate. Earlier studies used Na<sub>2</sub>Se [30, 35–39], but NaF is now more common because it is less hygroscopic, easier to handle, and gives the same improvements in performance. An external Na source allows for the use of Na-free substrates, such as flexible metal foils. If SLG is used along with an external Na source, an alkali diffusion barrier such as  $Al_2O_3$  or  $SiO_2$  is often deposited on SLG [32, 40] since very large amounts of Na can be detrimental to device performance [30, 41–44].

Na compounds can be added before [30, 32, 45–47], during [36–40, 43, 48, 49], or after CIGS depositions [20, 33, 43, 50], all with similar increases in efficiency. Na incorporation before CIGS deposition involves depositing a Na-precursor layer on either the substrate or Mo, however, thick precursor layers can cause adhesion problems if the precursor Na-compound layer is too thick [20]. An alternative to a precursor layer is to incorporate Na during the Mo deposition by doping the Mo sputter target with Na [18, 51–54]. Deposition of Na compounds during the CIGS deposition is commonly referred to as co-evaporation, and the exact time at which Na is added can alter electrical properties [43]. Na deposition after CIGS is known as a post deposition treatment (PDT).

#### 1.3.2 Effects of Na in CIGS

Na has been attributed with a number of changes to CIGS such as the formation of larger grains [34], preferential orientation of grains [55], increased p-type conductivity [46], and the inhibition of In/Ga interdiffusion [56]. It is unclear if the effects of Na are due to a single mechanism or from several beneficial effects. However, since the low temperatures used during NaF PDT cannot alter the CIGS grain structure, effects that require Na during growth, such as an increase in grain size with Na, cannot be the primary mechanism for improving CIGS [33]. Therefore, this dissertation places more focus on the non-structural effects of Na.

It is unclear if these effects of Na are due to its presence at grain boundaries or within grain interiors. It has long been established that Na in CIGS segregates at grain boundaries [57], but recent atom-probe tomography measurements reveal that a small amount of Na diffuses into the bulk reaching concentrations up to 100 ppm (Figure 1.7) [58]. At these concentrations, Na has the potential to impact device performance as discussed in Chapter 5. However, it is still not known if Na within grain interiors plays an active role in improving device performance, and this issue is one of the key focuses of this dissertation.



Figure 1.7: APT measurement of CIGS depicting the segregation of Na at grain boundaries and small amounts of Na at grain interiors. Reprinted from Ref. [58], Copyright 2010, with permission from Elsevier.

#### 1.4 Impact of Chemical Engineering Fundamentals

There are many opportunities for applying chemical engineering principles to CIGS research. The core chemical engineering fundamentals of thermodynamics, reaction kinetics, and transport phenomena each have important applications in studying these materials. Thermodynamics is useful for studying equilibrium phase behavior of CIGS as well as determining which atomic defects should be most prevalent based on defect formation enthalpies. The study of reaction kinetics is particularly applicable for the chemical vapor deposition of CIGS, since reaction rates of metallic precursors with the vapor phase Se precursor are very important in controlling the formation of device quality material.

This dissertation places particular emphasis on the transport of Na in CIGS to improve the current understanding of how Na benefits CIGS solar cells. The electrical effects of Na have been well characterized, but much less is known about its transport properties in CIGS. Diffusion impacts the incorporation and uniformity of Na into CIGS as well as its segregation at grain boundaries. The atomic diffusion mechanism provides information about which defects Na likely interacts with. For example, Na diffusion that proceeds along vacancy site will have a very different migration barrier than if it diffuses interstitially, and this can be estimated from activation energies measured in diffusion experiments.

### 1.5 Scope of Dissertation

Although the effects of Na in CIGS have been known for 22 years, the mechanism for how it improves device performance is still not fully understood and there are still several open questions, particularly regarding the transport of Na. As previously discussed, this dissertation places an emphasis on the diffusion of Na in CIGS-related materials to answer these questions and is organized as follows.

Chapter 2 begins by discussing experimental methods used including thin film deposition, materials characterization techniques, and electrical characterization techniques. Chapter 3 discusses the fundamentals of solid-state diffusion including how diffusion in solids differs from diffusion in fluids, how crystalline defects affect diffusion, and common solid-state diffusion measurement techniques. Chapters 4 to 6 are devoted to answering some of the open questions remaining about Na in CIGS:

- 1. What is the diffusion mechanism for Na in Mo and how does the Mo layer impact incorporation into CIGS when SLG is used as a source? (Chapter 4)
- 2. To what extent is Na incorporated into CIGS grain interiors, and by what diffusion mechanism? (Chapter 5)
- 3. Are the benefits of Na mostly due to its presence at grain boundaries or within grain interiors? (Chapter 6)
- 4. What crystalline defects are responsible for improving CIGS when Na is added? (Chapter 6)

Finally, Chapter 7 integrates these previous results and presents a mechanism for how Na impacts CIGS performance.

# Chapter 2 EXPERIMENTAL METHODS

## 2.1 Introduction

This dissertation involves the deposition of thin films as well as the electric and material characterization of these films. This chapter discusses deposition techniques followed by an explanations of the various analytical techniques used.

## 2.2 Thin Film Deposition

A completed CIGS device is comprised of several different layers deposited sequentially on a substrate as previously discussed with Section 1.2. CIGS devices in this dissertation were all deposited on  $1 \text{ in } \times 1$  in substrates of various materials with the most commonly used being soda-lime glass and Na-free alumina. This section provides details for each deposition step used in this dissertation.

### 2.2.1 Magnetron Sputtering of Molybdenum

All Mo films in this study were deposited by DC magnetron sputtering. In this technique, a DC bias is applied to a pure Mo target in the presence of Ar gas.  $Ar^+$  ions are formed and accelerated towards the target where they impact with enough energy to eject Mo ions. The ejected Mo then travels to the sample where it loses its energy and condenses to form a film. A magnetron confines ions near the surface of the target allowing the plasma to be sustained at lower pressures.
Sputter pressure has a large effect on Mo microstructure with lower pressures creating denser films and higher pressures creating more porous films [59–61]. This trend is due to sputtered atoms losing more energy with a higher pressure plasma which in turn reduces Mo mobility on sample [61]. It has been demonstrated that Na transport from SLG is enhanced in porous Mo layers, and this is likely due to increased oxygen at grain boundaries in porous films, which can aid in the transport of Na [62]. However, porous Mo films are less conductive because of an increase in grain boundary oxides [61].

For Mo depositions in this study, a sputter current of 1.5 A was maintained with an Ar pressure of 0.24 Pa and a rotation rate of five revolutions per minute for 75 min resulting in 700 nm thick films.

#### 2.2.2 Physical Vapor Deposition of CIGS

The CIGS absorber layer was deposited by the co-evaporation under vacuum of the individual elements from separate sources. Evaporation took place in a bell jar system shown in Figure 2.1 (figure used with permission from Ref. [12]). Elemental sources reside in Knudson cells for more reliable control over material flux. Evaporation rates are set based on the desired film composition and are controlled with the source temperature which is chosen based on vapor pressures for each element. The Cu / (In + Ga) ratio was usually targeted at 0.3 to 0.4.

During CIGS deposition the substrate is heated to promote large grain growth at a constant temperature that typically fell between 400 °C to 600 °C. The evaporation source temperature can follow a number of various profiles, and this dissertation utilized the common single stage and three-stage deposition methods.



Figure 2.1: Schematic of bell jar chamber used for CIGS co-evaporation. Figure used with permission from Ref. [12]. Copyright 2011, John Wiley and Sons.

### Single-stage deposition

The simplest deposition method is to maintain a constant evaporation rate from all sources over the duration of the run. While this process is simple, it can be difficult to maintain exact control over the target stoichiometry. It often takes several trials to determine the exact source temperature that gives the desired target composition.

# Three-stage deposition

An alternative to the single-stage process is the three-stage process, which gives finer control over the target composition. The first stage involves deposition of In, Ga, and Se without Cu to form an alloy of  $In_2Se_3$  and  $Ga_2Se_3$ . The second stage begins once the desired thickness of  $(In,Ga)_2Se_3$  is reached. The second stage involves deposition of Cu and Se to form  $Cu_2Se$  where it diffuses into  $(In,Ga)_2Se_3$ and reacts to form CIGS. This stage continues until stoichiometric  $CuIn_xGa_{1-x}Se_2$  is formed. At the end of the second stage  $Cu_2Se$  accumulates on the surface changing the emissivity of the sample allowing for in-situ end point detection. The final stage involves deposition of In, Ga, and Se to reduce the overall Cu content below stoichiometry to reach the target composition. Controlling the length of each stage along with evaporation rates gives more precise control over the final composition. This result also results in a gradient in Ga composition which can be beneficial to device efficiency. The exact details of the three-stage depositions performed in this study can be found in Ref. [63].

## 2.2.3 Chemical Bath Deposition of Cadmium Sulfide Buffer Layer

A thin layer of n-type cadmium sulfide deposited by CBD on the CIGS absorber completes the diode structure. An aqueous ammonia bath heated at 60 °C provides thiourea (0.075 M) and cadmium sulfate (0.0015 M) precursors that spontaneously react at the surface of a submerged CIGS sample to form the CdS layer. The deposition proceeds for 14 min to give a target thickness of 50 nm. CdS deposition was typically performed within two days of CIGS deposition to minimize oxidation of the CIGS surface caused by air exposure.

# 2.2.4 Deposition of Front Contact Layers

After CdS deposition a layer of intrinsic ZnO followed by a layer of indium tin oxide (ITO) are both deposited by reactive sputter deposition. This creates a coating that is nearly transparent and also electrically conductive. Anti-reflective coatings were not used in any of the cells from this dissertation, though they are common in commercial manufacturing. To enhance conductivity of the front contact an alloy of Ni and Al are deposited in a thin grid like pattern that is optimized to minimize the amount of light blocked. After deposition of the grid, cell boundaries were delineated by mechanical scribing to give a well defined area for efficiency calculations. Typically four cells are delineated on a single 1 inch substrate.

#### 2.2.5 Incorporation of Sodium

In this work, Na was incorporated using SLG substrates or by performing a NaF PDT with Na-free substrates. The entire NaF PDT process takes place in the same bell jar as the CIGS deposition without breaking vacuum. After the completion of the CIGS deposition, the sample is allowed to cool to room temperature, and NaF is deposited by heating a source at 1100 °C until the desired thickness, typically 50 nm, is achieved. After the NaF deposition, the sample is heated under vacuum to 400 °C for 30 min to induce the diffusion of Na into the CIGS film. The subsequent aqueous CBD dissolves any excess Na remaining on the surface after PDT.

# 2.3 Material Characterization

# 2.3.1 Energy-dispersive X-ray Spectroscopy (EDS) and X-ray Fluorescence Spectroscopy (XRF)

EDS and XRF were used to obtain the atomic composition of various films. EDS measurements were obtained using an AMRAY 1810 scanning electron microscope (SEM) and an Oxford Instruments silicon drift detector. XRF measurements were obtained using an Oxford Instruments X-Strata980 X-ray fluorescence spectrometer.

Both techniques identify specific elements by analyzing the energy of X-rays emitted from a sample during irradiation from an excitation source. EDS uses the electron beam from an electron microscope as an excitation source while XRF uses X-rays. Figure 2.2 shows how the emission process occurs. When the excitation



Figure 2.2: Illustration of X-ray emission process.

source interacts with the sample (step 1), core-level electrons with a binding energy less than the excitation energy can be ejected from the sample (step 2). When an electron is ejected, a higher energy electron quickly fills the vacancy left behind (step 3). During this transition X-rays can be emitted to conserve energy (step 4). The exact differences in energy levels are unique for each element so the energy of the emitted X-rays provide a fingerprint used for elemental analysis.

While both EDS and XRF give very similar information, they are typically used over very different length scales. The analysis depth of EDS varies based on the electron energy and material being analyzed, and a typical accelerating voltage of 20 kV gives an analysis depth of 1 µm to 2 µm. While the primary electron beam is finely focused, the spatial resolution of EDS is ultimately limited by the spreading of electrons so the minimum analysis area is ~0.5 µm. Analysis of a larger area can easily be obtained by operating the electron microscope at a lower magnification.

The analysis depth for XRF is  $\sim 10 \,\mu$ m making it ideal for simultaneously measuring both the Mo and CIGS layers. The analysis area for the XRF spectrometer used in this study is fixed at 0.5 mm.



Figure 2.3: Illustration of (a) the photoelectron and (b) Auger processes.

#### 2.3.2 X-ray Photoelectron Spectroscopy (XPS)

The surface atomic composition of various films was measured using XPS. In XPS, X-rays irradiate the sample causing core-level electrons to be ejected as photoelectrons (Figure 2.3a). The analyzer measures the kinetic energy of emitted photoelectrons so that the core-level binding energies can be calculated according to

$$BE = h\nu - KE - \phi_s \tag{2.1}$$

where BE is the electron binding energy,  $h\nu$  is the X-ray source energy, KE is the photoelectron kinetic energy, and  $\phi_s$  is the spectrometer work function. The inelastic mean free path of a photoelectron mostly depends on its kinetic energy and is typically 1 nm to 2 nm making XPS a very surface sensitive technique. The binding energies of the various core-level orbitals are unique for each element allowing easy identification and relative quantification of surface elements.

Shifts in binding energy provides additional information about chemical state of the element. For example metal oxides often show higher binding energies compared to the metallic state. The exact binding energy of various compounds is well documented, and use of binding energy shift greatly aids in the identification of chemical state.

For accurately determining chemical state, it is important to know if the sample is electrically insulating since any sample charging will cause an artificial shift in the measured binding energy across the entire spectrum. One way to compensate for charging is to use the C 1s peak as an internal standard. All samples in vacuum contain sub-monolayer amount of carbon referred to as adventitious carbon. The C 1s peak from this layer always has a binding energy of 284.8 eV, and the shift in this peak from charging can be used to correct the binding energy of other peaks.

Another method for determining chemical state is though the combined use of photoelectron and Auger electron peaks. The Auger electron emission process is similar to the X-ray emission process discussed in Section 2.3.1. Auger electrons are emitted when a higher energy electron fills the vacancy left by a photoelectron causing another electron to be ejected to conserve energy (Figure 2.3a). The difference in kinetic energy between a photoelectron peak and its corresponding Auger peak is very sensitive to changes in chemical state and is independent of sample charging. This is often measured using the modified Auger parameter ( $\alpha$ ), which is the sum of the photoelectron binding energy (BE<sub>PE</sub>) and Auger electron kinetic energy (KE<sub>AE</sub>) and is independent of the X-ray source energy.

$$\alpha = KE_{AE} + BE_{PE} \tag{2.2}$$

Like binding energy, the values for the modified Auger parameter are well documented for a wide variety of compounds. This dissertation used a Physical Electronics 5600 series XPS system equipped with a hemispherical analyzer, multi-channel detector, and dual Al/Mg anode X-ray source for all XPS measurements. The binding energy scale was calibrated by comparing the primary photoelectron peaks for elemental Au, Ag, and Cu to known literature values. Peaks were fit using a Shirley background and pseudo-Voigt Gaussian/Lorentzian product function with relevant spin orbital splitting constraints. The chamber is also equipped with a Ar<sup>+</sup> sputter gun for surface etching and a Ta filament heater for vacuum heat treatments.

# 2.3.3 Secondary Ion Mass Spectrometry (SIMS)

SIMS is a technique that measures concentration as a function of depth over a wide range of concentration. The fundamentals of this technique are shown in Figure 2.4 where a primary ion beam strikes the sample surface ejecting secondary ions from the sample, which are then collected and analyzed by a mass spectrometer. The primary ion beam continuously sputters away the sample so that the sample composition is obtained as a function of depth. With careful implantation standards, the mass spectrometer count rate can be calibrated to yield absolute concentrations, typically in units of atoms/cm<sup>3</sup> or simply cm<sup>-3</sup>. SIMS can analyze a very wide range of concentrations. Detection limits are typically around  $1 \times 10^{15}$  cm<sup>-3</sup> and concentrations as high as 100 at% can be measured.

When measuring depth profiles through a stack of multiple materials care must be taken to determine if sputter yield, the ratio of secondary ions to primary ions, changes between materials. If sputter yield changes, different sensitivity factor calibrations must be used in each material. If a single calibration is used, the concentration between different materials cannot be directly compared.



Figure 2.4: Illustration of SIMS at an atomic scale.

Another possible artifact during SIMS measurements is caused by surface mixing, where the energetic primary ion beam can drive surface atoms up to 10 nm into the film. This can lead to artificial concentration tails with concentrations higher than what is actually in the sample. The extent of surface mixing depends on a number of factors including, primary ion energy, type of target atom, and various matrix properties. To minimize the effects of surface mixing, samples in this dissertation were usually rinsed with water to remove accumulated surface Na.

Samples in this dissertation were analyzed by Evans Analytical Group using dynamic SIMS with a Cs<sup>+</sup> primary ion beam. Depending on the element of interest, either positive or negative mode was used. Sensitivity factors for elements of interest had been previously determined in CIGS for the quantification elemental composition were used and had a  $1\sigma$  accuracy of  $\pm 30\%$ . Since only calibrations measured from CIGS were used, Na concentrations measured in CdS and Mo layers may not be as accurate. The depth was calibrated based on stylus profilometry measurements on the resulting craters after the SIMS measurement and had a  $1\sigma$ accuracy of  $\pm 10\%$ .



Figure 2.5: Schematic of a Kelvin probe measurement.

# 2.4 Electronic Characterization

#### 2.4.1 Conductivity

The conductivity ( $\sigma$ ) was calculated from the resistance (R) measured across a gap in the Mo contact in the dark at room temperature using a Kelvin probe setup as shown in Figure 2.5. For Mo coated SLG substrates, the gap was made by laser scribing and was typically 30 um wide. Laser scribing could not be used for non-transparent substrates, such as alumina, and instead the substrate was masked during the Mo deposition to create a 1 mm gap. The Kelvin probe apparatus is a four-probe setup that measures resistance by passing current through one pair of probes and measuring the resulting voltage from the second pair of probes. This eliminates contact resistance allowing for much more accurate measurements compared to a two-probe setup. Conductivity is calculated from resistance using the following equation

$$\sigma = \frac{w}{hl} \frac{1}{R} \tag{2.3}$$

where w and l are the width and length of the gap in the Mo film, and h is the thickness of the CIGS film. Current tends to take the path of least resistance so this measurement cannot be made on films with a conductive substrate such as metal foils, otherwise the high conductivity of the substrate resistance would dominate the measurement.

#### 2.4.2 Seebeck Coefficient

The Seebeck effect is a thermoelectric phenomenon in which a voltage is induced by an applied thermal gradient and is the same effect used in thermocouples. The voltage is created by the diffusion of hot charge carriers towards colder areas of the material. The electric field created by accumulation of charge carriers opposes the diffusion of carriers until an equilibrium is reached. The polarity of the voltage is determined by the majority carrier type, and Seebeck effect measurements are useful for quickly determining whether a material is n or p-type. The Seebeck coefficient also provides information about charge carrier density and mobility making it a good compliment to the conductivity measurements described in the previous section.

This voltage is measured using an apparatus shown in Figure 2.6 which consists of two probes spaced 1 cm apart for measuring voltage. These probes are temperature controlled so voltage is measured at the exact location that the temperature gradient is applied. One probe is a thermocouple embedded within a heating block that is held at 100 °C while the second is a spring loaded stainless steel tip held near room temperature, ~23 °C. The probes are spring loaded to minimize the force applied to the film preventing damage to the surface. Measurements were taken in the dark to prevent photo-induced voltage differences across the film.

The Seebeck coefficient (S) is the ratio between the measured voltage  $(V_{\text{hot}} - V_{\text{cold}})$ , and applied temperature difference,  $(T_{\text{hot}} - T_{\text{cold}})$ , where

$$S = -\frac{V_{\text{hot}} - V_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}}$$
(2.4)

According to convention a positive coefficient denotes a p-type material. While this setup does not account for a contact potential between the probes and semiconductor [64], it is adequate for measuring relative changes.



Figure 2.6: Schematic of the apparatus used for measuring the Seebeck coefficient.

## 2.4.3 JV Characteristics

The primary method for assessing the performance of solar cells is to measure the cell current as a function of bias voltage under illumination equivalent to the sun, commonly referred to as a JV measurement. This measurement is performed with a carefully calibrated light source with the cell under temperature control. Figure 2.7 shows a typical JV curve for CIGS.

The most important parameters of this curve are the open circuit voltage  $(V_{OC})$ , short circuit current  $(J_{SC})$ , and max power point  $(P_{max})$ .  $V_{OC}$  is the voltage measured from an illuminated cell with an open circuit. Its value is limited by the band gap of the material, but there are several loss mechanisms that can result in a  $V_{OC}$  that is smaller than the band gap. Champion CIGS cells typically have



Figure 2.7: Diagram of a typical JV curve.

a V<sub>OC</sub> of around 730 mV. J<sub>SC</sub> is current density measured when the cell is short circuited under illumination, and champion CIGS cells typically have a J<sub>SC</sub> of around  $35 \text{ mA/cm}^2$ . P<sub>max</sub> is the maximum power that the cell can produce under the optimal load and standard illumination. From P<sub>max</sub> the cell efficiency ( $\eta$ ) can be calculated as

$$\eta = \frac{P_{max}}{P_{illumination}} \tag{2.5}$$

where  $P_{illumination}$  is the illumination power density which is always kept at  $1000 \text{ W/cm}^2$ during the measurement. Both  $V_{OC}$  and  $J_{SC}$  play a major role in determining cell efficiency.

Another parameter that affects cell efficiency is fill factor (FF). FF is defined as the ratio between  $P_{max}$  and the product of  $V_{OC}$  and  $J_{SC}$ .

$$FF = \frac{P_{max}}{J_{SC}V_{OC}} \tag{2.6}$$

FF represents the squareness of the JV curve and a value of 1 makes a perfect rectangle defined by  $V_{OC}$  and  $J_{SC}$ . It is represented graphically in Figure 2.7 as

the ratio between the rectangle defined by  $P_{max}$  and the rectangle defined by  $V_{OC}$  and  $J_{SC}$ . There are several mechanisms that cause reduction of FF but these are beyond the scope of this dissertation.

# Chapter 3 SOLID-STATE DIFFUSION

# 3.1 Introduction

Diffusion in solid materials often exhibits non-ideal behavior, and Fick's laws are not always an adequate description of solid-state transport. This non-ideal behavior is partly due to the important role that crystalline defects play in the diffusion mechanism as well as the non-ideality of many solid-state solvent-solute mixtures. This chapter describes techniques for measuring solid-state diffusion, mechanisms for diffusion in solids, and sources of non-ideal diffusion.

# 3.2 Measuring Diffusion in Solids

Measuring the diffusion coefficient in solids involves fitting experimental diffusion data to diffusion models that are based on Fick's laws of diffusion. Fick's first law describes the diffusive flux (J) [65] and can be written as

$$J = -D_i \nabla c_i \tag{3.1}$$

where  $c_i$  is the concentration of species i and  $D_i$  is the diffusion coefficient for species i and implies that the diffusive flux of component i is proportional to its concentration gradient. It should be noted that D often depends on the host material. Fick's second law is derived from the conservation of matter and is written as

$$\frac{\partial c_i}{\partial t} = D_i \nabla c_i \tag{3.2}$$

In some cases, such as diffusion through multiple materials, a single equation is insufficient to describe diffusion and multiple instances of Equation 3.2 must be used. The partial differential equation (PDE) (or system of PDEs) is solved according to the geometry and boundary constraints imposed by the system and experimental diffusion data is fit to the solution. Either concentration vs. depth data (Section 3.2.1) or surface accumulation data can be used to estimate the diffusion coefficient.

# 3.2.1 Depth Profiling Techniques

Depth profiling techniques involve inducing diffusion for a fixed period of time, followed by concentration measurements as a function of depth. Depth profiles are obtained using a wide variety of techniques, but this work exclusively uses secondary-ion mass spectroscopy (SIMS) for measuring depth profiles. The simplest model for analyzing depth profiles is diffusion from a constant source into a semi-infinite slab. A semi-infinite slab is an idealized system that can be applied whenever the sample is large enough to exclude edge effects and much thicker than the length of diffusion. The solution to Equation 3.2 for this system is

$$c_i = c_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{D_i t}}\right) \tag{3.3}$$

where erfc is the complementary error function,  $c_0$  is the source concentration, and x is the depth. A diffusion coefficient can be estimated from experimental data by fitting Equation 3.3 to the measured depth profile.

If the assumptions of a constant source or semi-infinite slab do not apply, Equation 3.2 must be solved using the relevant constraints. Crank provides in-depth analytical solutions to a wide variety of diffusion problems [66]. For problems that are too complex for an analytical solution, numerical methods should be used instead.

# 3.2.2 Surface Accumulation Techniques

In cases where it is not practical to obtain a depth profile, such as for diffusion through a thin film with low concentration, surface accumulation methods may instead be used. Since diffusion must occur through the entire sample, this technique is best suited for thin films. This technique involves allowing the diffusing substance to penetrate the entire sample and accumulate at the back surface. The surface concentration of the accumulating species is measured as a function of time and fit to diffusion models. Diffusion at the back surface creates added complexity for modeling since both diffusion through the film and diffusion on the accumulating surface must be accounted for. Often surface diffusion occurs much faster than bulk diffusion simplifying the analysis. XPS and Auger electron spectroscopy are both well suited for the measurements involved with the surface accumulation technique.

#### 3.3 Mechanisms for Diffusion in Solids

The mechanism for diffusion in a crystalline solid is significantly different than that through gas or liquid due to constraints imposed by the crystalline lattice. Ideal diffusion in a solid can be considered to be the result of a series of random jumps along the lattice [67]. Historically it was believed that diffusion in solids occurred by the direct exchange between adjacent atoms, however, it was later verified that this mechanism is very energetically unfavorable [68]. The pioneering work of Kirkendall proved that diffusion occurs by atomic jumps onto vacant lattice sites [69, 70]. The vacancy mechanism is now considered to be one of the most dominant solid diffusion mechanisms. If the diffusing atoms are considerably smaller than atoms of the host material, diffusion can occur by interstitial jumps between lattice sites.

Both the vacancy and interstitial mechanisms involve a transition state in which the diffusing atom is between sites (Figure 3.1a), and there is an associated activation energy for jumping between site as shown in Figure 3.1b. The activation energy causes diffusion in solids to have an Arrhenius relationship with temperature [71]. For vacancy diffusion, the apparent activation energy is a combination of the jump activation energy and vacancy formation activation energy. A consequence of this dependency on vacancy formation is that diffusion along grain boundaries occurs more quickly with a lower activation energy compared to diffusion through grain interiors due to the large amount of disorder at grain boundaries where vacancies are more likely to form. This difference between diffusion rates is one source of non-ideal diffusion observed in some polycrystalline materials.



Figure 3.1: (a) Vacancy mechanism with diffusing atom in transition state. (b) Energy vs. position of diffusing atom showing the activation energy of a lattice jump.

#### **3.4** Diffusion in Polycrystalline Materials

The grain boundary diffusion coefficient ( $D_b$ ) can be orders of magnitude larger than the grain interior diffusion coefficient ( $D_g$ ) creating complex twodimensional concentration profiles. Diffusion through polycrystalline materials was first analyzed for the case of a single isolated grain boundary [72, 73]. In this model, two-dimensional PDEs were set up for diffusion along the grain boundary and through the grain interior. Based on these results, diffusion in polycrystals was classified by Harrison according to the difference between the grain interior diffusion length ( $\sqrt{D_g t}$ ), the average grain width (w), and the grain boundary width ( $\delta$ ) [74]. These regimes are referred to as type A, B, and C.



**Figure 3.2:** Typical concentration profiles in polycrystalline materials for (a) type A, (b) type B, and (c) type C diffusion kinetics.

## 3.4.1 Type A Diffusion

Type A diffusion involves fast diffusion in the grain interior, where solute atoms can traverse several grains. This regime occurs when the diffusion length in the grain interior  $(\sqrt{D_g t})$  is at least 1.25 times larger than the average grain width [75]. The concentration profile is nearly uniform in the lateral direction as shown in Figure 3.2a and follows Fick's law as a function of depth. The experimentally measured diffusion coefficient for the type A regime is an average of the bulk and grain boundary coefficients weighted by their respective volume fractions. For this reason, diffusion experiments performed in the type A regime slightly overestimate the bulk diffusion coefficient due to the faster diffusion occurring along grain boundaries.

#### 3.4.2 Type B Diffusion

The type B regime involves a diffusion length in grain interiors that is less than the average grain width and greater than the grain boundary width. In this case, diffusion can be considered to be isolated within individual grains. The



Figure 3.3: (a) Concentration profile for type B diffusion in a thin film. (b) Depth profile from Gilmer and Farrel for diffusion in a thin film. Figure used with permission from Ref. [76]. Copyright 1976, AIP Publishing LLC.

concentration in this regime is highly non-uniform (Figure 3.2b) and depth profiles that are averaged over many grains do not appear to follow Fick's laws. This diffusion regime can be recognized if a plot of natural logarithm of concentration vs. depth raised to the 6/5 power appears to be linear.

In thin films, type B diffusion becomes even more complex due to accumulation at the back surface. The solute diffuses quickly through grain boundaries and accumulates at the back surface where it acts as a secondary diffusion source into the grain interiors (Figure 3.3a). Type B diffusion in thin films often shows gradients towards both the front and back surfaces as shown in Figure 3.3b due to both surfaces acting as a source (figure used with permission from Ref. [76]). Due to the complexity of models in this regime, an analytical solution is usually not feasible and instead numerical analysis must be performed as demonstrated by Gilmore and Farrell [76].

# 3.4.3 Type C Diffusion

Type C involves a characteristic diffusion length in the grain interior smaller than the width of grain boundaries. In this case diffusion is constrained solely to the grain boundaries as seen in Figure 3.2c. Diffusion in this case follows Fick's law, however, the concentration averaged over many grains is very low due to the small volume fraction of grain boundaries. This makes it difficult to measure depth profiles and surface accumulation techniques are often more appropriate for studying type C diffusion.

# 3.5 Chemical Potential Driving Force

An ideal mixture is defined as a mixture in which the intermolecular forces are identical between all combinations of species in the mixture. In this case the driving force for diffusion is the concentration gradient as depicted in Fick's first law (Equation 3.1).

In a non-ideal mixture, the difference in intermolecular interactions between different species creates an additional driving force that can either enhance or reduce the driving force created by the concentration gradient. A more general driving force that encompasses both ideal and non-ideal mixtures is a gradient in chemical potential ( $\mu$ ). Spontaneous processes always attempt to minimize free energy thus it is natural for a solute to move in the direction that lowers its chemical potential. The diffusive flux of solute i in an arbitrary matrix can be expressed as

$$J_i = -\frac{D_i c_i}{RT} \nabla \mu_i \tag{3.4}$$

where R is the gas constant, and T is the temperature.

# 3.5.1 Diffusion in Ideal Mixtures

Fick's law can be derived from Equation 3.4 for an ideal solution by starting with the expression for the chemical potential of an ideal mixture

$$\mu_i = \mu_i^0 + RT \ln x_i \tag{3.5}$$

where  $x_i$  is the mole fraction of component *i* and  $\mu_i^0$  is a reference chemical potential, usually taken to be the chemical potential of the pure substance. In an ideal solution, there is no enthalpy of mixing since the interaction between different components is the same as in the pure species. Therefore, Equation 3.5 is derived solely from the entropy of mixing.

Substituting Equation 3.5 into 3.4 gives

$$J_i = -\frac{D_i c_i}{RT} \nabla [\mu_i^0 + RT \ln x_i]$$
(3.6)

 $x_i$  can be expressed as  $c_i/c$ , where c is the total molar concentration of all species in the mixture, so that Equation 3.6 becomes

$$J_i = -\frac{D_i c_i}{RT} \nabla \left[ \mu_i^0 + RT \ln \frac{c_i}{c} \right]$$
(3.7)

$$J_i = -\frac{D_i c_i}{RT} \nabla [\mu_i^0 + RT \ln c_i - RT \ln c]$$
(3.8)

After removing the terms that have no spatial dependence, Equation 3.8 simplifies to Fick's first law.

$$J_i = -D_i c_i \nabla \ln c_i \tag{3.9}$$

$$J_i = -D_i \nabla c_i \tag{3.1}$$

Diffusion in this manner is inherently an entropy-driven process and Equation 3.1 only truly holds in the absence of a chemical gradient.  $D_i$  is obtained when measuring diffusion caused by the spontaneous mixing of isotopically labeled atoms in an otherwise pure material. For this reason,  $D_i$  is often called the tracer diffusion or self diffusion coefficient.

#### 3.5.2 Diffusion in Non-Ideal Mixtures

For a non-ideal solution, activity  $(a_i)$  must be used instead of  $x_i$  in the expression for chemical potential. Activity can be expressed as the product of the mole fraction and activity coefficient  $(\gamma_i)$  so that Equation 3.5 becomes

$$\mu_i = \mu_i^0 + RT \ln x_i \gamma_i \tag{3.10}$$

To facilitate the evaluation of  $\nabla \mu_i$  in Equation 3.4 for a non-ideal mixture, the chain rule can be applied yielding

$$J_i = -\frac{D_i c_i}{RT} \frac{\partial \mu_i}{\partial x_i} \nabla x_i \tag{3.11}$$

Substituting  $\nabla(c_i/c)$  into  $\nabla x_i$  gives

$$J_i = -\frac{D_i}{RT} x_i \frac{\partial \mu_i}{\partial x_i} \nabla c_i \tag{3.12}$$

$$J_i = -\frac{D_i}{RT} \frac{\partial \mu_i}{\partial \ln x_i} \nabla c_i \tag{3.13}$$

Substituting Equation 3.10 into  $\frac{\partial \mu_i}{\partial \ln x_i}$  yields

$$\frac{\partial}{\partial \ln x_i} \left[ RT(\ln x_i + \ln \gamma_i) \right] = RT\left( 1 + \frac{\partial \ln \gamma_i}{\partial \ln x_i} \right)$$
(3.14)

Substituting this result into Equation 3.13 gives

$$J_i = -D_i \left( 1 + \frac{\partial \ln \gamma_i}{\partial \ln x_i} \right) \nabla c_i \tag{3.15}$$

which can be expressed as

$$J_i = -D_i^C \nabla c_i \tag{3.16}$$

where  $D_i^C = (1 + \partial \ln \gamma_i / \partial \ln x_i) D_i$  and is termed the chemical diffusion coefficient. If the mixture is ideal,  $\gamma_i = 1$  and Equation 3.16 reduces to Fick's law. If the mixture is dilute  $\gamma_i$  is constant according to Henry's law and Equation 3.16 again reduces to Fick's law.

This derivation serves to demonstrate that there are two effects behind the diffusion driving force: (1) An entropic effect as seen by the spontaneous mixing of an ideal solution, and (2) a driving force created by the differences in intermolecular interactions between the diffusing particles and their surroundings. When the intermolecular interactions differ between different species in solution, i.e. there is a non-zero enthalpy of mixing, the second effect can not be ignored.

# Chapter 4

# SODIUM DIFFUSION THROUGH THE MOLYBDENUM BACK CONTACT LAYER

#### 4.1 Introduction

One of the simplest methods for incorporating Na is to allow it to diffuse from a SLG substrate through a thin molybdenum (Mo) layer during the CIGS deposition, where the Mo serves as an electrical contact to the back of the CIGS film. The high temperatures during deposition, typically greater than 450 °C, cause Na to diffuse through the Mo and into the CIGS. The amount of Na incorporated using this approach is not well controlled and can result in non-uniform distribution of Na over large areas [77, 78]. However, it remains an attractive option due to its simplicity and low cost. Developing a better understanding of the Na diffusion mechanism through Mo can potentially lead to solutions that overcome these controllability issues.

While there have been several studies on how the Mo back contact affects Na incorporation in CIG [59–62, 79–81], the specific diffusion mechanism is still not well understood. The current understanding is that at CIGS deposition temperatures, which range from 450 °C to 600 °C, Na is highly mobile along Mo grain boundaries [79] but does not diffuse into the grain interiors since the solubility of Na is negligible up to at least 2623 °C [82], the melting point of Mo. Therefore, it is unlikely that any bulk transport takes place within the grain interiors of Mo. Since grains in a typical Mo back contact are columnar and span the entire height of the film [83], the grain boundaries provide a fast diffusion path to the CIGS interface. Near the Mo/CIGS interface, Na tends to segregate, and this effect has been measured by different groups using secondary ion mass spectroscopy (SIMS) [62, 80]. The amount of Na that accumulates at the Mo surface may determine how much Na is incorporated into the rest of the CIGS film [62].

The void fraction or porosity has a large effect on the amount of Na that is incorporated into CIGS [59–62, 81] and less Na is observed in films grown on dense Mo compared to those grown on porous Mo [60–62, 81]. It is believed that Mo oxides form along the surfaces of these voids, which is known to facilitate Na diffusion because of the strong affinity of Na for oxygen [62, 79]. Previous work in our group has shown that Na does not accumulate on the Mo surface when heating under high vacuum in the absence of oxygen [84]. CIGS deposited on intentionally oxidized Mo has been shown to have a higher Na concentration [62], and CIGS devices made on intentionally oxidized Mo films show a small improvement in V<sub>OC</sub> and FF, likely due to increased incorporation of Na [85].

This chapter evaluates the role that oxygen plays on the accumulation of Na on the Mo film surface. Specifically, it shows that at a given temperature less Na accumulates on the Mo surface if oxygen is removed prior to Na diffusion and more accumulates if oxygen is added. Based on the experimental results, a diffusion model is used to explain Na diffusion from SLG and its accumulation on Mo. By fitting the model to diffusion data at different temperatures, the apparent activation energy for grain boundary diffusion of Na through Mo is determined.

#### 4.2 Sodium Diffusion through Molybdenum Thin Films.

Mo films were deposited on SLG substrates using DC magnetron sputtering as discussed in Section 2.2.1. The surface composition of these films was analyzed using the XPS system discussed in Section 2.3.2. Relative sensitivity factors (RSFs) for O and Mo were verified using MoO<sub>3</sub> powder, and the RSF for Na was verified using trisodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>6</sub>O<sub>7</sub>).

The XPS chamber was equipped with a differentially pumped ion gun for sputter cleaning. An accelerating voltage of 2 kV, an emission current of 25 mA, and an argon pressure of  $1.1 \times 10^{-2}$  Pa were used, resulting in a sputter current of approximately 3 µA at the sample surface and a sputter rate of ~0.5 nm/min. The ion beam raster size was 1 cm x 1 cm, which covered the entire sample.

Sample heating was performed in a separate process chamber attached to the XPS system through a gate valve. Samples could be transferred between the process chamber and the XPS analysis chamber under vacuum and without exposure to ambient air. In the process chamber, a resistive heater of Ta wire was located 5 mm above the sample. Temperature was measured using an identical Mo/SLG reference sample with a K-type thermocouple permanently attached. The sample of interest is assumed to have the same temperature as the reference sample since they are both located at the same distance away from the heater. This setup allows the sample of interest to freely move between the process and analysis chambers without restriction from an attached thermocouple.

#### 4.3 **Results and Discussion**

## 4.3.1 Characterization of Mo Films

Cross-sectional SEM images were used to characterize the grain structure of the Mo films, and the measured dimensions will be used as input parameters when modeling the diffusion of Na through Mo. Figure 4.1a shows an SEM image of a Mo film that is 680 nm thick having columnar grains with an average width of 50 nm extending through the entire thickness of the film. Figure 4.1b shows a simplified cross-sectional schematic of the Mo film with arrows denoting the diffusion path of Na. Figure 4.1c shows a schematic of a close up of a Mo grain boundary along with adjacent grains and denotes the dimensions that will be used in modeling the diffusion of Na. Notation from this figure is discussed in Section 4.3.4.

XPS scans of the Mo 3d, O 1s, and Na 1s regions were taken of the Mo/SLG surface and the composition was calculated from the peak areas divided by their RSF. The RSF adjusted peak area of an element was divided by the sum of the adjusted peak areas of all elements present to give an atomic percentage. Surface carbon was not included in this calculation.

Scans of the as-deposited Mo surface show 47 at% Mo and 53 at% O with no Na. The Mo 3d XPS spectrum shown in Figure 4.2a reveals that  $MoO_2$ ,  $MoO_3$ , and metallic Mo are all present on the surface. For this particular sample, 82% of the Mo 3d region is metallic, 3% is  $MoO_2$ , and 15% is  $MoO_3$ . These peak areas of the Mo oxides are in good agreement with the actual percentage of oxygen measured. XPS depth profiling (Figure 4.3a) reveals that  $MoO_3$  exists only with the first few nanometers of the film, and only  $MoO_2$  is detectable further in the film. Qualitative secondary ion mass spectroscopy (SIMS) measurements (Figure 4.3b) show that the oxygen level is nearly constant through the entire film and depth profiling with



Figure 4.1: (a) Cross-section SEM image of sputter deposited Mo on SLG. (b) Enlarged schematic of seven Mo grains with arrows denoting the diffusion path of Na. (c) Schematic depicting two adjacent Mo grains with their shared grain boundary. Dimensions used for diffusion modeling are depicted and are not shown to scale.

Auger electron spectroscopy (not shown) reveals that the oxygen concentration within the Mo film is about 2 at%. Oxygen impurities in sputtered Mo films have been shown to originate from the residual gas in the sputter chamber [86, 87]. Given the very low solubility of O in Mo [88], most of this O must reside at grain boundaries.

After heating the sample from Figure 4.2a for 10 minutes at 400 °C, Na appears with a concentration of 4 at%. The Na 1s peak was located at 1072.5 eV as shown in Figure 4.2b, which is in agreement with the binding energy of Na<sub>2</sub>O.

# 4.3.2 Controlling Surface Oxygen on Mo

To evaluate the relationship between the amount of oxygen on the Mo surface and the amount of Na accumulation, the concentration of surface oxygen was precisely controlled before diffusion experiments. The amount of oxygen on the surface of Mo was controlled by either sputtering to remove oxygen or heating in air to add oxygen.

Heat treating in ambient air at 200 °C for 30 min increased the surface oxygen content from roughly 50 at% for the as-deposited sample to 65 at%, and Figure 4.4a shows the increase in surface oxygen as measured by XPS as a function of heat treatment time. Depth profiling measurements with XPS reveal that this oxide layer is only a few nanometers thick. It was determined that Na diffusion in Mo at this temperature is too slow to cause any significant diffusion of Na out of the glass during this heat treatment.

To remove oxygen from the Mo surface, samples were sputter etched inside the XPS analysis chamber at a sputtering rate of  $\sim 0.5 \text{ nm/min}$ , and Figure 4.4b shows the decrease in surface oxygen with sputter time. The Mo thickness is



Figure 4.2: (a) XPS spectrum of Mo 3d region for as-deposited Mo surface with peaks for oxide and metallic species. (b) XPS spectrum of Na 1s region for SLG/Mo sample after heating at 400 °C for 10 min.



Figure 4.3: (a) XPS and (b) SIMS depth profile through surface of Mo coated SLG.



Figure 4.4: Surface oxygen content of Mo on SLG as measured by XPS for samples (a) heated in ambient air at 200 °C and (b) sputtered in vacuum.

reduced by less than 1% during sputtering, which will not significantly skew results from diffusion measurements. The oxygen concentration stabilizes at an artificially high concentration after long periods of etching, and it is most likely that a small amount of surface oxygen is pushed into the film during sputtering preventing the complete removal of oxygen from the surface. Surface oxygen concentrations as low as 16 at% can be achieved by using this procedure. Concentrations below this could not be achieved due to surface mixing from sputtering. Diffusion experiments were performed immediately after etching and without exposure to ambient air to prevent re-oxidation of the Mo surface.



**Figure 4.5:** Na concentration on Mo surface as measured by XPS as a function of heating time at 400 °C for samples with a high amount of surface oxygen (red diamonds) and low amount of surface oxygen (blue squares).

# 4.3.3 Relationship of Surface Oxygen to Na Segregation

The accumulation of Na on SLG/Mo during heating in vacuum was compared between a sample having 53 at% oxygen due to ambient air exposure, and a sample that had been sputter etched for 20 min to have 16 at% oxygen. These samples were heated in a vacuum of  $1 \times 10^{-5}$  Pa at 400 °C for 1 min to 2 min, cooled to near ambient temperature, then transferred to the XPS analysis chamber to measure the Na content. This process was repeated on the same sample until the concentration of Na stopped increasing. Figure 4.5 shows results of this experiment for both samples. Within 10 min of heating, the surface of both samples becomes saturated with Na, and the concentration no longer increases. The saturation concentration varies by nearly an order of magnitude between the low and high oxygen samples, suggesting that oxygen on the surface of Mo may affect the amount of Na that accumulates.



**Figure 4.6:** The saturation concentration of Na as a function of initial surface oxygen on the Mo film after heating in vacuum at 400 °C (blue squares) or 500 °C (red diamonds). Surface oxygen was varied from as-deposited films by either sputter etching or heating in air at 200 °C.

To clarify the relationship between surface oxygen and Na accumulation, similar heat treatments were performed where the oxygen concentration on SLG/Mo samples was varied from 27–59 at% using the techniques described above. These samples were heated under vacuum at either 400 °C or 500 °C until the Na concentration stopped increasing. In Figure 4.6 the saturation concentration is plotted against the amount of surface oxygen before heating. There is a linear relationship at both temperatures where samples with more surface oxygen accumulate more Na, which clearly demonstrates that surface oxygen plays a critical role in controlling the Na saturation concentration. At this point it is not clear why the saturation concentration is greater for samples that were heated to higher temperatures. Mathematical modeling was then performed to explain the observed relationships and quantify the diffusion process.
#### 4.3.4 Diffusion Modeling

The accumulation of Na on the surface of Mo was modeled according to Harrison's type C diffusion regime where the grain boundary diffusion coefficient is much larger than the bulk lattice diffusion coefficient  $(D_b >> D_l)$  (see Section 3.4.3). In this case, transport only takes place along grain boundaries and on the free surface, while diffusion through grain interior is negligible. Such diffusion behavior is usually observed at temperatures below 35% of the melting point [89]. Therefore, this analysis is appropriate for this system due to the high melting point of Mo at 2623 °C and the relatively low temperature range of 300 °C to 500 °C used in this study.

To obtain a mathematical solution, an analysis is adopted from the 2D model of Hwang and Balluffi describing type C diffusion through a thin film [90]. This analysis is performed for a single grain and can be extended to multi-grained structures due to the symmetry of the microstructure. Figure 4.1c shows a schematic of a single grain boundary and adjacent grains along with several parameters used in this model. Based on the previously discussed SEM cross-sectional images, Mo grains were approximated as evenly spaced, parallel square columns with the grain width  $(d_s)$  and the film thickness (h) having values of 50 nm and 680 nm, respectively. Based on TEM measurements of Mo films performed by other groups, a value of 3 nm was used for the grain boundary width  $(\delta)$  [91]. Lastly, the accumulation of Na is confined on the surface within a layer of fixed thickness  $\delta_s$ . This fixed accumulation layer thickness is well justified since after the Na reaches its saturation does not continue indefinitely. It is assumed that the accumulation of Na is limited to a single monolayer, which gives  $\delta_s$  a value of 0.2 nm. While this is a somewhat

arbitrary assumption, if diffusion does not occur in a perfect monolayer it should not significantly alter the estimation of the diffusion coefficient [92].

The analysis begins by assuming all Na transport takes place according to Fick's second law. The generalized form for this is:

$$\frac{\partial c(y,z,t)}{\partial t} = D(y,z) \nabla^2 c(y,z,t)$$
(4.1)

where c is the concentration of Na and D is the diffusion coefficient. z is defined as the direction parallel to the grain boundaries and y is the direction perpendicular.

Since diffusion only takes place along grain boundaries and on the surface, the expression can be separated into two equations. The first equation accounts for diffusion along grain boundaries and the second accounts for diffusion across the surface:

$$\frac{\partial c_b(z, t)}{\partial t} = D_b \frac{\partial^2 c_b(z, t)}{\partial z^2} \text{ for } 0 \le z \le h$$
(4.2)

$$\frac{\partial c_s(y, t)}{\partial t} = D_s \frac{\partial^2 c_s(y, t)}{\partial y^2} \text{ for } 0 \le y \le \frac{d_s}{2}$$

$$(4.3)$$

where  $c_b$  is the Na concentration along the grain boundaries,  $D_b$  is the grain boundary diffusion coefficient,  $c_s$  is the concentration of Na along the surface and  $D_s$  is the surface diffusion coefficient.

To fully constrain both of these partial differential equations, four boundary conditions and two initial conditions are needed. The two initial conditions arise since the grain boundary and surface are both free of Na at the start of heating.

$$c_b(z, 0) = c_s(y, 0) = 0 \text{ with } z \neq 0$$
 (4.4)

Since the amount of Na available from the glass greatly exceeds the total grain boundary and accumulation volume, a constant uniform Na concentration is assumed at the SLG/Mo interface. This can be expressed as the following boundary condition:

$$c_b(0, t) = c_0 \tag{4.5}$$

where  $c_0$  is the Na concentration within the SLG and at the SLG/Mo interface. This value is independent of position in y and does not vary with time.  $c_0$  was determined from XPS measurements on bare SLG giving a value of 4 at% both before and after heating to 500 °C for 10 min. This Na concentration is lower than expected for SLG and it is likely that near the surface the glass is Na poor.

The next two boundary conditions describe the transition of Na out of the grain boundaries and onto the Mo surface. The first condition accounts for the conservation of matter. The amount of Na leaving the grain boundary must equal the amount entering the surface:

$$\delta D_b \left. \frac{\partial c_b}{\partial z} \right|_{z=h} = 2\delta_s D_s \left. \frac{\partial c_s}{\partial y} \right|_{y=0}$$
(4.6)

where  $\delta_s$  is the thickness of the accumulation layer. The next boundary condition describes the segregation of Na between the grain boundaries and accumulation at the surface. It is assumed that a thermodynamic equilibrium can be maintained at this junction so that the concentration of Na is not necessarily continuous at the grain boundary exit, and that the amount of segregation is independent of concentration giving the following expression:

$$c_b s' = c_s at y = 0 with z = h$$

$$(4.7)$$

where s' is the surface segregation factor. This accounts for any discontinuity in the Na concentration due to surface segregation at the grain boundary exit. As s' approaches 1, segregation disappears and concentration becomes a continuous function during the transition to surface diffusion.

Finally, due to symmetry, the following condition on the sample surface must be met:

$$\frac{\partial c_s}{\partial y} = 0 \ at \ y = d_s/2 \tag{4.8}$$

The full analytical solution is obtained with the Laplace transform and can be found in Hwang and Balluffi's paper [90].

The problem and solution simplify as the surface diffusion coefficient becomes infinitely larger than the grain boundary diffusion coefficient  $(D_s >> D_b)$ . When this condition is met, one can assume that the surface concentration does not vary with position and changes only with time. In effect, diffusion is so rapid that the concentration is the same at all values of y along the surface. The analytical solution for this scenario was adapted from an analogous heat transfer problem originally solved by Carslaw and Jaeger [93] and is shown below [94]:

$$\frac{c_s}{c_0 s'} = 1 - 2\sum_{n=1}^{\infty} \exp\left(-\theta_n^2 \frac{D_b t}{h^2}\right) \frac{(\theta_n^2 + H^2)\sin\theta_n}{(\theta_n^2 + H^2 + H)\theta_n}$$
(4.9)

where  $\theta_n$  is the nth root of

$$\theta \tan \theta = H \tag{4.10}$$

Parameter	Description	Value
$c_0$	Source concentration	4  at%
$\delta$	GB width	$3\mathrm{nm}$
h	Mo thickness	$680\mathrm{nm}$
$d_s$	Grain width	$50\mathrm{nm}$
$\delta_s$	Accumulation layer thickness	$0.2\mathrm{nm}$
$D_b$	GB diffusion coefficient	Fit to data
s'	Surface segregation factor	Fit to data

 Table 4.1: List of parameters used in the diffusion model along with approximated values.

and H is a dimensionless quantity representing the ratio of grain boundary capacity to accumulation layer capacity

$$H = \frac{\delta h}{\delta_s d_s s'} \tag{4.11}$$

This fast surface diffusion approximation should be valid for the system used in this study based on experimental data of the amount of time it takes to reach saturation compared to the amount of time it takes Na to first appear. If surface diffusion were limiting, one would expect that it would take much longer for the surface to become saturated with Na. Additionally, when fitting the experimental data to the full Hwang-Balluffi solution, which includes surface diffusion, the optimized value of  $D_s$  is arbitrarily large (fit not shown), further validating the use of the Carslaw-Jaeger solution.

Table 4.1 summarizes all parameters used in the Carslaw-Jaeger solution along with estimations for their values. After accounting for the Mo microstructure, the only remaining unknown parameters are  $D_b$ , and s'. Since  $D_s$  is essentially infinite, it is no longer a parameter.



- Figure 4.7: The Hwang-Balluffi model (solid line) fit to experimental data (circles) for as-deposited SLG/Mo samples after diffusion at 400 °C, 350 °C, and 300 °C. Dashed lines denote the model with ±25% of the optimized grain boundary diffusion coefficient.
- **Table 4.2:** Optimized values of  $D_b$  and s' for various temperatures and surface oxygen concentrations.

Treatment	Initial O	T (°C)	$D_b \ (\mathrm{cm}^2/\mathrm{s})$	s'
	(at %)			
Sputter etched	11	400	$7.8\times10^{-12}$	0.12
None	53	400	$12 \times 10^{-12}$	1.02
None	44	350	$6.5\times10^{-13}$	1.18
None	54	300	$2.9\times10^{-13}$	0.31

Equation 4.9 was fit to experimental data using a downhill simplex algorithm to minimize the residual sum of squares while varying  $D_b$ , and s'. Figure 4.7 shows fits of the XPS diffusion data from as-deposited SLG/Mo heated at 300 °C, 350 °C, and 400 °C. Table 4.2 shows the optimized values for D<sub>b</sub> and s' from these three heat treatments and also compares the as-deposited sample at 400 °C to a sputter etched sample with a low amount of surface oxygen, also heated to 400 °C.

The optimized values of  $D_b$  at 400 °C for the as-deposited sample with high oxygen and sputter etched sample with low oxygen vary by only 50 %. The difference between these two values of  $D_b$  is not significant given the precision of these measurements. While the oxygen at grain boundaries plays a role in Na diffusion, sputter etching does not alter the amount of oxygen within the bulk of the film, and  $D_b$  remains unchanged. It has been demonstrated that Na diffusion is enhanced in Mo films with a greater bulk oxygen concentration [62, 95], and it is expected that the value of  $D_b$  would increase with the concentration of oxygen at the grain boundaries.

On the other hand, the surface segregation factor, s', is expected to be dependent on surface properties, and its value for the sample with a large amount of surface oxygen is nearly nine times greater than the sample with a low amount of surface oxygen. Surface adsorbates have been shown to alter surface segregation of the diffusing species [96] and this effect could contribute to the observation that samples with more surface oxygen accumulate more Na. Furthermore, the surface segregation factor is known to depend on temperature [97] which can explain the increase in Na saturation concentration for heat treatments at 500 °C and its decrease for the experiment performed at 300 °C.

As expected the grain boundary diffusion coefficient increases with temperature. Typically the temperature dependence of a diffusion coefficient follows an Arrhenius type relation:

$$D(T) = D_0 \exp\left(\frac{-E_a}{\mathrm{RT}}\right) \tag{4.12}$$

where  $D_0$  is the pre-exponential factor and  $E_a$  is the apparent activation energy for grain boundary diffusion. Figure 4.8 plots the natural logarithm of  $D_b$  against the inverse of temperature. This plot is linear confirming that Na diffusion through



Figure 4.8: Arrhenius plot for the grain boundary diffusion coefficient.

Mo has an Arrhenius type dependency on temperature. The slope resulted in an estimate of the apparent activation energy of 117 kJ/mol. As a rule of thumb for grain boundary diffusion in metals, Gupta suggests that the activation energy in calorie/mol should be 17 to 25 times melting temperature of the diffusion matrix in Kelvin [98]. For grain boundary diffusion in Mo, this gives an estimated activation energy of roughly 206 kJ/mol to 303 kJ/mol. Since activation energy measured for this system is so much lower than expected, it is likely that the transport of Na in Mo may not follow a standard mechanism for grain boundary diffusion. Arnoldy reports an activation energy of the Mo–O bond breaking during the reduction of MoO<sub>3</sub> to be 120 kJ/mol [99], which is in good agreement with activation energy from Figure 4.8, suggesting that the Mo–O bond is involved with the diffusion of Na.

Figure 4.9 shows an Ellingham diagram depicting the Gibbs free energy of formation for Na<sub>2</sub>O, MoO<sub>3</sub>, and MoO<sub>2</sub> calculated using published data [100]. Na<sub>2</sub>O is more stable than both Mo oxides suggesting that Na is thermodynamically capable of disrupting Mo-O bonds at the grain boundary.



Figure 4.9: Ellingham diagram depicting Gibbs free energy of formation for  $Na_2O$ ,  $MoO_2$ , and  $MoO_3$ .

## 4.4 Conclusions

By selectively adding or removing oxygen from the surface of Mo coated sodalime glass, a linear relationship was shown between the surface oxygen concentration and the amount of Na that ultimately accumulates. The diffusion and accumulation of Na was modeled using the Hwang-Balluffi method with a fast-surface diffusion approximation adapted from Carslaw and Jaeger. Fitting the solution of this model to experimental data revealed that the surface segregation parameter is the only parameter that significantly varies with oxygen content. Surface oxygen can affect the amount of surface segregation and thus the overall saturation concentration of Na. An apparent activation energy was also calculated for the diffusion of Na through Mo grain boundaries. Our reported value of  $117 \, \text{kJ/mol}$  is in good agreement with the activation energy for breaking the Mo–O bond in MoO<sub>3</sub>, suggesting Na–O bonds partially disrupt Mo–O bonds as Na diffuses through the grain boundary. As Na diffuses along Mo grain boundaries, the presence of Mo oxides provides a chemical driving force for Na diffusion due to the strong affinity of Na for oxygen. The interaction of Na with these oxides to form Na<sub>2</sub>O could partially disrupt Mo–O bonds explaining the observed activation energy.

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## Chapter 5

# DIFFUSION IN ${\rm CuInSe_2}$ SINGLE CRYSTALS: ROLE OF SODIUM IN THE GRAIN INTERIOR

## 5.1 Introduction

While it is well established that Na in CIGS resides primarily at grain boundaries, it has not been conclusively ruled out that very small amounts of Na within grain interiors affect device performance. Niles et al. [57] show with high resolution AES that Na is only detectable at grain boundaries, and measurements made on grain interiors fall below detection limits. However, the detection limit in this study was only ~0.1 at%, and lower concentrations could cause significant changes in electronic properties. It has been found that the addition of Na in CIGS can increase net carrier concentration from  $2.4 \times 10^{14}$  cm<sup>-3</sup> to  $6.5 \times 10^{15}$  cm<sup>-3</sup> along with a 85 mV increase in V<sub>OC</sub> [33]. An increase of this magnitude could easily be achieved by incorporation of Na in the bulk grains at concentrations that are well below the 0.1 at% detection limit.

Recently very small amounts of Na were detected within grain interiors using atom-probe tomography (APT), which is a technique that allows for the creation of a three-dimensional elemental map with sub-nanometer spatial resolution and a detection sensitivity of a few tens of atomic parts per million [102, 103]. Its low detection limits and fine spatial resolution make APT an ideal technique for distinguishing between Na in grain boundaries and interiors. ATP measurements on polycrystalline CIGS confirm that a majority of Na resides along grain boundaries, but small amounts of Na are also present in grain interiors at concentrations ranging from 30 ppm to 145 ppm [58, 104–106].

Despite confirming the presence of Na within grain interiors, current APT methods are not well suited to characterizing lattice diffusion of Na within the grain interior due to the small sample size and time consuming sample preparation procedure. Typical diffusion rates, their temperature dependence, and the solubility of Na in bulk CIGS are still not well understood. This is partly due to the small size of APT samples, which typically consist of a cone that is 500 nm across and 100 nm at the base. These small samples are usually not representative of the entire film making a comprehensive diffusion study with this technique impractical. Despite this, these measurements provide insight into the behavior of Na in bulk CIGS grains. APT usually shows a uniform Na concentration in the grain interior throughout an entire sample suggesting that lattice diffusion occurs fast enough that the grain is saturated with Na. Another study detects Na in grain interiors after a NaF PDT at 157 °C suggesting that Na lattice diffusion is rapid even at low temperatures [107].

Single crystals are ideal for studying bulk lattice diffusion since a larger analysis area can be used without interference from grain boundaries allowing depth-profiling techniques such as SIMS to be used to analyze diffusion. Schroeder and Rockett [108] incorporated Na into epitaxial single crystal CIGS from both Na<sub>2</sub>Se and NaOH at temperatures up to 600 °C and reported Na concentrations ranging from  $6 \times 10^{19}$  cm<sup>-3</sup> to  $10^{20}$  cm<sup>-3</sup>. Characterizing the diffusion of Na was not the objective of this study, and this paper does not report diffusion coefficients or investigate the possibility that Na transport occurred along extended defects. Champness's group has attempted to incorporate Na into the melt during crystal growth using either metallic Na [11, 109, 110] or  $Na_2Se$  [111]. Na was not detected in these crystals using AES [109] and EDS [110], however, the Na concentration in these materials may be below the detection limit of these techniques.

Another study attempts to incorporate Na into CIS single crystals by forming Na<sub>2</sub>Se in-situ by heating elemental Na and Se in a sealed ampule along with a CIS crystal [112]. Samples heated up to 500 °C in the presence of excess Na disintegrated due to the high reactivity of metallic Na. CIS crystals were also heated in the presence of equimolar amounts of elemental Na and Se and it was assumed that Na<sub>2</sub>Se is formed in the vapor phase and deposited on the crystal surface. SIMS depth profiles on these samples show no significant increase in Na concentration after the heat treatment. The downside of this approach is that it couples reaction rates, vapor transport, and lattice diffusion into a single experiment. Less volatile Na<sub>2</sub>Se likely forms quickly at the Na source preventing significant deposition on the crystal. The same study attempts to incorporate Na by heating single crystal CIS samples with Na<sub>2</sub>CO<sub>3</sub> in an ampule at 500 °C. The vapor pressure of Na<sub>2</sub>CO<sub>3</sub> is eleven orders of magnitude smaller than metallic Na [100], and it is not surprising that Na is not detected in the crystal after this treatment.

In this chapter, the diffusion of Na into single crystals is investigated by evaporating NaF directly onto the sample surface followed by heating to drive Na into the crystal. Diffusion is evaluated at two different temperatures and a rough estimate of the lattice diffusion activation energy is provided. The diffusion mechanism is investigated by comparing the diffusion behavior of Na in two crystals with different defect structures.

## 5.2 Sodium Incorporation into CuInSe<sub>2</sub> Single Crystal

## 5.2.1 Preparation of Single Crystals

Single crystals of  $CuInSe_2$  grown by both vertical Bridgman [113] and horizontal gradient freezing methods were used to evaluate the incorporation of Na. The Bridgman crystals were grown by vertical solidification of  $CuInSe_2$  melts in pyrolytic boron nitride crucibles at a maximum temperature of 1000 °C. The horizontal gradient crystals, also referred to as melt-grown crystals, were grown in evacuated fused silica ampoules by a three step process consisting of: 1.) isothermal reaction at 450 °C of 6N purity elements; 2.) isothermal ramping to 1000 °C; and 3.) slow-cooling at 100 °C/h to 750 °C with a 5 °C/cm gradient across the ampoule length, with overnight cooling to room temperature.

Crystals several mm in size were extracted from the obtained ingots with random growth facets and were first prepared by a room temperature mechanical polish with 0.02 µm alumina slurry in water. A room temperature chemical polish in bromine-water solution [114] was then carried out for 30 seconds, in a solution containing 0.05 vol%  $Br_2$ , and 150 g/L KBr, at an etch rate of ~1 nm/ sec which produces a Se excess on the surface. Finally, immediately prior to loading into the NaF deposition system, the Se excess layer was removed by immersion in 0.5 M aqueous KCN at 40 °C for 1 min.

## 5.2.2 Characterization of Crystals

Table 5.1 presents the atomic composition of each crystal as measured by XRF and shows the melt-grown crystal is stoichiometric and the Bridgman-grown crystal is slightly Cu-poor. The standard deviation for the measurement is ~0.1 at% so this difference in Cu content is statistically significant. CIS made by the vertical

Sample	Cu (at%)	In $(at\%)$	Se (at%)	$\mathrm{Cu/In}$	Metals/Se
Bridgman	24.2	26.1	51.3	0.93	0.98
Melt	25.1	25.5	49.9	0.98	1.01

 
 Table 5.1: Atomic composition for Bridgman and melt-grown crystals as measured by XRF.

Bridgman method is typically Cu-poor due to the segregation of  $Cu_2Se$  during growth [115].

Laue photos for each crystal are shown in Figure 5.1 and both show clearly defined diffraction spots confirming that both samples are single crystal. Also, both images show mirror symmetry, which is due to a terminating mixed cation-anion face. No indication of grain boundaries or micro-cracks were observed with SEM (not shown).

## 5.2.3 Sodium Treatment of Single Crystals

NaF was deposited on the crystals by evaporation with a base pressure of  $10^{-6}$  Torr. The NaF source was heated at 1100 °C for 30 min resulting in a film ~40 nm thick and the crystals were masked during deposition so that NaF was only deposited on an area of  $4 \text{ mm} \times 4 \text{ mm}$ .

After NaF deposition, the crystals were heated at 420 °C for 300 min within the same chamber without breaking vacuum to induce diffusion. After this treatment, excess NaF was rinsed from the surface with deionized water and the concentration profile was measured with SIMS. The crystals were recycled by repeating the polishing procedure on the backside of each crystal followed by deposition of NaF and 480 °C heat treatment. The polish removes several hundred micrometers from the surface eliminating any possible Na contamination from the first diffusion experiment.



(a)



(b)

Figure 5.1: Laue photographs of (a) Bridgman grown and (b) melt-grown CIS.

#### 5.3 Results and Discussion

## 5.3.1 Analysis of Diffusion Profile

Figure 5.2 shows Na concentration profiles for both crystals after heating at 420 °C and 480 °C. The Na concentration profile on the uncoated area of the Bridgman crystal after heating at 420 °C shown in Figure 5.2a is two orders of magnitude smaller than in the NaF-coated area of the same crystal. The residual amount of Na observed on the uncoated area is likely due to contamination either during crystal growth or during NaF deposition. The depth profile was modeled using the solution for diffusion from a constant source into a semi-infinite slab as discussed in Section 3.2.1. The best fit line depicted in these figures was obtained by varying the lattice diffusion coefficient  $(D_g)$  and source concentration  $(c_0)$  from the solution

$$c(z,t) = c_0 \operatorname{erfc}\left(\frac{z}{\sqrt{D_g t}}\right)$$
(5.1)

where z is depth, and t is diffusion time. Na has a limited solubility in CIS and  $c_0$  represents the solubility limit.

The semi-infinite slab model is justified because the crystal is much thicker than the diffusion length and 40 nm of NaF provides much more Na than what ultimately diffuses into the crystal.

Within the first few micrometers of each profile, the concentration steeply decreases in a manner that does not follow Equation 5.1. This is likely caused by an increase in defects near the surface that were introduced by the mechanical polish. For this reason z = 0 was set further into the crystal rather than at the surface. The optimized values for D and  $c_0$  are shown in Table 5.2.



Figure 5.2: SIMS Na depth profiles in the NaF-coated areas of the (a) Bridgman grown CIS and (b) melt-grown CIS after heating at 420 °C (orange) and 480 °C (red) along with best fit line (black). The Na profile on the masked uncoated area of the Bridgman crystal is shown in blue.

The diffusion coefficients are nearly identical for both samples and are comparable to the diffusion coefficients measured in other studies for both Na and Cu in CIS. One study estimates both grain boundary and bulk lattice diffusion coefficients of Na in polycrystalline CIGS using SIMS [107] where the lattice diffusion coefficient at 400 °C was  $9 \times 10^{-12}$  cm<sup>2</sup>/s, comparable to the diffusion coefficient measured at 420 °C in this chapter. Another study directly measures a diffusion coefficient of  $10^{-10}$  cm<sup>2</sup>/s for Cu diffusion in single crystal CIS at 400 °C using a radioactive tracer technique [116]. Na<sup>+</sup> is ~ 25% larger than Cu<sup>+</sup> and it is not surprising that Na diffusion is slower.

Since diffusion was only measured at two temperatures, these experiments cannot determine if Na diffusion in CIS has an Arrhenius relationship. However, another study observed an Arrhenius temperature dependence for Na diffusion in polycrystalline CIGS, so it is reasonable to assume that there is an Arrhenius dependence in single crystal CIS as well. The activation energy for diffusion is estimated to be 0.69 eV for the Bridgman crystal and 0.74 eV for the melt-grown crystal. Activation energy was only estimated from two temperatures, introducing a large margin of error so there is not a statistically significant different between these two estimates. The solubility of Na in melt-grown crystal was almost 10x lower and exhibited a stronger dependence on temperature compared to the Bridgman crystal.

## 5.3.2 Analysis of the Extended Defect Structure

Extended defects, which strongly affect diffusion behavior, were evaluated using TEM to measure the dislocation density of each crystal.<sup>†</sup> TEM samples were

 $<sup>^\</sup>dagger$  TEM measurements performed by Dr. A. Rockett & Dr. X. He at University Illinois at Urbana-Champaign.

Crystal	Temperature (°C)	$D (cm^2/s)$	$c_0 ~(at/cm^3)$
Bridgman	420	$2.4\times10^{-11}$	$3.25\times10^{18}$
Bridgman	480	$6.0\times10^{-11}$	$6.20\times10^{18}$
Melt	420	$2.0\times10^{-11}$	$2.7 \times 10^{17}$
Melt	480	$5.4\times10^{-11}$	$1.7  imes 10^{18}$

**Table 5.2:** Diffusion coefficients and solubility limits obtained from best fit toSIMS depth profiles of sodium in CIS.

prepared by a lift-out method in an FEI Focused Ion Beam instrument Helios Nano Lab 600i. The electron diffraction pattern of the Bridgman crystal taken along the  $\langle 001 \rangle$  zone-axis, shown in Figure 5.3, shows clearly defined spots with no evidence of twin boundaries. TEM bright field and dark field images were taken under a two beam condition with the deviation parameter s slightly positive in a JEM 2010 LaB6 microscope at 200 kV. The samples were intentionally tilted away from the zone axis to suppress the effect of strong dynamic contrast.

The dislocations in the crystals can be distinguished by comparison of two beam dark field images and the corresponding bright field images shown in Figure 5.4 and Figure 5.5. A higher density of dislocation was observed within 1 µm of the surface (not shown), which is likely caused by the mechanical polishing procedure as previously discussed. The melt grown specimen clearly has a much higher dislocation density and also has two isolated grains embedded in the CIGS matrix as seen in Figure 5.5a. The striation pattern in the larger grain is likely caused by a high density of stacking faults. The estimated dislocation density from these TEM images are  $10^7 \,\mathrm{cm}^{-2}$  and  $10^8 \,\mathrm{cm}^{-2}$  for the Bridgman and melt grown crystals, respectively. Extended defects are expected to increase diffusion and solubility, but the melt grown crystal has a lower Na solubility and the same



Figure 5.3: Electron diffraction pattern for the Bridgman crystal.

diffusion coefficient despite having a higher dislocation density, which suggests that dislocations are not the controlling factor for Na diffusion in these crystals.

## 5.3.3 Diffusion Kinetics at Dislocations

Diffusion through dislocations can be classified using the same system originally proposed by Harrison for grain boundary diffusion. Diffusion in this system is classified by three regimes based on the relationship between the bulk lattice diffusion distance  $(\sqrt{D_g t})$ , the mean distance between locations ( $\Lambda$ ), and the dislocation core width (a):

- **Type A** The bulk diffusion length in the bulk is greater than the dislocation distance  $(\sqrt{D_g t} > \Lambda)$  and diffusion appears to follow Fick's laws.
- **Type B** The bulk diffusion length is smaller than the dislocation distance  $(\Lambda >> \sqrt{D_g t})$  and diffusion can be modeled using an isolated dislocation model.
- **Type C** The bulk diffusion length is smaller than the dislocation core width  $(\Lambda \gg \sqrt{D_g t})$ , and diffusion is constrained to the dislocation with minimal diffusion into the bulk.



Figure 5.4: A series of BF and DF TEM images of the Bridgman crystal taken under a g = [224]\* two-beam condition. (a) A multi-beam BF image with no apparent contrast of dislocations. (b) and (c) are a pair of BF and DF images from the same region with dislocations circled.

The dislocation density either crystal is too low to accommodate the amount of Na measured with SIMS, and it is clear that diffusion cannot proceed solely along dislocations as described by type B or C diffusion.

Using a dislocation pipe model with a dislocation core diameter of 1 nm, the volume fraction occupied by dislocations with a density of  $10^7 \,\mathrm{cm}^{-2}$  would be  $\sim 10^{-7}$ . If dislocation cores were entirely occupied with Na, this would correspond to a concentration ranging from  $\sim 10^{15} \,\mathrm{at/cm}^3$  to  $10^{16} \,\mathrm{at/cm}^3$ , which is considerably lower than concentrations measured with SIMS. EDS measurements taken at dislocations were not able to detect Na, confirming that Na does not significantly accumulate at these areas. This rules out the possibility that Na is transported solely through dislocations according to type C kinetics. The concentration profile resulting from type B diffusion exhibits a tail that penetrates further into the sample than what would be observed with only bulk diffusion. This dislocation tail is linear with the logarithm of concentration and becomes prevalent at depths greater than  $\sim 3x$  the diffusion length. The average distance between dislocations







Figure 5.5: A series of BF and DF TEM images of the melt grown crystal taken under a g = [112]\* two-beam condition. (a) A multi-beam BF image showing two isolated grains embedded in the CIS matrix, and (b) a BF image with dislocations circled. can be approximated as the inverse of the square root of the dislocation density, assuming that dislocations are randomly located. This approximation gives an average dislocation distance of  $3 \mu m$  for the Bridgman crystal and  $1 \mu m$  for the melt grown crystal, so if type B diffusion is occurring the bulk diffusion length must be less than this and a dislocation tail should become prevalent at a depth greater than  $9 \mu m$  for the Bridgman crystal and  $1 \mu m$  for the melt grown crystal. The logarithm of the concentration profile beyond either of these distances is clearly not linear in either crystal (see Figure 5.2) showing that diffusion is not in the type B regime.

Thus, the SIMS measurements are inconsistent with type B and C, therefore Na diffusion in these samples must follow type A kinetics. The apparent diffusion coefficient measured for type A transport is an average between the dislocation and bulk diffusion coefficients weighted by their respective volume fractions. With a dislocation volume fraction of  $10^{-7}$ , the contribution of diffusion along dislocations is negligible.

#### 5.3.4 Mechanism for Lattice Diffusion of Sodium in CuInSe<sub>2</sub>

One possible mechanism for Na diffusion in CIS is a vacancy-substitution pathway where Na moves through the CIS bulk by a series of exchanges with vacancy sites. This mechanism would most likely be mediated through Na on a Cu vacancy, Na<sub>Cu</sub>, since Cu and Na are monovalent, and DFT calculations show that the substitution of Na with Cu is more favorable by ~1 eV to 2 eV compared to substitution with In or Se [117]. If diffusion was mediated entirely with copper vacancies, an increase in V<sub>Cu</sub> concentration would cause an increase in diffusion coefficient. The Bridgman crystal has a lower Cu content and should have a corresponding increase in  $V_{Cu}$ , however, both crystals show nearly identical diffusion coefficients. This suggests that  $V_{Cu}$  does not control the diffusion of Na in CIS. Furthermore, the unusually low activation energy is inconsistent with a vacancy-mediated mechanism. The measured activation energy for a vacancy-mediated diffusion mechanism will be a combination of activation energies for vacancy formation, vacancy migration, and solute site exchange. The migration barrier for  $V_{Cu}$  in CIS has been calculated to range from 1.09 eV to 1.26 eV [118, 119], which is inconsistent with the activation energy for Na diffusion estimated in this study.

Another possible mechanism is interstitial diffusion, which typically has activation energies lower than vacancy-mediated substitutional mechanisms. For example, the activation energy for migration of Cu interstitials in CIS is only 0.2 eV to 0.34 eV [118, 120]. However, the large size of Na<sup>+</sup> ions (1.16 Å) compared to other host ions (Cu<sup>+</sup>: 0.91 Å, In<sup>+3</sup>: 0.94 Å, Se:<sup>-2</sup>: 1.84 Å) will cause a low equilibrium concentration of Na interstitials which is inconsistent with the solubility measured with SIMS.

This disagreement between a low activation energy and high solubility can be explained using a hybrid interstitial-substitutional diffusion mechanism. In a hybrid mechanism most solute atoms reside on host lattice vacancies and only a small fraction of solute atoms exist interstitially [121] as shown in Figure 5.6. The interstitial diffusion is much faster than vacancy-substitutional diffusion, allowing for a relatively high solubility along with fast bulk diffusion. This mechanism was first experimentally confirmed for Cu diffusion in Ge [122] and since has been observed in a number of various semiconductors and metals [123–125]. It has been speculated that Cd and Fe diffusion in CIGS grains both proceed by an



Figure 5.6: Illustration of a hybrid interstitial-substitutional diffusion mechanism for an arbitrary solute/solvent system

interstitial-substitutional mechanism [126, 127]. Each of these diffusion studies involved a solute atom that is comparable in size or larger than the host solvent atoms.

Since the diffusion rate is controlled by interstitial transport, both crystals have comparable diffusion coefficients despite having different Cu contents. The higher concentration of  $V_{Cu}$  in the Cu-poor Bridgman crystal allows this crystal to accommodate more Na as observed by the increased solubility limit. The melt grown crystal exhibited a stronger temperature dependence because Cu-rich CIS has a greater  $V_{Cu}$  formation enthalpy of 1.43 eV compared to Cu-poor of  $0.64 \pm 0.15 \text{ eV}$  [118]. The activation energy for Na solubility estimated from SIMS data is 1.4 eV for the melt-grown crystal and 0.48 eV for the Bridgman crystal, both in good agreement with  $V_{Cu}$  formation energies for Cu-rich and Cu-poor CIS. It must be stressed that measurements at additional temperatures are needed to confirm that Na solubility has an Arrhenius relationship with temperature.

The results from this study are in good agreement with DFT calculations in the literature. Oikkonen et al. [118] calculate with DFT an activation energy for interstitial Na diffusion of  $0.51 \,\mathrm{eV}$  which is within error of the  $0.7 \,\mathrm{eV}$  value estimated in this study. Oikkonen notes that  $\mathrm{Na}_{\mathrm{Cu}}$  has a more favorable formation enthalpy compared to interstitial Na and proposes a hybrid interstitial-substitutional mechanism that is consistent with the SIMS measurements of this study.

## 5.4 Conclusions

Bridgman and melt grown CIS single crystals were used as a model system to represent the grain interiors of a polycrystalline CIGS film. Diffusion was studied by evaporating NaF onto a 4 mm × 4 mm, heating at both 420 °C and 480 °C, and then measuring Na concentration profiles with SIMS. The Na concentration of the NaF-coated area was two orders of magnitude higher than the uncoated area, demonstrating that the NaF treatment successfully incorporated Na into the single crystals. The activation energy of diffusion was ~0.7 eV for both crystals while the solubility of Na varied by an order of magnitude between the two crystals. This can be explained in terms of a hybrid interstitial-substitutional diffusion mechanism. Most Na sits on  $V_{Cu}$  sites so the Cu-poor Bridgman crystal has a higher Na solubility. The rate of diffusion is controlled by the diffusion of interstitial Na explaining why both crystals have the same activation energy of diffusion which is similar to previously computed values for interstitial Na diffusion in CIS.

## Chapter 6

## REVERSIBILITY OF ELECTRICAL PROPERTIES: ROLE OF SODIUM AT GRAIN BOUNDARIES

### 6.1 Introduction

A crucial aspect in the manufacturing of Cu(In,Ga)Se<sub>2</sub> (CIGS) solar cells is the introduction of a small amount of Na into the CIGS absorber layer. It is well known that a Na concentration on the order of  $1 \times 10^{19}$  atoms/cm<sup>3</sup> will increase both device open circuit voltage (V<sub>OC</sub>) and fill factor (FF) [22, 29, 30, 32]. Incorporation of Na can lead to a relative increase in efficiency as high as 60% [33] and is necessary for manufacture of high efficiency and cost-effective modules.

The presence of Na increases p-type conductivity in CIGS [37, 46, 128, 129], and the mechanism for this is attributed to a variety of point defects. If Na occupies In or Ga sites, denoted as  $Na_{In}$  and  $Na_{Ga}$ , respectively, it will directly act as an acceptor, increasing the hole concentration [130]. Niles et al. reported evidence, by X-ray photoelectron spectroscopy (XPS), of Na bound to Se and attributed this to the substitution of Na into In sites [130]. However, density functional theory (DFT) computations disagreed whether this defect is energetically favorable [117, 131, 132]. An alternate hypothesis suggests Na replaces  $In_{Cu}$  defects to form  $Na_{Cu}$  [37, 128].  $Na_{Cu}$  does not introduce energy levels within the band gap and thus is electrically inactive [131]. However, the  $In_{Cu}$  defect is an electrically active donor and replacing it would lower the concentration of compensating electrons.

It is also possible that Na improves device performance by passivating grain boundary defects. Both Mungan et al. [133] and Urbaniak et al. [134] provide models describing how the passivation of grain boundaries can enhance cell performance. The removal of grain boundary donor defects can increase carrier concentrations near grain boundaries and also reduce the amount of recombination traps at grain boundaries. Cahen and Noufi suggest that the primary electrically active defect at grain boundaries is the selenium vacancy ( $V_{Se}$ ) [135], and Kronik et al. present a model for  $V_{Se}$  passivation in which Na catalyzes the oxygenation of this defect to form electrically neutral  $O_{Se}$  [77]. A majority of Na in CIGS resides at grain boundaries [57, 58] supporting the grain boundary passivation model, but small amounts of Na below detection limits in grain interiors could still impact electronic properties. Rudmann et al. propose that Na does not affect grain interiors when incorporated with a NaF post-deposition treatment (PDT) because the lower temperatures used with this method do not allow Na to diffuse into grain interiors [33]. However, more recent atom-probe tomography measurements reveal the presence of a small amount of Na in CIGS grain interiors after NaF PDT [107] so the possibility that Na affects the electronic properties of grain interiors can not be entirely ruled out.

The incorporation of Ag into CIGS to form  $(Ag,Cu)(In,Ga)Se_2$  (ACIGS) has been of recent interest because of its ability to raise the band gap [136] while lowering defect density [137], providing a pathway for high efficiency devices [138]. ACIGS has the same chalcogenide structure as CIGS with Ag substituting with Cu. The effect of Na is much less studied in ACIGS, but it is known to increase  $V_{OC}$  and FF similar as in CIGS. Because of the similarities in structure, the same Na-related defects that improve CIGS may also be responsible for improvements in ACIGS.

This chapter discusses the effect of Na addition and removal on the electrical transport properties in ACIGS films. A novel procedure is used that allows Na to be cyclically removed and re-introduced into the film. A combination of conductivity and Seebeck effect measurements show how Na affects electrical transport properties, and the results are interpreted in terms of grain boundary chemistry.

## 6.2 Measuring Electrical Properties as a Function of Sodium Content

## 6.2.1 Sample Deposition

All ACIGS films were deposited on 2.5 cm x 2.5 cm alumina pieces (99.6% purity) rather than the typical soda-lime glass to eliminate the substrate as a source of Na, and it was confirmed that the Na content of these substrates fell below detection limits of both XPS and energy dispersive X-ray spectroscopy (EDS). To allow for both device and electrical measurements, the substrate was masked during the Mo deposition using a pattern that consists of a 1 mm gap for measuring conductivity and a 8 mm x 20 mm Mo-free area for measuring the Seebeck coefficient as shown in Figure 6.1.

ACIGS was deposited by three-stage co-evaporation with a substrate temperature of 580 °C, and the details of this process can be found elsewhere [63]. The sample composition was measured with an Oxford Instruments X-Strata980 X-ray fluorescence spectrometer (XRF) and had a composition of: Ag/(Cu+Ag) = 0.26, (Cu+Ag)/(In+Ga) = 0.78, and Ga/(In+Ga) = 0.54.

After the ACIGS deposition, a 20 nm layer of NaF was deposited at room temperature by electron beam evaporation, and after a brief exposure to air, the



Figure 6.1: Schematic of Mo pattern used with ACIGS samples on alumina substrates for conductivity and Seebeck measurements.

sample was transferred to a separate vacuum chamber where it was heated to 400 °C for 20 min to induce Na diffusion into the ACIGS film. After the sample had cooled, it was removed from vacuum and rinsed in water to remove excess NaF from the surface. An identical alumina/ACIGS sample was made without NaF treatment to serve as a Na-free control. Preliminary electrical measurements were carried out prior to Na removal.

## 6.2.2 Control of Na Concentration Within Films

Sodium was removed from the ACIGS samples by multiple cycles of briefly rinsing in  $18 \text{ M}\Omega \cdot \text{cm}$  deionized water at 60 °C followed by heating in air at 200 °C for 5 min to 10 min. Sodium compounds are typically very soluble in water, and water rinsing is expected to completely remove Na from the surface. XPS measurements, conducted with a pass energy of 23.5 eV and an energy step size of 0.05 eV, verified that the surface Na concentration after rinsing was below the detection limit of ~0.1 at%. Heating in air drives Na out of the film where it accumulates on the surface. The presence of oxygen has shown to greatly increase the rate of Na



Figure 6.2: Flow diagram depicting material deposition, Na removal, and electrical measurements.

diffusion [84, 101], so the presence of air during the heat treatment facilitates the accumulation of Na on the surface. The newly accumulated Na is once again rinsed away so that the combination of surface accumulation followed by dissolution lowers the Na concentration in the film, making it possible to control Na content by increasing the number of heat/rinse cycles. Secondary ion mass spectrometry (SIMS) measurements on previous samples have shown that this is an effective procedure for Na removal from (A)CIGS films [139]. The ACIGS samples in this chapter underwent multiple rinse/heat cycles, and the film conductivity and Seebeck coefficient were measured after each cycle as shown in Figure 6.2. After 31 cumulative minutes of heating, NaF was re-deposited using the previously described procedures and the electrical measurements along with the Na removal procedure were repeated.

The time scale and low temperature were chosen so that Na would be removed from grain boundaries rather than from grain interiors. To significantly deplete Na from grain interiors, the diffusion length,  $2\sqrt{Dt}$ , must be larger than the width of the grain. At 31 min of heating, the bulk diffusion coefficient must be  $1 \times 10^{-12} \text{ cm}^2/\text{s}$ to give a diffusion length of 1 µm which is unrealistically large for lattice diffusion at 200 °C. Extrapolating the results from Chapter 5 the diffusion coefficient of Na in single crystal CuInSe<sub>2</sub> at 200 °C is estimated to be  $\sim 1 \times 10^{-13} \text{ cm}^2/\text{s}$ , which is too slow to deplete the grains of Na in 31 min. Due to the low temperature and short heating times, the rate of Na diffusion out of grain interiors would most likely be too slow to account for the large changes observed in electric properties and it is more likely that Na is instead removed from grain boundaries.

## 6.2.3 Electrical Measurements

Cross-grain conductivity ( $\sigma$ ) of the ACIGS film was measured in the dark at room temperature across a 1 mm gap in the Mo back contact (Figure 6.1) using the procedure discussed in Section 2.4.1. The Seebeck coefficient (S) was measured using the procedure discussed in Section 2.4.2. Since  $\sigma$  and S are measured across many grains, they include contributions from both grain boundaries and grain interiors.

## 6.3 Results and Discussion

#### 6.3.1 Conductivity and Seebeck Effect

Figure 6.3 shows conductivity and Seebeck coefficient as a function of heat/rinse cycles, expressed as heating time at 200 °C, for both Na-free ACIGS and ACIGS with two sequential NaF depositions. The conductivity of the Na-treated sample was two orders of magnitude higher than the Na-free control, consistent with reports in the literature while the Seebeck coefficient was an order of magnitude higher than the control. Within 30 minutes of the Na removal procedure, both measurements decreased to values similar to the Na-free sample. After the second NaF treatment, conductivity and Seebeck coefficient returned to their original values and decreased again with subsequent Na removal, indicating that the effects of Na are reversible. The Na-free sample was subjected to the same heating procedure, and both measurements showed negligible change, demonstrating that the heat/rinse cycling did not itself affect the electrical properties of the film. The fact that removing Na from grain boundaries caused electrical properties to approach values measured with a completely Na-free sample is strong evidence that Na acts only at grain boundaries to improve device performance with minimal contributions from the grain interior.

The decrease in conductivity with Na removal is consistent with numerous observations that low Na CIGS films have lower in-plane conductivities [37, 46, 128, 129]. The relationship between conductivity and charge carrier properties can help identify the mechanism behind these electronic changes in ACIGS. For a p-type semiconductor,  $\sigma$  can be expressed as

$$\sigma = q(\mu_h p - \mu_e n) \tag{6.1}$$

where q is the elementary charge, p and n are the concentration of holes and electrons, and  $\mu_h$  and  $\mu_e$  are the hole and electron mobility, respectively. It is important to realize that in a polycrystalline film this relationship becomes more complex due to the presence of grain boundaries, but the fundamental concepts presented in Equation 6.1 are still valid. Hall mobility measurements from other groups suggest that carrier mobility is not affected by the presence of Na [128], therefore the observed decrease in conductivity is due to changes in either electron or hole concentration. A conductivity measurement alone cannot distinguish between carrier type, concentration, or mobility, therefore additional techniques and measurements are needed to determine which of the carrier properties are affected by the presence of Na.



Figure 6.3: (a) Room temperature ACIGS conductivity and (b) Seebeck coefficient as a function of heating time at 200 °C for the Na-free control (open circles), after the 1<sup>st</sup> NaF treatment (orange diamonds), and after the 2<sup>nd</sup> NaF treatment (red triangles).

The Seebeck coefficient, when measured together with conductivity, can be used to distinguish between these electrical properties. For a p-type semiconductor, the Seebeck coefficient can be expressed as [140]

$$S = \frac{k_B}{\sigma} \left\{ -n\mu_e \left[ \frac{5}{2} + r_e - \ln \frac{n}{N_c} \right] + p\mu_h \left[ \frac{5}{2} + r_h - \ln \frac{p}{N_v} \right] \right\}$$
(6.2)

where  $k_b$  is the Boltzmann constant,  $N_V$  and  $N_c$  are the effective density of states in the valence band and conduction band, respectively, and  $r_{e,h}$  is a parameter determined by the carrier scattering mechanism and ranges from -1/2 to 3/2. The Seebeck coefficient remains positive throughout the experiment as expected for a p-type semiconductor.

The effect of hole carrier concentration on Seebeck coefficient can be demonstrated more clearly by examining these expressions in the case of a strong p-type material where p >> n. In this regime, Equation 6.1 and 6.2 reduce to

$$\sigma = q\mu_h p \tag{6.3}$$

$$S = \frac{k_B}{q} \left( \frac{5}{2} + r_h - \ln \frac{p}{N_v} \right) \tag{6.4}$$

From these simplified expressions, conductivity and Seebeck coefficient exhibit opposite trends with respect to the hole concentration as depicted in Figure 6.4, and a decrease in the acceptor concentration alone, upon removal of Na, cannot explain the observed trends (Figure 6.3), where both parameters decrease with Na removal. Instead, we propose that Na removal increases compensating electrons, which in turn decreases both conductivity and Seebeck coefficient. This observation


Free Carrier Concentration (cm<sup>-3</sup>)

Figure 6.4: Seebeck coefficient (dashed red line) and conductivity (solid black line) as a function of majority carrier concentration for an arbitrary semiconductor with p >> n from Equations 6.3 to 6.4.

that Na suppresses compensating donor defects has also been observed in CIGS thin films [108, 141, 142] suggesting that the behavior of Na is similar for both CIGS and ACIGS.

# 6.3.2 Reversibility of Electrical Measurements

In light of these results, any proposed mechanism describing the effects of Na in (A)CIGS must be able to explain this reversibility in electrical properties when Na is added and removed. A common explanation for the behavior of Na at grain boundaries is that it reduces compensating donors by catalyzing the formation of  $O_{Se}$  [77], where the Na only acts as an oxygenation catalyst and does not directly participate in the passivation of defects. According to this hypothesis the removal of Na alone will cause no change in electrical properties. To reverse the effects of this mechanism, oxygen must also be removed allowing  $V_{Se}$  defects to reform. However,  $O_{Se}$  is directly bound to In and Ga [77] forming a very stable bond [143], and the passivation of  $V_{Se}$  with O was calculated to have a standard enthalpy of reaction of  $-4.3 \, \text{eV}$  [131]. Thus it is thermodynamically unfavorable to remove O



Figure 6.5: Schematic of the passivation of  $In_{Cu}$  defects with Na.

and form  $V_{Se}$  when Na is removed and therefore, this mechanism cannot explain the reversibility of the electrical properties.

Another commonly proposed mechanism is that Na replaces donor-type  $In_{Cu}$  defects to form neutral  $Na_{Cu}$  as shown in Figure 6.5, which results in a net increase in p-type conductivity. The formation of this defect is strongly exothermic with a free energy in the bulk as low as -1.0 eV and easily proceeds spontaneously [131].

The high solubility of Na compounds in water provides a driving force for the removal of the  $Na_{Cu}$  defect during the rinse/heat procedure which results in the re-formation of the  $In_{Cu}$  defects causing the conductivity to decrease when Na is removed. Additional research is needed to conclusively determine the defects responsible for the observed behavior.

### 6.4 Conclusions

In summary, the effects of Na on the electrical transport properties of ACIGS thin films were investigated using a novel back contact pattern that allows for conductivity and Seebeck coefficient to be measured on a single sample. Na was incorporated into the ACIGS by NaF evaporation then removed with water rinsing at 60 °C and heating at 200 °C. The removal of Na resulted in a decrease in both the conductivity and Seebeck coefficient to values comparable to Na-free ACIGS, consistent with an increase in compensating donor defects. As the rate of bulk

diffusion is expected to be very low at the temperatures used, it is most likely that the changes in electrical properties were due to the removal of Na from grain boundaries rather than the grain interiors. The changes in the electrical properties were completely reversible with the addition and removal of Na and cannot be easily attributed to the passivation of  $V_{Se}$  with oxygen due to the stability of the O–In and O–Ga bonds. An explanation consistent with both the conductivity and Seebeck results along with the reversibility is that Na passivates a donor-type  $In_{Cu}$  defect by forming a neutral  $Na_{Cu}$  defect where the process is reversible with the addition/removal of Na.

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# Chapter 7

# UNDERSTANDING THE EFFECT OF Na IN Cu(In,Ga)Se<sub>2</sub> FROM A SOLID-STATE DIFFUSION PERSPECTIVE

# 7.1 Introduction

Previous chapters of this dissertation explored various aspects of Na transport in CIGS related materials. These chapters establish that an understanding of Na diffusion in CIGS is essential for understanding the mechanism behind its beneficial effects. In particular the following issues were addressed:

- 1. The role of Mo in controlling Na incorporation from soda-lime glass.
- 2. The segregation of Na at grain boundaries and its diffusion into bulk CIGS.
- 3. Which crystalline point defects Na likely interacts with.

While Chapter 4 provides detail on the Na diffusion mechanism in Mo films, it does not consider how transport in this layer affects Na incorporation into CIGS. Comparing Chapters 4 to 5, the diffusion of Na in Mo is considerably slower than in CIGS, and diffusion through the Mo back contact is the controlling step for Na incorporation in CIGS.

Na segregates at CIGS grain boundaries [57, 58, 145] and the diffusion rates of Na will partly determine the final concentration within grain interiors. There remains some debate whether Na can affect device performance by acting in the bulk, therefore it is important to understand its diffusion behavior in both grain boundaries as well as within individual grains. The atomic diffusion mechanism provides information about how Na interacts with point defects at grain boundaries and within the crystalline lattice. Solid-state diffusion is usually mediated with vacancies [67] so Na must participate in various substitution defects as it diffuses through CIGS. Interaction with electrically active point defects could explain some effects of Na.

This chapter presents an integrated model for how Na behaves in CIGS focusing specifically on the diffusion of Na through CIGS related materials and is organized as follows. First, it discusses the effect of the Mo back contact in controlling Na incorporation into CIGS. Next it compares the transport of Na in grain boundaries and grain interiors. Lastly it discusses remaining opportunities and challenges for understanding Na in CIGS.

# 7.2 Effect of Mo Layer on Na Incorporation

When SLG is used as a Na source, the Mo back contact limits Na incorporation into CIGS [62, 87]. Chapter 4 discusses the mechanism for the diffusion of Na through the Mo back contact and describes the role of oxygen in promoting Na diffusion and accumulation on the surface of Mo. Mo coated SLG samples showed a correlation between the amount of surface oxidation and the amount Na accumulation after heating [141]. Mo films with less surface oxide ultimately accumulated less Na after long periods of heating. This correlation is due to the strong affinity of Na for oxygen, which provides a driving force for enhanced Na diffusion [84, 87, 146]. This chemically promoted diffusion has a lower activation energy than what would be possible with a purely physical diffusion mechanism.

Based on these results, it may be possible to enhance Na incorporation into CIGS by controlling the amount of surface oxygen on Mo substrates, which could increase the rate of diffusion so that more Na is incorporated into CIGS improving device performance. XPS measurements of oxygen on the Mo surface after brief air exposures can reach as high as 50 at%, and Mo samples that are exposed to air should inherently provide this enhancement. Also, due to the high temperatures during CIGS deposition, additional surface oxygen would only slightly improve Na incorporation. At a standard deposition temperature of 580 °C, Na would diffuse through a 1 µm film in 15 s based on the data in Chapter 4. With such a rapid diffusion rate, additional surface oxygen would only marginally enhance the Na incorporation explaining why the effect of Mo oxidation usually does not need to be accounted for. However, for manufacturing processes that involve sequential Mo and CIGS depositions without exposure to atmosphere, the complete lack of oxygen could make Na incorporation less favorable. Also, at lower deposition temperatures Na diffusion in Mo may become slow enough that Mo surface oxidation becomes a larger factor.

Although at high temperatures Mo surface oxygen only plays a minor role in the incorporation of Na, the amount of surface oxidation can still be optimized to provide slight improvements in  $V_{OC}$  and efficiency. A large number of devices must be analyzed to determine if such a correlation exists, any such efficiency increase would be relatively small and there are many other factors that also affect efficiency. The easiest way to control surface oxidation is to compare device performance against age of the Mo substrates before CIGS deposition. Mo samples that remain in storage longer will have greater exposure to air and will accumulate more surface oxygen. Figure 7.1 takes data from the Institute of Energy Conversion cell



Figure 7.1: ACIGS  $V_{OC}$  (a) and efficiency (b) vs. age of Mo before ACIGS deposition. Red lines are displayed to serve as a visual aid. Data provided by Chris Thompson.

performance database for 280 (Ag,Cu)(In,Ga)Se<sub>2</sub> devices and plots the efficiency and  $V_{OC}$  against the Mo age (data provided by Chris Thompson). The inclusion criteria for this plot were a Ga / (In + Ga) ratio between 0.47–0.53 and a Ag / (Cu + Ag) ratio between 0.2–0.4 to minimize the effect of composition on band gap and cell performance. Despite a few outliers from poor performing cells, this figure shows a slight increase in efficiency and  $V_{OC}$  consistent with the idea that an increase in surface Mo oxidation enhances Na incorporation. Due to the small sample size, data from Figure 7.1 is noisy and the trend is less clear. However, a increase in cell efficiency with Mo age has been independently observed by Salomé et al. [85] providing more support to this hypothesis. There appears to be less spread in  $V_{OC}$  for older Mo samples although a more extensive sample set is needed to confirm that this trend is real. If confirmed, this increased reliability may be of more importance than the minute increase in efficiency gained.

These results raise the possibility that the Mo substrates could undergo a partial oxidation treatment to optimize the amount of surface oxide. Care must be taken not to provide too much oxygen since an overly oxidized Mo surface would have several detrimental effects on device performance. It is well known that  $MoO_3$  acts as an intercalation host for Na [147] because its layered structure provides stable sites for alkali elements. The solubility in bulk  $MoO_3$  is expected to be larger than CIGS and large amounts of surface oxide on Mo could act as a Na sink preventing incorporation into CIGS. This is not a problem for low O concentration samples since sub-monolayer amounts of  $MoO_3$  would not form the typical layered structure and would not act as an intercalation host. Another detrimental effect is that excess amounts of surface oxygen would also compete with the formation of  $Mo_2$ Se, which is known to facilitate the formation of an ohmic back contact [24–26].

Lastly,  $MoO_3$  is not conductive and a thick oxide layer at the back contact would increase series resistance in devices.

### 7.3 Na Diffusion in CIGS

# 7.3.1 Na at CIGS Grain Boundaries

Chapter 6 establishes that Na acts only at grain boundaries. It shows that removing Na exclusively from ACIGS grain boundaries causes conductivity to decrease to values similar to Na-free films despite Na remaining in the grain interiors [144]. In this study, Na was removed by heating in air at 200 °C, and due to the low temperatures involved, Na was mostly removed from grain boundaries without significantly modifying the concentration within grains. The single crystal diffusion studies in Chapter 5 confirm that Na lattice diffusion is too slow at 200 °C for grains to become depleted from this procedure.

The Na removal procedure outlined in Section 6.2.2 was performed on a series of SLG/Mo/CIGS samples for a total of 6 cumulative hours of heating at 200 °C. Although the SLG substrate is a source of Na, diffusion through Mo proceeds too slowly at 200 °C to replenish CIGS. Extrapolating the data from Chapter 4, the diffusion length for Na in Mo after 6 hours of heating at 200 °C is 46 nm, which is much smaller than the 700 nm thickness of this layer. The SIMS depth profiles presented in Figure 7.2a show that this procedure lowered the Na concentration by a factor of 4. After the removal procedure, the minimum Na concentration is  $3 \times 10^{18}$  at/cm<sup>3</sup> which is very close to the solubility limit estimated for the Bridgman-grown crystal in Chapter 5 indicating that most remaining Na resides within grain interiors.



Figure 7.2: (a) Na SIMS depth profiles through CIGS for an as-deposited film and after Na removal. (b) JV curves for CIGS devices with standard Na (solid) and with Na removal (dashed).

Table 7.1:	JV	characteristi	cs and	d average	Na	concentrations	of the	devices	pre-
	sen	ted in Figure	7.2.						

Sample	Avg. Na Conc.	$V_{OC}$	$J_{SC}$	$\mathbf{FF}$	$\eta$
	$(at/cm^3)$	(V)	$(\mathrm{mA/cm^2})$	(%)	(%)
As-deposited	$1.7 \times 10^{19}$	0.65	29.8	76.7	14.9
After Na removal	$4.1\times10^{18}$	0.60	28.9	68.6	11.9

Devices were made before and after Na removal and JV results are shown in Figure 7.2b and device parameters are listed in Table 7.1. Na removal caused a decrease in  $V_{OC}$ , FF, and efficiency similar to what is seen in Na-free devices.

Chapter 6 also provides evidence that the removal of Na increases in the concentration of compensating donors. The presence of donor defects at grain boundaries can be detrimental to device performance [133, 134], and the effect of Na can be understood as the passivation of these donor defects at grain boundaries. Donor defects are positively charged after giving up their electrons which causes downward band bending along the grain surfaces of p-type (A)CIGS as shown in Figure 7.3a. Downward band bending creates depletions regions extending from grain boundaries, which can significantly lower the hole concentration in small grains [134]. Electrostatic repulsion from positively charged grain boundaries creates an energy barrier for holes moving between adjacent grains and this energy barrier contributes to the lower conductivity observed in the Na-free samples. Additionally, photogenerated electrons are attracted to positively charged grain boundaries where they can recombine, lowering  $V_{OC}$  and FF. Device simulations that account for electron attraction to positively charged grain boundaries shown significant improvements in device performance with the passivation of grain boundary defects [133]. Na passivates donor defects as previously discussed, creating flat bands along grain boundaries and eliminating the detrimental effects of a positively charged grain boundary. The creation of accumulation layers from a net negative charge at the grain boundaries could further enhance this benefit, however, only one report has found evidence of this [148].

There is ample evidence in the literature that grain boundaries contain positively charged donor defects [129, 149–151]. Downward band bending near grain



Figure 7.3: Band diagram of the region near a grain boundary in CIGS. A positively charged grain boundary (a) repels holes creating a depletion region and attracts electrons increasing recombination. Na can passivate donor defects at grain boundaries (b) eliminating the depletion region, possibly creating accumulation regions (dotted lines) and lowering electron recombination.

boundaries has been confirmed using Kelvin probe force microscopy (KPFM) [149], and temperature dependent resistivity and Hall measurements reveal an activation energy for hole transport that is in good agreement with the potential barriers measured with KPFM [150]. The potential barrier in Na-free films could be as high as 300 meV, while films with Na typically had barriers below 100 meV [129, 150, 151], further supporting the idea that Na passivates donor-like defects at grain boundaries.

The amount of positive charge can be roughly estimated from the density of donor defects at the grain boundaries as shown in Equation 7.1, assuming a uniform donor density and that each donor gives up two electrons. While there are more rigorous treatments for estimating grain boundary charge [150], this approach provides a acceptable first approximation.

$$Q_{GB} = 2qN_D^{GB} \tag{7.1}$$

 $Q_{GB}$  is the grain boundary surface charge density, q is the elementary charge, and  $N_D^{GB}$  is the surface density of donors along grain boundaries. From  $Q_{GB}$  the space charge width  $(w_{sc})$  can be estimated by maintaining charge neutrality between the grain boundary and the space charge region

$$Q_{GB} = N_A q w_{sc} \tag{7.2}$$

The magnitude of the band bending induced by the space charge region  $(V_b)$  can be estimated by solving Poisson's equation for a uniform doping density,  $N_A$ , and evaluating the solution at the grain boundary giving

$$V_b = \frac{qN_A}{2\epsilon} w_{sc}^2 \tag{7.3}$$

where  $\epsilon$  is the absolute dielectric constant for CIGS. From Equations 7.1 to 7.3, the 300 meV barrier height observed with a Na-free grain boundary gives a space charge width of ~100 nm and a grain boundary donor density of ~5 × 10<sup>11</sup> cm<sup>-2</sup> assuming  $N_A = 10^{17}$  cm<sup>-3</sup> and the relative dielectric constant is 7.5 [152]. The dangling bond density of a typical CIGS surface is ~10<sup>15</sup> cm<sup>-2</sup>, so under the stated conditions only a small fraction of surface sites need to be electrically active. In the case of a Na-containing grain boundary with a barrier height of 100 meV, the grain boundary donor density is calculated to be ~3 × 10<sup>11</sup> cm<sup>-2</sup>. Therefore, to reduce the barrier height below 100 meV, ~40% of active donor sites need to be passivated with Na. While the exact numbers may vary with the specific film, this example demonstrates the feasibility of forming a depletion region from grain boundary donor states.

### 7.3.2 Na Within CIGS Grains

It is clear from the diffusion of Na in single crystals that Na can be incorporated into CIGS grains, albeit at much smaller concentrations than in grain boundaries. The deposition temperature can be as high as 580 °C resulting in a bulk diffusion length of ~9  $\mu$ m1 h after an hour of heating, based on diffusion data from Chapter 5. This is significantly greater than the largest grains in CIGS films, so grains likely have a uniform concentration when Na is incorporated during the CIGS deposition. Even at the lower temperatures used for PDT, bulk Na diffusion proceeds fast enough that bulk Na incorporation can occurs. NaF post-deposition treatments typically involve heating NaF-coated CIGS for 30 min at a temperatures ranging from 300 °C to 400 °C. In this case the diffusion length after 30 min of heating extrapolated at 300 °C is 0.6  $\mu$ m. Although the grain will not be saturated, Na should still have penetrated a significant distance into the grain. While the data presented in this dissertation establishes that the beneficial effects of Na are due to its presence at grain boundaries rather than grain interiors, it cannot be ruled out that Na within CIGS grains has a slight negative impact on performance.

There is evidence that too much Na in CIGS can have a detrimental effect on device performance [30, 41–44]. Chapter 5 provides evidence that Na within CIGS grains primarily resides at copper vacancies, so the detrimental effect of too much Na could be a result of the annihilation of copper vacancies in the bulk by the formation of Na<sub>Cu</sub> thereby reducing net carrier concentration. Under normal circumstances, the positive effects of Na at grain boundaries greatly outweigh any detrimental effects of Na within grains resulting in a net enhancement in performance. However when the concentration of Na within bulk CIGS is exceedingly high, negative effects may become dominant which typically is not a problem for standard Na incorporation procedures. For Na post-deposition treatments, the low temperatures prevent too much bulk incorporation and detrimental effects do not occur. When SLG is used, the lower Na concentration within the glass prevents excessive Na within CIGS grains. More experimental evidence is needed to conclusively prove that Na detrimentally impacts CIGS in this way.

### 7.4 Opportunities and Challenges

Significant improvements have been made in understanding the role of Na in improving CIGS solar cells, but a few open questions still remain. This section addresses two opportunities for furthering the understanding of Na in CIGS. First, it discusses the challenges associated with determining the exact defects passivated by Na at grain boundaries. Second, it examines the possibility that Na could affect the CIGS/CdS junction.

#### 7.4.1 Atomic Defects Related to Na

While the results in Chapter 6 point towards a mechanism where Na passivates donor-like defects at grain boundaries, determining the exact atomic defects involved remains a challenge. This challenge arises in part because the small volume fraction that grain boundaries occupy. It is difficult to measure Na-related defects when concentrations of 1-2 at% are confined to sub-nanometer regions. Grain boundary composition and orientation greatly vary, even within the same film, and this wide variety of grain boundary properties further complicates the analysis of Na related defects. CIGS films typically contain a mix of several different types of twin and randomly oriented high angle grain boundaries [150, 153], and the orientation of the grain boundary will dictate which defects are prevalent. Twin grain boundaries are grain boundaries between adjacent grains with mirror symmetry. Due to their high symmetry, twin boundaries often have less defects compared to randomly oriented high angle grain boundaries. This boundaries are classified using  $\Sigma$  notation which is based on the coincidence-site lattice and details on this notation can be found in Ref. [153]. The lowest energy and most prevalent twin boundary orientation in CIGS is  $\Sigma 3$  [153]. The atomic composition varies significantly between different grain boundaries as demonstrated by Lei et al. [154] who took several hundred nano-EDS measurements of grain boundaries on films deposited by identical methods and observed a 5 at% variation in grain boundary composition. Such a wide variety of grain boundaries raises the possibility that Na may only be beneficial at some boundaries while having no effect at others.

KPFM [148, 155–157], CL [148, 158], and EBIC [158, 159] measurements across  $\Sigma 3$  twin boundaries indicate that these boundaries are mostly electrically inactive. Hanna et al. [148] show with cathodoluminescence (CL) that the grain boundaries of (220/204) textured films with Na exhibit less radiative recombination compared to grain boundaries of (112) oriented and randomly oriented films containing Na. The grain boundaries of Na-free (220/204) oriented films showed increased radiative recombination similar to the random oriented films with Na. (220) oriented films tend to be dominated by  $\Sigma 3$  twin grain boundaries [155] and these CL measurements suggest that Na is most effective at passivating these boundaries. On the other hand, KPFM measurements on CGS/GaAs with a single  $\Sigma 3$  boundary indicated that the boundary was neutral despite the absence of Na [155, 156]. If  $\Sigma 3$  boundaries are electrically neutral without the presence of Na, it would be more likely that Na acts primarily to passivate random grain boundaries instead. A systematic investigation is needed to resolve this apparent contradiction.

Even though the exact defects that Na passivates are unknown, inferences can be made based on previous observations. An argument is made in Section 6.3.2 that the passivation of  $V_{Se}$  by forming  $O_{Se}$  as described in Ref. [77] is not responsible for the beneficial effects of Na. This section does not argue against the idea that  $V_{Se}$ passivation is beneficial. Rather, it argues that benefits from  $V_{Se}$  passivation and benefits from Na incorporation are two separate and unrelated phenomena. The existence of  $O_{Se}$  at grain boundaries is supported by both APT [105] and EELS [160] measurements at grain boundaries which show an anti-correlation between oxygen and Se at grain boundaries [135, 161]. Furthermore, the beneficial effects of air heat treatments on device performance have long been attributed to the passivation of  $V_{Se}$  with oxygen.  $O_{Se}$  is a very stable defect and its formation should not be reversible. The device data in Figure 7.2b along with the electrical measurements in Chapter 6 clearly show that the effects of Na are reversible when Na is removed. This reversibility cannot be explained by the irreversible oxygenation of  $V_{Se}$  and the beneficial effects of Na must be due to another process.

The idea that  $V_{Se}$  is unrelated to Na is supported by several studies in the literature. Couzinié-Devy et al. [162] analyze a CIGS sample with APT where there is no difference in oxygen concentration between the grain boundary and bulk even though Na has segregated at the grain boundary. If Na acts as an oxygenation catalyst, oxygen would be expected to segregate at the grain boundary along with Na. In another study, Rockett et al. [42] analyzed 8 different CIGS samples with SIMS and showed that even though the Na concentration varied by 5 orders of magnitude, O concentration varied by less than a factor of 10, providing further evidence that oxygenation of  $V_{Se}$  is not related to sodium. Keller et al. [106] show a complete absence of O above the detection limit of 10 ppm when an alkali diffusion barrier is used. The authors conclude that the alkali diffusion barrier blocks oxygen from the SLG substrate, and without an air anneal there is no source of oxygen for the sample. It is well established that the beneficial effects of Na can be achieved on cells manufactured with a NaF PDT, an alkali diffusion barrier, and no air anneal [33], suggesting that the presence of oxygen is not necessary to achieve the beneficial effects of Na.

The electrically inactive nature of  $\Sigma$ 3 twins suggests that Na may not be necessary at these boundaries and the effects of Na may be due to its presence at randomly oriented high angle grain boundaries. EELS measurements with sub-nanometer resolution show that Cu and In concentrations are anti-correlated at random grain boundaries suggesting that Cu<sub>In</sub> and In<sub>Cu</sub> readily form at grain these grain boundaries [105, 160, 163].  $In_{Cu}$  is an electrically active donor, and it is possible that Na helps passivate this defect to improve the device performance.

### 7.4.2 Na at the CIGS/CdS Junction

One commonly dismissed mechanism is the possibility that Na acts at the CIGS/CdS junction. Na compounds are highly soluble in water, and the aqueous bath during CdS deposition dissolves nearly all Na at the surface of CIGS. For this reason, it is often stated that Na cannot exist near the CIGS/CdS junction. However, given the very fast Na diffusion rates presented in previous chapters it is almost certain that Na below the CIGS surface quickly diffuses back to the CdS interface. The CdS layer contains oxygen, which is known to enhance Na diffusion, providing an additional chemical driving force for Na incorporation at this junction. Figure 7.4a summarizes XPS measurements of the CIGS surface immediately after rinsing and as a function of the amount of time exposed to air after rinsing. Although Na disappears immediately after rinsing, it diffusion is fast enough at room temperature to diffuse back to the CdS interface in a completed device.

Figure 7.5 shows that the Na concentration in a CIGS/CdS sample remains around  $10^{18}$  at/cm<sup>3</sup> through the film without a significant drop near the CdS interface. The apparent increase in Na concentration in the CdS layer is likely an artifact caused by an increased sputter yield, the ratio of the amount of sputtered secondary ions to the amount of impinging primary ions. This observation that Na is not depleted at the CdS interface was also observed by Heske et al. [164] who used a combination of X-ray emission spectroscopy and photoelectron emission



Figure 7.4: (a) Na 1s spectra measured with XPS of CIGS after rinsing (blue) then after 16 hours exposure to room air at 25 °C. (b) Na accumulation on the surface of CIGS measured with XPS as a function of time exposed to room air.

spectroscopy to show that a significant amount of Na resides at the CdS junction. APT measurements of the CIGS/CdS junction reveal that in addition to segregating at the interface, Na also diffuses into CdS and can reach concentrations as high as 0.2 at% [145, 165].

Experimentally determining the role of Na at the CIGS/CdS is a challenge due to the fast diffusion rate of Na in CIGS. It becomes very difficult to exclusively incorporate Na at the junction because Na can quickly diffuse into grain boundaries. Despite this challenge, it is important to determine if the presence of Na near the CdS junction affects device performance. While there has not been much research into this issue, a few studies propose mechanisms for Na near the CdS junction. Heske et al. [164] propose that Na may affect the interface dipole and alter the electronic properties of the heterojunction. Erslev et al. [166] use a combination of capacitance-voltage profiling and drive level capacitance profiling to determine that low Na samples contain ~ $10^{17}$  cm<sup>-3</sup> defects within 50 nm of the CIGS/CdS junction which could explain the reduced V<sub>OC</sub> in Na free samples.



Figure 7.5: SIMS depth profiles on a CIGS/CdS for (a) the entire film and (b) near the CdS heterojunction. The dashed line denotes the nominal CdS interface.

### 7.5 Concluding Remarks

While the benefits of Na have been known for over two decades, the mechanisms behind its improvements are still debated today. This chapter focuses on understanding the effect of Na in CIGS by studying its diffusion behavior. First, it shows that the Mo back contact plays a role in the incorporation of Na and the presence of oxygen enhances Na diffusion in Mo. CIGS films deposited on aged Mo performed slightly better possibly due to enhanced Na incorporation caused by the oxidized Mo surface. Next, this chapter investigates the diffusion of Na through CIGS grain boundaries and grain interiors. Selectively removing Na from only grain boundaries causes  $V_{OC}$  and FF to drop to values nearly expected for a low Na device, proving that Na primarily acts at grain boundaries. A mechanism for passivation of donor defects at grain boundaries is presented that could explain increased device performance in Na-containing films. Based on reversibility of electrical measurements when Na is removed, it is unlikely that the effects of Na are related to the passivation of  $V_{Se}$  defects with oxygen. Lastly, this chapter discusses remaining opportunities and challenges for understanding the effects of Na. While Na appears to passivate donor defects at CIGS grain boundaries, the exact defects involved are still unknown. It is also unknown whether Na modifies electrical properties near the CdS/CIGS heterojunction.

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## Chapter 8

# CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

### 8.1 Summary of Results

This dissertation provides quantitative information that expands the current understanding of how Na benefits CIGS solar cells by evaluating the transport of Na in CIGS-related materials and its relationship to electrical and device properties. It begins by investigating diffusion of Na from soda-lime glass through Mo thin film and then looks at diffusion of Na through the grain boundaries and grain interiors of CIGS-related materials.

### 8.1.1 Na Diffusion Through Mo

The diffusion of Na through Mo was studied by heating Mo-coated SLG at various temperatures and using XPS to measure Na accumulation vs. heating time. Surface accumulation of Na was modeled using the Hwang-Balluffi method, and the results agreed well with the model indicating that diffusion followed Harrison's type C regime where the solute is confined to grain boundaries. Using this model, diffusion coefficients were determined for several different temperatures. The resulting activation energy was lower than expected for physical diffusion through Mo grain boundaries and instead was consistent with dissociation of the Mo–O bond in MoO<sub>3</sub>. To directly test if O is involved in Na diffusion, accumulation of Na was measured as a function of the amount surface oxide present before heating.

It was found that the amount of Na that ultimately accumulates on the surface increased linearly with the amount of surface oxide confirming that oxygen in Mo provides a driving force for enhanced Na diffusion.

The effect of Mo surface oxide on the incorporation of Na into CIGS devices was investigated by comparing ACIGS cell performance against age of the Mo substrates. The age of Mo determines the amount of air exposure that samples receive and therefore the amount of surface oxide that develops. It was shown that ACIGS cells deposited on Mo substrates older than 6 days had slightly higher efficiency and  $V_{OC}$ . These findings suggest that the amount of surface oxide on Mo substrates can be optimized to slightly boost performance of CIGS devices.

### 8.1.2 Na Diffusion in CIGS Grain Interiors

Single crystal CIS was used as a model system that represents the interior of CIGS grains. Na diffusion from a NaF source was studied in crystals made by the Bridgman method and by a horizontal gradient freezing method (referred to as melt grown). NaF diffusion was induced by evaporating a 40 nm layer on the surface of room temperature crystals followed by heating at 420 °C for 6 h. This procedure was repeated on each crystal at 480 °C. SIMS measurements revealed that this procedure resulted in a Na concentration that was two orders of magnitude higher than the concentration from regions on the crystal that did not receive NaF. Diffusion was modeled using the solution for transportation from a constant source into a semi-infinite slab, and experimental depth profiles were a good fit to the model. The Na diffusion coefficients in the Bridgman and melt grown crystals were the same at both temperatures, but the Na solubility in the melt grown crystal was ~10x lower at each temperature. The extended defect structure was studied using TEM, which revealed that the Bridgman and melt grown crystals had dislocation densities of  $10^7 \text{ cm}^{-2}$  and  $10^8 \text{ cm}^{-2}$ , respectively. The TEM specimen from the melt grown crystal also had an isolated grain embedded in the CIS matrix with a high density of stacking faults. These extended defects should increase both the diffusion coefficient and solubility of Na, but the melt grown crystal had a lower solubility and the same diffusion coefficient as the Bridgman crystal despite its higher defect density suggesting that dislocations are not the controlling factor for diffusion. Furthermore, the defect density in each crystal is too low to easily explain the high solubilities observed in each crystal.

Next, the role of composition on diffusion and solubility was investigated using XRF measurements on each crystal. The Bridgman crystal was slightly Cu-poor and the melt grown crystal was nearly stoichiometric. The Cu-poor composition of the Bridgman crystal is consistent with the observation that  $Cu_2Se$ segregated at one end of the crystal ingot. The possibility that Na diffusion occurs by substitutions with Cu vacancies is constant with solubility measurements but not diffusion coefficient estimates. The Cu-poor Bridgman sample has a greater concentration of Cu vacancies, which provides more sites for Na and consequently increases the Na solubility. An increase in Cu vacancy concentration should also increase the probability that any Na atom has a neighboring vacancy, and therefore the diffusion coefficient should increase in a Cu-poor sample. The Cu-poor Bridgman grown crystal had the same diffusion coefficient as the melt grown sample which is inconsistent with a diffusion mechanism that is entirely mediated by Cu vacancies.

To reconcile these inconsistencies, a hybrid interstitial-substitutional mechanism is proposed. This mechanism combines the fast diffusion rates of interstitial diffusion with the higher solubility of substitution onto Cu vacancies. Since the formation of Na interstitials is energetically unfavorable, only a small fraction of atoms are located interstitially. Instead, a majority of atoms reside at Cu vacancies and Na solubility is controlled by Cu content. The diffusion rate is controlled by transport of interstitials since the activation energy for interstitial migration is much lower than for vacancy formation and migration. This hybrid interstitial-substitutional mechanism has been established for nearly 60 years and has been experimentally verified for many systems that usually involve solute atoms comparable in size to the surrounding matrix atoms.

These results on single crystals verify that Na can easily diffuse into CIGS grains at temperatures as low as 400 °C and reach concentrations as high as  $10^{18} \,\mathrm{cm}^{-2}$ . For this reason, the possibility that Na effects bulk electronic properties cannot be neglected.

# 8.1.3 Na in CIGS Grain Boundaries

The effect of Na in CIGS grain boundaries was studied by selectively removing Na from grain boundaries without significantly modifying the Na concentration within grains. Due to the lower activation energy of grain boundary diffusion compared to bulk diffusion, at 200 °C Na at grain boundaries remains very mobile while Na diffusion within grain interiors is very slow. Na was removed from CIGS and ACIGS using repeated cycles of heating at 200 °C to drive Na out of grain boundaries and rinsing to remove Na that accumulates on the surface. SIMS verified that the average Na concentration decreased during this procedure, and the Na concentration after long periods of heating was similar to the solubility limit measured in CIS single crystals, showing that the only remaining Na resides within grains.

Electrical measurements of ACIGS films taken during this procedure showed that conductivity and Seebeck coefficient both decreased as Na was removed. After completion of the Na removal procedure, Na was re-introduced into the films and both electrical properties recovered to their original values. Na removal and re-introduction was repeated twice with the same result showing that changes in conductivity and Seebeck coefficient were due to the presence of Na and not an unrelated factor caused by the heat treatment. This simultaneous decrease in conductivity and Seebeck coefficient cannot be explained by a single carrier semiconductor but is consistent with an increase in compensating donors with the removal of Na.

After long periods of Na removal, the conductivity and Seebeck coefficient returned to values similar to Na-free films. Devices made after Na removal showed a decreased  $V_{OC}$  and FF similar to what is typically observed in Na-free devices. The observation that electrical and device properties return to values similar to Na-free films despite the presence of Na within grains proves that the major mechanism for the benefits of Na are due to its presence at grain boundaries rather than within grain interiors.

A model was presented that explains how passivation of charged grain boundary defects could enhance device performance. Donor defects at grain boundaries are positively charged after giving up their electrons which creates depletion regions near grain boundaries. Positive photo-generated holes experience a coulombic attraction to negatively charged grain boundaries, where they can easily recombine due to a large concentration of recombination centers caused by the high disorder at grain boundaries. Passivation of donor defects at grain boundaries eliminates the depletion region and photocarriers no longer experience attraction toward grain boundaries, resulting in less charge carrier recombination and a higher  $V_{OC}$ . If Na passivates enough donor defects so that grain boundaries become more p-type than the bulk, an accumulation layer will form repelling photo-generated holes from grain boundaries resulting in further improvements to device performance.

The reversibility of electrical properties contradicts the commonly proposed model that Na indirectly passivates charged selenium vacancies at grain boundaries. In this model, Na catalyzes the dissociation of oxygen, which then interacts with Se vacancies to form electrically inactive  $O_{Se}$ . These  $O_{Se}$  defects are inherently very stable and would not be easily reversed under the mild heat treatments used during the Na removal procedure. Oxygen occupying Se sites would not be removed along with Na, and therefore the  $V_{Se}$  passivation model cannot be responsible for the changes in electrical and device properties observed in these experiments.

#### 8.2 Recommendations for Future Work

# 8.2.1 Extended Single Crystal Diffusion Study

The results of Chapter 5 provide groundbreaking insight into the diffusion mechanism of Na in bulk CIGS. However, these experiments were performed with just two crystals and two temperatures, which only provides a semi-quantitative description of Na diffusion. Taking diffusion coefficient measurements over a wider range of temperatures can further refine the estimated activation energies from this study. Also, the effects of both dislocations and composition on Na diffusion can be better understood with additional single crystal diffusion studies. One possible mechanism for the benefits of Na is the passivation of dislocations. For this reason it is important to understand the diffusion of Na along dislocations, however, due to the low dislocation density of these two crystals this could not be studied. Samples with a higher dislocation density would be useful for understanding the segregation and diffusion of Na along these defects.

The composition of actual CIGS devices varies over a much wider range than what was studied with these two crystals. It is unknown if the trend that Na solubility increases with additional Cu vacancies extends into samples that are very Cu-poor. It is also unknown if Ga plays a role in controlling bulk Na diffusion and solubility. Lastly, commercial manufacturing processes often involve the selenization and sulfurization of metallic precursors, and it is unknown how the presence of sulfur would affect Na transport properties.

The Institute of Energy Conversion has a large collection of CIGS single crystals including crystals with gallium and with sulfur and also has the expertise to make new crystals. Repeating the experiments outlined in Chapter 5 would provide a more complete understanding of how Na behaves within CIGS grains.

### 8.2.2 Effect of Na at the CdS Junction

The idea that Na near the CIGS/CdS interface affects device performance is often discarded because the chemical bath deposition of CdS dissolves Na from the surface of CIGS. This dissertation provides evidence that Na diffusion in CIGS is fast enough at room temperature that the interface can be replenished with Na diffusing from deeper in the absorber. Given these results, it is important to understand if Na has any impact at the CdS interface. The fast diffusion rate of Na makes it difficult to distinguish between affects of Na at the interface and affects of Na at grain boundaries. Chapter 7 outlines an approach for determining how Na affects the CIGS/CdS interface.

#### 8.2.3 Effect of Na Migration on Long-Term Device Stability

The fast diffusion of Na in CIGS at room temperature raises the possibility that long-term stability could be affected by the migration of Na. While the impact of Na on stability has not been extensively studied, there are a few reports that low-Na devices exhibit better long term stability and less degradation compared to devices with high Na contents [167–169]. It is clear from these studies that there are multiple pathways in which Na migration affects device stability.

Theelen et al. [167] show that devices with Na underwent severe degradation caused by shunting after extended exposure to damp heat at 85 °C and 85% relative humidity while under illumination. However, low-Na devices were stable under the same conditions despite initially having a lower efficiency. Degradation did not occur during treatments performed in the dark indicating that illumination played a key role in the degradation process. Cells that were unstable during damp heat treatment had Na-rich areas extending throughout the ZnO:Al and CdS layers that likely caused shunting in these devices. In these samples, Na also decreased in the CIGS layer suggesting that the increased Na in the ZnO:Al layer originated from the absorber layer rather than the substrate. The author proposes that illumination creates a potential gradient that causes rapid Na diffusion towards the surface. Na initially does not diffuse into the CdS layer due to the potential barrier created by the p-n junction, but large amounts of Na cluster at the interface until the accumulated positive charge weakens the barrier allowing Na to migrate through CdS into the ZnO:Al. Since this mechanism relies on photo-generated charge carriers, samples that underwent heat treatment in the dark were stable and did not suffer from shunting.

Fjällström et al. [168] exposed cells of varying Na content to dry heat at 85 °C while biasing the cells at 50 V since the stability of devices at high voltage is relevant for cells at the high voltage end of a module. Significant degradation occurred in high-Na cells within 5 h of heating in the dark, while no degradation occurred in low-Na cells within the 50 h duration of the experiment. Also, no significant decrease in device performance took place in the absence of a high voltage bias. SIMS measurements showed an increase in Na in both the CIGS and CdS layers, and this extra Na appears to come from the glass substrate. Devices made on Na-free substrates with NaF PDT incorporation showed no significant degradation after this treatment in agreement with the hypothesis that Na migration from the substrate is responsible for degradation. It is demonstrated that glass with high Na mobility resulted in a larger concentrations of Na in the CdS and a lower device efficiency. The degradation in device performance is presumably due to the increased concentration of Na in CdS caused by migration of Na out of the substrate. Chapter 4 demonstrates that Na diffusion through Mo at 85 °C is too slow to cause a significant increase in concentration in CIGS within 5 h. The 50 V bias applied to these cells likely created an electric field that enhances the diffusion rate of Na ions through the Mo back contact.

Daume et al. [169] compared low and high Na cells supported on Na-free substrates exposed to damp heat at 85 °C and 85% relative humidity and observed that high Na-cells had a much faster degradation rate. This degradation mechanism is different from the previous two since it occurred in the dark, without a voltage bias, on Na-free substrates. Degradation was caused by an increase in series resistance, which the authors propose was caused oxidation of the Mo back contact enhanced by Na and H<sub>2</sub>O.

These three studies depict three separate degradation mechanisms caused by the migration of Na. Diffusion mechanisms presented in this dissertation are insufficient to understand these degradation mechanisms. The effects of illumination, voltage bias, and humidity on Na diffusion all need to be studied to better understand how Na migration affects long-term device stability.

# 8.2.4 Effects of Other Alkali Elements

In 2013 the discovery that potassium increases cell efficiency beyond the benefits of Na led to new pathways for creating high efficiency devices [5]. After this discovery, four separate institutions created five new world record efficiencies in a period of less than two years [5–9]. During this period, the champion efficiency increased from 20.3% to the current world record of 21.7%. Before this discovery, record efficiencies for CIGS were set every 1 to 2 years and the world record had only increased by 1.4% absolute over a period of 10 years.

Increases in efficiency caused by K are separate from the benefits of Na, and both Na and K were needed to achieve a record efficiency device [5]. CV measurements confirm that K increases the net hole concentration but not as effectively as Na [128, 170, 171]. The benefits of K have been attributed to the ability to deposit thinner CdS layers without loss of device performance [5, 9, 170]. These studies observe that the CIGS surface becomes Cu deficient after KF treatment, which could facilitate the diffusion of Cd through Cu vacancies. Diffusion of Cd into the CIGS is often speculated to enhance the junction [28, 172], and quicker diffusion of Cd into CIGS could allow for faster CdS deposition times that result in thinner CdS layers that absorb less light. Devices with thin CdS layers and low K usually suffer from increased interface recombination, but the addition of K eliminates this creating higher efficiencies [170].

It has also been observed that CIGS films with K can have a higher Ga content without the associated decrease in efficiency [6]. An increase in Ga leads to a larger band gap, which leads to a higher  $V_{OC}$  at lower Ga concentrations. However, at higher Ga concentrations  $V_{OC}$  levels off despite the continually increasing band gap. The increasing band gap also causes a decrease in  $J_{SC}$  because photons with energy below the band gap are not absorbed. At low Ga concentrations the decreasing  $J_{SC}$  is offset by increases in  $V_{OC}$ , but once  $V_{OC}$  levels off at higher Ga content the efficiency begins to decrease. Typically, the optimal Ga / (In + Ga) ratio for low-K devices is ~0.3, but when K is added the optimal ratio increases to 0.44. High Ga cells with K have a higher efficiency than lower Ga cells because the increased  $V_{OC}$  leads to lower resistive losses.

Further complicating the incorporation of potassium is the observation that  $K^+$  ions tend to displace Na<sup>+</sup> ions in CIGS. Chirilă et al. [5] show that the Na concentration in CIGS decreases after addition of K, which could be due to an ion exchange mechanism. This creates an additional challenge since too much potassium could potentially lower the Na concentration to a point where device efficiency suffers. Also, due to the size difference between Na<sup>+</sup> and K<sup>+</sup> ions, the activation energy of diffusion will differ making the final distribution of alkali elements very dependent upon the processing temperature.

The benefits of potassium are in the early stages of investigation, and a study of its diffusion in CIGS can help show how it impacts device performance. An understanding of how K interacts with Cu will provide insight into why its incorporation results in a Cu-poor surface. Equally important is an understanding of the Cd diffusion mechanism in CIGS. Finally, understanding how K interacts with Na in CIGS will aid in the optimization of Na and K incorporation procedures.

The effects of Li are far less studied, however, one report shows that incorporation of LiF into CIGS gave the same benefits as NaF but less pronounced citeArd2000. It was found that only half the amount of LiF could be incorporated, likely because it is more chemically stable than NaF. However, due to its smaller size Li may diffuse through CIGS faster with a higher solubility than Na. It is possible that alternative Li precursors could provide additional benefit not observed when using LiF. A comprehensive study of Li diffusion in CIGS could not only identify an alternative to Na incorporation, but also provide additional insight into the Na transport through CIGS.

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