Abstract

The chalcopyrite phase of ternary transition metal chalcogenides is an important family of materials for their ability to harness solar energy to generate electricity or fuel which offers the opportunity for sustainable energy production. This work provides a unique combination of physical property analysis and solar harnessing experimentation to explore the intimate connection between the fundamental properties of chalcopyrite materials and their performance in solar energy-harvesting applications.

Chapter 1 serves as the necessary foundation to understand this work: section 1.1 defines ternary transition metal chalcogenides and their chalcopyrite crystal structure; section 1.2 reviews the basics of semiconductor physics; and section 1.3 describes the four general steps used to execute the projects described in Parts I, II, and III.

Parts I, II, and III are divided by the chalcopyrite material of focus—CuIn(S_{1-x}Se_x)_2, CuInTe_2, and CuInS_2, respectively. Part I follows the polycrystalline synthesis and electrode fabrication of CuIn(S_{1-x}Se_x)_2 (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) for photoelectrochemical evolution of H_2 and CO_2 reduction. Part II follows the single crystal growth of CuInTe_2 and its characterization as a potential candidate for photoelectrochemical solar fuel production through thermodynamic photoelectrode analysis and electronic band structure studies. Part III follows the single crystal growth of CuInS_2 and analysis by electronic transport measurements, atomic-scale imaging, and photoexcitation experiments to interpret the source of detrimental metastability reported in chalcopyrite photovoltaic devices.
Acknowledgments

The work presented in this thesis was accomplished with the help of numerous, talented scientific collaborators. Their specific contributions are noted within each chapter. Many thanks to all those who, knowingly or unknowingly, enabled this graduate work, whether that be as a mentor, mentee, collaborator, administrative lifeline, confidant, friend, or emotional support animal.

Faculty
Prof. Andrew B. Bocarsly, Prof. Robert J. Cava, Prof. Leslie M. Schoop, Prof. Sigurd Wagner, Prof. Annabella Selloni, Prof. Bruce Koel

Imaging & Analysis Center
Dr. Nan Yao, John Schreiber, Dr. Guangming (Gary) Cheng, Dr. Yao-Wen Yeh, Dr. Daniel Gregory

Bocarsly Lab
Dr. Yuan Hu, Dr. James (Jim) White, Dr. Maor Baruch, Dr. Ivy Fortmeyer, Dr. James Pander, Dr. James Park, Dr. Aubrey Paris, Dr. Tao Zhang, Dr. Hsin-ya Kuo, Danrui Ni, Steve (Stove) Tignor, Michael Smith, Dr. Sonja Francis, Dr. Mike Kelly, Brian (little brian) Foster, Daniel Blasini-Pérez, Spyder-Ryder Sloman

Cava Lab
Dr. Satya Kushwaha, Prof. Fazel Tafti, Dr. Karoline Stolze, Prof. Weiwei Xie, Dr. Tai Kong, Dr. Huwien Ji, Dr. Jason Krizan, Prof. Huixia Luo, Prof. Fabian von Rhor, Prof. Tomasz Klimczuk, Dr. Brendan Phelan, Dr. Elizabeth (mama Liz) Seibel, Dr. Quinn Gibson, Dr. Marisa Sanders, Dr. François Alexandre (Alex) Cevallos, Dr. James Park, Dr. Elizabeth (baby Liz) Carnicom, Dr. Daniel Straus, Dr. Shu Guo, Dr. Ruidan Zhong, Danrui Ni, Kelly Powderly, Loi Nguyen

Former Students
Dr. Colleen Richardson, Dr. Esther Frederick, Dr. Girija Sahasrabudhe, Dr. Susanna Lilijegren Bergman, Dr. Matth Vallon, Dr. Jake Herb, Dr. Martina Lessio, Dr. Michelle Hofman, Dr. Andreas Topp

Administration & Staff
Jennifer Levine, Meredith LaSalle-Tarantin, Michael Checkovage, John Eng, Philip Fairall, Pattie Faranetta, Victoria Lloyd, Maura Matvey, C. Todd Reichart, Mike Souza, Susan Vanderkam, Kitty Wagner, Kevin Wilkes, Stanley Chidzik, William Dix

Emotional Support Animals
Matteo Ippoliti, Gnocchi (Chicken), Raviola (Ravi), Dr. Aubrey Paris, Dr. Nadia Leonard
List of Figures

1.1 Lineage of the Chalcopyrite Crystal Structure........................................3
1.2 Visible Spectrum Range of Chalcopyrite Semiconductors........................4
1.3 Band Theory Model of a Semiconductor and Metal..............................5
1.4 Silicon Doping For $n$- and $p$-Type Carriers.....................................6
1.5 Band Theory Model of Intrinsic and Extrinsic Semiconductors.............8
1.6 Temperature Dependence of Carrier Concentration............................10
1.7 Standard Solid-State Synthetic Methodology......................................12
1.8 Bridgman Furnace Schematic............................................................13
1.9 Microscopy and Spectroscopy Techniques for Material Identification......17
1.10 Solar Harnessing Device Fabrication................................................18
1.11 Band Diagram of $p$- and $n$-Type Semiconductors Reaching Equilibrium..21
1.12 Photoelectrochemical Water Splitting.............................................22
1.13 Photodetector Applications at Different Detection Wavelengths...........23
1.14 Photoconductor Schematic and its Relationship with Illumination........24

2.1 XRD and Lattice Parameters of CuIn(S$_{1-x}$Se$_x$)$_2$................................31
2.2 SEM, EDX, UV/Vis, and XPS Analysis of CuIn(S$_{1-x}$Se$_x$)$_2$..................34
2.3 Electronic Transport Measurements of CuIn(S$_{1-x}$Se$_x$)$_2$....................35

3.1 Band-Edge Thermodynamics of CuIn(S$_{1-x}$Se$_x$)$_2$ Photoelectrodes........47
3.2 CuIn(S$_{1-x}$Se$_x$)$_2$ Band-Bending Schematic and PEC H$_2$ Evolution Plot.....51
3.3 LSV Analysis of CuIn(S$_{1-x}$Se$_x$)$_2$; $x = 0.2, 1.0$.................................53
3.4 PEC H₂ Evolution Analysis of CuIn(S₁₋ₓSeₓ)₂ Photoelectrodes..........................55

4.1 Degradation of Bare CuInSe₂ Under Standard CO₂ Reduction Conditions.......68
4.2 LSV Analysis of CuInSe₂/Ni₃Al+TiO₂ Photoelectrode..................................69
4.3 Potential Dependence of CuInSe₂/Ni₃Al+TiO₂ Photoelectrode.....................70
4.4 Materials Characterization of CuInSe₂/Ni₃Al+TiO₂ Photoelectrode...........73

5.1 XRD, UV/Vis, and Electronic Transport Analysis of CuInTe₂.......................86
5.2 Tetragonal and Cubic BZ of CuInTe₂...............................................................90
5.3 ARPES Data and DFT Calculations of CuInTe₂.............................................92
5.4 Lineage of the Chalcopyrite Crystal Structure...........................................95
5.5 Band-Edge Thermodynamics of CuInTe₂ Photoelectrode.............................97

6.1 UV/Vis, XRD, and Electronic Transport Analysis of CuInS₂.......................110
6.2 Microstructure Characterization of Chalcopyrite CuInS₂.........................112
6.3 Quantitative Composition Analysis of Chalcopyrite CuInS₂.......................114
6.4 The Photoelectric Properties of CuInS₂.......................................................116
6.5 Additional Photocurrent Response Data for CuInS₂..................................117
6.6 Electronic Band Structure Model of CuInS₂ with Defect States...............123
## List of Tables

1.1 Electrical Transport Option (ETO) Measurements.................................................16

2.1 Lattice Parameters, EDX Analysis, and Optical $E_g$ of CuIn(S$_{1-x}$Se$_x$)$_2$.............32

2.2 Electronic Transport Values of CuIn(S$_{1-x}$Se$_x$)$_2$..................................................36

3.1 Flat-Band Potentials of CuIn(S$_{1-x}$Se$_x$)$_2$ Photoelectrodes.....................................48

3.2 PEC H$_2$ Evolution Rate ($\mu$mol h$^{-1}$ cm$^{-2}$) of CuIn(S$_{1-x}$Se$_x$)$_2$ Photoelectrodes......52
# Table of Contents

Abstract ............................................................................................................................... iii

Acknowledgments ............................................................................................................. iv

List of Figures ..................................................................................................................... v

List of Tables ...................................................................................................................... vii

**Chapter 1 Introduction** .................................................................................................. 1

1.1 Ternary Transition Metal Chalcogenides (TMCs) .................................................. 2

1.2 A Chemist’s Overview of Semiconductor Physics ................................................ 4

   *i. Energy Band Model* .............................................................................................. 4

   *ii. Charge Carriers* .................................................................................................. 6

   *iii. Influence of Doping on Semiconductor Properties* ......................................... 7

1.3 General Experimental Procedure .......................................................................... 11

   Step 1: Synthesis

   *i. Standard Solid-State Techniques* ................................................................. 11

   *ii. Single-Crystal Melt Growth* .......................................................................... 12

   Step 2: Characterization

   *i. Electronic Transport Measurements* ............................................................. 14

   *ii. Microscopy & Spectroscopy* .......................................................................... 17

   Step 3: Fabrication

   *i. Photoelectrodes* ............................................................................................... 18

   *ii. Photocells* ...................................................................................................... 19

   Step 4: Analysis
i. Photoelectrochemical H₂O Splitting..................................................19

ii. Photoconduction...............................................................................23

References.................................................................................................24

Part I CuIn(S₁₋ₓSeₓ)₂

Chapter 2 Characterization of Primary Carrier Transport Properties of the Light-Harvesting Chalcopyrite Semiconductors CuIn(S₁₋ₓSeₓ)₂

2.1 Introduction...........................................................................................28

2.2 Results & Discussion...........................................................................31

   i. Synthesis and Characterization of CuIn(S₁₋ₓSeₓ)₂.................................31

   ii. Transport Properties of CuIn(S₁₋ₓSeₓ)₂.................................................36

2.3 Conclusions............................................................................................38

2.4 Methods................................................................................................39

   i. Synthesis...............................................................................................39

   ii. Sample Characterization......................................................................39

   iii. Transport Property Measurements..................................................40

Chapter 3 Chalcopyrite CuIn(S₁₋ₓSeₓ)₂ for Photoelectrocatalytic H₂ Evolution: Unraveling the Energetics and Complex Kinetics of Photogenerated Charge Transfer in the Semiconductor Bulk

3.1 Introduction............................................................................................42

3.2 Results & Discussion............................................................................45

   i. Flat Band Potential................................................................................45

   ii. PEC H₂ Evolution Bulk Electrolysis......................................................50
Chapter 4 Photoelectrochemical CO\textsubscript{2} Reduction Using Chalcopyrite-Based Composite Electrode CuInSe\textsubscript{2}/Ni\textsubscript{3}Al+TiO\textsubscript{2}

4.1 Introduction.................................................................65
4.2 Results & Discussion.........................................................66
4.3 Conclusions...........................................................................71
4.4 Methods..............................................................................72

References..............................................................................74

Part II CuInTe\textsubscript{2}

Chapter 5 Single-Crystal Growth and Characterization of CuInTe\textsubscript{2} for Photoelectrochemical Solar Fuel Production

5.1 Introduction........................................................................81
5.2 Results & Discussion............................................................85

i. Synthesis, Growth, and Characterization of CuInTe\textsubscript{2}.........85

ii. Transport Properties of CuInTe\textsubscript{2} Single Crystals...............85

iii. CuInTe\textsubscript{2} Defect Chemistry........................................87
iv. Theoretical Electronic Band Structure ........................................ 89

v. ARPES Measurements .............................................................. 89

vi. Crystal Structure and Brillouin Zone of CuInTe$_2$ ....................... 94

vii. Thermodynamic Characterization of CuInTe$_2$ Photocathodes ...... 96

5.3 Conclusions .............................................................................. 98

5.4 Methods ..................................................................................... 98

i. Synthesis and Crystal Growth .................................................. 98

ii. CuInTe$_2$ Characterization and Physical Property Analysis .......... 99

iii. Electrode Fabrication ............................................................... 99

References ..................................................................................... 100

Part III CuInS$_2$

Chapter 6 Defect Origin of Metastability in Solar-Energy-Harvesting Chalcopyrites

6.1 Introduction ............................................................................. 105

6.2 Results & Discussion ............................................................. 108

i. Electronic Transport ................................................................. 108

ii. Microstructure Characterization ............................................. 111

iii. Photoconductivity ................................................................. 115

iv. Discussion ................................................................................ 118

6.3 Conclusions ............................................................................. 124

6.4 Methods ..................................................................................... 124

i. Single Crystal Growth & Characterization ................................. 124
CHAPTER 1
INTRODUCTION

Energy is a requirement in everyday life on Earth to meet basic human needs, including health, mobility, communication, lighting, cooking, hydration, and others. In parallel, Earth’s exponentially growing population has resulted in an increase in energy demand, which has largely been met by fossil fuel-based power generation. This, in turn, has introduced the greatest global challenge of the 21st century: climate change. According to the 2018 Global Risks Survey, environmental, economic, and societal risks directly or indirectly connected to climate change make up 7 of the top 10 greatest global risks in terms of both likelihood and impact. Fortunately, renewable and sustainable energy sources hold the key to creating an energy platform for Earth’s present and future energy demands while simultaneously mitigating climate change and its associated risks. Additionally, renewable energy provides opportunities for energy security and access, as well as human social and economic development.

These three opportunities are connected through renewable energy. Given the interdependence of economic growth and energy consumption, social and economic benefits will come from new job creation that is anticipated to employ 25 million people
by 2050, more than offsetting job losses from conventional energy sectors. The result is shifts in labor intensities and increase in personal health. Energy security and access will ensure uninterrupted running of the economic and political world for not only developed countries but also for developing countries; for example, in rural areas, a grid based renewable energy source offers nearby electricity access. Climate change mitigation will reduce health complications associated with pollutants from fossil fuel-based energy and reduce environmental implications from climate change such as natural disasters. Currently, renewable energy sources contribute 26% to global electricity generation, with solar sources leading the way.

This thesis will provide specialized insight into chalcopyrite phase ternary transition metal chalcogenides, a class of materials that will play an important role in solar harnessing applications to increase the standard of living on Earth. This work aims to broaden our scientific understanding of the connection between the fundamental physical properties of chalcopyrites—dictated by their synthetic method and environment—and their performance in solar energy-harvesting applications.

1.1 Ternary Transition Metal Chalcogenides (TMCs)

Ternary TMCs are a class of materials that have been identified as a major target for developing efficient solar harnessing devices such as photo(electro)catalysts, solar cells, and sensors. This stems from not only their ideal physical properties for light harvesting — i.e. a direct bandgap with a high absorption coefficient well matched to the solar spectrum on earth — but also from its energy production potential with respect to the availability and cost of its constituent elements.
Ternary TMCs possess a chalcopyrite crystal structure, which generically have MM’X₂ formulas, where M is typically a transition metal, M’ is a transition or other metal, and X is S, Se, or Te (the mineral “chalcopyrite”, for example, is CuFeS₂). Chalcopyrite semiconductors are often referred to as I-III-VI₂ semiconductors, an elaboration of the binary II-VI zinc blende crystal structure, which is itself an elaboration of the structure of the elemental indirect band gap semiconductor Si. Fig. 1.1 shows this lineage of semiconductors: IV → II-VI → I-III-VI₂. The addition of the second cation in the chalcopyrite structure offers the significant advantage of changing the electronic structure of the semiconductor to access direct band gap values not accessible in the binary materials, enabling efficient access to the entire visible spectrum, as seen in Fig. 1.2. 

**Figure 1.1:** Structural lineage of the chalcopyrite semiconductor: IV → II-VI → I-III-VI₂. (a) Diamond Structure, example: Si (cubic Fd̅3m), (b) Zinc Blende Structure, example: ZnTe (cubic F̅43m), (c) Chalcopyrite Structure, example: CuInTe₂ (tetragonal I4̅2d). Si, blue. Zn, gray. Te, purple. Cu, orange. In, aqua.
1.2 A Chemist’s Overview of Semiconductor Physics

This section will provide basic concepts and terminology for understanding semiconductors. Here we will review the energy band model, electron and hole charge carriers, and the influence of dopants on various semiconductor properties. For an in-depth and mathematical review of semiconductor physics, “Physics of Semiconductor Devices” \(^{15}\) and “Semiconductor Physics and Devices” \(^{16}\) are highly recommended, which are the sources of the information that follows.

**i. Energy Band Model.** Band theory is a useful way to visualize energy bands in solids by plotting overlapping delocalized orbitals that form bands. Semiconductors form a low-energy valence band (VB) and a high-energy conduction band (CB). These bands are separated by a quantum mechanically forbidden energy zone, called the band gap \((E_g)\). The band gap is a significant energy spacing between the two bands, which leads to the VB being almost filled, and the CB being almost vacant due to the higher energy required for

---

**Figure 1.2:** An illustration of the visible spectrum and where some typical chalcopyrite-type I–III–VI\(_2\) nanocrystals absorb when between 2 and 5 nm in size. Adapted with Permission from Reference 14. Copyright 2009 American Institute of Physics.
the transition between bands. The presence of an energy spacing between the two bands is
the critical difference between semiconductors and metals (Figure 1.3), and the source of
their fundamental difference in electrical conductivity. In metals, the VB and CB overlap,
forming a continuum of energy states for electrons. Metals exhibit high electrical mobilities
due to this energy continuum which enables electrons to move to the available set of
delocalized empty orbitals with small activation energy. However, electrical mobility can
be induced in semiconductors by exciting electrons from the VB to the CB with photons
of energy greater than or equal to $E_g$ (i.e. $h\nu \geq E_g$).

Semiconductors can exhibit direct or indirect band gap transitions. Direct band
gaps—those whose electron transitions between bands preserve the angular momentum of
the electron—require only the absorption of an optical photon of $h\nu \geq E_g$. On the other
hand, an indirect band gap requires a change in the electron momentum and therefore
necessitates the assistance of a phonon, or lattice vibration. The absorption or emission of
a phonon is less likely to occur, resulting in a much smaller absorption coefficient than that
of a direct transition. Regardless of these two different optical properties, the Fermi level
($E_F$) of semiconductors can be defined as the average energy of the electrons in the lattice,
which typically lies within the band gap where electron density is quantum mechanically forbidden. The relative position of the Fermi level within the gap is dictated by the qualitative ratio of charge carriers, discussed next.

**Figure 1.4:** Silicon doping to create extrinsic semiconductors of \( n \)- and \( p \)-type carriers. Doping Sb, a pentavalent group V element, contributes free electrons to the Si lattice which creates extra electron energy levels that give an \( n \)-type semiconductor. Conversely, doping B, a trivalent group III element, creates holes that will take electrons from the Si lattice. This creates extra hole energy levels that give a \( p \)-type semiconductor.

**ii. Charge Carriers.** When a semiconductor’s electrons are excited from the VB to the CB, an equal amount of positively charged states, or holes, are left behind. Both electrons and holes can be utilized as charge carriers. Semiconductors are known as *intrinsic semiconductors* if the densities of electrons and holes are equal, leading to its Fermi level lying close to the middle of the band gap. The density ratio of electrons to holes can be controlled through doping to produce *extrinsic semiconductors*, which have an excess of either electrons or holes. Doping is the intentional act of creating impurities within the semiconductor lattice by introducing (or extracting) an element. Impurities that provide electrons to the lattice are known as donors, creating \( n \)-type semiconductors that possess electrons as their majority charge carrier. Conversely, impurities that remove electrons from the lattice are known as acceptors, creating \( p \)-type semiconductors that possess holes.
as their majority charge carrier. Figure 1.4 shows a classic example of this phenomenon through doping Si with Sb and B to create \( n \)- and \( p \)-type Si, respectively.

The resulting imbalance in charge carriers through doping results in a shift of the material’s Fermi level. Band theory can be applied to \( n \)- and \( p \)-type semiconductors to visualize this shift. For \( n \)-type semiconductors, extra electron energy levels lie near the top of the band gap so they can be easily excited into the conduction band. The extra electron presence raises the average energy of electrons in the lattice, which therefore raises the Fermi level to lie between the new electron states and the CB. Conversely, \( p \)-type semiconductors possess extra hole energy levels near the bottom of the band gap so they can easily accept electrons excited from the VB. The extra hole presence lowers the average energy of electrons in the lattice, which therefore lowers the Fermi level to lie between the new hole states and the VB. Figure 1.5 reviews the band theory model of intrinsic and extrinsic semiconductors before and after photoexcitation.

**iii. Influence of Doping on Semiconductor Properties.** Doping occurs on a relatively small scale, roughly 1 mol % or less, and thus does not normally result in a change of the band gap energy or the potential energy position of the band edges. Doping can however enhance light absorption at longer wavelengths (i.e. \( h\nu < E_g \)) without changing the band gap by introducing shallow acceptor states, from which electrons can be photoexcited to the CB.\(^{17,18}\) However, the most important function of semiconductor doping is the ability to tune a material’s electronic transport properties (i.e. the process by which the charge carriers move).
Figure 1.5: Band theory model of intrinsic and extrinsic type semiconductors before and after photoexcitation. (a) Intrinsic semiconductor whose density of carriers is approximately equal leading to a Fermi level placed evenly between the VB and CB. Upon photoexcitation, electrons are excited from the VB to the CB, leaving behind holes. (b) n-type semiconductor formed from donor impurities. Extra electron energy levels are created near the CBM, shifting the Fermi Level higher in energy. Upon photoexcitation, electrons from both the VB and donor levels are excited to the CB, leaving behind holes. The electrons from the donor states have a lower energetic barrier to overcome. (c) p-type semiconductor formed from acceptor impurities. Extra hole energy levels are created near the VBM, shifting the Fermi level lower in energy. Upon photoexcitation, electrons from the VB are excited to both the CB and acceptor states, leaving behind holes. Excitation of electrons from the VB to the acceptor states have a lower energetic barrier to overcome.
The conductivity of a semiconductor is a function primarily of the concentration of the majority charge carrier. The electrical conductivity of a semiconductor can be altered through doping to simply increase the carrier concentration and thus, enable carrier migration in the dark under external bias.\textsuperscript{19,20} Carrier concentration itself is dependent on temperature as seen in Figure 1.6. Here we see a typical log-scale dependence of carrier concentration ($N$) on reciprocal temperature. The plot consists of three main regions: the ionization region, the extrinsic region, and the intrinsic region that occur at low temperature, moderate temperature, and high temperature, respectively. The absolute range of these regions are material dependent, but in general the ionization region begins just above absolute zero, and room temperature is within the extrinsic region. Band theory models each region and at absolute zero are presented in Figure 1.6 modeled after an n-type semiconductor.

At absolute zero all electrons, in the VB or donor states, are at rest and no excitation occurs. Once temperature begins to rise, carrier concentration is within the ionization region where some excitation from the donor states into the CB has occurred. Carrier concentration, and thus conductivity, begin to rise. In the extrinsic region, all shallow dopants are ionized and thus the carrier concentration remains stable. The material conductivity typically displays a bump throughout this region due to a relatively high contribution of mobility at this temperature range.\textsuperscript{21} The carrier concentration in this region can be equated to the concentration of the majority carrier. In the intrinsic region, the thermal energy is large enough to excite electrons directly from the VB to the CB (i.e. intrinsic carrier excitation). There is a sharp increase in both conductivity and carrier
concentration, which in this region can be equated to the number of total carriers (both electrons and holes).

**Figure 1.6:** Variation in carrier concentration ($N$) and conductivity ($\sigma$) with change in temperature ($T$). The inset features band theory models of an $n$-type semiconductor at different temperature ranges. At absolute zero all electrons are at rest and no excitation occurs. Once temperature begins to rise, carrier concentration is within the ionization region where some ionization of the donor states has occurred. Carrier concentration, and thus conductivity, begin to rise. In the extrinsic region, all shallow dopants are ionized and thus the carrier concentration remains stable. The material conductivity typically displays a bump throughout this region due to a relatively high contribution of mobility at this temperature range. The carrier concentration in this region can be equated to the concentration of the majority carrier, or electrons in this case. In the intrinsic region, the thermal energy is large enough to excite electrons directly from the VB to the CB (i.e. intrinsic carrier excitation). There is a sharp increase in both conductivity and carrier concentration, which in this region can be equated to the number of total carriers—the sum of the majority carriers (electrons) and minority carriers (holes).
1.3 General Experimental Procedure

Parts I, II, and III of this thesis were executed with the four general steps described here. Specific details of these steps, including how they were tailored for each project, can be found in the Methods section of each chapter.

Step 1: Synthesis

i. Standard Solid-State Technique. Polycrystalline samples were produced through basic solid-state synthetic techniques, meaning the elements were directly mixed in the desired stoichiometry and heated in a large box furnace. A typical polycrystalline synthetic method of CuInX₂ (X = S, Se, Te) can be seen in Figure 1.7: (1) Cu, In, and X are loaded into a quartz ampoule, then purged and sealed under vacuum to avoid oxidation; (2) sealed ampoules are placed in a box furnace at ~45° angle in order to keep the contents at one end; (3) the temperature of the furnace is very slowly increased stepwise from room temperature to 1100 °C (the melting point of CuInX₂ materials is ~1050 °C). The stepwise heating and holding at 400 °C and 700 °C is essential for CuInS₂ in particular. Sulfur has a very low boiling point (~450 °C) so the slow and steady heating method allows sufficient reaction
to reduce the possibility of the samples exploding (which, let’s say, I learned from experience, but it was never catastrophic enough to have the fire department called). What also helps is a little trick I came up with, which is simply allowing your sulfur to bake overnight at ~120 °C to rid of any moisture before adding it to the quartz ampoule; (4) depending on the desired outcome, the samples are cooled to room temperature at 180 °C/hour or quenched on the benchtop. I’m sure this method could be shortened if time is an issue, but I knew this method worked for all my materials, so I kept it to be consistent.

![Figure 1.7: Typical solid-state synthetic method used to make polycrystalline samples of CuInX$_2$ (X = S, Se, Te). The top left image shows the elemental starting materials vacuum sealed in quartz ampules. The top right image shows the final polycrystalline product.](image)

**ii. Single-Crystal Melt Growth.** The Bridgman technique was employed for single crystal growth. This technique grows crystals from the melt by passing molten material through a temperature gradient at a slow speed which solidifies when the temperature is below the melting point of the material. The Bridgman method is a well-known technique used specifically to grow crystals of wide-bandgap semiconductors like CdTe, ZnSe, and other chalcogenides because of the simplicity of the growth apparatus and the high growth rate.
A schematic of the Bridgman setup, and an image of the furnace used in the work, can be seen in Figure 1.8.

![Figure 1.8: Bridgman furnace set-up employed for all crystal growths of CuInX$_2$ material. Polycrystalline starting material is loaded into a double layer quartz ampoule, sealed under vacuum. It is suspended in the “hot zone” by a Pt wire connected to a motorized pulley. Once the sample is homogeneously liquid, the sample is driven through the furnace slowly, where crystallization will begin when the temperature is below the material’s melting point.](image)

All crystal growths were conducted with pre-reacted polycrystalline sample, formed by standard solid-state synthesis, in gram-scale (~10-20 g total). The polycrystalline material was loaded into a carbon-coated quartz tube, sealed under vacuum, then sealed under vacuum in a second quartz ampoule. The CuInX$_2$ materials tend to expand during the growth process—the double quartz layer prevents oxidation in case the first layer is punctured. A platinum wire, connected to a motorized pulley system, is connected to the growth container allowed it to be hung within the vertical furnace. The furnace temperature is raised to 1140 °C in order to get the core of the growth container
above the melting point (1050 °C) of the material. The setup is left for the afternoon and overnight, ~18 hours, in order to ensure all the polycrystalline material has melted. The pulley is then set to slowly lower the growth container from the “hot zone” through the length of the furnace at 0.1 mm/hour. The growth takes anywhere from 5-10 days, depending on the length of the growth container you need to get through. After the growth the container is carefully cut down and annealed at 400 °C for 24 hours to ensure high crystal quality.

**Step 2: Characterization**

**i. Electronic Transport Measurements.** Four-point resistance, Hall effect, and I-V curve tracing measurements were used to analyze CuInX₂ samples in either single crystal form or pelleted polycrystalline form. A physical property measurement system (PPMS) equipped with the Quantum Design Electrical Transport Option (ETO) was used for these experiments. Table 1.1 summarizes the basic setup and relevant equations of these techniques. ²³

*Four-point resistance* measurements consist of two leads that pass a current through the sample, and two separate leads that measure the potential drop across a section of the sample. Ohm’s law can then be used to calculate the resistance ($R$) of the sample for the region between two voltage leads. With the known dimensions of the sample, Eq. (1) can be used to calculate the resistivity ($\rho$) of the material. This experiment measures $R$ vs. temperature (T) which, through data transformation to ln($\rho$) vs 1/T, allows the semiconductor activation energy ($E_a$) to be extracted using Eq. (2), or the Arrhenius law.

*Hall effect* measures the Hall voltage, $V_{ih}$, as a function of magnetic field. The paired current and potential leads are placed perpendicular to each other. This placement
of the leads is key, for when charged particles move perpendicular to a magnetic field a force is exerted on them perpendicular to both the field and the direction of particle motion—i.e. $\vec{F} = q \vec{v} \times \vec{B}$. This transverse force causes charge carriers to build up on one edge of the material leading to a potential difference across the sample, i.e. $V_{H}$. The Hall voltage is defined as Eq. 3 which can be rewritten as Eq. 4 in terms of $R$ to extract the carrier concentration, $N$, of your semiconductor sample. With $N$ in hand, along with $\rho$ measured by the four-point resistance technique, Eq. 5 can be used to calculate mobility, $\mu$, of the sample.

*I-V curve tracing* measures a current response waveform from a voltage excitation waveform. The slope of this curve can be analyzed to interpret the free electron generation rate and lifetime via Eq. 6, outlined by Rose. $^{24}$ I-V measurements can also be performed at various light intensities in order to determine the dependence of photocurrent on light intensity using a simple power law, Eq. 7. $^{25}$ Though simple, the extracted information is powerful, as the value of $a$ can be associated with major patterns in photoconductor behavior revealing important system information such as the presence of recombination states, carrier-carrier interactions, and distribution of trap states. $^{24}$
Table 1.1: Electrical transport option measurements used in this work.

<table>
<thead>
<tr>
<th>4-POINT RESISTANCE</th>
<th>HALL EFFECT</th>
<th>I-V CURVE TRACING</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Setup</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Relevant Equations**

\( \rho = \frac{RA}{l} \)

\( V_H = \frac{IB}{Net} \)

\( I = e^{\frac{F\mu t}{L^2}} V \)

\( \rho = \rho_0 \exp \left( \frac{-E_a}{k_B T} \right) \)

\( \frac{1}{N} = \frac{Rt}{B} \)

\( I_{ph} = AP^\alpha \)

\( \sigma = Ne\mu \)

**Key**

- \( \rho \) resistivity
- \( R \) resistance
- \( A \) cross-sectional area
- \( l \) voltage lead separation
- \( \rho_0 \) pre-exponential term
- \( E_a \) activation energy
- \( k_B \) Boltzmann’s constant
- \( T \) temperature
- \( V_H \) Hall voltage
- \( I \) current
- \( e \) electron charge
- \( B \) magnetic field
- \( N \) carrier concentration
- \( \mu \) sample mobility
- \( F \) electron generation rate
- \( \tau \) free electron lifetime
- \( L \) spacing of electrodes
- \( V \) voltage
- \( t \) sample thickness
- \( \mu \) mobility
- \( \alpha \) exponent
- \( I_{ph} \) photocurrent
- \( A \) scaling constant
- \( P \) light power
**ii. Microscopy & Spectroscopy.** These characterization techniques use different ranges of the electromagnetic spectrum to image/visualize the material (microscopy) or extract information about the material from how it interacts with radiation (spectroscopy). Each is unique, providing necessary information to fully characterize the identity of a material. Figure 1.9 gives a basic overview of the many techniques used in this work. I will not be going into theoretical detail of these techniques, but if you are interested, I would recommend sitting in on Dr. Nan Yao’s class on “Characterization of Materials” or check out the course reading list. 26–28 All in all, these techniques were essential for this work,
and I must acknowledge the excellent instruction and guidance from the Imaging and Analysis Center: Dr. Nan Yao, John Schreiber, Dr. Yao-Wen Yeh, Dr. Daniel Gregory, and Dr. Guangming Cheng. Thank you all for your expert support and genuinely friendly, supportive, and respectful research atmosphere you provided at the IAC.

**Step 3: Fabrication**

**i. Photoelectrodes.** CuInX₂ material was fabricated into a photoelectrode when used for PEC reduction of H₂O. Polycrystalline samples were pressed into pellets ≥ 90% of the material’s theoretical density and single crystals were used as-extracted. Depending on the project, ohmic contact was achieved using Au or InGa eutectic. Ohmic contact was confirmed with current-voltage measurements. The ohmic contact was then connected to an external copper wire with conductive Ag epoxy. The unit was encased in a glass tube and sealed with a watertight epoxy to prevent leakage. Figure 1.10a shows an image and schematic of a typical photoelectrode used in this work.

![Figure 1.10: Solar harnessing device fabrication.](image)

**Figure 1.10:** Solar harnessing device fabrication. (a) Image and schematic of a photoelectrode used for PEC H₂O reduction. CuInX₂ densified pellet (or single crystal) is coated with Au to achieve ohmic contact, attached to a copper wire with conductive Ag epoxy, and encased in a glass tube sealed with a watertight epoxy. (b) SEM image and schematic of a rudimentary photovoltaic cell constructed with two contact points of InGa eutectic to achieve ohmic contact.
**ii. Photocells.** A photocell device was fabricated in order to analyze photo-electric properties of CuInX$_2$. Only the single crystal form of CuInX$_2$ was used in photocell fabrication. This device is very simple, consisting of just two ohmic contact points annealed to the crystal surface. Pt wires were used to complete the circuit during analysis. Figure 1.10b shows a scanning electron microscopy (SEM) image and schematic of a typical photocell used in this work.

**Step 4: Analysis**

The work presented in this thesis will focus on two solar energy harnessing applications through which the ternary TMC semiconductors were characterized in part: photoelectrochemical H$_2$O splitting and photoconduction.

**i. Photoelectrochemical H$_2$O Splitting.** Photoelectrochemistry is one of the oldest investigated techniques for converting sunlight into usable energy, dating back to 1839 when Edmond Becquerel discovered the photovoltaic effect while experimenting with two metal electrodes in an electrolytic cell. Since this seminal report, photoelectrochemistry has developed into two general fields: (1) the storage of solar energy in chemical bonds, such as splitting water to generate H$_2$ as an environmentally benign fuel, and (2) a chemically invariant system that generates electricity from combining a reversible redox couple and a dye-sensitized photoelectrode. Here, we will focus on type (1) systems defined as a monolithic process based on a semiconductor-liquid junction. For a discussion on type (2) systems please refer to other work.  

Catalytic splitting of pure water into H$_2$ and O$_2$ is an energetically costly transformation involving a large positive change in the Gibbs free energy ($\Delta G^\circ = 238$ kJ
The overall water splitting reaction consists of two half-reactions—the oxidation of water to $O_2$ and protons and subsequent reduction of protons to $H_2$:

*Overall water splitting:* $2H_2O \rightarrow 2H_2 + O_2$

*Oxidation half-reaction:* $2H_2O + 4h^+ \rightarrow O_2 + 4H^+$

*Reduction half-reaction:* $2H^+ + 2e^- \rightarrow H_2$

The oxidation and reduction potentials of water are +1.23 V and 0 V, respectively, vs. normal hydrogen electrode (NHE) which gives an overall $E^o$ cell = 1.23 V vs. NHE.

When a semiconductor is immersed in an electrolyte solution its free energy, $\Delta G_{\text{semi}}$ (Eq. 8), can be related to the free energy of the electrolyte, $\Delta G_{\text{electrolyte}}$ (Eq. 9):

$$\Delta G_{\text{semi}} = -nF E_F$$

$$\Delta G_{\text{electrolyte}} = -nF E_R$$

where $n$ is the number of electrons involved in the process, $F$ is Faraday’s constant, $E_F$ is the Fermi level, and $E_R$ is the redox potential of the electrolyte as given by the Nernst equation. Electron transfer takes place between the semiconductor and the electrolyte in order to equilibrate $E_F$ of the semiconductor with $E_R$ of the electrolyte solution. $^{34}$ If the semiconductor is $p$-type ($n$-type), the electrolyte solution accepts (donates) electrons from (to) the semiconductor when $E_F$ is more negative (positive) than the reduction potential of the electrolyte solution. Since the density of electrons in a semiconductor is finite—i.e. the number of mobile electrons in the semiconductor is much lower compared to the electrolyte, causing $E_F$ to change significantly with electron flow at the interface, whereas $E_R$ remains almost unchanged $^{35}$—and the potentials of the band positions at the interfaces can be assumed to be pinned, the electron transfer causes band bending (Figure 1.11). This electron flow across the interface creates a space-charge region near the junction inside the
semiconductor\textsuperscript{35,36} inducing an electric field that plays an important role in charge separation.\textsuperscript{34}

\begin{figure}
\centering
\begin{subfigure}{0.4\textwidth}
\centering
\includegraphics[width=\textwidth]{p_type_diagram}
\caption{p-type semiconductor}
\end{subfigure}
\begin{subfigure}{0.4\textwidth}
\centering
\includegraphics[width=\textwidth]{n_type_diagram}
\caption{n-type semiconductor}
\end{subfigure}
\caption{Band diagrams of p-type and n-type semiconductors with Fermi level $E_F$ immersed in an electrolyte with redox potential $E_R$ before equilibrium (a, c), and at equilibrium (b, d). Adapted with Permission from Reference 22. Copyright 2015 American Chemical Society.}
\end{figure}
The charge carrier moving toward the interface can then be utilized to perform electrochemical reactions. The opposite charge carrier, migrating toward the bulk, completes the photoelectrochemical redox cycle with the other half-cell reaction at another site for particles or on an auxiliary electrode connected via the external circuit for photoelectrochemical cells. Because the minority charge carrier is directed toward the semiconductor−electrolyte interface, the nature of this species determines whether an oxidation or reduction reaction is observed at the semiconductor interface. If the semiconductor is $p$-type ($n$-type), the electrons (holes) flow down (up) the potential gradient to perform photoreduction (photo-oxidation). These phenomena are illustrated for $p$- and $n$-type semiconductors (photocathode and photoanode) in Figure 1.12. 37

![Figure 1.12: Energy diagrams of photoelectrochemical water splitting using (a) a photocathode ($p$-type) and (b) a photoanode ($n$-type). Adapted with Permission from Reference 24. Copyright 2014 Royal Society of Chemistry.](image-url)
ii. Photoconduction. In the broadest terms, photodetectors are sensors used to detect change in light and send the information to other electronics. These sensors play a critical role in everyday human life, ranging from biotechnology, telecommunication, medicine, atmospheric studies, etc, depending on the desired spectral range (Figure 1.13). 38 This section will provide a basic review of photoconductors, the simplest type of photodetectors, defined as a material whose electrical conductivity increases upon absorption of light energy. Photoconductor devices consist simply of a semiconducting material between two ohmic contacts, shown in Figure 1.14a. Upon illumination of the exposed semiconductor, electron-hole pairs are produced which contribute to the increase in material conductivity. Figure 1.14b shows the qualitative current-voltage curves under dark and illuminated conditions. Figure 1.14c shows the inverse relationship between material resistance and illumination. Photoconductors can use either intrinsic absorptive processes (hv ≥ Eg) or extrinsic defect-mediated absorption for long-wavelength detection. 39

Figure 1.13: Photodetector applications at different detection wavelengths. Adapted with Permission from Reference 25. Copyright 2017 Wiley.
REFERENCES


Part I

CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2}
CHAPTER 2
CHARACTERIZATION OF PRIMARY CARRIER TRANSPORT PROPERTIES OF THE LIGHT-HARVESTING CHALCOPYRITE SEMICONDUCTORS CuIn(S_{1-x}Se_x)_2

This section is based on *J. Phys. Chem. C* 2017, 121, 17046-17052. Figures reprinted and adapted from those in the published article are used with permission from the American Chemical Society, copyright 2017. Dr. Satya Kushwaha, a coauthor on this work, served as my mentor in the Cava lab. He taught me everything—tube sealing, tube crafting, little lab tricks, how to grow crystals, work the PPMS, etc. Without his foundational teachings this thesis could not exist, nor could my current crystal growth project on the ISS. Thank you, Satya!

2.1 Introduction

To enhance optical to electrical conversion efficiencies in photoelectrochemical (PEC) measurements, work has been directed toward improving charge separation and transport at the surface of photocathodes. This has been achieved by Domen et al. \(^1\text{–}^3\) through surface modification of I–III–VI\(_2\) photocathodes with \(n\)-type layers to form a \(p-n\) junction—facilitating a more efficient photogenerated charge separation. However, the mobility of charge carriers through the bulk of the photoelectrode is another important factor, which has received little attention to date. For charge carriers to contribute to PEC half-reactions, they must first reach the semiconductor/electrolyte or semiconductor/substrate interface; therefore, the internal electrical transport of the charge carriers is significant. In support of
this statement, it is noted that several studies on hematite photoelectrodes for solar water splitting have taken a closer look at the poor bulk charge transport of this material to improve PEC water splitting.\textsuperscript{4–6} Recently, van de Krol et al.\textsuperscript{7} concluded that charge carrier transport is a major limiting factor in the photoconversion efficiency of \( p \)-CuBi\(_2\)O\(_4\) for PEC water splitting. It was noted that the poor charge carrier transport of holes (the majority charge carrier) reduced the obtainable photocurrent density by two orders of magnitude. \( n \)-BiVO\(_4\), a well-known and characterized metal oxide photoanode for PEC water splitting, is most limited in its photoresponse due to its poor bulk electronic conductivity.\textsuperscript{8,9} The poor bulk electronic conductivity has been confirmed by time-resolved microwave conductivity studies and temperature dependent bulk transport studies.\textsuperscript{10,11} It is clear from these studies on well-known PEC materials that the basic charge transport properties of other promising light-harvesting materials, like I–III–VI\(_2\) chalcopyrites, merit deeper study in order to optimize them for further PEC applications.

The utilization of ternary chalcopyrite semiconductors for light-harvesting processes, such as PEC water splitting, stems from their innate, high optical absorption coefficients. Among I–III–VI\(_2\) chalcopyrites, copper indium disulfide (CuInS\(_2\)) possesses a band gap that is well matched to the solar spectrum on Earth (1.5 eV). In addition to its spectral response, this material possesses favorable band edge energetics relative to \( \text{H}_2 \) evolution. Despite this favorable bandgap range and alignment, CuInS\(_2\)-based photocathodes have only been reported to achieve a maximum solar conversion efficiency of 1.82\% (at +0.25 V vs RHE).\textsuperscript{1} High bulk electrical resistivities have been reported as a contributing factor to the low efficiency of I–III–VI\(_2\) materials when used as photocathodes.
12–14, as charge transport properties are one of the major factors (along with spectral response and band gap alignment) to consider for PEC processes.

The bulk, electrical properties of I–III–VI2 materials largely depend on their atomic composition. 12,15–17 One method used to decrease resistivity in CuInS2 is to introduce an aliovalent impurity atom into the system. This technique was employed on CuInS2 thin films using an aliovalent Zn2+ impurity on the In3+ sites, which demonstrated a decrease in resistivity with an increase of Zn content up to 15%, generating the quaternary compound CuIn0.85Zn0.15S2. 18 In other work, such as in the CuGaS2−ZnS or AgInS2−ZnS solid solutions, Zn is present, but the ZnS substitution is not nominally expected to yield a change in dopant concentration. 19,20 A related approach is to modify the ratio of cations in the structure; when varying the ratio of the cations in CuInS2 thin films (0.98 ≤ Cu/In ≤ 1.02) the resistivity can vary by one order of magnitude 12,13, indium rich samples being the most resistive due to the compensation of the p-type defects present through the presence of donors. 21,22

Studies reporting on the effect of anion ratio in CuInS2 have introduced Se into the system, creating the series CuIn(S1−xSex)2 in nanoparticle or thin film form. 23–26 Although no transport studies on this series have been reported, these CuInS2−CuInSe2 alloys allow a linear tuning of the fundamental bandgap (Eg) from pure CuInS2 (1.5 eV) to pure CuInSe2 (1.0 eV). This Eg tuning could in turn increase efficiency of CuInS2 systems for PEC applications by manipulating the position of the valence band edge of photocathodes. 25,26

CuIn(S1−xSex)2 alloys not only offer the opportunity for Eg tuning, but also provide an environment for studying the effects of varying the bulk electrical resistivity on the efficiency of charge transport processes (like PEC H2 evolution). High Se content reduces
the absolute bandgap energy of the alloy away from optimal values and, additionally, shifts the absolute energy levels of the valence and conduction bands to potentials unsuitable for PEC applications.\textsuperscript{27,28} However, limited substitution of Se for S can be expected to alleviate high resistivity issues in CuInS\textsubscript{2} while keeping the bandgap energy within range of the visible spectrum. The purpose of the current work is to elucidate the transport properties and bandgap trends of well characterized bulk materials in this series as a context for future PEC studies.

### 2.2 Results & Discussion

#### i. Synthesis and Characterization of CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2}

PXRD patterns of CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2} (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) recorded at 300 K can be seen in Figure 2.1. The red and purple lines on the bottom of the plot correspond to the powder pattern of tetragonal phase (I\textsuperscript{4}2\textsuperscript{d}) for pure CuInS\textsubscript{2} and CuInSe\textsubscript{2}, respectively. (b) Lattice parameters $a$ and $c$ plotted as a function of composition (x) displaying a clear linear increase in the unit cell as Se content increases. The dotted, linear trendline is a guide for the eyes.

**Figure 2.1:** (a) PXRD patterns for the sintered pellets of CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2} for x = 0, 0.2, 0.4, 0.6, 0.8, and 1 recorded at 300 K. The red and purple lines on the bottom of the plot correspond to the powder pattern of tetragonal phase (I\textsuperscript{4}2\textsuperscript{d}) for pure CuInS\textsubscript{2} and CuInSe\textsubscript{2}, respectively. (b) Lattice parameters $a$ and $c$ plotted as a function of composition (x) displaying a clear linear increase in the unit cell as Se content increases. The dotted, linear trendline is a guide for the eyes.

#### 2.2 Results & Discussion

**i. Synthesis and Characterization of CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2}** PXRD patterns of CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2} (x = 0, 0.2, 0.4 0.6, 0.8, 1.0) sintered pellets can be seen in Figure 2.1. The variation of the S/Se ratio in the polycrystalline pellets is clearly reflected in the XRD data, without any evidence of a structural phase transition or phase separation throughout the series. The patterns show pure, tetragonal CuInS\textsubscript{2} chalcopyrite for x = 0, pure tetragonal CuInSe\textsubscript{2}
chalcopyrite for \( x = 1.0 \), and homogeneous solid solutions for \( x = 0.2, 0.4, 0.6, \) and \( 0.8 \). As the Se content increases, the diffraction peaks shift toward lower 2θ angles, attributed to the increased lattice spacings when substituting Se atoms for smaller S atoms. \( \text{CuIn(S}_{1-x}\text{Se}_x\text{)}_2 \) lattice parameters \( a \) and \( c \) for the tetragonal crystal structures were determined from the refined XRD patterns and are listed in Table 2.1. The lattice parameters as a function of composition \( (x) \) are plotted in Figure 2.1. The lattice parameters show a clear linear relationship with increasing Se content, consistent with Vegard’s law behavior.

**Table 2.1**: \( \text{CuIn(S}_{1-x}\text{Se}_x\text{)}_2 \) material characterization: lattice parameters \( a \) (Å) and \( c \) (Å); mole ratio of Cu, In, S, Se as measured by EDX; and \( E_g \) (eV) from UV-vis diffuse reflectance measurements.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( a )</th>
<th>( c )</th>
<th>( \text{Cu: In: S: Se} )</th>
<th>( E_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.5240(6)</td>
<td>11.140(1)</td>
<td>1.00: 1.00: 1.98: 0.0</td>
<td>1.39</td>
</tr>
<tr>
<td>0.2</td>
<td>5.572(1)</td>
<td>11.227(2)</td>
<td>1.17: 1.02: 1.69: 0.4</td>
<td>1.24</td>
</tr>
<tr>
<td>0.4</td>
<td>5.622(2)</td>
<td>11.315(3)</td>
<td>1.18: 1.02: 1.13: 0.8</td>
<td>1.16</td>
</tr>
<tr>
<td>0.6</td>
<td>5.677(1)</td>
<td>11.418(3)</td>
<td>1.01: 1.08: 0.8: 1.12</td>
<td>1.09</td>
</tr>
<tr>
<td>0.8</td>
<td>5.7312(6)</td>
<td>11.521(1)</td>
<td>1.18: 1.14: 0.4: 1.62</td>
<td>0.99</td>
</tr>
<tr>
<td>1.0</td>
<td>5.7838(5)</td>
<td>11.622(1)</td>
<td>1.08: 1.00: 0.0: 1.92</td>
<td>0.92</td>
</tr>
</tbody>
</table>

The bulk chemical composition of the pellets was analyzed by EDX. The quantitative analysis (listed in Table 2.1) shows the smooth evolution of the material from pure \( \text{CuInS}_2 \) to pure \( \text{CuInSe}_2 \). Although the precision of the technique employed for a specific element is 10%, the Se content increases linearly with increasing \( x \). This is shown in Figure 2.2, where the Se content as detected by EDX is plotted as a function of Se content in the synthetic feed. A representative SEM image and corresponding EDX data of a dense \( \text{CuIn(S}_{1-x}\text{Se}_x\text{)}_2 \) pellet used in this study can be seen in the inset of Figure 2.2(a). By SEM, the dense polycrystalline pellets display evenly distributed grain sizes along the entire pellet surface area. Several different points on each pellet were sampled. The 1% Mg
dopant could not be quantified by EDX analysis due to characteristic X-ray overlap of Mg Kα (1.253 keV) and Se Lα (1.379 keV).

Diffuse reflectance UV−vis was used to determine the optical bandgap of the opaque, dense pellets used in this study (Figure 2.2(b)). The inset of panel (b) shows the absorption spectra of the CuIn(S₁−ₓSeₓ)₂ series. The direct optical band gap (E₉) was established using a Tauc Plot considering the following relationship:

\[
(\alpha h\nu)^2 = \frac{A}{(h\nu - E_g)}
\]

where \(\alpha\) is the absorption coefficient, \(A\) is a constant, and \(h\nu\) is the radiation energy. The experimental values of \((\alpha h\nu)^2\) were plotted against \(h\nu\), and \(E_g\) was determined by extrapolating the absorption edge to the \(x\) intercept. These values are reported in Table 2.1. Figure 2.2(b) shows the linear decrease of the optical band gap \(E_g\) of CuIn(S₁−ₓSeₓ)₂ from 1.39 to 0.92 eV with composition varying from \(x = 0\) to 1. This linear relation agrees with previous optical bandgap studies on CuIn(S₁−ₓSeₓ)₂ thin films and, in addition, agrees with the prediction by Wu et al. in 2002 on the linear relationship of the band gap energy values of the mixed chalcopyrite CuIn(SₓSe₁−ₓ)₂ (\(x = 0.2, 0.4, 0.6, 0.8\)) solid solution with composition.

XPS was used to probe the chemical composition on the surface of the pellets. All binding energies were referenced to C 1s (284.5 eV). Representative XPS spectra of CuIn(S₁−ₓSeₓ)₂ where \(x = 0.6\) can be seen in Figure 2.2. Figure 2.2(c) shows Cu 2p core splitting into Cu 2p3/2 (932.0 eV) and Cu 2p1/2 (951.8 eV) peaks with a peak separation of 19.8 eV, signifying Cu is in the +1 oxidation state. Figure 2.2(d) shows the In 3d peaks located at 444.4 and 451.9 eV with a peak separation of 7.54 eV, signifying In is in the +3 oxidation state. Figure 2.2(e) shows the overlap region of S 2p and Se 3p. The S 2p3/2 is
located at 161.5 eV and S 2p1/2 at 162.7 eV with a peak separation of 1.18 eV. The Se 3p3/2 is found at 160.2 eV and Se 3p1/2 (166.0 eV) with a peak separation of 5.8 eV. Both S 2p and Se 3p peak positions support a −2 oxidation state. Figure 2.2(f) shows the Se 3d region with Se 3d5/2 at 53.9 eV and Se 3d3/2 at 54.8 eV with a peak separation of 0.86 eV. The 1% Mg dopant could not be identified by XPS due to peak overlap with the Mg 2p (51 eV) and Se 3d (54 eV) signals.

Figure 2.2: (a) Ratio of Se content in CuIn(S1−xSex)2 as measured by EDX as a function of Se content in the synthetic preparation feed. The dotted, linear trendline is a guide for the eyes. The inset is a representative SEM image at 558× magnification for sample CuIn(S1−xSex)2 with x = 0.6, showing evenly distributed grain size of the dense, polycrystalline pellet. (b) Energy bandgap vs composition (x) of CuIn(S1−xSex)2 recorded at room temperature. The inset is the diffuse reflectance UV−vis of CuIn(S1−xSex)2 series plotted as (αhν)² (eV/cm)² versus hν (eV). The optical bandgap energy, E_{g}, was estimated from extrapolating the linear absorption edge to the x axis. Panels (c)-(f) show representative XPS spectra of CuIn(S1−xSex)2 at x = 0.6. (c) Cu 2p peaks in the +1 oxidation state. (d) In 3d peaks in the +3 oxidation state. (e) Orbital deconvolution of the S 2p and Se 3p peak overlap. Both S and Se peaks are in the −2 oxidation state. (f) Se 3d peaks in the −2 oxidation state.
Figure 2.3: (a) Representative temperature profile of CuIn(S_{1-x}Se_{x})_2 for x = 0.8 ranging from 300-150 K. The same temperature profile is exhibited for all samples, with resistivity increasing as temperature decreases. The inset plots $\rho$ values at 300 K vs. composition (x). A general decreasing trend is seen from x = 0 to x = 1, with a total decrease in $\rho$ of four orders of magnitude. The dotted, linear trendline is a guide for the eyes. (b) Activation energy ($E_a$) vs. x for all the composition series. As Se content increases, it is kinetically easier for transport of holes through the valence band. The dotted, linear trendline is a guide for the eyes. The inset plots log($\rho$) vs 1000/T in the temperature range of 395-250 K. (c) The log($\rho$) vs 1000/T for the temperature range of 395-250 K comparing stoichiometric CuInSe$_2$ to the 1 % Mg-doped CuInSe$_2$. The difference in the slopes is clear, with stoichiometric CuInSe$_2$ displaying a much steeper slope—signifying a larger activation energy than 1 % Mg-doped CuInSe$_2$. The inset shows the $\rho_{xx}$ vs. T profile for both stoichiometric CuInSe$_2$ and 1% Mg doped CuInSe$_2$. (d) Representative Hall measurements for CuIn(S_{1-x}Se_{x})_2 for x = 0.8 and x = 0 measured from -9 T to +9 T. The positive slopes from this plot were extracted to calculate the $p$-type carrier concentrations. The red solid lines are the linear fit to the experimental data points.
ii. Transport Properties of CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2}. The temperature-dependent bulk resistivity of each sample was probed on cooling from 395 K. A representative temperature profile of the electrical resistivity, for CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2} at x = 0.8, is plotted in Figure 2.3(a) from 300 to 150 K. All samples display an exponentially increasing resistivity with decreasing temperature, a signature of semiconducting materials. The bulk resistivity of each sample at 300 K is listed in Table 2.2. To highlight the general decreasing trend in resistivity from x = 0 to 1, the resistivity (\(\rho\)) vs composition (x) at 300 K is plotted in the panel (a) inset. The plot shows that the transition from x = 0 to 1 does not have perfect linear behavior. This nonlinear behavior can be attributed to the interplay of both intrinsic defects and the Mg dopant in the crystal lattice.\textsuperscript{33} To elucidate the charge transport energetics present in the temperature range near room temperature (395−250 K), the resistivity data for all samples is plotted as log(\(\rho\)) vs T\(^{-1}\) in Figure 2.3(b) inset. The activation energy was thus estimated for each sample based on the relationship:

\[
\rho = \rho_0 \exp \left( \frac{-E_a}{k_B T} \right) \tag{Eq. 2.2}
\]

where \(\rho\) is the sample resistivity, \(\rho_0\) is the pre-exponential term, \(k_B\) is Boltzmann’s constant, and \(T\) is the temperature. When plotting log(\(\rho\)) vs T\(^{-1}\), a linear semilogarithmic fit can be made to estimate \(E_a\) values. The calculated \(E_a\)’s are much less than half of the optical band gaps measured by UV−vis diffuse reflectance spectrophotometry (Table 2.1), indicating

<table>
<thead>
<tr>
<th>x</th>
<th>Resistivity ((\Omega\cdot\text{cm}))</th>
<th>\textit{p}-type carrier concentration (cm(^{-3}))</th>
<th>Mobility (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>(E_a) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3300</td>
<td>(1.6 \times 10^{15})</td>
<td>1.2</td>
<td>70</td>
</tr>
<tr>
<td>0.2</td>
<td>650</td>
<td>(8.7 \times 10^{15})</td>
<td>1.1</td>
<td>49</td>
</tr>
<tr>
<td>0.4</td>
<td>46</td>
<td>(1.2 \times 10^{17})</td>
<td>1.2</td>
<td>35</td>
</tr>
<tr>
<td>0.6</td>
<td>19</td>
<td>(5.2 \times 10^{17})</td>
<td>6.1</td>
<td>33</td>
</tr>
<tr>
<td>0.8</td>
<td>2.9</td>
<td>(1.3 \times 10^{18})</td>
<td>1.6</td>
<td>25</td>
</tr>
<tr>
<td>1.0</td>
<td>0.26</td>
<td>(2.7 \times 10^{18})</td>
<td>8.9</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Table 2.2: Carrier transport properties for Mg-CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2}.
that all materials are in the extrinsic semiconductor regime near room temperature, with acceptor level defects dominating the transport. Thus, the $E_a$ values represent the estimated acceptor ionization energies for each sample and are reported in Table 2.2. Panel (b) in Figure 2.3 shows the $E_a$ values reported in Table 2.2 as a function of composition (x). A general decreasing trend is seen going from x = 0 to 1. This suggests that as the Se content increases the acceptor energies become shallower.

To clarify the identity of the extrinsic acceptor defect as our Mg dopant and indirectly validate the presence of Mg in our samples, a stoichiometric sample of CuInSe$_2$ was analyzed. The resistivity was probed in the same temperature range, and the resulting data was used to calculate its activation energy. Panel (c) in Figure 2.3 shows the log($\rho$) vs $T^{-1}$ plot (the inset shows the resistivity temperature profile) comparing the resistivities of stoichiometric CuInSe$_2$ and 1% Mg-doped CuInSe$_2$. It is clear from panel (c) that the slope of the stoichiometric sample is much steeper, signifying a higher activation energy. In the temperature regime near room temperature (395–250 K), the $E_a$ for stoichiometric CuInSe$_2$ $\approx$ 83 meV, over ten times the activation barrier found in the Mg-doped sample. We attribute the acceptor level defect to the presence of Mg dopant, showing the Mg dopant does indeed have acceptor levels lying below the Fermi level of all semiconductor samples. Similar measurements on stoichiometric CuInS$_2$ were attempted, but non-doped samples of this material had a resistivity above the measurement limit of our apparatus, supporting the presence of Mg dopant in our samples.

Majority carrier concentrations were estimated by Hall measurements. Representative Hall resistivity data as a function of magnetic field for CuIn(S$_{1-x}$Se$_x$)$_2$, x = 1 and 0.8 with 1% Mg dopant at 300 K are shown in panel (d) of Figure 2.3. The samples
exhibit a reliable linear fit of the Hall data ($R^2 \geq 0.90$) to applied field, allowing for the major-ity carrier concentrations ($n_p$) to be estimated (Table 2.2). For samples $x = 0.8$ and 1, $n_p \sim 10^{18}$ cm$^{-3}$ is three orders of magnitude greater than for samples $x = 0$ and 0.2 ($\sim 10^{15}$ cm$^{-3}$). Despite all samples being synthesized with the same amount of $p$-type dopant (1% Mg) this increase in $n_p$ at high values of $x$ is expected given the innate difference in acceptor level depths and band gap energies between pure CuInS$_2$ and CuInSe$_2$. Samples $x = 0.4$ and 0.6 display carrier concentrations of $\sim 10^{17}$ cm$^{-3}$.

Once the carrier concentrations were in hand, the mobilities of the majority carriers were estimated by assuming a single dominant carrier and band-like carrier motion. Using the measured quantities and the relationship:

$$\sigma = N\epsilon\mu$$

where $\sigma$ is the conductivity at 300 K, $\mu$ is the mobility of the carrier, $\epsilon$ is the electron charge, and $N$ is the carrier concentration, the mobilities were estimated (Table 2.2) as varying from approximately $1-10$ cm$^2$ V$^{-1}$ s$^{-1}$. The 4-order-of-magnitude decrease in bulk electrical resistivity seen as $x$ increases from 0 to 1 can therefore be primarily attributed to an increase in carrier concentration but also to a much smaller increase in mobility.

2.3 Conclusions

Temperature-dependent bulk resistivity and Hall effect measurements revealed a 4-order-of-magnitude decrease in electrical resistivity with increasing $x$ value in the quaternary alloy system CuIn(S$_{1-x}$Se$_x$)$_2$. Hall measurements revealed a corresponding 3-order-of-magnitude increase in $p$-type carrier concentration with increasing the $x$ value. The extrapolated electrical mobilities of the $p$-type majority carriers of CuIn(S$_{1-x}$Se$_x$)$_2$ were determined to increase somewhat with $x$. The use of 1% Mg-dopant in CuIn(S$_{1-x}$Se$_x$)$_2$
enabled the study of the bulk resistivity of the materials near ambient temperature. The bandgap and carrier transport properties presented here strongly suggest that the chalcopyrite series CuIn(S$_{1-x}$Se$_x$)$_2$ warrants further study as photoelectrodes to fully realize their potential for PEC applications.

2.4 Methods

i. Synthesis. Ternary and quaternary [we use the conventional term quaternary (four elements in major proportion) to describe the mixture of the two ternary compounds with different chalcogenide end members] CuIn(S$_{1-x}$Se$_x$)$_2$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) polycrystalline ingots were prepared by loading stoichiometric amounts of elemental Cu (Sigma-Aldrich 99.999%), In (Alfa Aesar 99.99%), S (Alfa Aesar), and Se (Alfa Aesar 99.99%) into quartz ampules. Mg (Sigma-Aldrich 99.99%) was used as a $p$-type dopant on the In site for all transport property measurements. All samples were doped with 1% Mg, which was chosen for the $p$-type dopant because of its high electropositive nature, ensuring efficient hole donation to the system. The ampules were purged with Ar and sealed under vacuum. The ampules were heated stepwise to 400, 700, and finally 1100 °C, annealing for 24 h at 400 and 700 °C to allow volatile S and Se vapor to react. After 6 h at 1100 °C, the samples were quenched to room temperature to allow maximum dopant dispersion in the crystal lattice. The resultant polycrystalline ingots were then ground into a powder and pressed into pellets (2.4 mm thickness, 3.17 cm$^2$ area) with two tons of pressure. The pellets were sintered under vacuum at 650 °C for 3 h. The resulting pellets (≥80% of theoretical density) were then used for subsequent characterization.

ii. Sample Characterization. All structural characterization presented in this manuscript was performed on stoichiometric CuIn(S$_{1-x}$Se$_x$)$_2$. First-principles calculations on ternary
chalcopyrites have revealed that divalent dopants like Mg are shallow acceptors on the group-III site. Thus, the 1% Mg dopant needed for transport property measurements is not expected to change the characterization data beyond the measurement error of the analytical techniques employed. The polycrystalline ingots and sintered pellets were analyzed using powder X-ray diffraction (PXRD) on a Bruker D8 Advance Eco with Cu Kα radiation and a LynxEye-XE detector. The scan parameters were 0.02°/step with 0.085 s/step, for a total scan time of 8 min. A Quanta 200 field emission gun environmental scanning electron microscope (SEM) equipped with an integrated Oxford System was employed for energy dispersive X-ray (EDX) analysis. The X-ray penetration depth was 1−2 mm, and the detection limit of a specific element was 10%. X-ray photoelectron spectra (XPS) were collected under 10−9 Torr using a ThermoFisher K-Alpha X-ray photoelectron spectrometer. All spectra were recorded using Al Kα radiation (1487 eV) with a survey and pass energy of 100 and 20 eV, respectively. Measured peaks were fit using Casa XPS software and a Shirley background. The C 1s peak at 284.5 eV of adventitious hydrocarbon was used as an internal binding energy reference. Optical bandgaps were measured with a UV−vis diffuse reflectance HITACHI 131-9007-1 model U3210/U3410 recording spectrophotometer with incident light from 200 to 1300 nm. KBr was used as a calibration standard. Each sample pellet for absorbance measurement was made from a homogeneously ground mixture of the powder and KBr (1:20 by weight).

**Transport Property Measurements.** Transport property measurements were performed on the sintered polycrystalline pellet samples with 1% Mg dopant. Hall effect data and electrical resistivities were collected using a Quantum Design Physical Property Measurement System. The samples were cut from the pellets into 1.20 mm-thick
rectangles, measuring approximately 1.5 mm × 0.5 mm in area. Hall effect data were obtained at 300 K by sweeping the magnetic field from −9 to +9 T at a constant current of 0.1 μA through the sample. The carrier concentration, $N$, was estimated by assuming a single dominant carrier type and the relationship:

$$\frac{1}{N e} = \frac{R t}{B}$$  \hspace{1cm} \text{Eq. 2.4}

where $e$ is the electron charge, $R/B$ is the slope obtained from the measured Hall resistance vs magnetic field measurement, and $t$ is the sample thickness. Resistivity ($\rho$) measurements were performed over a range of 395−10 K. Both Hall and resistivity four probe measurements were facilitated by attaching platinum wires to the samples using conductive Ag paint.
CHAPTER 3

CHALCOPYRITE CuIn(S_{1-x}Se_x)\textsubscript{2} FOR PHOTOELECTROCATALYTIC H\textsubscript{2} EVOLUTION: UNRAVELING THE ENERGETICS AND COMPLEX KINETICS OF PHOTOGENERATED CHARGE TRANSFER IN THE SEMICONDUCTOR BULK

This section is based on Chem. Mater. 2018, 30, 4422-4431. Figures reprinted and adapted from those in the published article are used with permission from the American Chemical Society, copyright 2018.

3.1 Introduction

Hydrogen is a next-generation energy carrier that can be produced from renewable energy sources. Photoelectrochemical (PEC) water splitting is one possible route toward solar-to-hydrogen energy conversion that is both sustainable and environmentally benign. To utilize solar energy, a photoelectrode must possess light absorption that is well matched to the solar spectrum on earth, and suitable conduction band positioning for water reduction.\textsuperscript{35,36}

In addition, efficient harnessing of solar energy for H\textsubscript{2} generation requires fast charge carrier generation, separation, and delivery in the semiconductor electrodes used in PEC processes.\textsuperscript{37}

Copper chalcopyrite semiconductors [Cu(In,Ga)(S,Se)\textsubscript{2}, termed CIGSSe and having an overall stoichiometry of A\textsuperscript{+}B\textsuperscript{3+}X\textsubscript{2}\textsuperscript{2−}] have attracted considerable attention as
photocathodes for PEC water reduction. The wide range of atomic ratio modification available in CIGSSe offers an ability to tune the physical properties to meet the desired solar absorption and conduction band position of an ideal electrolyzer photocathode. Tuning the band gap energy of CIGSSe is a well-known and well-represented experimental method in the literature. Some recent studies include varying the $A^+ / B^{3+}$ cation molar ratio in CuInS$_2$ nanoparticles from 0.7 to 2.9, subsequently decreasing the band gap from 1.45 to 1.19 eV. $^{38}$ Matsumura et al. $^{39}$ recently reported a study varying the cation $B^{3+}$ atomic percent in Cu(In,Ga)S$_2$ thin films that resulted in band gaps ranging from 1.52 to 1.80 eV. Varying the cation content of $A^+$ has also been reported by Kudo et al. $^{40}$ and gave a band gap range of 2.38–2.61 eV with an increasing $x$ value in the system Cu$_{1-x}$Ag$_x$GaS$_2$. Finally, varying the anion $X^{2-}$ atomic percent ratio was recently reported in our work $^{41}$ through the solid-state synthesis and characterization of CuIn(S$_{1-x}$Se$_x$)$_2$ producing a band gap energy range of 0.92–1.39 eV with an increasing $x$ value. The band edge position of CIGSSe can also be adjusted by the same method of atomic ratio modification, as the electronic structures of these materials strongly correlate with the atomic composition. $^{27,42,43}$

The third criterion for efficient H$_2$ evolution, carrier transportation/separation efficiency, is known to rely on the space charge region (SCR) that is formed at the semiconductor–electrolyte interface. $^{44}$ It is important that charge carrier generation take place in this region—where the carrier relaxation is at its minimum—so that delivery to the semiconductor surface is maximized. This rationale has been prioritized with a number of studies on CIGSSe by focusing on charge transfer at the semiconductor–electrolyte junction. Surface modification of CIGSSe photocathodes with $n$-type materials—such as CdS, TiO$_2$, or an additional CIGSSe analogue—is a common technique used to enhance
hydrogen evolution through the formation of a $p-n$ junction on the surface. $¹$-$³$ Net charge separation efficiency in CIGSSe has recently been shown by Hwang et al. $⁴⁵$ to critically depend on the minority carrier transfer at the semiconductor−electrolyte junction. This conclusion was reached after a decrease in quantum efficiency was observed for shorter wavelengths upon illumination of the back side of their CIGSSe thin films. However, the transport behavior of photocarriers in CIGSSe photocathodes outside of the SCR and its effect on the overall hydrogen evolution efficiency have received little attention. Charge carrier transportation beyond the SCR has been reported on photoelectrode materials other than CIGSSe and was found to be a nontrivial factor limiting the materials’ overall PEC performance, as charge carriers must first reach the semiconductor−electrolyte and semiconductor−back-contact boundaries to take part in water splitting redox reactions. For example, bismuth vanadate (BiVO$_4$), a promising metal oxide photoanode, is limited by poor majority carrier transport through the bulk, not by bulk defect states, surface states, or a Schottky barrier at the back-contact. $⁹$ This clearly identified obstacle has been subsequently addressed by a number of studies of BiVO$_4$. $¹⁰,¹¹,⁴⁶$ A recent report on ZnO films $⁴⁷$ concluded that charge transfer efficiency can significantly affect PEC performance depending on the direction of long-range diffusion of excitons through the bulk.

In this study, we report on the photoelectrochemical characterization and H$_2$ evolution rate of $p$-CuIn(S$_{1-x}$Se$_x$)$_2$ photocathodes. The flat band position of each CuIn(S$_{1-x}$Se$_x$)$_2$ electrode was determined to successively rise in energy with an increase in $x$, with all samples displaying band edges in an acceptable thermodynamic position for water reduction. However, despite the suitable band edge positions, normalized illumination, and identical induced potential bias, a two order of magnitude variance in the
H₂ evolution rate was determined for this series, and although the bulk majority carrier mobility of the materials has been found to be independent of x in CuIn(S₁₋ₓSeₓ)₂,⁴¹ we find a complex relationship between the H₂ evolution rate and the carrier concentration. This suggests that, like BiVO₄ and ZnO, charge transport behavior beyond the SCR has a substantial effect on the photoelectrochemical performance of CIGSSe photocathodes for H₂ evolution.

3.2 Results & Discussion

i. Flat Band Potential. To establish whether these materials have energetically favorable band positions for water reduction, their flat band potentials were experimentally determined. Upon comparison of pure CuInS₂ to pure CuInSe₂, substituting S for Se (an element of lesser electronegativity) is expected to alter the orbital character of the valence band and, consequently, alter its energy position relative to the water reduction potential and affect the overall performance for water splitting.²⁷,⁴²,⁴⁵ If the conduction band energies are not more negative than the water reduction potential, then no water reduction will occur as the energy levels for this transformation will be misaligned for the thermodynamic transfer of photoexcited electrons from the conduction band into solution. The fundamental characterization of the absolute band energy of these contemporary mixed anion chalcopyrites is imperative for considering these materials for photoelectrochemical hydrogen evolution.

Each CuIn(S₁₋ₓSeₓ)₂ electrode (in triplicate) was subjected to AC impedance measurements for Mott–Schottky (M–S) analysis to experimentally obtain the flat band potentials (Eₘₖ), which were then confirmed by chopped-light linear sweep voltammetry, both well-established techniques used to estimate the flat band potentials of metal
chalcogenides. 48 Linear sweep voltammetry (LSV) was performed on the CuIn(S$_{1-x}$Se$_x$)$_2$ series under dark, illuminated, and manually chopped conditions. The scanning window started at the open-circuit potential (OCP) determined for each electrode and was swept negatively to −1.2 V versus Ag/AgCl at a scan rate of 25 mV/s.

Figure 3.1(a) shows a representative chopped LSV plot for x = 0.6, with the inset showing the dark and illuminated LSV scans of the electrode. The dark current was subtracted from the chopped-light curve to create a $j$−$V$ curve strictly consisting of the photocurrent. The $E_{fb}$ was estimated from the chopped light curves, assigning $E_{fb}$ to the potential at which the photocurrent starts to grow in from its baseline.

Mott−Schottky analysis was performed at pH 14 in 0.1 M Na$_2$SO$_4$ (aq) to ensure a high double layer capacitance. Figure 3.1(b) shows a representative M−S plot for x = 0.8 in CuIn(S$_{1-x}$Se$_x$)$_2$. The negative slopes of the plots confirm the $p$-type behavior of the electrodes. The M−S equation (Eq. 3.8) used to fit these data assumes that the semiconductor−electrolyte interface is ideally capacitive. However, these interfaces are almost never perfectly capacitive, leading to frequency-dependent slopes (as seen in Figure 3.1(b)). 49 This class of frequency dependence gives plots with varying slopes that converge to a common intercept, giving a valid $E_{fb}$. 50 This behavior, exhibited in all of the electrodes used in this study, is attributed to interface states in the semiconductor, creating complicated surface capacitance. 44 M−S plots can also be used to calculate carrier concentration, $N$, (based on Eq. 3.8) if the slope of the plot is independent of frequency. However, because of the observed frequency dependence in our data, we were unable to confidently assess the carrier concentration of these samples in this manner.
Frequency-dependent slopes in M–S plots are commonly reported in the literature for water splitting electrodes like III–V and perovskite semiconductors, making accurate determinations of carrier concentration through this method rare. Instead, Hall effect measurements, a technique well-established in our research group, are used to characterize semiconductor material majority carrier concentration. For example, when calculating the

Figure 3.1: Determination of CuIn(S\(_{1-x}Se_x\))\(_2\) band-edge thermodynamics. (a) Representative chopped light LSV of CuIn(S\(_{0.4}Se_{0.6}\))\(_2\). Dark current is subtracted to give the differential current density. The top-right inset shows a close-up of the photocurrent onset (V\(_{on}\)). The bottom-right inset shows LSV scans in dark and illuminated conditions. LSV was performed in Ar purged 0.1 M Na\(_2\)SO\(_4\) with 1 M NaOH at a scan rate of 25 mV/s. (b) Representative M-S plot of CuIn(S\(_{0.2}Se_{0.8}\))\(_2\) at 1, 3, and 5 kHz measured under dark conditions. Capacitance measurements were performed in 0.1 M Na\(_2\)SO\(_4\) with 1 M NaOH. (c) Schematic diagram of the electronic band positions of CuIn(S\(_{1-x}Se_x\))\(_2\) with x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 at pH 14. Valence band edge values were approximated from the flat band potentials measured from photocurrent onset and M-S techniques. Conduction band edges were approximated based on the materials’ optically measured band gap values (E\(_g\)) labeled in gray text. The black dotted line represents the water reduction potential at pH 14. The dark blue coloring represents the filled states of the valence band, while the light blue coloring represents the empty states of the conduction band.

Frequency-dependent slopes in M–S plots are commonly reported in the literature for water splitting electrodes like III–V and perovskite semiconductors, making accurate determinations of carrier concentration through this method rare. Instead, Hall effect measurements, a technique well-established in our research group, are used to characterize semiconductor material majority carrier concentration. For example, when calculating the
hole diffusion length in BiVO₄ electrodes, Mullins et al. used the value of $N$ determined from ac Hall effect measurements instead of the values determined by their M–S plots due to frequency-dependent slopes. For these reasons, further discussion with regard to the majority carrier concentration of CuIn(S₁₋ₓSeₓ)₂ photocathodes will refer to the Hall effect measurements we previously reported for these materials.

Table 3.1: Flat-band potentials ($E_{FB}$) of CuIn(S₁₋ₓSeₓ)₂ measured from photocurrent onset (PCO) and M–S techniques.

<table>
<thead>
<tr>
<th>x in CuIn(S₁₋ₓSeₓ)₂</th>
<th>E (V vs Ag/AgCl) at pH 14</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PCO</td>
</tr>
<tr>
<td>0.0</td>
<td>-0.16 ± 0.046</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.29 ± 0.060</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.53 ± 0.035</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.60 ± 0.047</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.65 ± 0.014</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.69 ± 0.048</td>
</tr>
</tbody>
</table>

The flat band potentials from both photocurrent onset and M–S techniques are summarized in Table 3.1. The potentials estimated from photocurrent onset and M–S techniques are in excellent agreement for each electrode material. The values determined for the end members, CuInS₂ and CuInSe₂, are in good agreement with previously reported flat band potentials of these materials, after adjustment for the difference in pH value and reference electrode used to determine their positions. CuIn(S₁₋ₓSeₓ)₂ demonstrated Nernstian behavior as a function of electrolyte pH, with $E_{fb}$ varying by $0.056 ± 0.007$ V/pH unit. These flat band potentials, with consideration of their Nernstian behavior, were then used to approximate the position of the valence band maxima; because of the proximity of the Fermi level with the majority carrier edge, it is common practice to assign the $E_{fb}$ to the valence band position for $p$-type materials. Figure 3.1(c) shows a schematic diagram of the electronic band positions of CuIn(S₁₋ₓSeₓ)₂. The conduction band energies were determined by applying the reported optical band gap measurements. The schematic diagram includes the electronic band positions at pH 14 along with a dotted line
representing the potential at which H₂ evolution occurs at that pH. The dark blue coloring represents the filled states of the valence band, while the light blue coloring represents the empty states of the conduction band.

The relative valence and conduction band edges presented in Figure 3.1(c) follow the expected trend when considering the density of states (DOS) of the end members CuInS₂ and CuInSe₂. In multiple independent studies, density functional theory has predicted consistent elemental deconvolution of the DOS of CuInS₂, CuInSe₂, and other chalcopyrite-related compounds. The upper portion of the valence band primarily consists of Cu d and S/Se p states, while the lower portion of the conduction band primarily consists of s states. ⁵⁸–⁶⁰ Looking at Figure 3.1(c), we find the conduction band minimum (CBM) stays relatively constant with a change in x in CuIn(S₁−ₓSeₓ)₂, but there is a marked negative potential shift in the valence band maximum (VBM) with an increase in x. Because the sulfur and selenium anion states primarily contribute to the VB, this experimental change in the VBM is consistent with the change in anion.

The trend in VBM can be explained by looking at the difference in bonding energy of Cu and S/Se, which make up the valence band character. The ionic bond energy, \( E \), can be determined by the Born–Landé equation ⁶¹:

\[
E = -\frac{N_A A Z^+ Z^- e^2}{4\pi\varepsilon_0 r_0} \left( 1 - \frac{1}{n} \right)
\]

Eq. 3.1

where \( N_A \), \( A \), \( e \), \( Z^+ \), \( Z^- \), \( \varepsilon_0 \), and \( n \) are Avogadro’s constant, Madelung’s constant, the elementary charge, the cation charge, the anion charge, the permittivity of free space, and the Born exponent, respectively. \( r_0 \) stands for the nearest ionic bond distance and represents the factor influencing bond energy when interchanging S and Se anions. Given the difference in the Pauling electronegativity of S (1.58) and Se (1.55), the effective ionic
radius of six-coordinate $S^{2-}$ (1.84 Å) is understandably smaller than that of six-coordinate $Se^{2-}$ (1.98 Å). On the basis of the equation:

$$L = r_C + r_A$$

Eq. 3.2

where $L$ is the bond length and $r_C$ and $r_A$ are the ionic radii of the cation and anion, respectively, the $Cu^+−S^{2-}$ ionic bond distance is subsequently smaller than the $Cu^+−Se^{2-}$ ionic bond distance and results in a larger ionic bond energy. Thus, as $Se^{2-}$ is incorporated into the lattice in place of $S^{2-}$, the $Cu^+−X^{2-}$ bond weakens, resulting in an increase in valence band energy.

**ii. PEC $H_2$ Evolution Bulk Electrolysis.** In the previous section, we showed that all electrodes in the $CuIn(S_{1−x}Se_x)2$ series possess band edges energetically favorable for water reduction; thus, thermodynamic limitations are not present in $H_2$ evolution studies. After this checkpoint, the electrodes were in hydrogen evolution conditions subjected to the same electrolyte environment [0.1 M Na$_2$SO$_4$(aq) with 1 M NaOH and 1 M Na$_2$S], a light intensity of 100 mW/cm$^2$ at a wavelength greater than the materials’ band gap, and an applied potential bias to create $\sim$700 mV band bending based on each electrode’s measured flat band potential. A Pt mesh counter electrode was housed in a compartment connected to the photoelectrode half-cell via a fine-grade glass frit in all electrolysis experiments. A band bending schematic can be seen in Figure 3.2(a) illustrating the applied bias used to create 700 mV of band bending, and the relative energy positions of $CuIn(S_{1−x}Se_x)2$ (represented with $x = 0.6$ in this example) with respect to the solution redox potential for $H_2$ evolution. The colors of the bands represent the major elements contributing to the valence and conduction bands: Cu, S, and Se states in the valence band and In states in the conduction band. Figure 3.2(b) shows a representative plot of evolved $H_2$ versus time in hours for
CuIn(S$_{0.8}$Se$_{0.2}$)$_2$. The red symbols show the experimentally gathered data, and the blue line plots the theoretical 100% FE based on charge passed. The inset of Figure 3.2(b) shows the corresponding $j$−$t$ curve. The dotted lines mark the time at which H$_2$ gas collection data were taken. With all CuIn(S$_{1-x}$Se$_x$)$_2$ electrodes, there is a nonlinear trend of the total micromoles of H$_2$ evolved in the first $\sim$1−2 h, despite a constant current flow during this time. We attribute this nonlinearity at the beginning of the electrolyses to the time it takes for enough H$_2$ to be produced to saturate the electrolyte and fill the sampling headspace of the electrolysis cell.
The rate of $\text{H}_2$ evolution for each electrode was calculated by taking the slope of evolved $\text{H}_2$ versus time between the 2 and 10 h time points of stable $\text{H}_2$ production. The $\text{H}_2$ evolution rate of each electrode is listed in Table 3.2. The rates range from $0.25 \pm 0.04$ to $22.5 \pm 0.69 \mu\text{mol of } \text{H}_2 \text{ h}^{-1} \text{ cm}^{-2}$, a remarkable two order of magnitude difference in the $\text{H}_2$ evolution rate. This variability in rate may at first be considered anomalous given our effort to normalize the photoelectrochemical conditions for each electrode (i.e., normalize kinetic contributions). We first investigated the possibility of Fermi level pinning as an explanation to the varying $\text{H}_2$ evolution rates, but no sign of this phenomenon presented itself. Then, to confirm that the electrodes were indeed kinetically limited, the implication of the rate variation, current density was probed as a function of light intensity for a low value and a high value of $x$ in CuIn(S$_{1-x}$Se$_x$)$_2$ (Figure 3.3). In photoconductive devices, the photocurrent ($I_{\text{PH}}$) depends on the incident optical power ($P$) in a power law relation of $I_{\text{PH}} \propto P^y$, where $0.5 < y < 1$. $I_{\text{PH}}$ should therefore increase linearly to a point of saturation. The LSV plots in Figure 3.3 clearly show a lack of dependence of photocurrent density on light intensity. This confirms a significant kinetic limitation in our electrodes, as despite the number of electron–hole pairs generated with an increase in light intensity, the reductive current is limited by an internal charge carrier process.

### Table 3.2: $\text{H}_2$ evolution rate of CuIn(S$_{1-x}$Se$_x$)$_2$ over 10-12 h at ~700 meV band bending.

<table>
<thead>
<tr>
<th>$x$ in CuIn(S$_{1-x}$Se$_x$)$_2$</th>
<th>$\text{H}_2$ evolution rate $(\mu\text{mol h}^{-1} \text{ cm}^{-2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>$0.25 \pm 0.04$</td>
</tr>
<tr>
<td>0.2</td>
<td>$7.56 \pm 0.16$</td>
</tr>
<tr>
<td>0.4</td>
<td>$22.5 \pm 0.69$</td>
</tr>
<tr>
<td>0.6</td>
<td>$3.28 \pm 0.47$</td>
</tr>
<tr>
<td>0.8</td>
<td>$1.29 \pm 0.08$</td>
</tr>
<tr>
<td>1.0</td>
<td>$2.21 \pm 0.14$</td>
</tr>
</tbody>
</table>
Figure 3.3: LSV plots of (a) CuIn(S_{0.8}Se_{0.2})_{2} and (b) CuInSe_{2}, electrodes with relatively low and high carrier concentrations, respectively, as a function of light intensity. The insignificant change in photocurrent density as light intensity increases is a clear marker for kinetic limitations for electrodes on either end of the x in the CuIn(S_{1-x}Se_{x})_{2} spectrum.

Possible charge carrier factors affecting the rate of transformation include (1) the majority carrier delivery rate due to the presence of a Schottky barrier on the back-contact, (2) the minority carrier separation and rate of delivery to the solution, and (3) the charge carrier recombination rate in the bulk. We have shown that our electrodes display ohmic behavior \textsuperscript{56}, so for our case, the accumulation of positive charge in the bulk due to a Schottky barrier can be ruled out. In our experiments, the applied potential bias used for each electrode gave \( \sim 700 \text{ mV} \) band bending (based on their \( \text{E}_{\text{fb}} \)); this induced electric field is more than sufficient for performing nonlimiting e\(^{-}\) movement from the SCR into solution. \textsuperscript{66} Although surface states are inevitably present (given the frequency dependence displayed in our M–S plots), the \( \sim 90\% \) FE attests to the thermodynamic preference for H\(_2\) production over trapped charge formation. The Mg dopant used is a shallow acceptor in ternary chalcopyrites on the group III site \textsuperscript{34}, which, unlike deep acceptors, will not act as an optically active center or as a catalytic surface site. \textsuperscript{67} Additionally, any change in surface electrocatalytic activity with different S:Se ratios can be discounted because of the normalized driving force of 700 mV band bending and the FE of \( \geq 90\% \) for all samples.

This leaves us to consider charge carrier recombination in the bulk, which is influenced by the bulk mobility of the majority charge carriers. Considering our earlier
characterization, the bulk majority carrier mobilities of these materials are effectively the same at $1 \times 10^0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This suggests that carrier recombination in the bulk should be normalized throughout the CuIn(S$_{1-x}$Se$_x$)$_2$ series. To investigate this hypothesis, we considered the relationship between conductivity and carrier concentration. Carrier mobility ($\mu$) can be calculated with the following equation:

$$\mu = \frac{\sigma}{N} \frac{1}{e}$$  \hspace{1cm} \text{Eq. 3.3}

where $\sigma$ is the conductivity, $N$ is the carrier concentration, and $e$ is the electron charge. A plot of the CuIn(S$_{1-x}$Se$_x$)$_2$ series’ conductivity versus carrier concentration (Figure 3.4(a)) produces a positive trend line as previously reported. The increase in conductivity with an increased carrier concentration (known to increase lattice scattering contributions at room temperature) seems to compensate for one another to produce the same mobility from $x = 0.0$ to $x = 1.0$ in CuIn(S$_{1-x}$Se$_x$)$_2$. The constant carrier mobility with composition rules out bulk conductivity as the source of the observed charge transfer limitation.

Despite this normalized bulk mobility, there is a clear maximum in H$_2$ evolution at $x = 0.4$. In Figure 3.4(a), a color map from white to blue is presented to visually symbolize the relative rates of H$_2$ evolution. The inset of Figure 3.4(a) gives the relative rates of H$_2$ evolution versus $N$, which shows the peak of H$_2$ evolution occurring for $x = 0.4$, at a carrier concentration of $\sim 1 \times 10^{17} \text{ cm}^{-3}$. Clearly a “sweet spot” in carrier concentration exists in these materials but is unrelated to the bulk mobility of the majority carrier concentration. How else could carrier concentration impact this complex system?

The carrier concentration influences the energetic position of the semiconductor’s Fermi level: electron donors raise the Fermi level closer to the conduction band creating $n$-type semiconductors, while electron acceptors lower the Fermi level closer to the valence
Figure 3.4: (a) Conductivity vs carrier concentration of CuIn(S$_{1-x}$Se$_x$)$_2$, showing a positive trend line. The color map from white to blue represents the relative rate of H$_2$ evolution. The inset gives the rate of H$_2$ evolution vs carrier concentration, which shows a clear peak in H$_2$ evolution rate at $x = 0.4$ with a carrier concentration of $\sim 1 \times 10^{17}$. (b) Schematic of the three regions emerging in a semiconductor under illumination: R1, SCR; R2, diffusion region; and R3, dark region. Photocarriers generated in R2 diffuse to R1 at probability $e^{-b/\ell_n}$ before reaching the electrolyte to contribute to H$_2$ evolution. However, as the carrier concentration increases, the probability of this diffusion rate significantly decreases. Schematic (c) shows the impact of increased carrier concentration, which is a decrease in R1 width ($\Delta R_1$) creating a decrease in the diffusion rate, $e^{-(b+\Delta R_1)/\ell_n}$. At a constant photon flux, this phenomenon will lead to fewer photocarriers generated in R2 reaching R1 and contributing to water reduction, thus decreasing the rate of H$_2$ evolution.
band creating \( p \)-type semiconductors. In either case, below a carrier concentration of \( \sim 10^{16} \) cm\(^{-3} \), the Fermi level energy cannot be displaced from its intrinsic state to a position optimal for band bending and subsequent photoactivity. Low carrier concentrations giving lower or no photoactivity for water reduction/oxidation are commonly reported in the literature. For example, Huang et al. \(^6\) investigated the influence of carrier concentration on water oxidation with \((\text{GaN})_{1-x}\text{(ZnO)}_2\) semiconductors, showing that as they decreased from high to low concentrations, the photoactivity decreased and eventually no photoactivity was seen with samples having relatively low carrier concentrations. Their work also observed a complex dependence on carrier concentration at intermediate carrier concentrations, but an explanation for this complex dependence in their system was not offered.

For our system, a possible explanation for the decrease in \( \text{H}_2 \) evolution rate with samples of relatively high carrier concentrations involves looking at how the carrier concentration might affect the material when under illumination. Upon illumination, three regions emerge in a semiconductor: R1, the SCR, closest to the solution interface; R2, the diffusion region; and R3, the dark region, closest to the back-contact. A schematic representation of these regions is presented in Figure 3.4. As mentioned, R1 is where the majority of charge carrier creation and separation occur because of surface-light absorption and the induced electric field. For our system, the width of R1 ranges from \( 7 \times 10^{-5} \) to \( 2 \times 10^{-6} \) cm. R3 exists far enough away from the illuminated surface (starting at \( 0.1783 \pm 0.0209 \) cm in our 0.24 cm thick electrodes) to remain in the dark, contributing no photogenerated carriers to the \( \text{H}_2\text{O} \) reduction transformation. R2 is the middle ground in this situation, where light penetration can still reach, but no electric field is present. The
thickness of each region was determined through calculation of the SCR width and absorption depth from ultraviolet–visible measurements. A thorough overview of calculating the region thicknesses can be found in the supporting information of this work.

Now, any photogenerated minority carriers created in R2 have the potential to contribute to H₂ evolution, if diffusional drift into R1 is faster than carrier recombination following the canonical Gärtner model ⁷⁰, the photocarriers generated in R2 will diffuse to R1, which we will call here the probability of diffusion (P_D), at a constant rate of

\[ P_D = e^{-b/L_n} \]  

where \( L_n \) is the minority carrier diffusion length (in our case the electron diffusion length) and \( b \) is the photocarrier’s initial distance from R1 (Figure 3.4(b)). \( L_n \) has been measured on \( p \)-type polycrystalline CuInS₂ and other chalcopyrite materials by both the photoelectromagnetic effect and electron beam-induced current (EBIC) experiments, giving a minority carrier diffusion length on the order of \( 1 \times 10^{-5} \) cm. ⁷¹,⁷²

However, it is worth mentioning this value is indirectly dependent on carrier concentration, as \( L_n = \sqrt{D\tau} \), where \( D \) is the diffusion constant and \( \tau \) is the carrier lifetime. \( D \) is independent of \( N \); however, \( \tau \propto 1/N \), leading to a decrease in \( L_n \) with an increase in \( N \). ⁶⁸ These measurements were taken on samples at relatively low carrier concentrations, \( 10^{14}–10^{15} \) cm⁻³, so for samples with higher carrier concentrations, \( L_n \) will be even shorter. It is also worth noting that because our materials are polycrystalline the grain size (if smaller than \( L_n \)) could demand a more involved interpretation of the diffusion probability. However, this is not a problem for our material; the supporting information of this work shows a scanning electron microscopy (SEM) image at a large magnitude that has been
used to measure the average grain size of the electrodes, which are indeed on a scale sufficiently larger than $L_n$.\textsuperscript{56}

Now, focusing on $b$ in Eq. 3.4, we find that $b$ is indirectly affected by $N$. Despite a constant photon flux on the electrode, this distance, $b$, from R1 can change depending on the width of R1. The width of R1 ($L$) is dictated by the following equation:

$$L = \left(\frac{2\varepsilon\varepsilon_0}{eN}\Delta\varphi\right)^{1/2} \text{cm}$$ \hspace{1cm} \text{Eq. 3.5}

where $\varepsilon$ is the permittivity of free space, $\varepsilon_0$ is the dielectric constant, $e$ is the electron charge, $N$ is the carrier concentration, and $\Delta\varphi$ is the potential drop in the SCR (0.7 V in our case). I–III–VI$_2$ semiconductors have, on average, a dielectric constant of $\sim 10.47$ With this consideration, we can condense Eq. 3.5 to the following:

$$L = \left(7.7 \times 10^6 \frac{1}{N}\right)^{1/2} \text{cm}$$ \hspace{1cm} \text{Eq. 3.6}

We find that in our case, $L$ is highly dependent on $N$. As $N$ increases, the SCR width becomes smaller. Now, in addition to the initial distance $b$ in Eq. 3.4, the shift in the R1–R2 boundary position (due to an increase in $N$) must be taken into account. This scenario can be seen in Figure 3.4(c), where an increase in carrier concentration changes the probability of diffusion to:

$$P_D = e^{-(b+\Delta R_1)/L_n}$$ \hspace{1cm} \text{Eq. 3.7}

where $\Delta R_1$ is the change in the width of R1 after an increase in carrier concentration, despite photon flux remaining constant.

From this exercise, we can conclude the following: samples with relatively high carrier concentrations have an inherently lower probability of their minority carriers reaching R1 and are thus limited by charge recombination in the bulk leading to a lower rate of $H_2$ evolution. The relationship between carrier concentration and diffusion
probability can be seen in the supporting information of this work, where we have plotted $P_D$ versus $N$ with photocarriers generated $1 \times 10^{-4}$ cm into the electrode. 

After considering the consequences of relative carrier concentrations, we can rationalize that a possible explanation for the peak in H$_2$ evolution rate we see at $x = 0.4$ in CuIn(S$_{1-x}$Se$_x$)$_2$ is due to a complex balancing act between the pros and cons associated with both relatively low and high carrier concentrations.

**iii. Post-electrolysis Material Analysis.** Powder X-ray diffraction (XRD), SEM, and energy dispersive X-ray (EDX) analysis were used to analyze the bulk of the electrode material both pre- and post-electrolysis and can be found in the supporting information of this work. 

Through these techniques, we affirmed no major transformations of the bulk occurred during the 10−12 h bulk electrolysis each electrode performed. Neither binary phase segregation nor neutral metals were observed in any of the CuIn(S$_{1-x}$Se$_x$)$_2$ polycrystalline pellets. The electrode surfaces display an evenly distributed grain size with no obvious chipping or pitting into the densified pellet. The post-electrolysis bulk ratios of elements are comparable to the elemental ratios obtained pre-electrolysis.

X-ray photoelectron spectroscopy (XPS) was also used to survey the electrode materials both pre- and post-electrolysis to determine any change in the chemical composition of the electrode surface. This data can be found in the supporting information of this work. The binding energies were referenced to C 1s (284.8 eV) in all instances. The elemental fingerprint of each elemental component supports the integrity of the electrode material after H$_2$ evolution for 10 h. With Cu chalcopyrites as photocathodes, there is well documented concern with the stability of the Cu$^+$ oxidation state. Keeping a constant reductive potential for H$_2$O reduction opens the possibility of Cu$^+$ being reduced.
to Cu\(^0\) on the surface, leading to possible co-catalyst considerations or unwanted binaries forming on the surface of the electrode.\(^{75,76}\) The highly oxidative electrolysis environment, coupled with the presence of stabilizing polysulfides, sufficiently prevented any trace of Cu\(^+\) reduction, and like the bulk analysis, no binary phases or Cu metal was observed on the surface of the electrode material either pre- or post-electrolysis.

### 3.3 Conclusions

In this study, CuIn(S\(_{1-x}\)S\(_x\))\(_2\) electrodes were prepared from densified polycrystalline pellets using a layer of Au to create a back-side ohmic contact. The photocathodes were characterized by M–S plots and chopped-light LSV techniques to accurately determine their flat band potentials relative to the thermodynamic potential for H\(_2\) evolution. All x values tested in the CuIn(S\(_{1-x}\)S\(_x\))\(_2\) series were found to be thermodynamically fit to reduce water to H\(_2\). Despite their thermodynamic compatibility for photoelectrochemical reduction of water, the CuIn(S\(_{1-x}\)S\(_x\))\(_2\) electrodes displayed severe kinetic limitations. Bulk electrolysis studies revealed H\(_2\) evolution rates varying by two orders of magnitude depending on the x value in CuIn(S\(_{1-x}\)S\(_x\))\(_2\), peaking at x = 0.4. Through the use of the Gärtner model and the SCR width approximation, we suggest a likely explanation for peak H\(_2\) evolution rates that are indirectly influenced by charge carrier concentrations. Our studies support a nontrivial contribution of charge transport behavior beyond the SCR, advocating consideration of this influential factor for future optimization of CIGS derivatives in photoelectrochemical H\(_2\) generation.

### 3.4 Methods

**i. Sample and Electrode Preparation.** Polycrystalline CuIn(S\(_{1-x}\)S\(_x\))\(_2\) pressed pellets were made using our previously described method.\(^{41}\) Mg was used as a p-type dopant on the In
sites to enable transport property measurements and photoelectrochemical characterization. All samples contain 1 wt % of this dopant, normalizing any influence the dopant has on photoelectrochemical analysis. A full discussion of the incorporation of a Mg dopant can be found in our previous work. The synthesis was monitored by XRD on a Bruker D8 Focus X-ray diffractometer with a Cu Kα X-ray source and a graphite diffracted beam monochromator. Diffraction experiments on the surface of the electrodes were performed before and after electrolysis.

Ohmic contact was confirmed by sputtering 100 nm thick layers of gold on each side of the pellet samples using a Leica Sputter Coater. A linear current–voltage curve, found in the supporting information of this work, was obtained by performing a linear sweep experiment with this configuration, indicating the formation of ohmic contacts. To assemble the electrodes used in this study, one side of a pellet of CuIn(S$_{1−x}$Se$_x$)$_2$ was gold sputtered and connected to an external copper wire with conducting silver epoxy (Epoxy Technology H31). The layers were then covered with a glass tube and sealed with insulating epoxy cement (Loctite 0151 Hysol).

Prior studies involving CIGSSe photocathodes typically involved adding a passivating surface layer, such as ZnS or CdS, and a photocatalyst layer like Pt. However, because we wanted the studies presented in this work to focus solely on CuIn(S$_{1−x}$Se$_x$)$_2$ performance, without the added complexity of engineering passivated samples, surface modification was not employed.

**ii. Band Characterization.** AC impedance data were collected using a CuIn(S$_{1−x}$Se$_x$)$_2$ working electrode, a Ag/AgCl reference electrode, and a Pt mesh counter electrode in a one-compartment electrochemical cell; 0.1 M Na$_2$SO$_4$ (aq) was used as the electrolyte and
adjusted to pH 14 using 1 M NaOH. Capacitance–voltage measurements were taken using a CHI 760D electrochemical workstation operating at 1, 3, and 5 kHz and employing a dc potential range from −1.2 to −0.2 V with a 5 mV peak-to-peak AC potential perturbation. The flat band potential was determined from the M–S equation in linear form \(^{44}\):

\[
\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon_r \varepsilon_0 A^2 e N} \left( E - E_{fb} - \frac{kT}{e} \right)
\]

where \(C_{SC}\) is the capacitance of the space charge layer, \(e\) is the electron charge, \(\varepsilon_r\) is the dielectric constant of the material, \(\varepsilon_0\) is the permittivity of a vacuum, \(N\) is the majority carrier concentration, \(E\) is the applied potential, \(E_{fb}\) is the flat band potential, \(k\) is Boltzmann’s constant, \(T\) is the temperature at which the experiment was conducted, and \(A\) is the surface area contact with the electrolyte. When the semiconductor band bending generates a space charge region depleted of the majority carrier, a straight line will be obtained in a plot of \(1/C_{SC}^2\) versus \(E\). Extrapolating to \(1/C_{SC}^2 = 0\) produces an x-intercept of \(E_{fb} + kT/e\). Because the term \(kT/e\) is small at room temperature compared to \(E_{fb}\), it can be neglected.

Photocurrent onset potentials were obtained through linear sweep voltammetry measurements under chopped-light conditions using a Pyrex ultraviolet cutoff and infrared cutoff filter. Three-electrode \(j-V\) curves were obtained using CuIn(S\(_{1-x}\)Se\(_x\))\(_2\) as the working electrode, a Ag/AgCl reference electrode, and a Pt mesh counter electrode. A 150 W Xe arc lamp (USHIO UXL 151H, 350–1350 nm) operating at 100 mW/cm\(^2\) was used for illumination; 0.1 M Na\(_2\)SO\(_4\) (aq) was used as the electrolyte and was adjusted to basic pH using 1 M NaOH. The flat band potential was estimated from the photocurrent onset potential under chopped light.
iii. Sample Morphology and Composition. The morphology of CuIn(S$_{1-x}$Se$_x$)$_2$ electrodes was investigated using a Quanta 200 field emission gun environmental scanning electron microscope equipped with an integrated Oxford System used for EDX analysis. SEM and EDX data were collected both before and after electrolysis.

X-ray photoelectron spectra were collected under 10$^{-9}$ Torr in a ThermoFisher K-Alpha X-ray photoelectron spectrometer. All spectra were recorded using Al Kα radiation (1487 eV) with survey and pass energies of 100 and 20 eV, respectively. Measured peaks were fit using Casa XPS software and employing a Shirley background correction. The C 1s peak at 284.8 eV of the adventitious hydrocarbon was used as an internal binding energy reference. XPS data were collected both before and after electrolysis.

iv. Bulk Electrolysis. Bulk electrolysis measurements were taken with CH Instruments potentiostats (CH Instruments 760 and 1140). A custom-made two-compartment electrolysis cell with gastight ports was used to trap evolved H$_2$ in the headspace and to house the semiconductor working electrode, the Hg/HgO reference electrode, and the Pt mesh counter electrode. The 0.1 M Na$_2$SO$_4$ (aq) electrolyte was brought to pH 14 with 1 M NaOH. A pH 14 environment was used to create a sufficiently oxidizing environment to prevent degradation of Cu$^+$ to Cu$^0$. This practice has been successfully described in our past work on CuRhO$_2$. 52 To further maintain electrode photostability, the electrolyte contained 1 M Na$_2$S; a polysulfide rich environment is commonly used to stabilize sulfide and selenide materials in photoelectrochemical studies, without which the chalcogenide materials would degrade over the hours long bulk electrolyses. 78–81 The reaction solutions were purged with Ar for 1 h prior to electrolysis.
All electrolyses were conducted with a 150 W xenon arc lamp with an irradiance of 100 mW/cm². A digital hand-held optical power meter (model PM100D, Thorlabs) coupled with a thermal absorber (model S302C, Thorlabs) was used to obtain solar power data. Bulk electrolyses were performed with ~700 mV band bending. This was controlled by applying a working potential that was 700 mV more negative than the electrode’s predetermined flat band potential.

The bulk electrolyses were performed for hour-long periods of time over which the headspace was sampled for gas chromatography detection. The evolved H₂ was analyzed with an SRI 8610C gas chromatograph using a TCD detector and a Molsieve column. Argon was used as the carrier gas. A 7 min isotherm at 80 °C was employed. The gaseous product was quantified using 30-point calibration curves with R² values of ≥0.99. Faradaic efficiencies were calculated on the basis of the total charge passed during each experiment and the quantity of H₂ determined by gas chromatography.
CHAPTER 4

PHOTOELECTROCHEMICAL CO₂ REDUCTION USING CHALCOPYRITE-BASED COMPOSITE ELECTRODE CuInSe₂/Ni₃Al+TiO₂

This section is based on the submitted work by Foster, B. M.; Paris, A. R.; Frick, J. J.; Blasini-Pérez, D. A.; Cava, R. J.; Bocarsly, A. B. “Catalytic Mismatching of CuInSe₂ and Ni₃Al Demonstrates Selective Photoelectrochemical CO₂ Reduction to Methanol”. BMF and DABP conducted most (photo)electrochemical experiments. ARP performed isotopic labeling and CO feedstock experiments. ARP and JFF collected materials characterization data and oversaw project development and progress. All authors contributed to data analysis.

4.1 Introduction

This section will focus on the role of the photoabsorber, CuInSe₂, in this system and present the conclusions of this study. For a full picture of this work please refer to the submitted manuscript. ⁸² For detail on Ni₃Al as a CO₂ reduction electrocatalyst please refer to work by Paris et al. ⁸³

A broad conclusion that can be drawn from Chapter 3 is that the surface of the chalcopyrite series CuIn(S₁-xSex)₂ is not particularly catalytic toward water reduction. An obvious branch of this project in the Bocarsly Lab would be to test these photoelectrodes for CO₂ reduction. This is an electrochemically more-challenging transformation to perform, but by applying the simple rationale that if a material’s surface is not catalytic toward H₂ evolution (the main competing transformation for aqueous CO₂ reduction) it
could perhaps be useful as a photocathode in CO₂ reduction. That is, very basically, what stemmed this collaborative project with Dr. Aubrey Paris, Ph.D. and our shared undergraduate student, Brian Foster.

Brian is a fantastic scientist and I am very proud of my young Gryffindor for all he has accomplished thus far and will undoubtedly achieve throughout his life. This project would not exist without his dedication to the lab and budding scientific writing skills—which was all voluntary on his part, in addition to his heavy sophomore year course load, and job! “Fly high Gryffindor!” Collaborating with Dr. Paris, my fellow Slytherin, on this project started as a fun challenge to bridge our seemingly unrelated research areas in the Bocarsly lab. It soon became a milestone project for me personally, learning how to collaborate with, and simultaneously co-mentor a student with, a decisive scientist like Dr. Paris. I think I grew a lot from this project as a scientist, collaborator, and mentor. I believe our friendship grew stronger through it all and (is it sad to admit this?) working with Dr. Paris and Brian on this project was a highlight during my last year at Princeton :)

4.2 Results & Discussion

CuInSe₂ was selected out of the series chalcopyrite series discussed in Chapters 2 & 3 because it has the highest mobility (8.9 cm² V⁻¹ s⁻¹) and a low H₂ evolution rate, both desired characteristics for a CO₂ reduction photocathode. This material has a direct bandgap of 0.92 eV, which is well-matched to the solar spectrum under AM1.5 conditions. Despite the material’s sluggish kinetics as a H₂ evolution photoelectrocatalyst, its optical formation of electron-hole pairs was an efficient process at energies just slightly larger than the band gap energy. While the conduction band edge of the material is energetically well-situated for CO₂ reduction (Chapter 3) the reaction dynamics are expected to make
generation of carbon-containing products insignificant. To convert this electrode interface into an electrochemically interesting material, we have supplied the semiconductor surface with Ni₃Al and TiO₂, modifying agents which suppress photodecomposition and turn on CO₂ reduction activity. This composite photoelectrochemical system, hereafter referred to as CuInSe₂/Ni₃Al+TiO₂, produces methanol at a Faradaic efficiency 25 times greater than that achieved using the purely electrochemical Ni₃Al system ⁸³, while simultaneously lowering the operating potential requirement by 600 mV when compared to the same catalyst applied to a glassy carbon surface.

Preliminary electrochemical testing performed using bare CuInSe₂ electrodes supported our hypothesis that CO₂ reduction would not be facilitated by the pure, unmodified semiconductor. Namely, bulk electrolysis conducted in a custom two-compartment cell with a Pt mesh counter electrode, Ag/AgCl reference electrode, 0.1 M Na₂SO₄ electrolyte (pH 4.5 under CO₂ purge), and an operating potential of –1.4 V vs. Ag/AgCl (i.e., within the potential window of many CO₂-reducing electrocatalysts) failed to yield CO₂ reduction products. Instead, the semiconductor degraded under these conditions, as evidenced in Figure 4.1 by orange discoloration on the electrode surface and wall of the electrochemical cell. As noted in Chapter 3, this behavior is characteristic of Cu reduction (i.e., from the semiconductor, Cu⁺ to Cu⁰). ⁴¹,⁵² Switching the electrolyte from Na₂SO₄ to KHCO₃, which has a pH of approximately 7 when saturated with CO₂, failed to prevent electrode degradation even though CuInSe₂ is reported to be more stable at higher pH values (Chapter 3) We note in passing that Yuan et al. claims to have observed that the related p-type chalcopyrite CuInS₂ photoelectrochemically reduces CO₂ in the presence of
dissolved pyridine \textsuperscript{84,85}; however, these studies lack a critical \textsuperscript{13}CO\textsubscript{2} labeling experiment needed to substantiate this claim.

Applying a coating of TiO\textsubscript{2}, a known protective layer for chalcopyrite semiconductor surface stabilization \textsuperscript{1,86}, onto the CuInSe\textsubscript{2} electrode also did not protect against corrosion, which occurred more quickly than it did for bare CuInSe\textsubscript{2}. Current-voltage characterization revealed the presence of a Schottky barrier in this system, thereby facilitating—rather than preventing—material degradation. More information on preliminary electrode preparation trials can be found in the supporting information of this manuscript. \textsuperscript{82}

Since initial results suggested that CuInSe\textsubscript{2} was incapable of facilitating CO\textsubscript{2} reduction on its own, supporting our initial hypothesis, it served as an ideal semiconductor material with which to pair an active CO\textsubscript{2}-reducing electrocatalyst, thereby testing the concept of catalytic mismatching—strategically pairing a catalytically inactive, optically proficient semiconductor with a selective electrocatalyst. Given its ability to generate

\textbf{Figure 4.1:} Electrochemical reduction of the working electrode CuInSe\textsubscript{2}, Cu\textsuperscript{+1} to Cu\textsuperscript{0}, aka “Cheeto Dust”. Pt mesh counter electrode, Ag/AgCl reference electrode, 0.1 M Na\textsubscript{2}SO\textsubscript{4} electrolyte (pH 4.5 under CO\textsubscript{2} purge), and an operating potential of –1.4 V vs. Ag/AgCl.
highly reduced products from CO₂, the intermetallic Ni₃Al was selected as the electrocatalyst. Alternative literature systems that combine photoabsorbers and CO₂-reducing electrocatalysts have been limited to photo- or photoelectrochemical generation of formate, a two-electron-reduced product, as the dominant liquid-phase species and, critically, have not been designed specifically based on the principle of catalytic mismatching.

To assess the photoelectrochemical CO₂ reduction activity of the CuInSe₂/Ni₃Al+TiO₂ composite electrode, linear sweep voltammetry (LSV) was performed. As shown in Figure 4.2(a), current enhancement occurred around −0.4 V vs. Ag/AgCl under CO₂ saturation compared to Ar, suggesting the onset of CO₂ reduction. The presence of a photocurrent was also revealed using chopped-light LSVs obtained in a CO₂-saturated environment, Figure 4.2(b). This confirmed that the incident light successfully
penetrated beyond the 2–3 µm layer of Ni₃Al+TiO₂, in agreement with the absorbance measurements and subsequent absorption depth calculations reported in Chapters 2 & 3. This result is further supported by LSVs obtained separately under light and dark conditions, inset of Figure 4.2(b), which show a noticeable difference in current density.

Based on ¹H-NMR analysis of the electrolyte following preliminary electrolysis experiments, methanol was the primary CO₂ reduction product achieved. This product assignment was confirmed using isotopically labeled ¹³CO₂ starting material, provided in the supporting information of the work. ⁸² Preliminary testing also revealed that stable current densities around –0.1 mA/cm² could be achieved at –1.0 V vs. Ag/AgCl during a 16-h period, seen in Figure 4.3(a). During this time, CO₂ reduction competed with H₂ evolution—a frequent challenge ⁸⁹—and CO was not evident in the gas-phase. A sample Faradaic efficiency plot, shown in the supporting information of this work ⁸², indicated that the charge passed was divided between CO₂ reduction and H₂ production. These results

Figure 4.3: Performance of the CuInSe₂/Ni₃Al+TiO₂ composite electrode during bulk photoelectrolysis. (a) At –1.0 V vs. Ag/AgCl, stable photoelectrochemical current could be achieved for nearly 16 h, resulting in no physical degradation of the electrode (inset). (b) Faradaic efficiencies for photoelectrochemical CO₂ reduction to methanol are reported at various operating potentials, where a maximum value of 25 ± 3% was recorded at –0.8 V vs. Ag/AgCl. Experiments were conducted in 0.1 M KHCO₃ (pH 7) using a light intensity of 200 mW/cm².
confirmed charge and mass balance, so subsequent photoelectrolysis experiments were conducted under a constant flow of CO₂ (i.e., not sampling the gas phase).

Remaining bulk photoelectrolysis experiments were performed using 0.1 M KHCO₃ electrolyte, a 200 mW/cm² light source, and operating potentials ranging from –0.6 to –1.4 V vs. Ag/AgCl. The results of these experiments are shown in Figure 4.3(b), which plots the Faradaic efficiencies for methanol achieved using this composite electrode. At most operating potentials, methanol Faradaic efficiencies ranged from 2–6%. However, the CO₂ reduction activity of this system is highly potential-dependent, signifying a reintroduction of potential-based control compared to the expected behavior of an ideal semiconductor-electrolyte system. This is evidenced by a maximum Faradaic efficiency of 25% achieved at –0.8 V vs. Ag/AgCl, representing nearly five times higher methanol production than the second highest Faradaic efficiency. To the best of our knowledge, this is the first example of combining a chalcopyrite material with an electrocatalyst to generate methanol in photoelectrochemical CO₂ reduction.

4.3 Conclusions

Ultimately, the CuInSe₂/Ni₃Al+TiO₂ composite electrode presented in this work represents the formative case study combining a ternary chalcopyrite photoabsorber with a CO₂-reducing catalyst to achieve photoelectrochemical reduction of CO₂ to methanol, with Faradaic efficiencies reaching up to 25%. In doing so, this system affirms the utility of a novel photoelectrode design strategy—combining a catalytically inactive yet optically proficient semiconductor with a known electrocatalyst—in facilitating efficient and selective CO₂ reduction. The results of this study leave much room for exploring additional combinations of chalcopyrite photoabsorbers, as well as other electrochemically unreactive
semiconductors, with heterogeneous electrocatalysts to unlock new photoelectrochemical CO₂ reduction activity, though alternative catalytic processes should also be possible. As such, the composite CuInSe₂/Ni₃Al+TiO₂ system motivates the use and exemplifies the importance of catalytic mismatching as a strategy for future photoelectrochemical design.

4.4 Methods

The composite electrodes consisted of a CuInSe₂ semiconductor pellet coated with a mixture of TiO₂ (25 nm nanoparticle powder) and Ni₃Al alloy. Synthetic procedures for the CuInSe₂ semiconductor pellets ⁴¹ and Ni₃Al alloy ⁸³ were reported previously. The following provides condensed information on the material characterization for this work. For full experimental details please refer to the supporting information of this paper.⁸²

To achieve a uniform layer of Ni₃Al on the semiconductor surface, the intermetallic powder was mixed with an equal quantity of TiO₂ (by volume) in water and coated onto the electrode. Materials characterization was conducted on the final CuInSe₂/Ni₃Al+TiO₂ composite (pre- and post-electrolysis) to further support the validity of the established electrode fabrication method. X-ray diffraction in Figure 4.4(a) and (b) performed on the as-fabricated electrode confirmed the presence of CuInSe₂, Ni₃Al, and TiO₂, with CuInSe₂ appropriately dominating the bulk composition. As seen in the scanning electron microscopy (SEM) images in Figure 4.4(c) and (d), the intermetallic and TiO₂ were uniformly distributed across the surface of the electrode. This coating exhibited a thickness of approximately 2–3 µm, thereby providing substantial coverage of the semiconductor surface. Energy-dispersive X-ray spectroscopy (EDX) analysis further supported the homogeneity of the electrode surface. X-ray photoelectron spectroscopy (XPS) revealed that the surface composition matched that expected based on the previously reported
electrode components. EDX and XPS data can be seen in the supporting information of this work.

**Figure 4.4:** Materials characterization of CuInSe$_2$/Ni$_3$Al+TiO$_2$. XRD pattern of the as-synthesized composite pellet (a) pre- and (b) post-electrolysis. Reference peaks correspond to PDF patterns as follows: CuInSe$_2$ (00-063-0126); Ni$_3$Al (01-071-5883); anatase TiO$_2$ (01-070-6826). SEM image (c) pre- and (d) post-electrolysis, confirming both surface homogeneity and morphological stability. Based on analysis of the pellet cross-section, (c) inset, the thickness of the Ni$_3$Al+TiO$_2$ layer is 2–3 µm. Images were obtained using a 5 keV electron beam.
REFERENCES


Part II

CuInTe$_2$
CHAPTER 5
SINGLE-CRYSTAL GROWTH AND CHARACTERIZATION OF CuInTe₂ FOR PHOTOELECTROCHEMICAL SOLAR FUEL PRODUCTION

5.1 Introduction

Photoelectrochemical conversion of solar to chemical energy is an attractive approach for sustainable production of storable and transportable hydrogen fuel. ¹⁻³ However, to efficiently harness light to reduce water involves thermodynamic criteria and kinetic challenges. Thermodynamic considerations of a semiconductor’s electronic structure, such as absolute band gap energy and band edge positions, often provide a starting point for evaluating a material class for photoelectrochemical performance. ⁴ Using these criteria, ternary transition metal chalcogenides with the chalcopyrite crystal structure have been
identified as major targets for future sustainable light-harvesting materials. These ternary chalcogenides have the general composition $M_xM'_yE_n$ ($M$ = metal, $E$ = S, Se, Te). The two metal cations, $M_x$ and $M'_y$, adopt the oxidation state $+1$ and $+3$, respectively, resulting in a charge balanced semiconductor. In general, this class of materials possesses the two thermodynamic requirements for water reduction: light absorption well-matched to the terrestrial solar spectrum, and a conduction band energy more negative than the reduction potential of water. A wide range of studies have demonstrated the tunability of ternary chalcopyrites to meet both these thermodynamic requirements. For example, by varying the cation ratio $M_x/M'_y$, or the anion ratio $E_n/E'_m$, the energetics of the valence and/or the conduction band can be manipulated to shift the absolute energy and position of the bandgap. This approach has been used to study water splitting with chalcopyrite variants such as $\text{Cu(In,Ga)}(\text{S,Se})_2$ and $\text{CuIn(S_xSe_{1-x})}_2$ and $(\text{Ag_xCu}_{1-x})(\text{Ga_yIn}_{1-y})\text{S}_2$ in our own work.

Though thermodynamic considerations provide an initial screening for photoelectrode materials, kinetic factors also play a dominant role in achieving efficient photoelectrodes for water reduction or oxidation. Upon illumination of a photocathode composed of a $p$-type semiconductor, two types of charge transfer must be considered: that of the dominant holes (majority carriers) and the non-dominant electrons (minority carriers). Charge transfer of majority carriers through the semiconductor bulk has been identified as a major kinetic limitation for photoelectrodes. The bulk structure of a material’s valence band—through which majority carriers are transported—can provide hints about the intrinsic recombination rates of a photocathode and therefore its qualitative efficiency as a photocathode. A material that possesses a band structure composed of very
steep bands in k-space is advantageous for photovoltaic applications, since the slope of a band is directly proportional to its band velocity. In addition, a linear band dispersion results in zero effective mass and thus, high mobility.\textsuperscript{18–21} Carriers with high mobility have a higher chance to avoid charge recombination, especially those that are generated within a diffusion distance of the space charge region.\textsuperscript{14} However, few experimental electronic structure studies exist on such kinetic factors influencing the majority charge carrier transport through the bulk of a ternary chalcopyrite (or most other) light-harvesting semiconductor materials.

Take the popular \textit{photoanode} material $n$-BiVO$_4$ as an example. It is well known that BiVO$_4$ possesses poor majority charge carrier mobility as its major limiting factor for photoelectrochemical water splitting.\textsuperscript{17,22–26} Despite considerable attention drawn to this kinetic limitation, the literature has not yet come to a consensus on the nature of BiVO$_4$’s fundamental bandgap and valence band structure—an understanding of which is key to interpreting its majority carrier mobility limitations.\textsuperscript{16,27} Similar to BiVO$_4$, computational studies predicting the bandgap of ternary chalcopyrite derivatives, such as CuInTe$_2$, are mostly inaccurate and imprecise—with the majority of calculations underestimating the reported optically measured bandgap due to typical limitations of density functional theory (DFT).\textsuperscript{28–31} CuInTe$_2$ has been known for decades to possess a direct bandgap, determined through electroreflectance measurements\textsuperscript{32}, which gives rise to the material’s high optical absorption coefficient. However, experimental determination of the momentum resolved valence band structure of CuInTe$_2$ has not been determined. But it is exactly this property which will give important insight into the carrier mobility and thus, it is important for assessing the ability of CuInTe$_2$ to act as an efficient photoelectrode. Knowledge of the
momentum resolved electronic structure will therefore help establish rational approaches to improved photoelectrochemical quantum yield and energy conversion efficiency.

While experimental momentum resolved electronic structure studies have been widely used to understand physical properties in semimetals (such as for example, the ultra-high mobility in graphene 33) they have been used less frequently in the study of photoactive materials. A reason might be that the most common technique for studying the electronic structure, angle-resolved photoemission spectroscopy (ARPES), is hard to perform on materials with a bandgap that exceeds 1.5 eV in magnitude. For this reason, we chose to investigate the electronic structure of CuInTe2, which has a band gap of 0.9 ± 0.03 eV, which both meets the ARPES requirements and is a reasonable value with respect to the absorption of solar insolation.

Utilizing a combination of traditional methods, including X-ray diffraction and UV-Vis absorption spectroscopy, we have provided experimental verification of the known structural and optical properties of a bulk single crystal of CuInTe2 grown by the vertical Bridgman method. Bulk transport property measurements were used to estimate $p$-type carrier concentration and carrier mobility. Then, for the first time, ARPES is used to experimentally characterize CuInTe2’s valence electronic structure, revealing information about the slope and number of bands composing the valence band and indicating a high Fermi velocity. The measured data is compared with electronic structure calculations using DFT and is found to be in good agreement with our experimentally determined bandgap value and valence band structure. Finally, we show evidence that the band edge position of CuInTe2 enables this variant of ternary chalcopyrite to serve as a photocathode for photoelectrochemical water splitting. The electronic structure characterization presented
here provides critical insight into kinetic factors that govern efficiency of light-harvesting photocathodes similar to CuInTe$_2$ that will influence future optimization of ternary chalcopyrites in photoelectrochemical H$_2$ generation.

5.2 Results & Discussion

i. Synthesis, Growth, and Characterization of CuInTe$_2$. The PXRD pattern of pre-reacted polycrystalline CuInTe$_2$ is shown in Figure 5.1(a) (black). The purple lines correspond to the tetragonal CuInTe$_2$ chalcopyrite structure, which is derived from the cubic, zinc blende structure shown in gray. The dotted purple lines are a guide for the eye, showing our CuInTe$_2$ material matches with the tetragonal phase rather than the cubic phase—resulting in two distinct lattice parameters where $c > 2a$. Refining the XRD pattern resulted in a tetragonal unit cell with lattice parameters $a$ and $c$ equal to 6.191(4) Å and 12.391(2) Å, respectively. The composition of the material was confirmed with EDX and XPS was used to probe the chemical composition and oxidation state of freshly cleaved CuInTe$_2$ surfaces. These data can be found in the supporting information of this work. 34 The direct optical bandgap ($E_g$) measurement is shown in Figure 5.1(b) along with an inset plotting the material’s absorption coefficient ($\alpha$). CuInTe$_2$’s $E_g$ measured 0.9 ± 0.03 eV, with $\alpha$ on the order of $10^4$ cm$^{-1}$, with calculation details given in the supporting information of this work. 34

ii. Transport Properties of CuInTe$_2$ Single Crystals. The temperature-dependent bulk resistivity of CuInTe$_2$ was probed on cooling from 300 K using a four-point probe configuration. A representative temperature profile of electrical resistivity from 300 to 10 K is plotted in Figure 5.1(c). The sample displays an exponentially increasing resistivity with decreasing temperature, expected for a semiconducting material. At room temperature
The resistivity ($\rho$) is $6 \times 10^{-3} \text{ } \Omega \cdot \text{cm}$. The inset of this panel shows log($\rho$) vs. $1/k_BT$ in order to extract the activation energy ($E_a$) from the slope at high temperatures by utilizing the

\[ E_a = \frac{k_B T}{\gamma} \left( \frac{d \ln \rho}{d (1/k_BT)} \right)_T \]
Arrhenius equation. Details on extracting $E_a$ from this data can be found in the supporting information of this work.  

The majority carrier concentration of the CuInTe$_2$ crystals were estimated by Hall measurements. Representative Hall resistivity data as a function of magnetic field (-9 to +9 T) at 300 K is shown in Figure 5.1(d). The positive trend of resistivity with magnetic field further confirms $p$-type carriers as the dominant carrier type in the CuInTe$_2$ crystals. A reliable linear fit ($R^2 = 0.99$) allowed a confident calculation of the hole concentration $n_p = 1.2 \times 10^{18}$ cm$^{-3}$. With the resistivity and majority carrier concentration in hand, the mobility ($\mu$) of the $p$-type carriers was estimated to be 870 cm$^2$ V$^{-1}$ s$^{-1}$, a startling two-orders-of-magnitude greater than mobilities found for polycrystalline samples of CuInS$_2$ and CuInSe$_2$ reported from our lab.  

Compared to other common light-harvesting semiconductors, this calculated mobility is eight times larger than that of a single crystalline CH$_3$NH$_3$PbI$_3$ perovskite ($10^5$ cm$^2$ V$^{-1}$s$^{-1}$ by Hall measurements) and is three orders of magnitude greater than recently reported mobilities of $n$-type BiVO$_4$ single crystals measured by Hall measurements, 0.2 cm$^2$ V$^{-1}$s$^{-1}$. In the case of halide perovskite materials, the mobility has, at least theoretically, been shown to stem from high band velocities, which are common in perovskite-type materials. The link between carrier velocity and reduced recombination rates has also been drawn in the same publication. Details on the calculations of $n_p$ and $\mu$ can be found in the supporting information of this work.

### iii. CuInTe$_2$ Defect Chemistry

Chalcopyrite semiconductors are known for tolerating a large range of off-stoichiometries while maintaining their crystal structure. They can act as $p$- or $n$-type semiconductors depending on the type of native or extrinsic defects. In our case, the defects creating the observed $p$-type behavior must be native, as no extrinsic
elements were employed in the synthetic process. The possible $p$-type, intrinsic point defects in a ternary chalcopyrite structure are as follows $^{40}$:

1. $V'_{Cu} + h^*$
2. $V'''_{In} + 3h^*$
3. $Cu''_{In} + 2h^*$
4. $Te'' + 2h^*$

Looking closer at these four possible dominating defects, we must consider two key aspects dictating their presence: defect formation energy and defect ionization energy. These defect energies have been studied on CuInS$_2$ and CuInSe$_2$, the sister compounds of CuInTe$_2$. Focusing first on defect formation energy, Pohl et al. $^{41}$ studied the intrinsic point defects in CuInSe$_2$ and their formation energies. Comparing the four $p$-type inducing defects listed above, the order from lowest to highest defect formation energy goes (1) $< (3) < (4) < (2)$. This qualitative order in defect formation energy holds for earlier CuInSe$_2$ defect energy studies $^{42,43}$ and studies on CuInS$_2$ by Chen et al. $^{44}$

Now, considering the ionization energy of these $p$-type defects in CuInSe$_2$, Pohl et al. $^{41}$ calculated the same energetic ordering from lowest to highest energy: (1) $< (3) < (4) < (2)$. Which agrees with ionization energies calculated by Chen et al. $^{44}$ for CuInS$_2$. Although these defect energy calculations were not specifically performed on CuInTe$_2$, its defect chemistry is expected to be highly analogous to CuInS$_2$ and CuInSe$_2$, whose defect energy calculations are themselves consistent with one another. Thus, the $p$-type conductivity in our intrinsic CuInTe$_2$ crystals is likely due to ionized $V_{Cu}$ defects, which has been calculated to possess the lowest energy of formulation and ionization energy for all possible $p$-type intrinsic point defects in the chalcopyrite crystal lattice.
iv. Theoretical Electronic Band Structure. The band structure of CuInTe$_2$ has been theoretically reported numerous times using several different methods of calculations which have been compiled in the supporting information of this work. While these calculations all agree that CuInTe$_2$ has a direct band gap at the $\Gamma$ point, with highly dispersed conduction and valence bands, which is ideal for light harvesting materials, the vast majority of these calculations greatly underestimate the bandgap of CuInTe$_2$. On the other hand, DFT calculations using the modified Becke-Johnson (mBJ) functional, which has been shown to result in more accurate band gaps, overestimates the band gap in the CuInTe$_2$ case. To date, no previous studies have included spin orbit coupling (SOC) effects, to the best of our knowledge, although optical measurements have suggested that SOC has an effect on the electronic structure of CuInTe$_2$. In our calculations—with detail provided in the supporting information of this work—we compute a band gap of 0.77 eV if we employ the mBJ functional and include SOC, and 0.91 eV if we omit SOC. Even if the latter value is in excellent agreement with the experimental band gap, we will show below that SOC has an effect on the experimentally determined electronic structure and can therefore not be omitted in the calculation. The obvious failure of DFT to provide a conclusive description of CuInTe$_2$’s electronic structure highlights the importance of experimental investigations.

v. ARPES Measurements. The unit cell type and size influence the resulting Brillouin zone (BZ) of a crystal lattice. For CuInTe$_2$, a body centered tetragonal BZ is anticipated, with a smaller size compared to a cubic BZ due to the larger unit cell. However, instead of observing the tetragonal BZ, our ARPES data only reveals the cubic BZ. Figure 5.2(a) shows the different lattice vectors (blue for cubic; black for tetragonal) and the resulting
combination of both BZs with their relative sizes. This BZ phenomenon has been previously reported by Pettenkofer et al. 48 for CuInSe₂, the sister compound of CuInTe₂. In addition, orthorhombic structures such as the perovskite CaTiO₃ have also been reported to display pseudo-cubic unit cells in experimental band structure measurements. 49

Since the ARPES data only features the cubic BZ, it is important to understand how the high symmetry points of the different BZ’s relate to each other in order to compare the measured data with the calculated electronic structure, as the latter is based on the tetragonal BZ. Figure 5.2(b) shows different orthographic projections on the two BZs from panel (a). The natural cleavage plane of CuInTe₂ is the (112) plane, which is the pseudo-hexagonal plane, and thus the packing density is maximized. As can be seen from Figure

![Figure 5.2](image)

Figure 5.2: Panel (a) shows the Cu and In cations in the CuInTe₂ unit cell with the corresponding primitive vectors a₁, a₂, and a₃ for both the tetragonal (black) and cubic (blue) symmetry. Their corresponding Brillouin zones are presented in black and blue. Panel (b) shows two orthographic side views on the two BZs. The projections of the tetragonal bulk high symmetry points onto the [112] surface are indicated. (c) Top view on the [112] surface. The black and blue dots indicate projections of the bulk Γ points of the cubic and tetragonal BZ respectively.
5.2, cuts along k_x therefore correspond to the Γ-N, while cuts along k_y correspond to the Γ-Z direction. Note that the exact high symmetry point correspondence of the k∥ directions depends on the chosen photon energy. However, a photon energy of 80 eV in the following Figure 5.3 agrees well with the aforementioned directional determination.

Having the directions in momentum space resolved we now proceed to investigate the ARPES spectra. Figure 5.3 shows ARPES data gathered at hν = 80 eV. Figure 5.3(a) displays an overview over the BZ in the form of constant energy cuts at E_i = 0 eV (at the Fermi level) and E_i = -0.8 eV. At E_i = 0 eV, the Fermi surface is only composed of very weak intensity spots at the \( \bar{\Gamma} \) and \( \bar{\Gamma'} \) point, indicating that the valence band maximum is at \( \bar{\Gamma} \), consistent with DFT. Lower initial state energies show a clover-shaped feature surrounding \( \bar{\Gamma} \) and \( \bar{\Gamma'} \), indicating that the valence bands disperse away from the \( \bar{\Gamma} \) point. The distance between \( \bar{\Gamma} \) and \( \bar{\Gamma'} \) is 1.66 Å\(^{-1}\), matching the expected distances within the cubic BZ projected along the (112) direction. Figure 5.3(b) shows several constant energy cuts, which are stacked to give insight to the band dispersion. Cuts along k_y = 0 Å\(^{-1}\) (Γ-Z) and k_x = 0 Å\(^{-1}\) (Γ-N), shown in Figure 5.3(c), reveal that the bands are steeply dispersed in energy. The Shirley background subtracted and 2\(^{nd}\) derivative ARPES data both show a pair of bands meeting close to the Fermi level at \( \bar{\Gamma} \). A third band has its maximum at roughly -0.8 eV and is responsible for the inner structure of Figure 5.3(b) at lower initial state energies. All identified bands are schematically superimposed on the ARPES data and marked with arrows in the 2\(^{nd}\) derivative plots. Since the calculated band structure was plotted for the tetragonal BZ, the DFT data must be stretched by a factor of two in k_x and k_y, which was also included in the high-symmetry point positions superimposed on the ARPES data of Figure 5.3(a) and (c). In comparison to the experimental band structure,
Figure 5.3: ARPES data of CuInTe$_2$. (a) Constant energy slices at $E_i = 0$ eV ($E_F$) and $E_i = -0.87$ eV, integrated over 15.5 meV. At the Fermi surface, there is only weak intensity visible at the $\Gamma$ points corresponding to the cubic bulk BZ. The lower initial state energy was chosen to visualize the point positions better. The evolution in energy around $\Gamma$ is shown in (b). (c) Band structure dispersions along $k_y = 0$ Å$^{-1}$ and $k_x = 0$ Å$^{-1}$ with Shirley background subtraction and in negative 2nd derivative representation. Three bands can be identified, which are schematically superposed in the ARPES data and marked with arrows in the 2nd derivative plots. (d) DFT calculations of the respective k directions of (c). The three visible ARPES bands are matched by theory except for a necessary stretching of the theoretical energy axis. A further small splitting of the theoretical bands by SOC along N-$\Gamma$-N is too small in energy to be resolved by ARPES.
the calculated bands in Figure 5.3(d), furthermore, must be stretched by a factor of 1.9 in energy to match the measured dispersion. Note that this trend is opposite to the commonly found reduced band width in experimentally determined band structures, which is a result of electron-electron correlations. Thus, DFT underestimated the slope of the bands. Measuring the slope below the Fermi level, we find a band velocity of $2.5 - 5.4 \times 10^5$ m/s, depending on which band is considered. This is about 25-50% of the value found in graphene, $\approx 1 \times 10^6$ m/s. The conclusion that the band velocity is the reason for the high carrier mobility measured suggests itself, even though the velocity of course decreases at close vicinity to the Fermi level due to the parabolic band shape. However, since photo-absorption processes excite electrons well below the Fermi level, the initial band velocity of the created holes can still be very high.

A closer look at the measured band dispersions reveals a few more interesting details about the electronic structure of CuInTe$_2$. The three bands identified along the Z-$\Gamma$-Z direction are not reproduced in the DFT calculations without SOC, which only predicts two bands along this cut—shown in the supporting information of this work. As can be seen in Figure 5.3(d), if SOC is included in the calculation, the upper of the two bands along Z-$\Gamma$-Z splits into two, while the lower band is shifted to lower binding energies. This matches the expected splitting of p bands in the chalcopyrite structure. The shift is relatively large, about 0.8 eV, and is clearly resolved in the measurement, meaning that SOC strongly affects the electronic structure of CuInTe$_2$. Along N-$\Gamma$-N, in contrast, all three visible bands are already predicted in the calculation excluding SOC, seen in the supporting information of this work. Since CuInTe$_2$ lacks inversion symmetry, SOC has the potential to also spin split bulk bands (of the p or d type) according to the
Rashba/Dresselhaus effect. 52,53 This SOC induced splitting, visible in Figure 5.3(d), is much smaller and thus not resolvable in experiment. Nevertheless, the lowest band maximum is again shifted to lower binding energies when considering SOC, matching the ARPES data. Therefore, we can unambiguously conclude that SOC influences the electronic structure of CuInTe2 and must be included in the discussion. It has previously been suggested that the resulting spin splitting is advantageous for light harvesting materials. 54 Thus, the observed SOC effect could also contribute to good performance of CuInTe2. A more in-depth discussion of the phenomena is given in the supporting information of this work. 34

Having resolved the valence band structure of CuInTe2, we can now compare the results to other light harvesting materials such as CH3NH3PbI3 or BiVO4. While, with the exception of a low resolution ARPES experiment on CH3NH3PbBr3 54, the electronic structures of these materials have not been experimentally determined (likely due to their large band gap sizes) band structure calculations have been performed instead. 55 One could predict the slow charge transport kinetics of BiVO4, given the flat slopes seen in its band structure. Similarly, the high performance of CH3NH3PbI3 has been attributed to its calculated steep bands. 18,19 But, as we have shown here, band velocity is another variable (such as bandgap size) that DFT frequently fails to accurately determine. Hence, ARPES provides important insight into the potential of (small-gap) semiconductors as photoactive materials.

vi. Crystal Structure and Brillouin Zone of CuInTe2. To understand the experimental ARPES measurements, it is necessary to review the ancestry of the CuInTe2 crystal structure. The chalcopyrite crystal structure is derived from the zinc blende structure as
shown in Figure 5.4(a). Starting from the II-VI semiconductor ZnTe, the Group II element is replaced by two cations—Cu$^{+1}$ and In$^{+3}$—from the neighboring Groups I and III to create the I-III-VI$_2$ semiconductor CuInTe$_2$, Figure 5.4(b). To accommodate two cation species in the crystal lattice, the starting zinc blende structure with cubic unit cell is extended along the $c$-axis which allows ordering in the cation sublattice—creating a tetragonal unit cell with two distinct lattice parameters $a$ and $c$, where $c > 2a$. However, this particular tetragonal structure has lattice parameters where $c \approx 2a$, resulting in a stacked zinc blende structure, shown in panel (c). The stacking is visualized by the gray plane placed halfway along the $z$-axis and treating the Cu and In cations as equal. This creates a pseudo-cubic unit cell with lattice parameters $a = 6.191(4)$ Å and $\sim a = 6.196$ Å, a lattice mismatch of just 0.1%.

Figure 5.4: Ancestry of the chalcopyrite crystal structure from zinc blende. (a) ZnTe, a II-VI semiconductor, has a cubic lattice with a single lattice constant $a$. The Zn atom can be divided into two neighboring cations, Cu and In, to create a new material, (b) CuInTe$_2$, a I-III-VI$_2$ semiconductor. This stretches the crystal lattice in the $z$ direction, creating a tetragonal crystal structure with two distinct lattice parameters, $a$ and $c$ where $c > 2a$. However, this particular tetragonal structure has lattice parameters where $c \approx 2a$, resulting in a stacked zinc blende structure, shown in panel (c). The stacking is visualized by the gray plane placed halfway through the $z$-axis and treating the Cu and In cations as equal. This creates a pseudo-cubic unit cell with lattice parameters $a = 6.191(4)$ Å and $\sim a = 6.196$ Å, a lattice mismatch of just 0.1%.
0.1%. Thus, the tetragonal cell is only given by the elemental difference of Cu and In, a property that can be picked up in diffraction but seems to be invisible to ARPES.

**vii. Thermodynamic Characterization of CuInTe₂ Photocathodes.** To our knowledge, CuInTe₂ has not been studied for photoelectrocatalytic water reduction. Until this work, the only reported photoelectrochemical characterization of CuInTe₂ was of *n*-type nanoplates by Zhang et al. ⁵⁷ reporting on the photocurrent density at positive applied potentials. The band edge energy of the photoanode was not reported. To ensure our *p*-type single crystal material is thermodynamically suitable for water reduction, its flat band potential (*E*_ₐₐ) was experimentally determined. In triplicate, CuInTe₂ photoelectrodes were subjected to AC impedance measurements for Mott—Schottky (M—S) analysis and chopped-light linear sweep voltammetry (LSV).

Figure 5.5(a) shows a representative M—S plot for CuInTe₂. M—S analysis was performed at pH 9 in 0.6 M Na₂SO₄(aq) to ensure a high double layer capacitance, thus, allowing the space charge capacitance to dominate. The negative slopes of each curve confirm the *p*-type behavior of the electrodes. The M—S equation (Eq. 3.8) used to fit the data assumes that a semiconductor-electrolyte interface is ideally capacitive. However, these interfaces are almost never perfectly capacitive, leading to frequency-dependent slopes. ⁵⁸ This class of frequency dependence gives plots with varying slopes that converge to a common intercept, giving a valid *E*_ₐₐ. ⁵⁹ The *E*_ₐₐ determined by M—S analysis was -0.62 ± 0.041 V vs. Ag/AgCl at pH 9. Figure 5.5(b) shows a representative chopped LSV plot with the inset showing the dark and illuminated LSV scans. The dark current was subtracted from the chopped-light curve to form a *j*-*V* curve emphasizing the photocurrent. The *E*_ₐₐ is estimated by identifying the potential at which the photocurrent starts to grow.
from its baseline, namely the photocurrent onset potential (V_{onset}). The $E_{fb}$ determined by $V_{onset}$ was $-0.58 \pm 0.073$ V vs. Ag/AgCl at pH 9. The $E_{fb}$ determined by each technique is well within the experimental error, enabling a confident approximation of the valence band edge with respect to Ag/AgCl at pH 9. Based on this data, Figure 5.5(c) shows a schematic diagram of the electronic band positions of CuInTe$_2$. The conduction band edge was approximated based on the material’s optically measured band gap. The black dashed line represents the water reduction potential at pH 9.
dotted line representing the potential vs. Ag/AgCl for H₂ evolution at pH 9. The valence and conduction band edges of CuInTe₂ straddle this potential, confirming this material is indeed thermodynamically capable of photoelectrochemical water reduction.

5.3 Conclusions

The merit of a semiconductor for light harvesting applications depends heavily on its electronic structure. Thermodynamic factors such as band edge positions and band gap sizes are commonly investigated in this respect. Here, we showed that the momentum-resolved electronic structure is another important aspect of the electronic structure to consider. We showed with ARPES, that the band velocity of the valence band in CuInTe₂ can reach values of up to 50% of the value found in graphene – a material with extremely high mobility. Due to the parabolic (rather than linear) band dispersion, this value decreases in the vicinity to the Fermi level. Since photo-absorption processes excite electrons well below the Fermi level, this region of steep band dispersion can be accessed in the light harvesting process. We further show evidence that CuInTe₂ has energetically suitable band edges for photoelectrocatalytic water reduction, enforcing the argument that it possesses a favorable electronic band structure to efficiently harness solar energy for H₂ fuel production.

5.4 Methods

i. Synthesis and Crystal Growth. CuInTe₂ polycrystalline ingots were prepared by loading stoichiometric amounts of elemental Cu (Sigma-Aldrich 99.999%), In (Alfa Aesar 99.99%), and Te (Alfa Aesar 99.99%) into quartz ampules. The ampules were purged with Ar and sealed under vacuum. The samples were heated stepwise to 1100 °C. After 6 h at 1100 °C, the samples were cooled to room temperature by 3 °C per hour. The resultant
polycrystalline ingots were then ground into small particles for crystal growth. The bulk single crystals were grown by the Bridgman technique. Gram-scale amounts of the pre-reacted CuInTe₂ particles were loaded in a carbon-coated, bottom-pointed quartz ampoule with an inner diameter of 6 mm. The crystal growth ampoules were then sealed under vacuum at ≈10⁻⁵ mbar. The crystal growth was performed at 1200 °C with an ampoule translation rate of 1 mm h⁻¹ through the hot zone.

**ii. CuInTe₂ Characterization and Physical Property Analysis.** The crystals were analyzed by X-ray diffraction on a Bruker D8 Advance Eco with Cu Kα radiation and a LynxEye-XE detector. The optical bandgap was measured with the Agilent Technologies Cary 5000 UV-Vis-NIR spectrometer and was determined using the same method described in Chapter 2 using Eq. 2.1. Detail on the single crystal data, data collection, and refinement can be found in the supporting information of this work. Transport measurements were performed with a Quantum Design Physical Property Measurement System with the methods described in Chapter 2 using Eq. 2.2 and Eq. 2.3. ARPES spectra were recorded with the 12 experiment on the UE112-PGM2a beamline at the BESSY II synchrotron facility. Experimental details for this measurement can be found in the supporting information of this work. DFT calculations were performed within the framework of Wien2k using the modified Becke Johnson functional.

**iii. Electrode Fabrication.** Crystals with surface area of ≈0.120 cm² were extracted from the single crystal boule to be used as the electrode faces. A 100 nm thick layer of gold was applied to the back of the electrode face, followed by conductive silver epoxy (Epoxy Technology H31) to connect to an external copper wire. The layers were then covered with a glass tube and sealed with insulating epoxy cement (Loctite 0151 Hysol).
REFERENCES


Part III

CuInS$_2$
CHAPTER 6

DEFECT ORIGIN OF METASTABILITY IN SOLAR-ENERGY-HARVESTING CHALCOPYRITES

105

6.1 Introduction

Chalcopyrites have been the subject of many studies within the past century in order to better understand and apply their impressive ability to harness solar energy to produce electricity. 1,2 These direct bandgap semiconductors have been used in a range of solar-absorbing applications, including solar cells 3, sensors 4–6, and photoelectrodes for hydrolyzing water. 7,8 Chalcopyrites generically have MM’X₂ formulas, where M is typically a transition metal, M’ is a transition or other metal, and X is S, Se, or Te. (The mineral “chalcopyrite”, for example, is CuFeS₂). Ternary semiconducting I-III-VI₂ materials frequently display the chalcopyrite crystal structure, which is an elaboration of
the binary II-VI zinc blende crystal structure, which is itself an elaboration of the structure of the elemental indirect band gap semiconductor Si. The categorical difference between chalcopyrite and zinc blende (MX) semiconductors is the additional metal, resulting in cation valencies of +1 and +3 rather than solely +2. The addition of the second cation offers the significant advantage of changing the electronic structure of the semiconductor to access direct band gap values not accessible in the binary materials, enabling efficient access to the entire visible spectrum. 9 Chalcopyrites are known to tolerate a large range of off-stoichiometry without changing their crystal structure. 10,11 However, the second metal in chalcopyrites compared to zinc blends introduces the possibility for complex defect formation, which can lead to detrimental carrier self-compensation, producing an electrically inactive material. 12 As solar energy device efficiencies are critically dependent on the defect chemistry of their active semiconductors, it is imperative to understand how the self-compensation phenomena in chalcopyrites are promoted and how they influence the photoinduced metastable effects that occur in these systems.

Photoinduced metastability is one of the most significant performance challenges faced by chalcopyrite-based photovoltaic devices. 13 These effects in chalcopyrites range from sub-bandgap absorption 14, to persistent photoconductivity 15, to light-soaking effects. 16,17 Although these phenomena can be caused by device layer junctions 13, the underlying metastability of chalcopyrites under illumination, as an intrinsic property of the photoabsorber, is a major factor that is attributed to intrinsic defects in the crystal lattice. 18,19 Many theoretical and experimental studies on chalcopyrites have addressed the formation and ionization energies of the point defects that can form in the chalcopyrite lattice, i.e. cation antisite defects (M_{M'} and M'_{M}), vacancies on any of the sites (V_{M,M',X}),
and interstitials of any of the atoms (M_i,M'_i,X_i). In addition to these point defects, some theorists have argued that more complex defect modes are possible for ternary chalcopyrites involving the pairing of single point defects. The cation divacancy complex (V_{Se}+V_{Cu}) has been theoretically predicted, for example, to be the origin of metastable electronic properties in $p$-type Cu(In,Ga)Se$_2$ after an electrical bias or illumination switches this defect complex from a donor into an acceptor. This is detrimental because it simultaneously increases hole concentration and creates new carrier recombination pathways, decreasing carrier lifetimes. This prediction has been supported experimentally, with an expansion of the model identifying a sub-band gap optical transition that upon excitation induces an increase in acceptor concentration and a decrease in carrier lifetime. Further theoretical work proposed that the defect pair (In$_{Cu}^+$+2V$_{Cu}$) in chalcopyrite CuInSe$_2$ can serve as a source of metastability similar to the (V$_{Se}^+$+V$_{Cu}$) divacancy complex.

Here we present the characterization and defect analysis of a single crystal of the ternary chalcopyrite semiconductor CuInS$_2$, which support metastability as an intrinsic property of the photoabsorber. The crystal was intentionally grown in a Cu-poor environment (1 mol % Cu deficiency) to stimulate self-compensation and experimentally study the potential existence of the proposed (In$_{Cu}^+$+2V$_{Cu}$) defect pair, and its ability to facilitate photoinduced metastable effects. We first present results at face value, categorized by measurement technique: electronic transport measurements to study the general physical properties of the CuInS$_2$ crystal, then scanning/transmission electron microscopy (STEM) to image the atomic structure and atomically map the fine structure in conjunction with atomic scale electron dispersive spectroscopy (EDS), and finally the photoconductive properties using current-voltage measurements interpreted via a widely-
accepted model. 27 Our STEM images and atomic-scale EDS analyses reveal the presence of metastable, disk-like defect layers consisting of paired In_{Cu} and V_{Cu} defects in a remarkable extended ordered array. The discussion section then interprets these results in a self-consistent manner, allowing us to propose a structure-property model for this system.

6.2 Results & Discussion

i. Electronic Transport. The crystal structure of our 1 mol % Cu-deficient single crystal of \( n\)-CuInS\(_2\), seen in Figure 6.1a inset, was confirmed as a tetragonal chalcopyrite (space group, 122) by powder X-ray diffraction (PXRD), and Laue diffraction confirmed that the crystal orientation of the cleavage plane is (112) (Figure 6.1b). 28 The absorbance spectrum of our CuInS\(_2\), in Figure 6.1a, shows the optical bandgap of 1.47 eV. Additional spectroscopic characterization can be found in Extended Data Figures 1 and 2 of this work. 29

The basic electronic property characterization of this crystal is presented in Figure 6.1c, d. Note that all data presented in Figure 6.1 was collected on the same crystal sample, see in Extended Data Figure 1 of this work. 29 The resistivity vs. temperature data was collected from 395 K to 300 K and shows the typical temperature profile for a semiconductor (at temperatures below 300 K the resistance of the sample became out of range). The resistivity, \( \rho_{xx} \), of this crystal was measured to be \( 2.7 \times 10^6 \) \( \Omega \)-cm at 300 K. This data was then transformed into \( \log(\rho) \) vs. \( 1/T \) (Figure 6.1c inset) to extract the resistivity activation energy of 87 meV. To determine the carrier concentration, the Hall resistivity \( (\rho_{xy}) \) vs. magnetic field experiments, shown in Figure 6.1d, were performed by sweeping the magnetic field from \( \mu_0H = -3 \) to 3 T at 300 K. This allows us to extract the carrier concentration, \( n_n \), of \( n\)-type carriers, as \( 2.3 \times 10^{13} \) cm\(^{-3}\). With the values of \( \rho_{xx} \) and
n_0 in hand, the carrier mobility, μ, is calculated at 0.1 cm² V⁻¹ s⁻¹. The total carrier concentration is quite low, despite the relatively high percentage (1 mol %, about 1 part in 10²¹) of Cu deficiency, suggesting the existence of a complicated defect chemistry in this material, and many inactive dopants, which results in a crystal that is nearly fully compensated.
**Figure 6.1 | The basic electronic and structural characterization of our 1 mol % Cu deficient CuInS$_2$ single crystal.**

a, The absorption spectrum of CuInS$_2$, showing a sharp onset of absorption at the optical bandgap at 1.47 eV. A freshly cleaved (112) crystal surface was exposed for this measurement. The inset shows the tetragonal chalcopyrite structure of CuInS$_2$. 

b, XRD pattern of the single crystal face (green), powder form (orange), and database pattern match (black). The inset shows a Laue diffraction pattern of the (112) crystal surface.

c, Resistivity ($\rho_{xx}$) vs. temperature profile from 395-300 K. The inset plots this data as log of the resistivity vs. 1/T from which an activation energy of 87 meV can be extracted. d, Hall resistivity ($\rho_{xy}$) vs. magnetic field from $\mu_0 H = -3$ to 3 T at 300 K. The actual quantity plotted is $\rho_{xy}$ with an admixture of some $\rho_{xx}$ because the Hall contacts were not made exactly orthogonal to the current and field directions; however, it is the slope of this curve that is important for our purposes and not the absolute value of the resistivity. The negative slope denotes electrons as the crystal’s majority carrier type. From this data we can calculate the majority carrier concentration, equaling $2.3 \times 10^{13}$ cm$^{-3}$. The same crystal sample was used to collect data shown in panels c, d.
ii. Microstructure Characterization. To explore the effect of internal defects on the physical properties, a further investigation of the fine microstructures in CuInS$_2$ was carried out via electron microscopy. Note that the sample used here was extracted from the same section of the crystal boule used in the electronic transport measurements. The transmission electron microscope (TEM) image in Figure 6.2a shows that it exhibits a lamellar structure with grain boundaries inside, viewing from the $\langle 1\bar{1}0 \rangle$ direction. The thickness of the lamellae ranges from several hundreds of nanometers. The corresponding composite diffraction patterns are shown in the bottom panels of Figure 6.2a, taken from the $\langle 1\bar{1}0 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$ zone axes, respectively. It indicates that the grain boundary plane is $\{112\}$, which is consistent with the XRD analysis in Figure 6.1b.

Interestingly, periodic interfacial structures were observed at the grain boundary, as characterized by aberration-corrected STEM shown in Figure 6.2b, c, viewing from the $\langle 1\bar{1}0 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$ directions, respectively. There exist single or double layered interfacial structures at the grain boundaries, which dominate the defect makeup of the crystal, as shown in the schematic in Figure 6.2d. The grain boundary is a rotational-twin boundary (a 180° rotation) and has been theorized to be the most energetically favored twin boundary of chalcopyrites, avoiding reconstruction that would be inevitable in anion- and cation-terminated twin boundaries. 30,31 The rotational-twin boundary occurs either by itself as an extended defect through its entire crystal plane, or the boundary expands to include the single- or double-layer interfacial phase creating a disk-like layer defect shown in Figure 6.2e, f viewing from the $\langle 1\bar{1}0 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$ directions, respectively. The interfacial phase, present in only single or double lines, possesses a unique crystal structure unlike the
Figure 6.2 | Microstructure characterization of chalcopyrite CuInS₂.  

a, A low magnification bright-field TEM image showing the layered structure of CuInS₂ with its arrangement of rotational-twins inside. The rotational-twin plane is \{112\}. The corresponding diffraction patterns are shown in the bottom panels, taken from \{110\} and \{111\} zone axes, respectively. Scale bar, 500 nm. 

b, c, High-resolution HAADF-STEM images showing the rotational-twins with single and double interfacial layers inside, viewing from \{110\} and \{111\} directions, respectively. The chalcopyrite structure (Cu, red; In, blue; S, yellow) is overlaid on the images to illustrate the corresponding atomic configuration. Scale bar, 1 nm. 

d, A schematic to illustrate the distribution of rotational-twins with single (white) or double (green) layered interfacial structures along the \{221\} direction. 

e, f High-resolution HAADF-STEM images of the extended defect plane, viewing from \{1\overline{1}0\} and \{\overline{1}11\}, respectively. This defect plane is composed of a rotational-twin boundary expanding into a single-interfacial phase, creating a disk-like defect layer. The dotted white line outlines the disk-like shape. Scale bar, 1 nm.
surrounding chalcopyrite phase that, to our knowledge, has never been reported for this class of material.

Atomic-level STEM energy-dispersive X-ray spectroscopy (EDS) was used to map the different elements in the perfect crystal structure viewed from \langle 1\bar{1}0 \rangle \text{ and } \langle \bar{1}\bar{1}1 \rangle \text{ directions (Figure 6.3a, b), respectively. The identities of Cu, In, and S atoms are shown in blue, green, and red. Here we show the high-angle annular dark-field (HAADF) images and the element mappings of Cu/In and Cu/In/S, respectively (see more details of single elemental mappings in Extended Data Figure 3 of this work \textsuperscript{29}). Note that the atomic composition in the perfect structure is 25.2% Cu, 24.3% In and 50.5% S, which is within error of the stoichiometry of CuInS\textsubscript{2}. A unit cell is marked in the images showing the positions of different elements in the structure. It is clear that Cu and In atoms are overlaid in the \langle 1\bar{1}0 \rangle \text{ projection (Figure 6.3a), while periodically arranged in the } \langle \bar{1}\bar{1}1 \rangle \text{ projection (bright, In; weak, Cu in Figure 6.3b).}

To elucidate the compositional change at the rotational-twin boundary, Figure 6.3c shows a line-profile EDS mapping across the interfacial phase (the labeled arrow in the HAADF-STEM image). It is clear from the elemental mappings that both In and S are enriched at the interfacial layers while Cu is deficient in the same region. The plot in the bottom-left panel shows line-profile EDS analysis of composition change across a single- and double-interfacial phase, corresponding to the marked arrow in the HAADF-STEM image. The approximate atomic percent (at\%) change of each element at the single and double interfacial phase can be found in Extended Data Table 1.\textsuperscript{29} An additional example is given in Extended Data Figure 4 taken from the \langle \bar{1}\bar{1}1 \rangle \text{ direction, which shows a similar tendency in the composition change across the interfacial phase at the rotational-twin
boundary. This indicates that the stoichiometry of the interfacial phase is unlike that in the perfect CuInS$_2$ structure, that is, fewer Cu and more In and S atoms at the interfacial layer.

**Figure 6.3 | Quantitative composition analysis of chalcopyrite CuInS$_2$.** a,b, Atomic-level STEM-EDS mapping showing the occupations of Cu (red), In (green) and S (blue) in chalcopyrite CuInS$_2$, viewing from ⟨110⟩ and ⟨111⟩ directions, respectively. Here we show the HAADF-STEM image and the element mappings of Cu/In and Cu/In/S, respectively (see more details of single element mapping in Extended Data Figure 3). A unit cell is marked in the images showing the positions of different elements in the structure. Cu and In atoms are overlaid in the ⟨110⟩ projection, while separated in the ⟨111⟩ projection. Scale bar, 1 nm. c, STEM-EDS mapping of rotational-twin boundaries with single, I, and double, II, interfacial layers. The top-left panel shows the two rotational-twin boundaries. The right panel shows the element mappings of Cu (red), In (green) and S (blue), respectively. The bottom-left panel shows line-profile EDS analysis of composition change across the pseudo-twin boundaries, corresponding to the marked arrow in the HAADF image. Both In and S are enriched at the boundaries while Cu is deficient. Scale bar, 5 nm.
iii. Photoconductivity. Photoconductivity data was collected using a physical property measurement system (PPMS) with potential range +/- 10 V. LEDs of varying wavelength at various light intensities were used. It is important to note that the sample used for these measurements is the exact sample analyzed by TEM. The inset of Figure 6.4a shows a schematic of the rudimentary setup used in these studies. A rectangular shaped crystal piece (of thickness 290 ± 53 µm) was illuminated on its exposed (112) oriented surface—the same orientation discussed in Figure 6.2. InGa eutectic was used to make Pt-wire contacts on the crystal surface.

Figure 6.4a shows a representative photocurrent vs. voltage plot taken at room temperature under 780 nm illumination at intensities ranging from 0.33 to 70 mW/cm². The illumination results in a four-orders-of-magnitude decrease in resistivity from the original $\rho_{xx}$ value on the order of $10^6$ Ω·cm to an order of $10^2$ Ω·cm at 70 mW/cm² illumination (780 nm). A detailed plot of resistivity vs. light intensity can be found in Extended Data Figure 5 of this work. Under both positive and negative bias, the photocurrent increases with increasing applied potential and increasing light intensity. The symmetric I-V curves demonstrate a smooth ohmic contact at both wire contact points showing that non-ohmic contacts are not the origin of the observed effects. The linear slope of the I-V curves indicate that the system’s free electron lifetime remains constant, given the relationship:

$$I = e \frac{F\mu \tau}{L^2} V$$

where $e$ is the electron charge, $F$ is the free electron generation rate, $\mu$ is the sample mobility, $\tau$ is the free electron lifetime, and $L$ is the spacing of electrodes. Figure 6.4b shows the responsivity vs. wavelength for various voltage biases. Of the wavelengths tested, the responsivity peaks at 780 nm. The dotted lines are a guide for the eye.
Figure 6.4 | The photo-electric properties of CuInS$_2$. a, IV-curve of CuInS$_2$ under illuminated (780 nm) conditions. The cartoon inset shows the rudimentary setup used for the photoconductivity measurements: Pt wires were connected to the crystal using an InGa eutectic, with illumination occurring on the crystal’s (112) face. b, Responsivity vs. wavelength at varying potential biases. Of the wavelengths tested, 780 nm gave the highest responsivity at all applied voltages. c, Photocurrent vs. light intensity at 780 nm illumination with varying applied biases. These plots were fit with a simple power law (solid lines) resulting in an exponent equal to 0.54. d, Responsivity vs. light intensity at 780 nm with varying applied biases. A power law was also used to fit these data (solid lines). The power law used to fit data in panels c and d can be found in the text.

Figure 6.4c and d show log-log plots of the photocurrent and responsivity vs 780 nm light intensity, respectively. To quantitatively assess the dependence of photocurrent on light intensity, one can fit the data presented in panel c with a simple power law: $I_{ph} = AP^\alpha$ where $I_{ph}$ is the photocurrent, $A$ is a scaling constant, $P$ is the light power, and $\alpha$ is an exponent. The solid lines in panel c represent this fit. The exponent of these fits gives an
exponent equal to 0.54, indicating an odd power dependence on light intensity \((0.5 \leq \alpha \leq 1)\)—that is, the electron lifetime remains constant, as discussed above, but the electron response time decreases. The model accounting for this behavior, by definition of the standard model for photoconductivity\(^{27}\), consists of a distribution of states in energy within the bandgap. The spectral response of this photoconductor can then in theory include photon energies less than the band gap energy if a sufficient density of recombination centers exists. This holds in our material. The optical bandgap is 1.47 eV and, reexamining Figure 6.4b, we find that there is indeed a photoconductive response at lower energy excitations of 850 nm, 940 nm, and even a comparatively small amount at 1050 nm. Figure 6.5a shows the photocurrent vs. voltage plot of this material under 1050 nm illumination—further supporting the existence of states within the bandgap. The implication of these sub-band gap photocurrents will be discussed in the next section.

**Figure 6.5 | Additional photocurrent response data for CuInS\(_2\). a**, IV-curve of CuInS\(_2\) under illuminated (1050 nm) conditions. Pt wires were connected to the crystal using an InGa eutectic, with illumination occurring on the crystal’s (112) face. This high-wavelength induced photocurrent supports existence of a sufficient amount of states distributed within the bandgap (1.47 eV). **b**, Qualitative defect state schematic of CuInS\(_2\) under 1050 nm irradiation. The defect states at VBM + 0.3 eV are attributed to charged defect complexes of \((\text{In}_{\text{Cu}^+} + 2\text{V}_{\text{Cu}})^{\text{oc}}\).
Figure 6.4d shows a standard decrease in responsivity with increase in light intensity. The negative slope is a consequence of defect concentration within the gap decaying exponentially from the band edge to mid-gap, and as light intensity increases a smaller ratio of charge carriers will be separated. The responsivity of our rudimentary photoconductor device reaches 0.9 mA/W at a 5 V bias, which, for reference, is the same order of magnitude achieved by the first graphene photodetectors. We would like to emphasize that the focus of this manuscript is not a full investigation of an engineered photoconductive device made from CuInS₂, but rather the connection between CuInS₂’s photoconductive behavior and defect chemistry—which will be discussed in the next section.

iv. Discussion. Having described the material’s photoconductive behavior, pertinent physical properties, and its extended defects, a comprehensive picture can be made by drawing connections between them. Given the sample thickness of 0.06 cm, these defects are well within range of the penetration depth for all wavelengths studied as the absorption length of all wavelengths used in our photoconductivity measurements is ≤ 1.8x10⁻³ cm. And it is important to remind the reader that these defect layers are the sole defect present in significant quantities in the crystal lattice and therefore the contribution of the microstructure to the optoelectronic properties must lie within these defects.

The Hall effect results show that the material is n-type. The thermal activation energy of the electrical resistivity of 87 meV is surprisingly low, given that the free electron concentration is small, at 2.3 x10¹³ cm⁻³. The combination of low free electron concentration with low thermal activation energy suggests a donor defect that is largely depleted of electrons because these are trapped by a deep acceptor. When the free electron
concentration is smaller than the concentration of deep acceptors, the thermal activation energy of electrons out of the sparsely occupied donor level is equal to the energy of the donor level below the conduction band minimum, here 87 meV. Based solely on our electronic transport data, it is difficult to identify this shallow donor level at 87 meV (Figure 6.1c). Turning to the literature, defect activation energy in CuInS$_2$, and its sister compound CuInSe$_2$, has been studied both theoretically and experimentally and, in some instances, there is an encouraging agreement in these studies. For example, acceptors at ~50 meV and ~170 meV are confidently assigned as $V_{\text{Cu}}$ and $V_{\text{In}}$, respectively. However, the literature is still not in agreement on the assignments of similarly shallow donor levels. $^{12,19,21,22,26,35}$ Fortunately, though, our STEM analysis helps to solve this puzzle.

The first characteristic of our STEM data to note is the row of atoms just above the interfacial phase in Figure 6.2c. When viewing the crystal from this orientation it is clear there is no cation overlap—the relatively brighter atoms are In, due to its higher Z contrast, and the duller atoms are Cu. The row of atoms just above the interfacial phase is worth noting because the atoms are no longer alternating by brightness, but rather the entire row is of relative high brightness. Since the coordination and lattice spacings stay true to the chalcopyrite CuInS$_2$ phase, we can postulate that this row is composed of cation antisite defects on the major lattice: $\text{In}_{\text{Cu}}$ antisite point defects.

With this information in hand, we can reflect on the shallow donor level detected at 87 meV in Figure 6.1c and assign this to $\text{In}_{\text{Cu}}$ antisite defects, in agreement with other experimental studies on shallow level donors in CuInS$_2$ and CuInSe$_2$. $^{12,35}$ This donor gives the material its overall $n$-type identity. However, we must rationalize why the carrier concentration is relatively low ($2.3 \times 10^{13}$ cm$^{-3}$) and the connection that these physical
properties have to its photoconductive behavior. The reasoning behind both these questions lies in highly compensated defect chemistry.

The second STEM characteristic we would like to note is the rotational-twin boundary that can occur independent of the interfacial phase, seen most clearly in Figure 6.2e, outlined by a dotted white line. This type of twin-boundary has been reported in the literature as a benign, electrically inactive, grain boundary found in chalcopyrite structures and we can therefore discount this feature as a source of the optoelectronic properties we observe. \(^{36,37}\)

The last STEM characteristic we would like to note is the interfacial phase itself, along with the quantitative composition analysis of this region presented in Figure 6.3c. It is obvious that the interfacial phase is distinct from the surrounding chalcopyrite phase. A detailed structural characterization and analysis of this phase is forth-coming from our research team. However, for this study, the most critical piece of data gathered from this phase is its quantitative change in atomic percent composition as the interfacial phase transforms at the rotational-twin boundary from a chalcopyrite phase. As seen in Figure 6.3c, the stoichiometry of the interfacial phase consists of a significantly higher at% of In, a relatively small increase of at% S, and significantly lower at% of Cu. Bearing in mind that the starting material purposely contained a large deficiency in Cu, we interpret this STEM characteristic as follows: moving from the stoichiometric chalcopyrite phase to the In-rich interfacial phase leaves a high density of Cu vacancies, i.e. \(V_{Cu}\) point defects. Additionally, the presence of \(V_{Cu}\) defects is highly plausible as these vacancies are known to form easily in ternary chalcopyrites (especially under Cu-poor conditions) due to their low formation energy. \(^{25,38,39}\)
Now we turn to the deep acceptor that very nearly compensates the 87 meV donor. The strong photoconductive responsivity around $\lambda = 1050$ nm indicates an abundant electron-occupied gap state that lies 290 meV above the valence band minimum (VBM). We believe that this is the acceptor in question. Interpretation of S/TEM data suggests that this level is the ($\text{InCu}^+2\text{VCu}$) complex, and that it functions as an acceptor in its 0/-1 transition. The arguments are laid out below.

Having inferred the presence of $\text{VCu}$ induced point defects at the disk-like defect layers, we can discuss how highly compensated defect chemistry is created in this material. As previously mentioned, ternary chalcopyrites are known to self-compensate due to the additional degree of freedom inherent in a two-cation structure of differing valency.\(^{38-41}\) We rationalize that the high resistivity ($2.7 \times 10^6 \ \Omega\text{-cm}$) and low carrier concentration ($2.3 \times 10^{13} \ \text{cm}^{-3}$), both measured in the dark, are due to a neutralized defect pairing that compensates $\text{InCu}$ donors and $\text{VCu}$ acceptors. We interpret these compensating point defects as the ($\text{InCu}^+2\text{VCu}$) complex, the theoretically proposed defect pair in chalcopyrites that serve as a source of metastability, similar to the ($\text{VSe}^+\text{VCu}$) divacancy complex.\(^{23,25,26}\) In this case, most of the $\text{InCu}$ and $\text{VCu}$ defects will be compensated within these neutral defect complexes and the remaining uncompensated, isolated $\text{InCu}$ donors will contribute to the low, $n$-type carrier concentration. This phenomenon has been reported for ternary chalcopyrite semiconductors, with the neutral defect reported to have a low calculated formation energy.\(^{25,38,39}\)

This metastable complex has been reported to function as a recombination center ($N_r$) that reside within the bandgap and account for metastable, photoinduced effects.\(^{42,43}\) $N_r$ centers have been reported to occur in binary transition metal chalcogenides like ZnSe.
with the introduction of the extrinsic cation impurity, Ga. It should also be noted that the binding energy of paired InCu and VCu defect complex has been calculated and has been proposed as too weak to contribute to defect energy levels; however, the new data our manuscript presents offers a true supercell of atoms that we encourage theorists to accommodate in their calculations for Cu-poor growth environments of chalcopyrite semiconductors.

To complete the picture, we must now discuss how this self-compensating defect behavior actually generates its photoconductive response. We use the definitions laid out by Rose in “Concepts in Photoconductivity and Allied Problems” to describe the components of our model: trap states (N_t) will refer to states between the conduction band minimum (CBM) and the steady-state Fermi level defined by the density of n (E_Fn), and N_r will refer to the states below E_Fn and the steady-state Fermi level defined by the density of p (E_Fp). Figure 6.6a represents a qualitative model of the band-structure in the dark. The overall dominant shallow donor point defect InCu is positioned close to the CBM. As previously discussed in reference to Figure 6.4, the defect concentration within the gap decays exponentially from the CBM. The N_t states, between the CBM and E_F, represent trap states for electrons (i.e. the electrons can be trapped in these states, lengthening their response time, before reaching the CB). At this point, E_F is located near the shallow level donors just below the CBM. We rationalize that the defect states within the bandgap, VBM + 0.3 eV (Figure 6.5b), are attributed to the (InCu+2VCu) complex, despite theoretical work saying these states should occur further from the VBM. These states are filled and act as N_r states for excited electrons. Figure 6.6b shows how this model evolves under full illumination. At this point, E_F can essentially be thought of as two levels, E_Fn and E_Fp,
representing the Fermi level defined by the density of $n$ and $p$, respectively. Electrons from the VB and $N_t$ states make their way up to the CB and $N_t$ states. The number of original $N_t$ states lying between the CBM and $E_F$ has now decreased while the number of $N_r$ states has increased. This causes an overall decrease in electron response time, while the electron lifetime remains the same, leading to the observed odd power dependence on light intensity. The probability of recombination increases, which limits the efficiency of solar absorbing applications.

**Figure 6.6 | Defect states within the band gap and their contribution to sub-band gap photocurrent.** Electronic band structure models for the $I_{ph} = P^\alpha$ ($0.5 \leq \alpha \leq 1$) system of Cu-deficient CuInS$_2$ in the dark upon, a, and at full illumination, b. In the dark, isolated In$_{Cu}$ antisite defects make up an array of shallow donor levels near the CBM. These donor levels are trap states, $N_r$, for excited electrons. $E_F$ lies near these shallow donors just below the CBM. The states around VBM $+ 0.3$ eV are attributed to the defect complex (In$_{Cu}$+2V$_{Cu}$). Given the position of $E_F$, these states are filled and function as $N_r$ states for excited electrons to recombine with holes. Under continued illumination, the defect pair can act as either acceptors or donors and continue to serve as recombination sites. The $E_F$ can now essentially be thought of in two parts, $E_{Fn}$ and $E_{Fp}$, representing the steady state Fermi level defined by the density of $n$ and $p$, respectively. The number of $N_r$ states has now increased, occupying the defect level located between $E_{Fn}$ and $E_{Fp}$. Consequently, the number of $N_t$ states has decreased, which subsequently decreases the electron response time. With prolonged and/or increased illumination, this effect is exacerbated, leading to photoinduced metastability.
6.3 Conclusions

A CuInS$_2$ single crystal grown in a 1 mol % Cu-poor environment had a resistivity on the order of $10^6$ ohm-cm at room temperature and a low carrier concentration, on the order of $10^{13}$ cm$^{-3}$ in spite of the relatively large Cu deficiency. STEM imaging and EDS analysis revealed that the Cu deficiency was accommodated in extended defects—metastable, disk-like defect layers parallel to the chalcopyrite (112) planes. Photoconductivity studies reveal an odd power dependence on light intensity as a result of the decrease in electron response time due to the increased concentration of trap states. The culmination of our experimental studies is an electronic structure model that explains how the presence of the (In$_{Cu^+2}$V$_{Cu}$) paired defect levels can, upon illumination, activate a pathway for detrimental metastable effects. Our findings provide critical evidence that metastability in chalcopyrite semiconductors is an intrinsic property that arises at the borders of extended defects due to composition variation—indicating why the synthetic growth environment must be carefully considered when incorporating these photoabsorbers into solar energy devices. Further, they indicate that there is an intrinsic limit to the amount of $p$-type doping that is possible through copper deficiency due to the formation of extended defects and suggest that other avenues to optimizing chalcopyrites may be limited by similar defect mechanisms.

6.4 Methods

i. Single Crystal Growth & Characterization. Polycrystalline chunks of CuInS$_2$, with 1% Cu deficiency, were first synthesized using elemental starting materials Cu (99.99%), In (99.99%), and S (99.99%). The elements were loaded into a quartz tube and sealed under vacuum and then heated to a maximum temperature of 1100 °C. Detailed heating technique
for the polycrystalline material can be found in a previous publication. Once the polycrystalline material was characterized to ensure its purity, approximately 20 g of the CuInS2 polycrystalline chunks were ground into large grains and loaded into a specially crafted, carbon-coated quartz tube, and then sealed under vacuum. A specially designed vertical Bridgman furnace was used to grow the CuInS2 single crystal inside the quartz tube. During the crystal growth the hot zone was controlled at a temperature of 1140 °C. The quartz tube containing the polycrystalline CuInS2 was held in the hot zone for 24 hours, then driven through the length of the furnace at 0.1 mm/hour. Post Bridgman-growth, the crystal was annealed its quartz tube at 400 °C for 24 hours to ensure top crystal quality.

X-ray analysis in the form of powder X-ray diffraction (PXRD) and back-reflection X-ray Laue diffraction was used to characterize the CuInS2 polycrystalline pre-cursor material and the CuInS2 single crystal. PXRD analysis was performed on a Bruker D8 Advance Eco with Cu Ka radiation and a LynxEye-XE detector. The scan parameters were 0.02°/step with 0.085 s/step, for a total scan time of 8 min. A Quanta 200 field emission gun environmental scanning electron microscope (SEM) equipped with an integrated Oxford System was employed for energy dispersive X-ray (EDS) analysis. The X-ray penetration depth was 1−2 mm, and the detection limit of a specific element was 10%. X-ray photoelectron spectra (XPS) were collected under 10−9 Torr using a ThermoFisher K-Alpha X-ray photoelectron spectrometer. All spectra were recorded using Al Kα radiation (1487 eV) with a survey and pass energy of 100 and 20 eV, respectively. Measured peaks were fit using Casa XPS software and a Shirley background. The C 1s peak at 284.5 eV of adventitious hydrocarbon was used as an internal binding energy reference. The optical bandgap was measured with the Agilent Technologies Cary 5000 UV-Vis-NIR
spectrometer equipped with a Universal Measurement Accessory (UMA) with incident light from 200 to 1300 nm. At wavelengths less than 650 nm the absorbance became saturated. That being said, the absorption coefficients and absorption depths of these short wavelengths could not be accurately calculated.

**ii. Transport Property Measurements.** Please refer to the Method Section of Chapters 3 and 5 for details on data presented in Figure 6.1.

**iii. Scanning/Transmission Electron Microscopy.** TEM thin lamella for microstructure characterization were prepared by focus ion beam cutting via FEI Helios NanoLab™ 600 dual beam system (FIB/SEM). Conventional TEM imaging, atomic resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging and atomic-level energy dispersive X-ray spectroscopy (EDS) mapping were performed on a double Cs-corrected FEI Titan Cubed Themis 300 scanning/transmission Electron Microscope (S/TEM) equipped with an X-FEG source operated at 300 kV and Super-X EDS system.

**iv. Photoconductivity Measurements.** Photoconductivity measurements were performed on the same instrument as the electronic transport measurements, a Quantum Design Physical Property Measurement System, using a custom dark-room setup. Ohmic contact was made with Pt wires connected to the (112) surface with InGa eutectic. Current-voltage curves were plotted in real time as the potential was swept between -10 and 10 V at varying light intensities with each wavelength tested (365 nm, 395 nm, 462 nm, 537 nm, 640 nm, 780 nm, 850 nm, 940 nm, and 1050 nm). These measurements were performed at room temperature.
REFERENCES


### APPENDIX A

**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle-resolved photoemission spectroscopy</td>
<td>ARPES</td>
</tr>
<tr>
<td>Brillouin zone</td>
<td>BZ</td>
</tr>
<tr>
<td>Chalcogen</td>
<td>X/E</td>
</tr>
<tr>
<td>Conduction band minimum</td>
<td>CBM</td>
</tr>
<tr>
<td>Cu(In,Ga)(S,Se)$_2$</td>
<td>CIGS/CIGSSe</td>
</tr>
<tr>
<td>Density functional theory</td>
<td>DFT</td>
</tr>
<tr>
<td>Density of states</td>
<td>DOS</td>
</tr>
<tr>
<td>Electronic transport option</td>
<td>ETO</td>
</tr>
<tr>
<td>Energy-dispersive X-ray spectroscopy</td>
<td>EDX/EDS</td>
</tr>
<tr>
<td>Faradaic efficiency</td>
<td>FE</td>
</tr>
<tr>
<td>High-angle annular dark-field</td>
<td>HAADDF</td>
</tr>
<tr>
<td>Linear sweep voltammetry</td>
<td>LSV</td>
</tr>
<tr>
<td>Mott–Schottky</td>
<td>M–S</td>
</tr>
<tr>
<td>Normal hydrogen electrode</td>
<td>NHE</td>
</tr>
<tr>
<td>Photocurrent onset</td>
<td>PCO</td>
</tr>
<tr>
<td>Photoelectrochemical</td>
<td>PEC</td>
</tr>
<tr>
<td>Physical property measurement system</td>
<td>PPMS</td>
</tr>
<tr>
<td>Powder diffraction file</td>
<td>PDF</td>
</tr>
<tr>
<td>Powder X-ray diffraction</td>
<td>PXRD</td>
</tr>
<tr>
<td>Reversible hydrogen electrode</td>
<td>RHE</td>
</tr>
<tr>
<td>Scanning electron microscopy</td>
<td>SEM</td>
</tr>
<tr>
<td>Scanning/transmission electron microscopy</td>
<td>STEM</td>
</tr>
<tr>
<td>Space charge region</td>
<td>SCR</td>
</tr>
<tr>
<td>Spin orbit coupling</td>
<td>SOC</td>
</tr>
<tr>
<td>Transmission electron microscopy</td>
<td>TEM</td>
</tr>
<tr>
<td>Transition metal</td>
<td>M</td>
</tr>
<tr>
<td>Transition metal chalcogenide</td>
<td>TMC</td>
</tr>
<tr>
<td>Transition or other metal</td>
<td>M’</td>
</tr>
<tr>
<td>Ultraviolet–visible spectroscopy</td>
<td>UV/Vis</td>
</tr>
<tr>
<td>Valence band maximum</td>
<td>VBM</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>XRD</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy</td>
<td>XPS</td>
</tr>
</tbody>
</table>
APPENDIX B

PSYCHOLOGY OF A GRADUATE STUDENT

My time in graduate school, and at Princeton in general, has been the happiest and healthiest of my life. I truly mean this, and I owe this experience to both my amazing advisers (Andy & Boss) for giving me space to grow as a scientist and person while also providing a supportive, safe, and healthy environment to do so. However, one cannot simply go through graduate school without dealing with a higher-than-average amount of stress—which for me manifested itself in dreams. Thanks to Aubrey’s suggestion, sometime in early 2017, I started keeping a journal of all my work-related dreams which served as a productive stress-relief. I felt I could not present my graduate thesis without including a selection of dreams that comically showcase the struggles my inner psyche endured during the process. Please enjoy.

1. Andy turns into a skeleton and runs away. The Bocarsly lab looks for him everywhere but cannot find him.

2. Andy is going to jail so I cannot be a joint Bocarsly student anymore. I tell Liz (Seibel) Andy is going to jail and she says, “You need to talk to Boss now about becoming a full student in his group before it’s too late”. I run around lab frantically looking for Boss. I start crying because I don’t want to be a full-Cava student because Boss will make me work on superconductors which I don’t want to do.

3. The Bocarsly lab needs more dark room space so we have to build a room in the back of the lab using cardboard boxes because the department won’t give us a real room to use.
4. In the Cava lab, the element “copper” is known as “chicken”. I refer to my material as “Chicken Indium Sulfide” and “ChInS$_2$”.

5. Thomasz was visiting the Cava lab again and he stole my PPMS time.

6. The Bocarsly lab had a glove box that was only used to store glove bags. An undergrad (unspecified) broke a glove bag within the glove box by stabbing it with a needle. Hsinya and I were very pissed off at the undergrad, who ran away and did not help us fix it, which took a long time.

7. Andy and his wife came into lab. Andy had us switch desks around to accommodate the incoming undergrads while Andy’s wife made us tea that did not taste good.

8. I keep checking on Andy’s office wanting to talk to him, but every time RPL is in there talking to him.

9. The Bruker XRD is not working because someone took apart the wire attachments. Boss was very angry and told us (the entire Cava lab) to go in search for the wires. The Cava lab then went off on an adventure looking for the wires in the wild. Alex suggested we look in the woods nearby the building.

10. James (Park) and I were in lab late one night and were trying to put together quartz echem cells. James got frustrated, picked up a glass flower vase and threw it on the floor where it shattered. He then laughed maniacally.

11. Nadia and I were walking on the 3rd floor bridge and realized all the blue carpet in the building was being replaced by purple carpet. We were very upset because we thought the blue carpet matched the building way better than purple.

12. Andy told me the day before a conference was starting that he wanted me to present a poster at it. I didn’t have a poster, so I asked Aubrey and Hsinya to borrow of
theirs but they both said no. I was annoyed at them and secretly planned to take their posters that night after they both left lab (hehe). I went to the conference to present a poster but had to leave early to make it to a Cava lab dinner the next day. I was worried Andy would be angry I had to leave early to attend the Cava group dinner.

13. Boss was disappointed/angry I couldn’t interpret a particular sample using the Bruker so he came into lab to do the experiment himself. He did not know what he was doing and ended up BLOWING UP THE BRUKER and the sample inside (which was very bright blue) went everywhere in the lab. He then just walked out of the lab (in a very grumpy mood) leaving his mess behind him for us to clean up.

14. We had to take a Cava group photo and Jennifer wanted us to do a very “fancy” photoshoot at a far-off location in nature. The lab was not pleased with this idea and wanted to stay indoors, in Frick to take the photo.

15. The Chemistry Department created another required seminar presentation (in addition to the 3rd year seminar). I was unprepared for my presentation, so I presented my current manuscript while sitting down in the first row of Taylor Auditorium. Andy & Boss were laughing at me (not in a mean way) from their seats in the auditorium and Selloni was confused and asking questions.

16. I’ve titled this one, “The South Wing Battle”. One day I walked into the Bocarsly lab and saw that two research groups (in addition to Leslie’s and Jeff’s) from different schools had moved into the lab space. We found out that Tom (Muir) was having the five labs “battle it out” for the entirety of the 3rd floor south wing lab space. All the graduate students were forced to live in the lab while this was going
on. Tom had our clothes moved in and had a shower installed in one of the hallway bathrooms for us to use. Aubrey and I were pissed but determined to win the lab space for the Bocarsly lab. Unfortunately, I woke up before this dream came to any conclusions, but I’m sure Aubrey and I would have led our lab to victory.

17. I went into the dark room and found the Xenon arc lamp broken.

18. Sulfur-containing samples in the Cava lab blow up while in the furnace. This is a recurring dream I’ve had countless times.

19. Tao took apart my cardboard box and xenon arc lamp set-up. I was very angry at him and he tried putting it back together but could not find all the pieces.

20. Andy allowed 8-10 high school and undergrad-aged students to join the lab. I had to meet with them in a conference room to talk about all the projects going on in the Bocarsly lab. I went through all the active projects, including Aubrey’s Cr-Ga project. They ALL were most interested in that project and want to work with her. I thought to myself, “OMG Aubrey is going to kill me now that she has to mentor all these students at once”.

21. Andy told Steve and I that we had to make dinner for visiting students, but that the meal-prep had to involve “internal combustion” (?). Steve and I were very confused while Andy played his guessing-game with us about what to make for dinner. I thought maybe re-hydrating de-hydrated mashed potatoes would fit Andy’s weird criteria.

22. I was at my desk on the 3rd floor and Boss came up to talk to me which startled me so much (because he’s never on that floor) that I woke up.
23. There was a dinner taking place in the atrium and Aubrey, Hsinya, and I had to change into semi-formal clothes to attend. Luckily, Hsinya had moved her entire wardrobe to the back corner of the lab where we went “shopping” for dinner clothes.

24. The Bocarsly lab was moved into its own, secluded lab space, but it was the size of the group room and had only two hoods and no sinks. Michael and I had our desks right next to a hood where Danrui was synthesizing something. I asked Andy if I could move my desk because I didn’t feel safe next to the hood. He said no and that we all must focus on grant writing so that we can afford a sink and bench space for the new lab.

25. Aubrey came into the group room to get chips from our chip drawer. She found it was empty and judged me for eating all the chips.

26. There were three hidden conference rooms on the south end of the 1st, 2nd, and 3rd floors. Nadia and I discovered the room on the 3rd floor and found it was full of clothing racks of sequin dresses we could try on.

27. I was at a water-park and saw Andy and Jeff (Schwartz). I took a picture of them going down a waterslide together.