Accelerating the Development of Novel Photovoltaic Materials

by

Riley E. Brandt

Bachelor of Science, Massachusetts Institute of Technology (2011)
Master of Science, Massachusetts Institute of Technology (2013)

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Author .................................................................
Department of Mechanical Engineering
May 2, 2016

Certified by ..............................................................
Tonio Buonassisi
Associate Professor of Mechanical Engineering
Thesis Supervisor

Accepted by ............................................................
Rohan Abeyaratne
Professor of Mechanical Engineering
Chairman, Department Committee on Graduate Theses
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Abstract

To restrict the warming effects of climate change to less than a 2°C increase, we must deploy terawatts of solar photovoltaics (PV) and other renewables in the next 10–15 years — yet, historically novel PV materials have taken decades to go from discovery to commercial relevance. In this thesis, several strategies are outlined for faster screening of novel PV materials, including absorber layers and their respective carrier selective contacts, with the goal to reduce the materials development cycles from years to days or weeks through smarter design, modeling, and characterization.

First, “smart” theoretical screening criteria are established by considering the electronic structure features that produce tolerance to defects in semiconductors. Data mining a repository of tens of thousands of materials using these insights reveals a class of partially oxidized cation compounds that could offer promising PV properties. A fast experimental protocol is developed to quickly synthesize these materials and evaluate their minority carrier properties. This is then applied to bismuth halides and related compounds, revealing several materials with carrier lifetimes in excess of 1 ns.

Next, X-ray photoelectron spectroscopy (XPS) and related tools are used to design and predict optimal electron and hole selective contacts for thin-film PV absorbers. In particular, contacts are designed for cuprous oxide (Cu₂O) and tin monosulfide (SnS), resulting in state-of-the art open-circuit voltages for both materials. These XPS measurements are then compared to temperature- and illumination-dependent electrical measurements on Cu₂O solar cells to achieve comparable precision and accuracy to spectroscopy in a fraction of the time.

Finally, new numerical fitting approaches are applied to these electrical measurements in order to infer the underlying materials properties from purely electrical measurements. Using Bayesian inference, fundamental materials properties of SnS and other semiconductors are inferred from electrical measurements, allowing for full quantification of efficiency loss mechanisms in a new solar cell material in the time scale of one day. Together, these results point towards leveraging smarter theory and modeling to accelerate and improve how new PV materials are developed.
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Chapter 1

Motivation and Overview

Of the potential alternative energy sources available as fossil fuel replacements, solar offers the greatest resource base. Over 120,000 TW of solar radiation strike the Earth’s surface continuously, in comparison to our current global power consumption of 18 TW_{ave}. Yet in 2011, at the beginning of this thesis, only 70 GW_{peak} of solar photovoltaic (PV) power had been installed worldwide.

The barriers to growing the share of primary energy coming from the sun were significant, but the last five years have shown remarkable growth. In 2015, new PV installations reached 58 GW_{peak}, for a cumulative PV capacity worldwide of over 230 GW_{peak},[1] exceeding 1% of the world’s electricity production. This required dramatic reductions in prices, improvements in technology, and favorable policies in countries from Germany to China. However, there remains a significant gulf between our current installed PV capacity, and the levels of penetration necessary to combat global climate change. Overcoming this challenge presents a conflict of timelines — the need for rapid deployment of PV, and the historically slow process of bringing new materials discoveries to market.

1.1 Climate Change and Solar Power

To solve the pressing challenge presented by global climate change, scientists and citizens alike must reconcile two competing timelines. The first timeline is that of
anthropogenic carbon dioxide emissions, instigated by the industrial revolution and accelerated by the growing population and rising standard of living over the last 60 years. Climate models suggest that an upper limit in temperature rise of 2°C will be necessary to limit the most catastrophic effects of climate change. To do so would require a rapid scale-up in PV manufacturing capacity to 7–10 TW$_{\text{peak}}$ of installed capacity by 2030, which greatly outpaces the current trends in PV capacity additions.[2] In Fig. 1-1, this aggressive deployment scenario is compared against the current “business-as-usual” and potential alternative projections. This comparison demonstrates that with present technology and costs, it will be very difficult to deploy sufficient PV power in the next 10–15 years to limit the impact of greenhouse gas-induced warming.

As a potential alternative to the prevailing PV technology of crystalline sili-
con, thin-film PV modules could help answer the problem of rapid scale-up of solar power.[3][4] Of the competitive technologies, polycrystalline thin-film PV offers numerous advantages including reduced materials consumption (lower variable costs), faster and less energy-intensive production methods (lower capital costs), and the promise of lighter, flexible modules (with lower installation costs and higher specific power).[5][6][7]

Two particular thin-film PV technologies, made from cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS), have already demonstrated commercial applications, but their market penetration is small relative to crystalline silicon, and there are still fundamental scientific and manufacturing breakthroughs necessary to push these materials ahead of crystalline silicon. In addition to these materials, there are many other underinvested absorber materials that could offer potential scaling, manufacturing, and performance advantages over CIGS and CdTe.

First, to achieve terawatt-level capacity, CIGS and CdTe may encounter material scarcity bottlenecks. Fig. 1-2 plots all non-radioactive elements by present (2010), known information — price ($/kg) and annual global production (tonnes/yr). Generally, the elements follow a power-law demand curve in which lower production correlates with higher prices. Elements that are produced as byproducts of larger mining processes (including In, Ga, and Te) are less expensive as they are largely subsidized by the primary element extraction. In addition, toxic elements such as Hg, As, and Cd are cheaper due to lower demand. To put these figures in the context of PV production, Fig. 1-3 offers upper and lower bounds on the scaling capacity of elements depending upon different assumptions for the technology. For example, one can estimate the mass of element needed to produce one terawatt (peak rating) of thin-film modules — assuming the element comprises 50% of a binary semiconductor, with average density of 6 g/cm³, in a 1 micron thick, 20% efficient module. This suggests a production bound of 15,000 tonnes/TW_{peak}, drawn in Fig. 1-2 for comparison. Te, In, and Ga currently offer <1,000 tonnes of production annually, and while new economic sources may yet be discovered, alternative absorber materials could help satisfy growing demand for PV.
Figure 1-2: Global production in metric tonnes vs. price of element in $/kg for 2010, reflecting general trends in abundance of elements. Thresholds for price and volume are denoted in red dashed lines.[8]
Second, abundance, and specifically materials costs, are not sufficient to guarantee economic competitiveness. In crystalline silicon, the capital and processing costs alone make up a growing fraction of module cost. Thin-film CdTe modules, on the other hand, offer the lowest capital costs and factory footprint of any PV technology. Still other materials amenable to lower-temperature and higher rate deposition, such as solution processing, can augment this advantage and enable new substrate materials. Another key technical differentiator is absorber deposition uniformity and reproducibility; some compounds may have manufacturing advantages intrinsic to their elemental constitution. This could include congruent or stoichiometric sublimation of their constituent elements, a property that CdTe shares with several iodides and sulfides such as tin monosulfide (SnS). This may also include the presence of discrete, energetically favoured phases in their respective equilibrium phase diagrams especially in the presence of oxygen and at processing temperatures. New absorbers possessing these properties offer inherent manufacturing advantages over certain incumbents.
Finally, new device architectures demand new materials. To exceed the Shockley-Queisser efficiency limit, multi-junction configurations require absorbers with bandgaps of a wider range about the optimal 1.4 eV single-junction bandgap. For many third-generation PV or thermophotovoltaic cells, high quantum efficiencies are required over a narrow spectral bandwidth, offering a less constrained path to commercial adoption for novel materials. Other examples of high-value PV applications that could benefit from novel absorbers include high-temperature combined PV and solar thermal systems that require wide-bandgap absorbers that are thermally stable to several hundred degrees Celsius,[9] or applications involving electrochemistry, e.g., water-splitting devices that require resistance to corrosion or degradation in water.[10]

The pressing need for innovation in materials to allow for terawatt-level solar penetration is clear, and Chapters 2 and 3 will discuss the design of these materials and where they may offer intrinsic advantages. Before venturing further though, we must acknowledge the second, competing timeline.

### 1.2 Rate of Discovery of New Materials

The historical record of materials innovation is remarkably consistent over the last several decades: across many industries, it typically takes 15–20 years between the discovery of a novel material and its first commercial success. Ceder and Curtarolo documented this phenomenon across many industries, and find that on average 18 years elapse between discovery and commercial success for materials from Li-ion batteries to Velcro.

There are many reasons for this slow path to commercialization for materials. Musso [12] suggests that this rests in the fact that materials are functionally fungible, but simultaneously are difficult to change due to their complexity, and their position early in the value chain as commodities. Essentially, end users demand functionality, not the underlying materials. Manufacturers view new materials as risky, given the complexity of the products they are building. This fungibility and risk provides a relatively small market pull for new materials.
This situation puts materials innovators into the position of making a technology push (as opposed to a market pull), and the onus is on the materials scientist to demonstrate the capability of the technology. The adoption of a new material won’t occur until the innovators can sufficiently overcome all of the scientific and manufacturing challenges — many of which are formidable for a new material. Without the market pull that would prompt investment dollars though, progress in overcoming these scientific hurdles can be slow.

PV is no exception to this model of materials discovery and development. Fig. 1-5 is an iconic plot in the PV community, showing the steady progress of record solar-to-electricity conversion efficiencies across many different PV materials. For the industry standards, these materials took over two decades to break 20% in conversion efficiency, with only public funding and academic research. With recent increases in investment in these materials, some, like CdTe, have shown a surge in conversion efficiencies — however, this heavier commercial interest only occurred after multiple decades of slow development. During this long, arduous development period, very little revenue was generated by these materials.

The story appears more dire for the many dozens of materials that don’t feature on the official record chart. A slew of sulfides, oxides, selenides, and more exotic silicides, pnictides, and halides have been explored for their PV potential as well. A selection of these materials is plotted in Fig. 1-6.[14] These “Earth-abundant” materials include Cu₂O, SnS, and FeS₂, for example. In the case of Cu₂O, the material was explored for over 80 years before breaking the 2% threshold in conversion efficiency. This
Figure 1-5: Timeline of record efficiencies across many PV materials, showing the multi-decade process typical of many materials. Reproduced from Ref. [13].

raises two critical questions for the development of novel PV materials: (1) How can we accelerate the rate of discovery and development of these new materials to time periods less than a decade, and (2) how do we screen materials and determine when they are not worth pursuing further, so as to save the opportunity cost and focus on the most promising candidates?

It is clear that the 20+ year development cycle, combined with the high probability of failure, is incommensurate with the need to act now to prevent climate change. If materials scientists and engineers can develop tools to improve the ways in which we design, select, and develop new semiconductors for PV, this may help reduce the time period, and with that cost, of commercialization for PV — as well as related materials in other nascent industries.

1.3 Overview of Thesis

Motivated by the preceding discussion, this thesis aims to develop tools for the materials scientist to expedite the development of solar power in the 21st century. Chapter
Figure 1-6: Record efficiency improvements over time for various Earth-abundant thin-film photovoltaic technologies.[14]

2 begins by reviewing the design criteria for selecting PV materials, grounded in the physics of solar cell operation and an efficiency loss analysis of present-day materials. Then, Chapters 3-6 each contain a self-sufficient focus on one particular tool development — including methods, a selection of results, and a brief discussion connecting these results to prior and ongoing work.

Chapter 3 focuses on computational and experimental screening and selection criteria for the PV absorber layer. The central themes of this chapter are data mining, materials discovery, and experimental screening. Chapter 4 focuses on the next important design step, selecting optimal $n$- and $p$-type contact materials for the chosen absorber. The central themes of this chapter are the control of band energy levels and spectroscopic techniques for measuring them. Chapter 5 points towards accelerating the measurement of contact alignment, and more generally the quantification of recombination rates, through the use of cell electrical measurements. This includes tool development and a case study using cuprous oxide. Finally, Chapter 6 offers a framework for how to perform and analyze cell electrical data more quickly, by using
Bayesian inference to fit materials properties from cell data. The central themes of this chapter are probability, statistics, and machine learning.

To conclude, Chapter 7 pulls together the discussions from each chapter and offers some thoughts on where the work could go next. The conclusion section will be a brief summary of the thesis contributions. The appendices include derivations of the formulas used in Chapters 2–4, tables of materials values used in simulations, and the raw scripts used in Chapters 3, 5, &6.
Chapter 2

Design Considerations for Photovoltaics

2.1 The Importance of a Smart Search

Consider, for a moment, the pursuit of the optimal PV material to be similar to taking shots at the net in ice hockey. Our objective is equivalent: to score the most goals in a certain period of time; alternatively, to discover the most promising semiconductors for PV applications. A scientist may take one of two strategies. The first is to take more shots on net; in other words to try more materials per unit time. In later chapters, I will discuss techniques for speeding up the rate of learning on a new material, so as to enable more shots on net.

The second strategy is to take smarter shots, or, to be more selective about the materials one chooses to explore in depth. The filters applied to screen or down-select materials need not be perfect, but if they are better than random selection then they may greatly enhance the rate of discovery of new materials.

These two strategies are summarized by a simple statistical experimental, the binomial experiment. If one makes \( n \) independent trials, all of which have some
probability of success $p$, the probability distribution of successes, $P(x)$ is:

$$P(x) = \frac{n!}{(n-x)!x!} p^x (1-p)^{n-x}. \quad (2.1)$$

The expectation value, $E(x)$ of this distribution is equal to $np$; in other words, increasing the number of trials and the probability of success both lead to more successes. However, increasing $n$ requires a linear increase in cost and time, while increasing $p$ may be relatively inexpensive. This motivates the dual strategies: (a) lowering the cost per trial so as to increase $n$, and (b) using smarter search filters to increase $p$.

To determine how to increase $p$ in our search, the best place to start is with the physics of a solar cell and the underlying materials properties that enable high performance.

## 2.2 Overview of Solar Cell Physics

### 2.2.1 Thermodynamics of the Photovoltaic Effect

There are many routes to understanding the physics of how solar cells convert the energy of photons to electrical energy. The most complete route is the thermodynamic approach, but a convenient abstraction is the electrical engineering approach — to consider the solar cell as a superposition of competing currents.

A semiconductor is characterized by bands of available states for electrons to occupy, produced from the combination of many unique atomic orbitals of the semiconductor's constituent elements. Most relevant for PV operation are the valence band, which is the highest-energy, fully-occupied band, and the conduction band, the first mostly unoccupied band above the valence band. At 0 K, the valence band is completely full of electrons, and the conduction band is empty. This state minimizes the internal energy of the system, as each electron sits at its lowest possible energy relative to its surrounding electrons.

In Fig. 2-1, this 0 K picture is depicted at left. The energy difference between
Figure 2-1: The conduction and valence bands of a model semiconductor are depicted here for three scenarios. At 0 K, the system is at its lowest possible internal energy with electrons occupying all possible states in the valence band. The density of states in the valence band is denoted by \( N_V \). At higher temperatures, some electrons have enough thermal energy to jump to the conduction band, leaving behind corresponding holes. Under illumination, many more electrons are excited across the bandgap, leaving behind holes.

valence and conduction bands is the bandgap, \( E_G \), and the density (number per unit volume) of states available in the valence band and conduction band are denoted by \( N_V \) and \( N_C \), respectively. At elevated temperatures, some of these electrons jump across the bandgap to the conduction band. They leave behind an unoccupied valence band state, which we term a hole, as it acts in itself like a particle. The Fermi level, \( E_f \), marks the energy level at which electrons and holes have a 50% probability of occupancy. For an intrinsic semiconductor, the Fermi level is found very near the middle of the bandgap.

While the presence of electrons in the conduction band does not minimize internal energy \( (U) \), it still minimizes the free energy of the system, \( F = U - TS \), where \( S \) is the entropy of the system. By having a small number of electrons in the conduction band, where there are many empty energy levels, the entropy of the system is increased according to statistical mechanics:

\[
S = k_B \ln(\Omega),
\]  

(2.2)
where $k_B$ is the Boltzmann constant and $\Omega$ is the number of microstates available to the system (only one if all of the electrons were in the valence band). In other words, there are more redundant microstates (larger $\Omega$) when a small number of electrons can sample states in the conduction band. This particular picture of electron and hole occupancy applies to all intrinsic semiconductors in equilibrium, in the dark, at temperatures above 0 K. It is important to recognize this as the equilibrium state, because in this state where free energy is minimized, the system is incapable of performing any work.

The photovoltaic cell can perform work only when this equilibrium occupation is disrupted by the arrival of a photon. If the photon has energy in excess of the bandgap, it excites an electron from the valence band up to the conduction band. The arrival of many photons means many excess electrons and holes are injected into the conduction and valence bands, respectively. Now, the system is capable of doing work, because the electrons are at a higher electrochemical potential than in their equilibrium state (and the holes, lower). These electrochemical potentials are also known as the electron and hole quasi-Fermi levels ($E_{f,n}$ and $E_{f,p}$ respectively). This electrochemical potential difference translates into the open-circuit voltage ($V_{OC}$) of the material: the maximum voltage difference between electrons and holes in the semiconductor if it is not connected to an external circuit. The electrochemical potential difference can then be defined in terms of the free energy:

$$qV_{OC} = E_{f,n} - E_{f,p} = E_G - k_B T \ln \left( \frac{N_C N_V}{(n_e + \Delta n)(p_h + \Delta p)} \right),$$

(2.3)

where $n_e + \Delta n$ and $p_h + \Delta p$ are the concentration of electrons and holes in the conduction band and valence band above the dark background level, respectively. If the entire conduction band is full of electrons, and the same is true for holes in the valence band, the entropy goes to zero and the maximum amount of voltage the semiconductor can produce is equal to the bandgap. In the other extreme, when the carrier concentrations are equal to the intrinsic, background carrier concentration from the center panel of Fig. 2-1, the voltage goes to zero — the cell cannot do any
work, as expected. This is reflected in the fact that the intrinsic carrier concentrations \( (n_i) \) in the dark are equal to:

\[
n_{e}p_{h} = n_{i}^{2} = N_{C}N_{V} \exp(-E_{G}/k_{B}T).
\] (2.4)

That is, where \( \Delta n = \Delta p = 0 \), the \( V_{OC} = 0 \) V.

Unfortunately, the ability to absorb a photon and fill the conduction band with electrons is a double-edged sword — electrons may also fall back down to the valence band and recombine with holes. This recombination will become the most important topic of this thesis, and much of the research work on photovoltaics to-date. The symmetry of absorption and recombination sets an upper bound on the concentration of electrons that can be sustained in the conduction band, and therefore, sets an upper bound on the \( V_{OC} \). The \( V_{OC} \) will reappear frequently in the following chapters.

### 2.2.2 Extracting Power

This thermodynamic picture may remind one of a hydraulic dam, with two bodies of water at different altitudes, two tanks of compressed air at different pressures, or of a thermal engine with a hot and cold reservoir. The ability to do work is related to the magnitude of the potential energy, pressure, or temperature difference between the two reservoirs. However, isolated reservoirs are only capable of doing work if there is a pathway for conduction between them.

To extract power from a PV cell, the cell must separate the electrons and holes at
Figure 2-3: Cartoon of an energy band diagram that "filters" electrons (dark circles) and holes (open circles) to separate contacts by providing an energy barrier to each carrier type at the opposing contact. This forces all electrons to flow out one side, and all holes to flow out the other.

their respective electrochemical potentials, by providing a driving force for separation. Fig. 2-2 is a simple cartoon of how this works. One contact is a preferential sink for electrons, or the electron selective contact, while the other contact preferentially selects for holes. When a wire lead is connected to both the electron and hole selective contacts, the electron and hole can find one another and recombine in the external circuit. Those that escape into the external circuit produce a net current, while those that recombine before reaching their respective wire contact are lost, and do not produce valuable current.

The simplest device structure for producing this selective collection of holes and electrons is depicted in Fig. 2-3. In this scheme, the selective contacts simply provide an energy barrier to electrons or holes, and no energy barrier for the opposite type. In practice, real PV cells approximate this idealized structure in a variety of different ways explored in this paper.

This diffusive driving force, which drives electrons to escape through one contact and holes through the other, is the first important electrical current to consider in a solar cell. In an ideal cell, it is insensitive to the voltage applied across the contacts, and only sensitive to the number of incoming photons (or the number of electron-hole pairs created). In Chapter 5, the non-ideal case is discussed, where the ability of a
free carrier to find its selective contact depends upon the surrounding electric field, resistivity, or temperature. For now, the simplest cell model assumes that the light-generated current, or photocurrent $J_{ph}$ is a constant depending upon light intensity. From an electrical engineering point of view, it is a current source.

### 2.2.3 Recombination Currents

A fixed current source which is independent of voltage sounds too good to be true — and it is. It would imply that a PV cell could break the second law of thermodynamics. The counterbalance to this photocurrent source is electron-hole recombination that occurs within the cell.

At all times, free electron-hole pairs recombine through a variety of different mechanisms. This includes radiative recombination with the emission of a photon, defect-assisted recombination where carriers are trapped in defect states and recombine, and Auger recombination where the recombination event excites a third charged carrier to a higher energy state. These are depicted as cartoons in Fig. 2-4. Each of these mechanisms is dependent upon the concentration of electrons and holes around, and analogous to a chemical reaction, one can model the rate of each process based on the concentration of “reactant”, or the concentration of holes and electrons in this case. Trap-assisted recombination is often called monomolecular recombination, as one carrier type is the rate-limiting reactant. Radiative recombination and Auger recombination may similarly be referred to as bimolecular and trimolecular, respectively. Together, the functional form for the recombination rate in a semiconductor can be written as:

$$U = \frac{dn}{dt} = -An - Bn^2 - Cn^3,$$

where $A$, $B$, and $C$ are the respective rate constants, and will be explored more in detail later.

The important feature to note here is that recombination is strongly dependent upon the concentration of carriers present. As noted above, the voltage (or electrochemical potential) in a cell is strongly tied to the carrier concentration. When a solar
cell is brought into forward voltage bias (positive voltage applied to the hole-selective contact), this raises the electrochemical potential of electrons (in the electron-selective contact) and exponentially increases the concentration capable of diffusing from the selective contact back into the absorber layer. The result is that a diffusive “recombination current”, $J_0$, begins to flow as the voltage is increased, in direct opposition to the forward current. The operation of a solar cell, and the ability to extract power, rests upon this constant competition between the forward photocurrent and the reverse recombination current. Both currents are driven by recombination — the former driven by recombination in an external circuit, and the latter driven by recombination internal to the cell.

### 2.2.4 Electrical Engineering Model of a Solar Cell

This competition of currents sets up a convenient equivalent circuit model for a photovoltaic cell. In Fig. 2-5, the current source is placed in parallel with multiple
recombination diodes. These diodes pass minimal current for small applied biases, but at further forward bias they begin to pass exponentially more current. The resulting current-voltage behaviour is plotted in the same figure. At zero voltage bias, the cell outputs a short-circuit current. As soon as a load is added to the external circuit, which introduces a voltage drop, the cell is shifted into forward bias. Far enough into forward bias at the open-circuit voltage point, all photogenerated carriers recombine internally in the cell, and the cell achieves its maximum quasi-Fermi level separation (though unable to do any positive work). The maximum power point for the cell, where it operates most efficiently, occurs at a slightly lower voltage where the cell still produces net current. When we refer to the efficiency $\eta$ of a solar cell, it is defined as the power output at this maximum power point relative to the incoming power of sunlight. The ratio of the power produced at the maximum power point to the product of $J_{SC}$ and $V_{OC}$ is called the fill factor, $FF$.

### 2.3 Sources of Efficiency Loss

Much attention has been devoted to calculating the limiting thermodynamic efficiency of a solar cell. These Shockley-Queisser or detailed-balance analyses account for Carnot, Boltzmann, sub-bandgap optical, and above-bandgap thermalization losses,\[15\][16] and compute the maximum efficiency by balancing the flow of currents in a solar cell. While the present discussion focuses more critically on devices that perform below their thermodynamic limit, they may be treated with a similar current balance, beginning with the photocurrent.
2.3.1 Photocurrent and Collection Lengths

The photocurrent may be reduced from its theoretical maximum by optical losses (reflection, shading, or parasitic absorption of the light in the contacts), or electrical losses — that is, not all photons absorbed make it to their respective contacts. The average distance that an electron or hole may diffuse in a material, $L_{\text{diff}}$, is related to the carrier lifetime $\tau$ and the carrier mobility $\mu$:

$$L_{\text{diff}} = \sqrt{\frac{k_B T}{q} \mu \tau}. \quad (2.6)$$

Despite efforts to minimize optical losses, there are practical upper limits due to shading by metal electrodes, free-carrier absorption in transparent electrodes, and reflection. Top performing devices experience short-circuit current losses of 5–10% from their theoretical limit for optical reasons alone. Having insufficiently large $\mu$ and $\tau$, on the other hand, is a problem that plagues predominantly new PV absorbers. The semiconductor tin monosulfide (SnS) offers a representative case of this, in Fig. 2-6.

In this figure, I model the quantum efficiency, or ratio of current output to incoming photons for every wavelength. Measured optical data is used to separate the different current loss mechanisms for above-bandgap light ($\lambda < 1100$ nm). Current densities are calculated by integrating the wavelength-resolved loss mechanisms over the AM 1.5 spectrum. Reflectance and shading losses are determined by measuring the reflectance of the finished device. Parasitic absorption and lost absorption in the SnS layer are calculated using measured absorption coefficients of the window layer materials and of SnS, then assuming a Beer-Lambert law for absorption.\(^1\) 8.4 mA/cm\(^2\) is absorbed but not collected at the junction, representing the largest single loss mechanism.\(^{[17]}\)

The story for SnS is characteristic of a wide variety of novel PV materials, and is the first step towards prioritizing particular materials properties that enable high performance in PV: minority carrier lifetime, carrier mobilities, and the absorption

\(^1\)More details in co-authored manuscript, Ref. [17].
2.3.2 Recombination Currents and Voltage

In thin-film devices, there may be many recombination pathways that depend differently on applied bias. Electrons may recombine with a hole at the contact/absorber interface, in the space-charge region, or in the bulk — in all cases leaving a concentration gradient that pulls in successively more carriers. The flow of charge in a recombination current is opposite to that depicted for photocurrent in Fig. 2-3. This reverse diffusion is minimized near short-circuit conditions, as there is a potential energy barrier provided by the built-in voltage of the junction. This barrier is set by the separation in the electrochemical potentials between the $p$-type absorber and the $n$-type electron contact, for example.

Because of this energetic barrier for carriers to diffuse the wrong way back across the junction, these recombination currents tend to be exponentially activated with voltage, and with temperature. Recombination currents can be modeled as exponential...
tials with applied voltage:

\[ J = J_0 (\exp[qV/AT] - 1) \]  

\[ J_0 = J_{00} \exp[-\phi_B/AKT], \]

where \( J_{00} \) is a pre-factor corresponding to the number of recombination pathways, \( \phi_B \) is the barrier height for the recombination pathway, and \( A \) is the ideality factor of the diode.

By equating the photocurrent and recombination currents at the open-circuit condition, a simple expression is obtained for the \( V_{OC} \):

\[ V_{OC} = \frac{\phi_B}{q} - \frac{AKT}{q} \ln \left( \frac{J_{00}}{J_{ph}} \right). \]

In other words, the \( V_{OC} \) is strongly set by the number of potential recombination pathways, the type of recombination (related to \( A \)), and the activation energy or barrier for this recombination. In Chapter 5, this concept will be explored in more depth.

### 2.4 Review and Comparison of Existing Materials

In the following chapters, several techniques will be explored for separating and quantifying recombination currents in semiconductors. These will focus on primarily the minority carrier lifetime, and the electronic band alignments between semiconductors. To set the stage for this and to begin to develop an intuition for the ranges of these material properties, it is useful to consider the ranges for these properties extant in literature materials.

#### 2.4.1 Minority Carrier Lifetime

Perhaps the most pernicious recombination pathway in most photovoltaics is trap-assisted or Shockley-Read-Hall recombination. This is reflected in the first term in
Figure 2-7: PV conversion efficiency plotted vs. minority carrier lifetime for a number of PV materials, showing a strong correlation both within materials systems and across different device architectures. Data for this figure was collected in concert with Rafael Jaramillo and Michael Lloyd, and is reproduced from Ref. [20].

Eq. 2.5, and parametrized by a Shockley-Read-Hall lifetime, $\tau_{SRH}$:

$$U_{SRH} = \frac{dn}{dt} = -\Delta n / \tau_{SRH}. \quad (2.10)$$

In Chapter 3, this form of recombination will be explored in more depth. For now, its effect on the photocurrent and recombination currents is best explained through the experimental data available. In Fig. 2-7, the PV conversion efficiency is plotted vs. minority carrier lifetime (typically a SRH-limited lifetime) for a number of PV materials. The high photocurrent and lower recombination currents achievable with a longer lifetime are a necessity for achieving high efficiency. A takeaway from this plot is that one can make a bad solar cell with a high-lifetime material (through other failure modes), but cannot produce a good solar cell with a low-lifetime material.

In addition, it is important to note that a minority carrier lifetime of 1 ns is an
approximate threshold for being able to produce high-performance (>10% efficient) solar cells. This will become a relevant benchmark in the subsequent chapters. Given this benchmark, it is interesting to note that the number of thin-film polycrystalline PV absorbers that are known to surpass this threshold to-date is surprisingly small.

### 2.4.2 Contact Band Alignment

In Chapter 4, I will explore further the important role of electronic band alignment between the absorber material and its selective contacts. The importance was initially made evident in Fig. 2-3; here contacts are critical for blocking electrons or holes and ensuring high quasi-Fermi level separation. In practice, achieving these optimal band offsets is difficult, given that there are surprisingly few high-quality semiconductors to choose from, and only a subset of these may align well electronically, not chemically react, and have an appropriate bandgap for transmissivity and conductivity.

Alignment between two different semiconductors, to first order, follows the Anderson rule: the conduction band offset between two materials is equal to the difference in the electron affinity ($\chi$) of each material at its free surface.[21] In practice, there are many phenomena that can shift the alignment from this vacuum alignment — often referred to as interface dipoles. The various models for interface dipoles and band offsets are reviewed elsewhere.[22] In Chapter 4, variation in band offsets will be discussed in greater detail.

For now, it is useful to survey the literature on a variety of semiconductors to understand their relative electronic alignment, for the purposes of designing devices. Fig. 2-8 displays an array of semiconductors compared relative to the vacuum energy level. There are three general trends to note from this survey. First, in isostructural compounds, moving down a periodic table column in the cation or anion leads to a deeper conduction band or shallower valence band, respectively. Fully oxidized cations tend to form the conduction band states, as their outer orbitals become unoccupied, while valence band states are formed from fully reduced anions. As a result, as the atomic size of the anion increases and the outer valence orbitals are less strongly bound by the nucleus, the valence band states tend to move up in energy. Secondly, in
a related trend, compounds with a larger lattice constant and with less ionic bonding typically demonstrate smaller bandgaps. For example, the more ionic oxides tend to exhibit larger bandgaps than the sulfides and selenides. Finally, generally the ability to dope each semiconductor $p$- or $n$-type tends to follow trends in conduction and valence band energies — a higher valence band energy is correlated with higher $p$-type dopability, while a lower conduction band is correlated with increased $n$-type dopability. This is because higher valence band energies typically make the formation of acceptors more favourable, while the converse is true for deeper conduction band energies making donors more favourable. These trends in material properties are helpful to understand, as a variety of new semiconductors are introduced in the upcoming chapters.
Chapter 3

High-Throughput Screening of Novel PV Absorbers

In Chapter 2, several criteria were proposed for a high-performance absorber layer used in PV: the material must have a high absorption coefficient, a large minority carrier mobility, and a large minority carrier lifetime. The latter two properties relate to how far a minority carrier can diffuse through the film before recombining, and as a result these strongly determine the total current achievable from an absorber layer. However, this diffusion length is only relevant in comparison to the distance between where electron-hole pairs are created, and the contacts where they are collected. This distance, in turn, is typically set based on the thickness of material necessary to absorb all incoming photons. The result is that these three critical design criteria can be grouped together into a non-dimensional figure of merit for all PV materials:

\[ \nu = \frac{k_B T}{q} \mu \tau \alpha^2. \]  

(3.1)

In other words, the ratio of the diffusion length to the absorption length in an absorber material must be maximized in order to produce high photocurrent — as well as a high operating voltage for the solar cell.

The present chapter discusses how to go about finding materials that maximize this figure of merit, starting from computational screening, and finally moving into
strategies for experimentally screening novel PV absorbers.¹

3.1 Perovskites and Re-Focusing Screening Criteria

The last decade has seen a growing interest in screening of new PV materials, both computationally and experimentally, with the goal of increasing the probability of discovering a promising PV material. These efforts have focused predominantly on the absorption coefficient,²⁺³ primarily for reasons of accessibility and expediency. However, many materials have met the criteria of high optical absorption, and have not yet achieved >10% solar conversion efficiencies, e.g., in the case of Cu₂ZnSn(S,Se)₄,²⁺⁶ SnS,²⁷ and others.²⁶Meanwhile, PV devices have emerged based on methyl-ammonium lead iodide (MAPbI₃) and closely related halides (herein referred to as MAPbX₃). MAPbI₃ is a semiconductor which has demonstrated exceptional minority carrier lifetimes over 280 ns²⁸ and diffusion lengths up to 175 µm,²⁹ comparable to the best single-crystal semiconductors. This, in addition to meeting the criteria of high optical absorption, has resulted in a dramatic realization of photovoltaic conversion efficiencies over 20%¹³ in 2015, from <4% in 2009.³⁰

This chapter examines whether the dramatic success of MAPbX₃ in PVs can be used as a basis to expand design criteria to identify new potential high-performance optoelectronic materials. One of the most compelling questions engendered by MAPbX₃ as an optoelectronic material is the degree to which it is unique, and whether its success can lead to the identification of materials with improved stability and lower toxicity, yet similar high performance. Clearly, as in previous design criteria the high optical absorption coefficient is important, but also essential are the long carrier diffusion lengths observed in MAPbX₃, enabled by high minority-carrier lifetimes and mobilities.

The importance of τ and μ for device performance, established in Chapter 2, has been known in the field for decades. Oddly, these transport parameters are

¹Sections 3.1-3.3 of this chapter are reproduced largely from a first-author manuscript, Ref. [23]; copyright 2015 MRS Communications.
not traditionally considered essential screening criteria for early-stage candidate PV materials. This may be partially a consequence of the difficulty in measuring and/or calculating these parameters. The direct measurement of minority carrier $\tau$ and $\mu$ requires ultrafast electronic or optical sensors to capture transients,[31][20][32] or strong steady-state signals,[33][34] and must be performed with PV-device-relevant illumination conditions, electrical fields, and transport directions. Calculating $\tau$ and $\mu$ from first principles is even more challenging, given the lack of well established and high-throughput methods to directly calculate electron-phonon interactions and/or trap capture cross sections. While it is possible to obtain some information about carrier mobility from effective masses, and maximum radiative lifetime from the band structure, these are known to be insufficient and can be misleading when point and structural defects limit these transport properties.[35]

### 3.1.1 Theoretical Learnings from the Perovskites

This thesis proposes that a deeper electronic structure theory, combined with recombination and transport models, can help identify the properties of MAPbX$_3$ that are likely to underpin the high experimentally observed $\tau$ and $\mu$. [23] Specifically, this revolves around their long non-radiative minority carrier lifetime, even in the presence of defects.

A “defect tolerant” material is expected to either (a) form relatively few intrinsic or structural defects under high-throughput, low-temperature processing conditions, and/or more importantly (b) the extrinsic, intrinsic, or structural defects that do form have a very minimal effect on $\tau$ and $\mu$. There are several models for how a material may achieve this defect tolerance, and in developing such a model we hope to find that this property is not unique to MAPbX$_3$, but rather shared with a broader class of compounds.

Many authors have proposed explanations for the success of MAPbX$_3$ as a photovoltaic material. These include its large absorption coefficient, long electron and hole diffusion lengths, low exciton binding energies, low effective masses and high mobilities, and the presence of only shallow defects in the bandgap.[28][36][37][38]
The existence of only shallow defects, and the disperse valence band, have both been tied to the presence of filled Pb 6s orbitals, deriving from the partial oxidation of Pb relative to its Pb$^{4+}$ oxidation state. This orbital character has been identified by several other authors, and explains both the shallow binding energy of defects and the atypical dependence of bandgap on strain or temperature in MAPbI$_3$.[39][40][41] This model for explaining the defect-tolerance and shallow defects has direct analogy to those developed earlier for CuInSe$_2$[42] and Cu$_3$N,[43] where instead the Cu$^+$ cation contributes Cu $3d$ states to the valence band.

In addition, device-level observations support the claims that MAPbI$_3$ has excellent transport properties, including the long carrier diffusion lengths previously mentioned. Low non-radiative minority carrier recombination rates are also supported by measurements of high photoluminescence quantum yield (PLQY),[44] long carrier lifetimes,[45] and the high $V_{OC}$ demonstrated by many devices. These properties are made more exceptional by the way in which MAPbI$_3$ is processed: low temperature solution processing results in equal or better performance to vacuum synthesis, which runs contrary to the higher purity, higher temperature, and more equipment-intensive fabrication strategies used to obtain high performance in conventional crystalline semiconductor materials.

These findings are substantiated by applying density functional theory (DFT) to MAPbI$_3$.$^2$ In the model pioneered by Zhang, Lany, Zakutayev et al,[42][43] defect tolerance emerges from having bonding orbitals at the conduction band minimum (CBM), and antibonding orbitals at the valence band maximum (VBM). This band structure is markedly different than that in most semiconductors, where the valence band is composed predominantly of bonding states, while the conduction band is composed of wavefunctions with dominant antibonding character. The defect tolerance that emerges from such an electronic structure is easily described using atomic vacancies as examples. Namely, if predominantly antibonding orbitals occur at the VBM and bonding at the CBM, the dangling (broken) bonds that are formed upon creating the vacancy (of any kind) will likely appear as resonances inside the bands.

$^2$DFT performed by collaborator, Vladan Stevanović.
leaving the bandgap free of deep states that could act as carrier traps. As shown in Fig. 3-1 for the valence band of MAPbI$_3$, this is a consequence of the position of valence atomic orbitals relative to the bonding and antibonding bands formed due to interactions. Analogous arguments are also valid for other types of intrinsic defects, such as interstitials and/or antisites, as well as for structural defects such as grain boundaries, which consist of many dangling bonds. Extrinsic impurities could, however, still introduce deep traps inside the bandgap depending on the position of their atomic orbitals relative to the energy bands of the host material.

These situations, in particular the antibonding character of the VBM, can frequently be found in metal-nonmetal systems with partially oxidized cations such as binary group-III halides or group-IV chalcogenides in 1:1 stoichiometry (e.g. TlBr, SnTe). Due to the partial oxidation of Pb, the MAPbI$_3$ compound also exhibits similar electronic structure features. As shown in Fig. 3-1, there are three types of interactions that contribute to the valence band in MAPbI$_3$. The first results from the overlap of Pb(6$p$)-I(5$p$) atomic orbitals leading to the creation of the deeper portion of the valence band, which is predominantly of I(5$p$) character, and the bottom part of the conduction band, which is composed mostly of Pb(6$p$) atomic orbitals. This interaction is responsible for chemical bonding as it implies charge transfer from the Pb(6$p$) to the I(5$p$) orbitals. In addition, Pb(6$s$)-I(5$p$) interaction leads to the creation of two bands: a deeper valence band (bonding), and the antibonding maximum of the valence band. Finally, only one of the I(5$p$) orbitals is oriented along the Pb-I bond, which is a favorable direction to interact with Pb(6$s$) and Pb(6$p$). The other two, oriented orthogonally, can only interact with the 5$p$ orbitals from other iodine atoms forming the middle of the valence band as shown in Fig. 3-1.

As a result of these interactions, the electronic bandgap is formed between the antibonding top of the valence band originating from the Pb(6$s$)-I(5$p$) interactions and the antibonding conduction band minimum resulting from the Pb(6$p$)-I(5$p$) interactions. Bonding-type defect-tolerance arguments can therefore only be applied to the defects that would tend to create valence band-derived states such as cation (Pb or MA) vacancies. On the other hand, if anion (iodine) vacancies form, the resulting
dangling bonds will appear as resonances inside the conduction band only if the band-width and the dispersion of the conduction band are such that the CBM falls well below the energy of the Pb(6p) atomic orbitals. In the case of Pb, contrary to Sn and Ge compounds for example, this condition is more likely due to relativistic[46] spin-orbit interaction effects that increase the width of the Pb(6p) conduction band by 2 eV based on our calculations. Thus, the fact that vacancy-type defects in MAPbI$_3$ are resonant in the bands is attributed to: (a) the presence of antibonding orbitals within the valence band that push the VBM energy up, and (b) relativistic effects which push the CBM energy down. In related work, some authors have suggested that the shallow nature of the anion vacancies in MAPbX$_3$ is related to the low anion coordination number of 2 — this leads to minimal hybridization between the two Pb 6p orbitals remaining.[47]

In summary, an emerging conclusion from both experimental measurements and first principles calculations is that MAPbX$_3$ benefits from an inherently defect-tolerant electronic structure. While these features are convenient for the methylammonium lead halide perovskite family, the critical question is whether they generalize to a broader subset of materials. To evaluate this, I will revisit models for transport in
the presence of defects.

3.2 Developing New Theoretical Design Criteria

3.2.1 Modeling Electronic Transport in the Presence of Defects

To provide physical context for the claims above, and to translate them into electronic structure design criteria, transport models in defective materials offer important insights: in particular, models for defect-limited $\tau$ and $\mu$. These are semiconductor models (distinct from the Langevin recombination model, which is inappropriate for MAPbI$_3$).[45]

Defect-limited, monomolecular, or trap-assisted non-radiative recombination, $U_{\text{SRH}}$, is modeled by Shockley-Read-Hall (SRH) recombination statistics:

$$U_{\text{SRH}} = \frac{np - n_i^2}{\tau_{0,h}(n + n_1) + \tau_{0,e}(p + p_1)},$$

(3.2)

where $n$, $p$, and $n_i$ are the electron, hole and intrinsic carrier concentrations, respectively.[48] The SRH recombination rate is inversely proportional to the SRH minority carrier lifetime, hence a promising PV absorber must minimize $U_{\text{SRH}}$. The low-injection electron and hole lifetimes $\tau_{0,e}$ and $\tau_{0,h}$, which in turn should be maximized, are:

$$\tau_{0,e} = \frac{1}{N_t \sigma_{t,e} v_{\text{th},e}}$$

(3.3)

$$\tau_{0,h} = \frac{1}{N_t \sigma_{t,h} v_{\text{th},h}}$$

(3.4)

where $N_t$ is the trap density, $\sigma_t$ is the capture cross section for electrons or holes, and $v_{\text{th}}$ is the drift velocity of carriers. At low injection conditions, the hole and electron lifetimes tend toward $\tau_h = \tau_{0,h}$ and $\tau_e = \tau_{0,e}$, respectively; at high injection conditions, both hole and electron lifetimes tend toward $\tau_h = \tau_e = \tau_{0,h} + \tau_{0,e}$, or the SRH lifetime. The terms $n_1$ and $p_1$ reflect the occupancy of trap states, where $E_t$
is the energy level of the trap state and $E_i$ the Fermi level in the intrinsic material (near mid-gap):

$$n_1 = n_i \exp \left( \frac{E_t - E_i}{k_B T} \right)$$  \hspace{1cm} (3.5)$$

$$p_1 = n_i \exp \left( \frac{E_i - E_t}{k_B T} \right).$$  \hspace{1cm} (3.6)$$

From this model, three conditions are necessary to limit SRH (trap-assisted) recombination: defect energy levels far from mid-gap, as these exponentially impact lifetime; low trap density $N_t$; and low capture cross-sections $\sigma$. Operating in high-injection conditions is helpful (where photogenerated carrier concentrations greatly exceed background doping densities), especially when strongly injection-dependent defects limit lifetime.

To give some perspective to the role of trap binding energy, one can plot the SRH-limited recombination rate, and therefore lifetime, as shown in Fig. 3-2. There are many assumptions implicit in this plot, but the general trends are representative.
As the trap energy moves from the band edge to the mid-gap, the effective lifetime drops by one order of magnitude for every 60 meV deeper into the bandgap the trap becomes. Eventually, the lifetime reaches a minimum, which is independent of the trap energy level. The point at which it reaches this level depends upon the doping density and the ratio of capture cross sections (assumed here to be 1). Asymmetric capture cross sections show more complicated behaviour. In a p-type material, defects with a higher electron capture cross section (than for holes) tend to be less detrimental when closer to the conduction band, while defects with a higher hole capture cross section are less detrimental when closer to the valence band, but generally have a lower impact in p-type materials.

$E_t$ and $N_t$ may be calculated from first principles, however this calculation is computationally expensive. They may be approximated by building models from more fundamental electronic properties, which themselves are accessible by high-throughput screening. The first, and most important property is the relative static permittivity, or dielectric constant $\varepsilon_r$. A higher dielectric constant indicates a greater ability to screen charge, and may arise from electronic or ionic contributions, as well as the methylammonium molecular dipoles in the lattice.[49]

This screening means that the capture cross-section of a charged defect will be influenced by the dielectric constant. Assuming a Coulombic model for capture cross section, a capture event will occur when the electrostatic potential energy from a charged defect exceeds the thermal energy, $k_B T$, which occurs at a specific radius,[50] therefore:

$$\sigma_t = \frac{q^4}{16\pi(\varepsilon_r\varepsilon_0 k_B T)^2}.$$  \hspace{1cm} (3.7)

where $q$ is the elementary charge (assuming here that the charge state of the defect, $Z$, is 1), and $\varepsilon_0$ is the vacuum permittivity. MAPbI$_3$ has demonstrated a large static dielectric constant of 60–70 or higher,[36] due to electronic, ionic, and molecular dipole contributions from the organic cation.[51] This charge screening is very beneficial, given the inverse square dependence of carrier capture cross-section, and in turn recombination rate, on the dielectric constant.
In addition, for a simple “hydrogenic” defect under Effective Mass Theory, the energy level of the defect sits deeper in the gap for lower dielectric constants,\cite{i} \( i.e. \) the binding energy of a donor relative to the conduction band, \( E_C \) is:

\[
E_t - E_C = \frac{m_e^*}{\epsilon_t^2} \frac{q^4}{2(4\pi \epsilon_0 \hbar)^2}
\]

(3.8)

where \( m_e^* \) is the effective mass of an electron, and \( \hbar \) is the reduced Planck constant. Similar charge screening behavior has been used to explain the low binding energy of excitons in MAPbI\textsubscript{3}\cite{ii} and shallow effective mass-like states.\cite{iii}

More important, however, is the energy level of non effective-mass like traps formed by vacancies and structural defects. As discussed above, band structures containing antibonding orbitals in the VBM, bonding in the CBM, and/or high dispersion within a band can lead to shallower defects, as defect energy levels are resonant with the conduction or valence bands. A second model proposed to explain the lack of deep trap states is that MAPbI\textsubscript{3} is more ionic than other semiconductors,\cite{iii} resulting in shallower or fewer defect states associated with dangling bonds. Analogous arguments have been made to explain defect tolerance in GaN\cite{iv} and (Cd,Zn)Te.\cite{v}

A third model suggests that the depth of the trap relates to the degree of hybridization between the orbitals left behind on the dangling bonds when an atom is removed. In this model, the low iodine coordination number (2) and large lattice constant of MAPbI\textsubscript{3} create minimal Pb 6\textit{p} hybridization between the two remaining Pb atoms at an iodine vacancy, resulting a shallow level.\cite{vi}

To summarize, the following electronic structure features likely enable MAPb\textsubscript{3} and other semiconductors to achieve longer SRH-limited minority carrier lifetimes:

- Shallow trap energy levels, or large \( |E_t - E_i| \)
- Low trap density, \( N_t \)
- Low trap capture cross section, \( \sigma_t \)
- Low charge state of defect, \( Zq \)
- High static dielectric constant, $\epsilon_r$
- Low band-effective masses, $m^*$
- Bonding character – antibonding orbitals at VBM, possibly high ionicity and low coordination number

The second critical transport property is the minority-carrier mobility, which is influenced by the effective masses of free carriers and by the frequency of scattering events. The lower the effective mass, or the more disperse the band edges, the higher the mobility. However, in typical polycrystalline materials at room temperature, the mobility will not reach this intrinsic limit due to several forms of scattering.

One way in which the mobility will be limited is by charged defect scattering, either at ionized impurities or grain boundaries. Again, a high dielectric constant reduces the spatial extent and the potential barrier of a charged defect, lowering its propensity to scatter free carriers. For ionized impurities, the mobility $\mu_{H,ii}$ is given by:

$$\mu_{H,ii} = r_{H,ii} \frac{128\sqrt{2\pi}(\epsilon_r\epsilon_0)^2 (k_B T)^{3/2}}{\sqrt{m^* N_i Z^2 q^3}} \left[ \ln(1 + b) - \frac{b}{1 - b} \right]^{-1}$$

(3.9)

where $r_{H,ii}$ is the Hall coefficient for ionized impurity scattering, $b = 24m^* k_B T / \hbar^2 \beta_S^2$, and $\beta_S$ is the inverse screening length.[55] Thus, to reduce the impact of ionized impurities on mobility, it is again ideal to have a high dielectric constant, low effective mass, and low trap density. Grain boundary scattering is also reduced for larger dielectric constants, and when the defect levels associated with grain boundaries become shallower.[56]

Alternatively, the mobility limit may come from phonon scattering. The phonon-limited mobility is generally smaller in softer materials, given their higher concentration of phonons at a given temperature. In Ref. [57], the bulk modulus, $B$, and phonon-limited mobility $\mu_{ph}$ were found to be correlated, where $A_0$ is a constant:

$$\mu_{ph} = A_0 B (m^*)^{-2.5}.$$  

(3.10)

MAPbI$_3$ is a relatively soft material, with a bulk modulus predicted to be 22.2 GPa.
for the cubic phase. This may explain why its mobility, measured around 10 cm$^2$/V/s, is not large relative to III-V and group IV semiconductors. Claims of “high” mobilities may be relative to dyes and organic absorber materials from which much of the perovskite PV work derived. Thus, similar to the absorption coefficient of MAPbI$_3$, its mobility is necessary but insufficient to explain its high performance.

To summarize, the following electronic structure features likely enable MAPb$_3$ and other semiconductors to achieve higher minority carrier mobilities:

- Low trap density, $N_t$
- Low charge state of defect, $Zq$
- High static dielectric constant, $\varepsilon_r$
- Low band-effective masses, $m^*$
- High bulk modulus, $B$

Finally, it is worth mentioning that beyond point and structural defects, a disordered crystal structure can limit the conversion efficiency by introducing defect states near the band edges (Urbach tail). MAPbI$_3$ demonstrates a very small Urbach tail energy. This may be due to its low melting temperature, such that the material develops more crystalline order at lower processing temperatures (higher homologous temperatures). In comparison, many III-V, II-VI, and unary group IV semiconductors require processing temperatures in excess of 800°C to achieve high crystalline quality.

Many properties have been discussed for screening high-performance, low cost PV absorbers in this and the preceding chapter. In Fig. 3-8, these different criteria are categorized. Given the critical importance of minority carrier transport properties, the present screening will focus specifically on electronic structure properties that have a direct impact on transport, highlighted in bold.
3.2.2 Toward Ideal Electronic Structure: The Importance of Partially Oxidized, Heavy Post-Transition Metals

Materials that contain a lone 6s² or 5s² pair of electrons (that do not participate in bonding) have the potential to share the high dielectric constant, low effective masses, and VB antibonding character that lead to defect-tolerant transport properties. As a broad class, these are compounds formed from partially oxidized post-transition metals including In, Sn, Sb, Tl, Pb, and Bi. In the case of MAPbI₃, the partially oxidized Pb atom in its Pb²⁺ charge state lends these beneficial properties due to a large, polarizable cation leads to high Born effective charge and therefore large dielectric constants,[41] as well as a conduction band with greater bandwidth due to spin-orbit coupling, while filled 6s orbitals lead to a disperse valence band (low effective mass)[38] and antibonding orbital character in the valence band maximum.

Other partially oxidized post-transition metals including In⁺, Sn²⁺, Sb³⁺, Tl⁺, Pb²⁺, and Bi³⁺ share these properties, and are present in a wide variety of materials. This N – 2 oxidation state is more commonly observed for compounds of Tl, Pb, and Bi, due to relativistic effects leading to tighter binding of the remaining s elec-
Table 3.1: Sns and related materials’ properties

<table>
<thead>
<tr>
<th>Formula</th>
<th>CaS</th>
<th>SnS</th>
<th>SnS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>Ca²⁺</td>
<td>Sn²⁺</td>
<td>Sn⁴⁺</td>
</tr>
<tr>
<td>Bandgap [eV]</td>
<td>4</td>
<td>1.1</td>
<td>2.3</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>5-7</td>
<td>32-48</td>
<td>17-20</td>
</tr>
</tbody>
</table>

trons; however, lighter cations may also be stabilized in these oxidation states. Given their many beneficial properties, these cations appear increasingly in many optoelectronic applications: PbS and lead halide perovskites in PV; TlBr, PbI₂, and BiI₃ in X-ray detectors and scintillators; Sn²⁺-based TCOs; Pb and Bi-based ferroelectrics, photoferroelectrics, piezoelectrics, and thermoelectrics. For the thallous halides, analogous 6s²6p⁰ orbital explanations for low effective mass, antibonding VBM states, and a high dielectric constant were offered several years before similar work on MAPbX₃.

As an example to illustrate the effect such a cation has on electronic properties, consider the family of sulfides related to tin monosulfide, SnS. In Table 3.1, it is clear that the partially oxidized Sn cation offers a smaller bandgap and higher dielectric constant relative to its smaller, fully oxidized 4+ charge state. The presence of Sn 5s orbitals in the valence band also helps to reduce the bandgap by producing a broader valence band. In a more extreme example, the equivalently sized Ca²⁺ cation produces a material with a larger bandgap and lower dielectric constant, thanks to reduced covalent bonding and reduced polarizability of the cation.

Given the promising properties exhibited by materials in this class, the next question is how to spot these materials and identify their promise for PV applications, using properties which are easily computable from first principles. There are multiple signatures of this bonding behaviour that could lend clues. One is to look directly for the presence of antibonding orbitals with cation s-character at the top of the valence band. Another could be to look for the high Born effective charge of the cation, indicative of a potentially high dielectric constant. A third approach could be to use the unique property of the band structure in these materials — because of the pres-
Figure 3-4: Several conventional semiconductors compared with Pb-based semiconductors, which show opposite trends of bandgap with respect to temperature (and with respect to pressure). Conventional materials show a decrease in bandgap upon heating, while the Pb perovskites and other Pb compounds show the opposite.\cite{65}\cite{66}\cite{67}\cite{68}

ence of antibonding orbitals at the VBM, Pauli repulsion forces the valence bands to become more disperse as the lattice is compressed. This overcomes the usual increase in the bandgap due to a similar Pauli repulsion, and results in an anomalous negative pressure coefficient or positive temperature coefficient to the bandgap. This can be seen in Fig. 3-4.

3.2.3 Importance of Optical Absorption and Radiative Lifetime

Returning to the original figure of merit proposed, it is clear that optical absorption also plays an important role. Achieving a high optical absorption coefficient requires a strong coupling between valence band and conduction band states, or a high optical transition matrix element. This is most likely to occur in a direct-bandgap material, with a high density of states at both band edges, and a strong degree of coupling
between these states.

The MAPbI$_3$ perovskites exhibit several of these properties — including a direct gap, and the fact that the valence-band to conduction band-transition could occur between Pb 6s and Pb 6p orbitals, in other words on the same atom. This coupling could be responsible for a larger optical absorption coefficient. Typically, having a high band edge density of states might imply having flat bands and relatively high carrier effective masses as a result, which falls in direct conflict with the earlier assertion that low band effective masses are critical. However, a material may simultaneously achieve high density of states at the band edges and disperse band edges with low effective masses, as long as there is a high band degeneracy. In other words, having multiple disperse bands implies efficient carrier transport, but more states to allow for more probable optical transitions. This combination of properties may help lead to strong absorption in MAPbI$_3$, though this absorption is still not exceptional relative to other semiconductors.

An unfortunate consequence of having a direct bandgap and high optical absorption means that the inverse process of radiative recombination is also more efficient. Thus, a highly absorptive material may be expected to have a shorter radiative minority carrier lifetime. This may appear in direct conflict with the figure of merit above, but remember that an electron-hole pair that recombines radiatively produces a photon, which may be reabsorbed. Radiative recombination like this need not be detrimental to solar cell performance. In fact, the maximum achievable $V_{OC}$ is limited to

$$ V_{OC,rad} - k_B T \ln\left(\frac{U_{rad}}{U_{rad} + U_{SRH}}\right) $$

or the ratio of radiative recombination rate to total recombination rate.$[69]$ By enhancing the radiative recombination rate relative to the SRH term (achieving a shorter radiative lifetime), one may improve solar cell performance. In that way, a highly absorptive material may gain an additional advantage.
3.3 Mining Materials Databases

Screening for novel, promising PV absorbers requires multiple steps, the first of which is a broad computational search to narrow down the field of materials.

To identify promising materials with the electronic structure proposed above, I developed a script to search through all materials in the Materials Project.org (MP) database.[70] This is implemented using the Materials Project API and the pymatgen library, to access information on calculated crystal and electronic structure for all compounds in the database.[71] This search examines approximately 27,000 non-metallic inorganic compounds with full band structures calculated, and extracts information on crystallographic point group, stability, band structure, and in particular the fractional density of states by element and orbital. To screen for the properties described above, one can calculate the $s$-orbital fraction in the top 1 eV of the valence band density of states. This metric is a rough filter, and may mistakenly identify materials with band-inversion, as well as many metal hydrides and Au-anion compounds, wherein the anion species contributes a filled $s$ orbital at the valence band edge. However, it offers a starting point for filtering a large number of materials down.

In Fig. 3-5, a random subset of the materials from this broad search are plotted. Note the stark differences in VBM DOS character for different classes of materials. Conventional tetrahedrally coordinated III-V and II-VI compounds all demonstrate almost exclusive $p$-orbital character at the VBM, as do the majority of compounds. Other defect tolerant Cu-chalcogenide semiconductors, such as CuInSe$_2$, demonstrate a large $d$-orbital character in the valence band due to full 3$d$ cation orbitals. Meanwhile, the inorganic I-II-VII$_3$ family of perovskites sit along the bottom axis, reflecting their larger $s$-orbital fraction in the valence band DOS. However, they are not unique in this property.

In addition, a random fraction (30%) of the Materials Project Sn-cation compounds are plotted on these axes as well, separating them by those with Sn$^{2+}$ and Sn$^{4+}$ cations. The Sn$^{2+}$ cation-compounds cluster in the same region as the halide perovskites, whereas Sn$^{4+}$ compounds resemble the vast majority of semiconductors.
with anion $p$-orbital or transition metal cation $d$-orbital character.

The same trends are observed when splitting the other post-transition metal cations by their oxidation states. In Fig. 3-6, In, Sn, Sb, Tl, Pb, and Bi compounds are all plotted. There are several trends that these plots make apparent. Firstly, the frequency of partial oxidation state relative to the full oxidation state increases between row 5 and row 6 of the periodic table, and generally increases from group III to group V. The heavier row 6 nuclei tend to bind their $s$ electrons more strongly due to relativistic effects, increasing the energy associated with removing these two additional electrons. For Bi, with the most strongly bound $s$ electrons, only F and O are electronegative enough to produce the Bi$^{5+}$ oxidation state. For a similar reason, the degree of cation $s$ orbital mixing in the valence band also shifts across these six cations. As the lone pair of $s$ electrons become deeper in energy, they hybridize less with the anion $p$ orbitals. For In and Sn, with more weakly bound $s$ electrons, there is a strong degree of orbital hybridization and a large presence of cation $s$ orbitals at the VBM.
Figure 3-6: Ternary plots demonstrating the partial density of states of the valence band maximum by orbital type, for partially and fully oxidized cations. At left, row 5 cations In, Sn, and Sb. At right, row 6 cations Tl, Pb, and Bi.
Finding good candidate semiconductors with the $N - 2$ oxidation state is not straightforward, for several reasons. Firstly, the use of more electronegative anions (oxygen, fluorine, and chlorine) tends to fully oxidize these cations. By pairing them with sulfur, selenium, iodine, and bromine, or by including a less electronegative cation such as an alkali metal, it is possible to stabilize the lower oxidation state. Secondly, the lone $s$ orbitals are often stereochemically active,[72] leading to lower symmetry point groups, and a higher likelihood of indirect gaps. Lower symmetry in the crystal structure appears to be correlated with lower symmetry in the electronic structure, including flatter, less disperse valence bands and indirect bandgaps. This trend is demonstrated by Fig. 3-7. All 27,000 compounds screened from MaterialsProject are classified by the 32 distinct point groups for crystals, each of which can be characterized by the number of symmetry operations available to it (rotation, translation, inversion). For example, for Sn compounds from the Materials Project database, only 29% of those with Sn$^{2+}$ are found to have direct band gaps, whereas for Sn$^{4+}$, 47% have direct band gaps. Anisotropic crystal structures may also lead to anisotropic transport properties and surface potentials,[73] which may adversely influence device performance. Lastly, these cations may convert to the higher oxidation states inadvertently, when exposed to oxidizers such as oxygen or moisture. In CsSnI$_3$ and MASnI$_3$, this Sn$^{4+}$ formation results in metallic behavior with very high carrier concentrations.[74]

Lastly, note that all of the materials identified in the MaterialsProject.org search are inorganic, yet the asymmetric, molecular cations such as methylammonium play an important role in achieving large dielectric constants in the hybrid perovskites. Converting the inorganic materials identified herein into hybrid organic-inorganic analogues could lead to improved defect tolerance, but the presence of MA or other molecular cations is not expected to be the most important criteria in achieving defect-tolerance.
Figure 3-7: Scatter plot of the frequency of direct bandgap transitions for all 32 different crystal symmetry point groups, plotted by their number of symmetry operations (higher number of operations means more symmetry, with cubic point groups being the highest).

### 3.3.1 Materials Classes Identified

By filtering the materials data drawn from the Materials Project database, several interesting classes of materials emerge. The search first identifies the class of halide perovskites (CsPbI$_3$, CsSnI$_3$, RbPbBr$_3$, etc.); prior optoelectronic screening efforts had not identified these as promising materials.

Pb and Tl-containing compounds are excluded based on toxicity, however there are many promising optoelectronic materials containing these atoms. Unfortunately, the beneficial properties of Pb$^{2+}$ and Tl$^+$ are also connected to their toxicity, as they mimic the large ionic sizes of Ca$^{2+}$ and K$^+$ in the human body. This excludes the binary lead and thallium halides and chalcogenides such as TlBr, as well as a number of ternary chalcohalides or chalcogenides such as TlBiS$_2$.

In addition, this search is limited to materials existing in the MaterialsProject.org database. New materials may be discovered or designed using the present framework, for example the recently discovered Bi$_2$FeCrO$_6$ perovskite,[75] or the double perovskite Cs$_2$AgBiBr$_6$,[76] which have shown promising PV potential. This screening effort
strongly focused on one particular characteristic available: the valence band electronic structure. As our understanding of what makes a good PV absorber grows over time, such a search could be performed again with new intelligence, in the hopes of discovering a promising material.

The following classes of materials are considered for further experimental study:

1. Binary chalcogenides and halides (BiI$_3$, Bi$_2$S$_3$, SbI$_3$, Sb$_2$S$_3$, SnI$_2$, InI, etc.). In addition, polymorphs or alloys of these materials stabilized in cubic structures such as NaCl or CsCl.

2. Chalcohalides (BiOI, BiSI, BiSeI, SbSI, SbSeI, BiSBr, BiSeBr, etc.).

3. Ternary alkali chalcogenides (LiBiS$_2$, NaBiS$_2$ KBiS$_2$, RbBiS$_2$, CsBiS$_2$, etc.), which form rocksalt or related structures.

4. Ternary halides: (In$_3$SnI$_5$, InAlI$_4$, etc.), encompassing a variety of different crystal structures.

5. In$^{+}$-II-VI$_3$ ternary halides (CdInBr$_3$, CaInBr$_3$, etc.).

6. Octahedrally coordinated metal halides (Cs$_3$Bi$_2$I$_9$, Rb$_3$Bi$_2$I$_9$, K$_3$Bi$_2$I$_9$, Cs$_3$Sb$_2$I$_9$, etc.).

7. Cs-containing compounds, substituting 1+ molecular cations [e.g., (MA)$_3$Bi$_2$I$_9$, (FA)$_3$Bi$_2$I$_9$]. The inorganic compounds above could be converted to hybrid materials by the substitution of the Cs with an alkylammonium or other molecular cation.

In Ref. [23], more detailed DFT calculations with spin-orbit (SO) coupling are performed on many of these materials to explore them in more detail, and several additional conclusions emerge. First, many of these materials are relatively ionic, like MAPbI$_3$. Second, anisotropic crystal structures with stereochemically active lone pairs do appear to lead to higher hole effective masses. Third, most of the materials

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$^3$DFT calculations performed by Vladan Stevanović.
presented here demonstrate large ionic dielectric constants, independent of whether they have a polar space group. Finally, compounds formed with $6p$ block cations show a significantly larger contribution of SO coupling in the conduction band, versus those formed from the $5p$ block. While Pb and Tl compounds are not included here, the Bi compounds show a much stronger SO contribution than do the In, Sn, and Sb compounds. This may suggest that the Bi-containing compounds are most suitable for achieving similarly shallow anion vacancy levels as in MAPbI$_3$.

It is clear that MAPbI$_3$ offers an unusual mix of ionicity, high dielectric constant, low effective masses, and a lower band gap for PV; few semiconductors can claim excellent performance across all categories. To see if any such materials may be identified from the list above, it is necessary to experimentally screen them in more detail.

3.4 Experimental Screening Methods

As mentioned previously, the theoretical design criteria established here are only a first filter to reduce the subset of materials of interest for PV. Many of these materials may not achieve promising minority carrier transport properties, which necessitates performing proper experimental characterization of the materials to fully screen them. In Fig. 3-8, the series of screening steps is outlined. By combining the high-throughput, but less thorough nature of computational screening with the more thorough but time intensive experimental characterization, we can potentially capture the advantages of both approaches.

3.4.1 Material Fabrication

The first step, and perhaps most challenging, is materials synthesis. To synthesize materials quickly and with high quality is important, yet few growth techniques offer both of these features. Molecular beam epitaxy and chemical vapor deposition can offer high-quality phase-pure materials, but it is time intensive to build a separate tool and optimize the process for each material, and cross-contamination is always a
Figure 3-8: Flowchart reflecting the combined theoretical and experimental screening approach, which begins with identified a promising subset material and then focusing on achieving the desired phase and evaluating its minority carrier lifetime as swiftly as possible — without sacrificing accuracy.

risk. Faster deposition techniques like sputtering and thermal evaporation are more convenient but can produce less homogeneous materials and again suffer from the potential for cross-contamination between materials in different growth runs.

To address this challenge, three particular growth techniques were chosen for the synthesis: physical vapor transport (PVT) or sublimation in a tube furnace, solution processing by spin coating, and growth of single crystals from the melt. Together these techniques offer:

- High throughput — in the case of spin coating, dozens of unique samples can be fabricated per hour, and PVT can achieve thin-film depositions in approximately one hour. In the case of PVT and melt synthesis, it is relatively easy to select precursors and processing conditions based on phase diagrams, as distinct from the lengthy precursor development process of reactive synthesis techniques.

- High purity — In all three techniques, the growth environment consists of relatively cheap, disposable parts such as quartz tubes for PVT and bulk crystal growth. This allows for interchanging of parts between different materials and reduces cross-contamination, which is often prohibitively expensive in vacuum growth systems.

- Low structural defect densities — Growth from the melt can allow formation of
relatively large grains and low structural defect densities. For thin-films, spin coating can use the presence of a solvent effectively to increase the diffusivity of species during film formation, beyond the solid state diffusivity that would exist at those temperatures. This can allow for forming relatively crystalline films at temperatures below $100^\circ C$.

- Multiple form factors — for different characterization techniques, it is advantageous to be able to characterize single crystals and powders formed thereof; for other techniques and for devices, thin-films are more appropriate.

Fig. 3-9 illustrates the three general growth systems used for the materials presented in this chapter. The following growth techniques appear in Ref. [77] and Ref. [78] in more detail.\(^4\)

\(^4\)Robert Hoye and Rachel Kurchin assisted with the growth of MBI and BiI$_3$, respectively.
For all thin films, substrates of glass, quartz, and silicon/silicon dioxide were sequentially cleaned ultrasonically in deionized water, acetone, ethanol and isopropanol for 5 min at 50°C. For spin-coated films, the substrates were subsequently oxygen plasma cleaned for 5–10 min at -90 kPa (gauge).

Bismuth triiodide is grown by all three techniques. For PVT, BiI$_3$ powder (Alfa Aesar, 99.999% metals basis) is placed in a quartz crucible at the center of the hot zone of a quartz tube furnace. The hot zone is a 12" section of a 2"-diameter quartz tube. The furnace is evacuated to a base pressure of <10 mTorr. During deposition, inert nitrogen gas flows through the furnace at a flow rate of 10 mL/min, resulting in an operating pressure of 1.3–1.7 Torr. Substrates are placed downstream in the tube furnace at the end of the single hot zone; for the source temperature of 280°C used here, substrate temperatures range from 60–200°C. Films are deposited on bare quartz, soda lime glass, or on glass coated with a 200nm of Au, with similar morphologies achieved for each. The leading edge of the substrates experiences both the highest temperature and fastest growth rate, thus the films are thicker for hotter substrate temperatures, while the coolest substrate region produces very thin films.

For solution-processed films, 100 mg of BiI$_3$ powder (99.999% purity from Alfa Aesar) is dissolved in 0.25 mL anhydrous N,N-dimethylformamide (DMF, from Sigma-Aldrich). The solution is filtered through 0.45 µm PTFE filters, producing a translucent orange liquid (cloudy before filtering). 10 µL of the saturated solution are spun onto glass or quartz substrates in a N$_2$ glove box at room temperature. After spinning at 3500 RPM for 35 seconds, the films are dried at room temperature for over an hour, producing a black film.[77]

Methylammonium bismuth iodide (MBI) is grown beginning with the aforementioned technique for spin coating of BiI$_3$. The film is annealed at 100°C. It is converted to MBI by two approaches: first, by reacting with MAI solution in isopropanol to intercalate with MA and I, followed by a final drying step at 100°C. The second method for converting to MBI is vapor-assisted hot-casting (VAHC), this method involves spin-casting BiI$_3$ in solution on a substrate heated to 150°C (instead of room temperature) and converting to MBI by reacting with MAI vapour (instead of in so-
olution). For this, the film was suspended over MAI powder and heated at 150°C for four hours under vacuum (-100 kPa gauge pressure). This was cooled to room temperature before taking out of the oven and cleaning with anhydrous isopropanol. The MBI film was then annealed at 100°C for one hour inside a nitrogen-filled glovebox.

Indium monoiodide (InI) was fabricated by two different techniques. First, thin films of InI were produced by spin coating. Anhydrous InI pellets (99.999% pure, Sigma Aldrich) were dissolved at a concentration of 200–400 mg/mL in DMF and dimethyl sulfoxide. To encourage dissolution, the solvent was heated to 70°C overnight. In DMF, this produced a bright yellow liquid with In metal collected at the bottom; dissolved in DMSO instead, the solvent reacted with the solute and produced a white solid, most likely In$_2$S$_3$. The DMF solution is filtered through 0.45µm PTFE filters, and 20µL of the solution are spun onto glass or quartz substrates in a N$_2$ glove box at room temperature. After spinning at 2000–3000 RPM for 35 seconds, the films are annealed at 50°C, producing a dark, milky red film. Phase analysis suggests that the material produced is a mixture of InI and InI$_3$, indicating that the In$^+$ disproportionates into In metal and In$^{3+}$ in solution, resulting in a low fractional phase content of InI.

Instead, an alternative growth technique from the melt was used for InI. 0.2 g each of indium metal (99.995% pure) and iodine pellets were measured out and placed into a clean quartz ampule. The ends were sealed with a torch while the tube was filled with an argon atmosphere of approximately 2 Torr (to eliminate reactive oxygen and water vapor from the growth environment). This sealed ampoule was placed at a 10° angle into a larger horizontal tube furnace wrapped with heater tape and insulation. A K-type thermocouple was inserted into the center of the tube furnace, to monitor the internal temperature. The In-I mixture was then heated to 400°C over a period of 12 hours, during which the In and I melt and react to form InI, which itself melts at 351°C. The melt was held at 400°C for 12 hours to ensure a complete reaction, and then was cooled at a rate of 8°C/hour for 48 hours. 0.4 g bulk polycrystals grow in the bottom of the ampoule, and are removed and cleaved for characterization of
a fresh surface on the inside of the crystal. In the present work, three crystals were
grown under identical processing conditions, but with three In-I compositions in the
melt: 49%/51% In-rich and In-poor samples, and one 50%/50% composition.

Single crystals of SbSI, SbSeI, and BiI$_3$ are grown by a modified Bridgman-
Stockbarger growth from the melt. Details for the synthesis of these compounds
are provided in the literature.[77] [79]

3.4.2 Phase and Morphology Characterization

Phase identification is performed primarily through X-ray diffraction (XRD), which
identifies lattice positions based on the diffraction of X-rays by the periodic lattice
planes at different angles. This is the fastest technique for the experimental feedback
loop described above. Diffraction measurements are performed with multiple tools
depending upon the need. For fast scans and quick phase identification, a Bruker
GADDS tool is used. For performing Rietveld refinement of the crystal structure
based on diffraction peak positions and intensities, a Rigaku SmartLab was used for
grazing incidence XRD using Cu $K\alpha$ radiation (1.5406 Å wavelength) at an incident
angle of 0.5°.

Powder X-ray diffraction was performed with a PANalytical X’Pert PRO XRPD
instrument using Cu $K\alpha$ radiation (1.5406 Å wavelength). Powder samples were
mounted onto off-cut silicon (PANalytical, miscut from (510) plane), which introduces
no background to the diffraction pattern.$^5$

To characterize stoichiometry, X-ray fluorescence (XRF), Rutherford back-scattering
(RBS), and X-ray photoelectron spectroscopy (XPS) were used; details can be found
in Ref. [78].

Film micrographs are performed using multiple tools. For more insulating sam-
ples, or thin films on insulating substrates, micrographs were performed with a Zeiss
ORION He-ion microscope using an electron flood gun to offset charging. For more
conductive thin films, a Zeiss SUPRA 55VP Scanning Electron Microscope (SEM)
was used.

$^5$Grazing incidence and powder XRD were performed by Robert Hoye and Rachel Kurchin.
3.4.3 Optical Characterization

Optical absorption measurements were performed using a PerkinElmer Lambda 950 UV-VIS-NIR spectrophotometer. The samples were mounted on the front or back plane of an integrating sphere, after the instrument was calibrated with 0% and 100% reflectance and transmittance standards before measuring the samples. Substrate absorptance was also measured and subtracted out.

To compute the optical absorption coefficient as a function of wavelength, the transmittance ($T$) and reflectance ($R$) of the film are measured. Knowing the film thickness, the absorption coefficient can be inferred with the following equation:

$$\alpha = \frac{-\ln(T/(1-R))}{d} \quad (3.11)$$

3.4.4 Photoluminescence Measurements

Steady-state, spectral photoluminescence (PL) measurements are performed using two different tools. The first is a FluoroMax-3 (Horiba Scientific), typically using an excitation wavelength of 360 nm, slit size of 5 nm for the incident beam and detector and longpass filters in front of the detector. The second tool is a Horiba LabRAM HR Evolution Raman spectrometer. Typically this tool uses a 532 nm wavelength excitation laser with an intensity of 20 µW.

To measure time-resolved photoluminescence, a technique called time-correlated single photon counting (TCSPC) is used. In this apparatus, photoluminescence is detected based on the arrival time of a single photon after the excitation pulse. By repeatedly pulsing the laser and measuring arrival times, a histogram of arrival times can be used to build a picture of the transient decay of photoluminescence. A 532 nm wavelength laser (PicoQuant LDH-P-FA-530B) is used to excited the sample with a train of excitation pulses at a frequency of 2.5 MHz. Each pulse has a FWHM of 80 ps, but a longer exponential tail (approximately 200 ps).

The emission from the film was collected using reflective optics and directed to

---

6Jeremy Poindexter, Lea Nienhaus, and Mark Wilson assisted with collecting TCSPC data.
a single-photon-sensitive avalanche photodiode (SPAD) with 30 ps time resolution (Micro Photon Devices $PD-100-C0C$). Dielectric filters (Chroma Technology Corp. and ThorLabs) were used to remove scattered light from the primary excitation pulse. Photon arrivals were correlated with the excitation pulse using a PicoQuant PicoHarp 300. To avoid inaccuracies due to pile-up, the excitation intensity was varied as necessary to ensure that the probability of detecting a photon during a single excitation cycle was below five percent.

The power was tuned from 1 nW up to 30 µW to evaluate the fluence-dependence of the TCSPC decay. Over this range of incident laser powers, it is possible to calculate the injection level relative to 1-sun. Assuming a laser pulse rate of 2.5 MHz and pulse width of 80 ps, a photon energy of 2.33 eV (532 nm), and spot size of 200 microns in diameter, the pulse photon fluence would range from $8 \times 10^7$ – $2.4 \times 10^{11}$ photons/cm$^2$/pulse over the power range tested. Given that the 1-sun generation rate in a material with a 1.8 eV bandgap should be around $10^{21}$ cm$^{-3}$/s, a material with a lifetime of 100 ns would have a steady-state 1-sun injection level of $10^{14}$ cm$^{-3}$. For an absorption depth of 100 nm, this means that 1-sun injection corresponds to roughly 100 nW for the laser power.

### 3.5 Case Study: Bismuth Triiodide

The first material screened through these techniques was bismuth triiodide (BiI$_3$). BiI$_3$ has a long history of study in X-ray detectors,[80][81] given its high density and high atomic number of constituent elements, few competing phases in the Bi-I system,[81] wide bandgap of 1.67 eV,[82] large static dielectric constant (albeit anisotropic),[83] and an electron mobility that has been measured as high as 260±50 cm$^2$/V/s or 1000±200 cm$^2$/V/s with Sb-doping.[81][84] The hole mobility is expected to be much lower due to the difference in carrier effective masses; previously we calculated the hole and electron effective masses in the BiI$_3$ R$\bar{3}$ phase to be 10.39

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7 This section is reproduced in large part from a first-author manuscript, Ref. [77]; copyright 2015 American Chemical Society.
Figure 3-10: Crystal structure and electronic structure of BiI$_3$ (R$\bar{3}$): (a) Four unit cells showing the octahedrally coordinated Bi atoms; (b) a single layer plane showing 1/3 vacant cation sites; (c) dispersion relation showing energy vs. momentum throughout the Brillouin zone; (d) partial density of states by atomic orbital. Reproduced from Ref. [77]; copyright 2015 ACS.

and 1.85, respectively.[23] Electron mobility-lifetime products of $1.4 \times 10^{-6}$ cm$^2$/V and $9.5 \times 10^{-6}$ cm$^2$/V have been reported,[80][85] corresponding to electron diffusion lengths of 1.9 microns or 4.9 microns, respectively. These diffusion lengths are on the order of the thickness of typical thin-film solar cells, suggesting that the electronic properties of BiI$_3$ may enable PV performance. A high resistivity up to $10^8 - 10^9$ ohm-cm [81][85] suggests that the material may require extrinsic doping or a high photoinduced carrier concentration (high injection) to achieve reasonable conductivity and low series resistance.

The crystal structure of BiI$_3$ is a layered, 2D structure built from BiI$_6$ octahedra and related to the CdI$_2$ crystal structure with 2/3 of cation sites occupied. As a result, the central Bi atoms are symmetrically coordinated by six iodine atoms, and the lone pair of electrons on the Bi$^{3+}$ cation are not stereochemically active. The crystal structure (space group R$\bar{3}$) is shown in Fig. 3-10(a), demonstrating the stacked layer planes. In Fig. 3-10(b), a single layer plane is shown, highlighting the vacant cation sites.

The electronic structure of BiI$_3$ in this phase is calculated from first principles.
by our collaborators (V. Stevanović) using density functional theory (DFT). Incorporating spin-orbit coupling, he computes the indirect bandgap of BiI$_3$ (R$\bar{3}$) to be 1.73 eV (2.51 eV without spin-orbit interactions), which agrees well with earlier DFT results.[82] In Fig. 3-10(d), the fractional density of states in the valence and conduction bands are plotted together, with the anion contributions and cation contributions on the positive and negative $y$-axes, respectively. Similar to MAPbI$_3$, the partially oxidized Bi$^{3+}$ cation contributes antibonding $6s$ character to the top of the valence band. In addition, spin-orbit coupling along with the large atomic weight of the Bi$^{3+}$ cation leads to a more disperse conduction band and lower electron effective mass, as compared to DFT calculations minus spin-orbit coupling, or as compared to the isostructural, lighter SbI$_3$ compound. The computed dispersion relation for this material is plotted in Fig. 3-10(c), showing the indirect bandgap with a direct optical transition slightly higher in energy.

To evaluate the potential of BiI$_3$ as a photovoltaic absorber, it is critical to grow a phase-pure material. Thin films are grown using an open-flow PVT or sublimation furnace over a range of substrate temperatures, and by solution processing via spin-coating (see Experimental Methods section above). Collaborators at the University of Florida (J.C. Nino) grow single crystals by a modified vertical Bridgman method using electrodynamc gradient techniques. Fig. 3-11 plots the XRD spectra for PVT and solution processed films (grown on gold to avoid amorphous background and overlapping crystalline peaks), as well as micrographs shown for different regions. As the substrate temperature of PVT BiI$_3$ increases, the preferred orientation of the BiI$_3$ layer planes moves from perpendicular to parallel to the substrate, resulting in a different morphology (as noted previously[86]). At the lowest PVT substrate temperature, the film is very thin (due to the single zone furnace design, in which growth occurs via a thermal gradient) and shows minimal long-range order, hence its XRD pattern is dominated by the peaks of the Au substrate. The morphology of films on Au or glass substrates are very similar.

Assuming an indirect bandgap, in Fig. 3-12(a) the Tauc method is used to fit a linear absorption edge in a plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$. Finding the intersection of this
edge with sub-bandgap absorption, the bandgap is found to be 1.79±0.05 eV and 1.80±0.05 eV for the PVT and solution-processed films respectively. Given the high absorption of BiI$_3$ above 2 eV, the absorption saturates and results in an underestimate of the absorption coefficient. However prior literature suggests that it exceeds $10^5$ cm$^{-1}$ above 2 eV.[82] Use of a thinner film or spectroscopic ellipsometry would allow for a more accurate determination of $\alpha$. In addition, the high absorption below the bandgap suggests that the present material may have a secondary phase (e.g., Bi metal) resulting in broadband sub-bandgap absorption. The non-monotonic rise in sub-bandgap absorption is a result of optical interference fringes.

Next, room-temperature spectrally-resolved PL reveals that BiI$_3$ thin films and single crystals luminesce at room temperature. Using a pump wavelength of 532 nm, PL peaks are observed centered between 1.76–1.83 eV. This data is plotted in Fig. 3-12. The samples show a clear band-edge PL peak above the substrate emission and above background, suggesting that time-resolved PL can be used to quantify the recombination kinetics.

Finally, the carrier recombination lifetime may be measuring by time-resolved photoluminescence using TCSPC. In Fig. 3-13, a 532 nm wavelength laser is used to excite the sample. Because the instrument response function (IRF) of the TCSPC
Figure 3-12: (a) Tauc plot of absorption coefficient calculated from PVT and solution processed BiI$_3$, where $(\alpha h\nu)^{1/2}$ is linearly extrapolated to the band edge assuming an indirect gap; (b) normalized photoluminescence spectra for both types of thin films and the single crystal. PVT films measured here were deposited at a substrate temperature of 110 ± 10°C, though the bandgap is found to be independent of growth temperature. Reproduced from Ref. [77]; copyright 2015 ACS.
technique is on the same timescale as the time-resolved photoluminescence decay, the former must be decoupled from the latter to extract a carrier lifetime.[87] First, the IRF is convolved with a monoexponential decay function. Then, this function is fit using a least-squares method to the TCSPC data. The effective lifetimes are found to be within the range of 180 ps and 190 ps for the PVT and solution-processed films, respectively. The single crystal sample shows biexponential decay with time scales of 160 ps and 1.3 ns. Given the fact that BiI$_3$ is reported to be intrinsic (majority carrier type unknown), this recombination lifetime may reflect the sum of electron and hole lifetimes. The monoexponential decay times of the thin films may be strongly limited by surface recombination, so these may be lower bounds on the bulk Shockley-Read-Hall lifetime. In the single crystal sample, the initial fast decay is expected to be indicative of surface recombination, while the longer component may indicate bulk recombination — more rigorous modeling is still in progress.

After performing the complete synthesis and characterization loop on BiI$_3$, it is worth revisiting whether the material shows compelling properties for PV applications. First, its bandgap of approximately 1.8 eV is well positioned for use as a top cell material in a multi-junction solar cell, as this represents a near-ideal bandgap

Figure 3-13: TCSPC decay curves for IRF, thin film PVT ($T_{\text{growth}} = 110 \pm 10^\circ\text{C}$), solution processed, and single crystal BiI$_3$. Fitted raw data is shown in (a). In (b), the data has been fit by convolution with the instrument response function. Thin-film samples are fit with monoexponential decays, while the single crystal data is fit with a biexponential model; time constants shown inset. Reproduced from Ref. [77]; copyright 2015 ACS.
to be paired with silicon as the bottom cell.\textsuperscript{88} Furthermore, BiI\textsubscript{3} demonstrates an absorption coefficient $>10^5$ cm$^{-1}$ in the visible region of the solar spectrum, suggesting the possibility to obtain high photocurrents with a film $<1$ micron thick, even without light-trapping designs.

However, not all of its properties are compelling for PV applications. Some of these may be resolved through further materials development, and some may be intrinsic to BiI\textsubscript{3}. First, at present, the carrier lifetime of thin films is too short to produce high-performance PV devices. Other thin-film devices based on CdTe and Cu\textsubscript{2}ZnSnSe\textsubscript{4}, with comparable PL decay lifetimes (between 100$-$200 ps) have produced efficiencies of 8$-$9\%\textsuperscript{89} and $<$1\%\textsuperscript{90} respectively. Critically, highly resistive materials such as methylammonium lead halide and BiI\textsubscript{3} require high lifetimes to achieve reasonable fill factors, because the series resistance is governed by the photoexcited carrier concentration, which is proportional to carrier lifetime. The prospects to improve lifetime in BiI\textsubscript{3} are suggested by the lifetime difference between single crystal and polycrystalline thin film materials (Fig. 3-13). Likely, improved controls of phase purity, elemental purity (i.e., controlling contamination), and intragranular structural defect (i.e., dislocation, stacking fault) density will prove essential to increasing lifetime.

Concerning phase purity, several authors have argued that BiI\textsubscript{3} begins to dissociate as the melting point is approached.\textsuperscript{60,80} This dissociation in the window of 250$-$300\degree C may result in an off-stoichiometry of several percent. This may result in small quantities of Bi metal, which could be consistent with the strong sub-bandgap absorption visible in Fig. 3-12. Note that Bi metal XRD peaks overlap with BiI\textsubscript{3}, and would thus be indistinguishable. Regarding extrinsic contaminants and intragranular structural defects, Du and Singh\textsuperscript{83} have suggested that the anisotropic crystal structure in BiI\textsubscript{3} may be partially responsible for its lower $\mu\tau$ product, as it may be more likely to form structural defects, and should exhibit anisotropy in dielectric screening. However, they do not rule out the possibility that impurities may limit the transport properties. In other halide materials such as TlBr, extensive purification efforts through zone refining have resulted in over two orders of magnitude improvement in mobility lifetime products,\textsuperscript{91} which mirrors the pioneering success.
in purifying crystalline silicon.[92]

The measurement of lower lifetimes than those achieved in MAPbX\textsubscript{3} may lead to further insights on its defect tolerance. Firstly, despite Bi\textsuperscript{3+} being isoelectronic with Pb\textsuperscript{2+}, its larger atomic mass leads to deeper 6s orbitals and less of a contribution to the valence band. That, in addition to its anisotropic crystal structure, leads to a much higher hole effective mass in Bi\textsubscript{3}. This is distinct from some other post transition metal halides such as MAPbI\textsubscript{3} and TlBr, which are symmetric crystal structures and demonstrate isotropic electronic properties as well as low hole effective masses. Recent DFT results have also suggested that, while the \textit{V}\textsubscript{I} defect is shallow (as in MAPbI\textsubscript{3}), \textit{V}\textsubscript{Bi} lies deeper in the gap,[84] perhaps related to the less disperse valence band maximum and the higher oxidation state of Bi, with more charge transition levels. These results re-emphasize, rather than contradict, the strategies for achieving defect-tolerant transport properties: the high hole effective mass, relatively low static dielectric constant, and potential deep defects all point to this material being inferior to MAPbI\textsubscript{3}.

### 3.6 Additional Materials Screened

Following initial publication of this screening perspective and results on Bi\textsubscript{3}, multiple external collaborators offered to share their materials for characterization. Table 3.2 summarizes these materials grown internally and grown by external collaborators to-date. Each of these materials has been subjected to the theory, growth, phase characterization, and carrier lifetime characterization explained in the previous sections.

The partial densities of states for these compounds are plotted in Fig. 3-14, mined from MaterialsProject.org.[70] Each compound displays cation \textit{s} antibonding orbitals at the top of the valence band, but they are different for each compound. Going across the periodic table from In to Sn to Sb, the relative contribution of the \textit{s}-orbitals decreases, as the bonding \textit{s} states move deeper into the valence band and hybridize less with anion \textit{p} states. In a related trend, the valence bands across this
Table 3.2: List of “perovskite-inspired” semiconductors screened to-date

<table>
<thead>
<tr>
<th>Material</th>
<th>Growth Technique</th>
<th>Institute</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiI$_3$</td>
<td>Spin coating, PVT, Single crystals</td>
<td>MIT PV Lab, U. of Florida</td>
</tr>
<tr>
<td>(MA)$_3$Bi$_2$I$_9$</td>
<td>Spin coating, vapor conversion</td>
<td>MIT PV Lab</td>
</tr>
<tr>
<td>InI</td>
<td>Crystals from melt, spin coating</td>
<td>MIT PV Lab</td>
</tr>
<tr>
<td>SnS</td>
<td>Thermal evaporation, PVT</td>
<td>MIT PV Lab</td>
</tr>
<tr>
<td>SbSI</td>
<td>Bridgman single crystals</td>
<td>Lithuanian Univ. of Edu. Sci.</td>
</tr>
<tr>
<td>SbSeI</td>
<td>Bridgman single crystals</td>
<td>Lithuanian Univ. of Edu. Sci.</td>
</tr>
<tr>
<td>BiOI</td>
<td>Chemical vapor deposition</td>
<td>University of Cambridge</td>
</tr>
<tr>
<td>NaBiS$_2$</td>
<td>Crystals from melt</td>
<td>Northwestern University</td>
</tr>
</tbody>
</table>

series become less disperse, due to the increased stereochemical distortion of the lone pair of electrons. The result is that the hole effective masses increase across this series of compounds from InI to SnS to SbSeI. However, it is not entirely the cation that produces such behavior; the choice of anion and the crystal structure are also critical.

In the top row of Fig. 3-14, all of these materials contain Bi. While the $s$-orbital contributions to the valence band in these materials are smaller than in the bottom row, they are highest in NaBiS$_2$. This is due in part to the deeper sulfur $p$-orbitals and in part to the symmetric crystal structure of NaBiS$_2$, which is most similar to the PbS rocksalt structure. The bismuth halides experimentally surveyed here show relatively low $s$-orbital contributions to the VBM, and relatively flat valence bands with high hole effective masses.

3.6.1 Methylammonium Bismuth Iodide

Methylammonium bismuth iodide (MBI) is another candidate photovoltaic absorber identified from computational screening.\(^8\) There are several reports of MBI from the ferroelectrics community,[93][94][95][96] and since the publication of our work there have been several papers exploring it for PV applications.[97][98]

Phase-pure MBI is synthesized by low temperature solution-processing techniques described above, and its phase is identified through Rietveld refinement of XRD

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\(^8\)This section is reproduced with permission from a second-author paper, Ref. [78].
spectra. Through optical absorption measurements, MBI is found to have an indirect bandgap of 2 eV, making it potentially suitable as a top absorber in tandem solar cells. In addition, despite being synthesized at lower temperatures, it achieves room temperature photoluminescence. The crystal structure and optical properties are plotted in Fig. 3-15.

After verifying the phase and stoichiometry, the PL decay of MBI is measured using pulsed excitation through TCSPC spectroscopy. In Fig. 3-16, the PL decay time of thin-film MBI is plotted for several different fabrication conditions. The decay time constant can be improved over the baseline two-step solution synthesis by treating it with pyridine vapour. Pyridine treatment has been shown to increase the lifetime of hybrid lead perovskites[99] and it is thought that this occurs due to the lone electron pair on the nitrogen atom in pyridine passivating under-coordinated Pb ions in the perovskite.[99] A similar process may occur with under-coordinated bismuth ions on the surface of MBI.

Further increases in PL decay time are obtained by using VAHC MBI (Fig. 3-16). The time for VAHC MBI to decay to $1/e$ of the peak value is 760 ps, which can be taken as a characteristic PL decay time. Note that the PL decay initially
Figure 3-15: (a) MBI crystal structure with a unit cell indicated by the dashed lines, showing the separated Bi$_2$I$_9^-$ anions. The atomic positions and lattice parameters are obtained through Rietveld refinement of the powder diffraction pattern. (b) Photoluminescence (PL) and absorption coefficient of two-step MBI measured in air. The PL of the same MBI film before and after pyridine treatment is shown, using an excitation wavelength of 360 nm for both. The PL spectrum of the quartz substrate is given, showing that the luminescence from the substrate is not responsible for the PL peaks measured from the MBI film. Partial density of states (DOS) of MBI calculated through DFT. The DOS corresponds to the lowest energy configuration of the rotatable methylammonium cation, but different orientations of this cation have negligible effects on the DOS due to its small contribution to the band-edges. The indirect bandgap ($E_G$) and direct transition 0.1 eV above it ($E_{\text{direct}}$) are indicated, as are the bonding and antibonding orbitals. Reproduced with permission from Ref. [78].
deviates from a monoexponential, which may be due to the signal being dominated by surface recombination as a result of the shallow absorption depth (115 nm) in the >400 nm thick film. CdTe also has a high absorption coefficient and its surface decay lifetime has been measured to be two orders of magnitude shorter than its bulk lifetime.[100] But after the first 10 ns, the PL decay of VAHC MBI tends towards a monoexponential decay, with a time constant of 5.6 ns. Detailed and careful studies are needed to model the PL decay of MBI in order to determine the recombination rate and mechanism for this particular material, as to whether this is a surface-bulk recombination phenomenon, or perhaps non-SRH recombination mechanisms influencing the decay time. Regardless, these results suggest that the lifetime of VAHC MBI is at least 760 ps, and potentially as high as 5.6 ns.

Aside from these lifetime measurements, another interesting feature of MBI is that it exhibits higher air-stability than methylammonium lead iodide perovskite and does not degrade to BiI$_3$ over a one-month testing period under ambient conditions ((61±4)% relative humidity, (21.8±0.7)°C). By contrast, MAPbI$_3$ degrades to PbI$_2$ after 5 days under these conditions. This air-stability is found to be at least in part be due to MBI preferentially forming a surface BiOI or Bi$_2$O$_3$ layer instead of degrading.

Figure 3-16: Normalized PL decay of two-step MBI as-deposited and after pyridine treatment. A comparison is made with MBI made by vapour-assisted hot-casting at 150°C. 600 nm and 425 nm wavelength longpass filters were used for all three measurements. Reproduced with permission from Ref. [78].
to BiI₃. Other hybrid ternary bismuth halides share the features of MBI that are amenable to it having a promising lifetime and air-stability.

In summary, MBI offers an enhanced lifetime over BiI₃, raising interesting questions about the differences between these two very similar materials. In addition, it offers higher moisture stability than the prototypical perovskite material, and the mechanism by which it achieves this could hint at future design criteria for air-stable semiconductors for PV.

### 3.6.2 Indium Monoiodide

Indium monoiodide (InI) shares many similarities with BiI₃, but offers a counterpoint in terms of electronic properties and more closely approximates some of the features of the lead halide perovskites. It is expected to have a direct bandgap, respective hole and electron DOS effective masses of 0.25 and 0.15, and it is expected to have a much higher ionic dielectric constant of 33.5.[23]

InI has been explored already for X-ray detectors,[101][102][103] yielding promising optoelectronic properties. The hole $\mu\tau$ product was measured at $4 \times 10^{-5}$ cm$^2$/V based on alpha particle radiation, and $1.2 \times 10^{-3}$ cm$^2$/V based on steady-state photoconductivity measurements.[104]

As spin coating did not produce phase pure films, the material studied here was based on a large polycrystalline bulk crystal grown from the melt. The orthorhombic Ccmm phase was confirmed by crushing the crystal with a mortar and pestle and
performing XRD on the resulting powder, as shown in Fig. 3-17.\textsuperscript{9} Next, spectral PL measurements were used to evaluate the direct bandgap, which was found to be 2.0 eV. The PL emission intensity and peak position were comparable across the melt compositions tested. Given that InI and In metal are immiscible, the In metal appears to separate out and leaves pure-phase InI in the interior of the crystals formed.

Crystals were grown with differing In-I compositions in the melt. The highest performing crystals were found to come from 1% In-rich melts, which may be due to suppression of higher iodide phases. The excess In metal is not miscible with InI, and was rejected to the edge of the crystal as a ball of molten In, which solidified upon cooling. The following measurements are performed on crystals cleaved from this In-rich batch, however crystals formed from a 50/50 composition melt were found to have similar properties.

The spectral PL is plotted in Fig. 3-18(a), showing a relatively sharp emission line (129 meV FWHM) and no evidence of an Urbach tail on the sub-bandgap edge. Furthermore, no emission is observed down to 1.3 eV, suggesting minimal radiative emission from sub-bandgap states.

Finally, the lifetime was measured by TCSPC. Using a laser intensity of 1 µW at 532 nm excitation, the TCSPC decay was integrated over one hour. A long pass filter at 550 nm, short pass filter at 800 nm, and notch filter at 532 nm all ensured that the only PL signal was from band-edge emission of InI. From the plot in Fig. 3-18(b), there are two distinct regimes for the TCSPC decay, as in previous samples. The time constant of the initial decay was 0.80 ns, while the time constant of the extended monoexponential tail was found to be 4.1 ns.

3.6.3 Lifetime Measurement Summary

To compare all of the materials above, grown or acquired for the purposes of evaluation PV performance, the TCSPC decay curves are plotted together in Fig. 3-19. To date, the highest lifetimes have been observed on MBI and InI, though SbSI and BiOI also show decay time constants in excess of 1 ns at longer time scales. The extracted

\textsuperscript{9}Rachel Kurchin assisted with performing XRD.
Figure 3-18: (a) Photoluminescence of indium moniodide crystals (InI) showing sharp emission at the 2.0 eV band edge, and little emission into the gap. (b) TCSPC decay curve taken on InI, showing a fast initial decay time constant of 0.80 ns, and a slower time constant of 4.1 ns at longer time scales.

Lifetimes are tabulated in Table 3.3.

3.7 Learnings from Initial Materials Screening

This chapter proposed new search criteria for the discovery of semiconductors for optoelectronic applications, building upon the recent success of methyl-ammonium lead iodide as a PV material, which achieves excellent device efficiencies in the presence of defects. Multiple materials were explored and their lifetimes were characterized.

<table>
<thead>
<tr>
<th>Table 3.3: Lifetimes tabulated for materials screened to-date</th>
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<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>BiI₃ films</td>
</tr>
<tr>
<td>BiI₃ crystals</td>
</tr>
<tr>
<td>(MA)₃Bi₂I₉</td>
</tr>
<tr>
<td>InI</td>
</tr>
<tr>
<td>SbSI</td>
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<tr>
<td>BiOI</td>
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</table>
From the experimental screening effort, several important lessons were learned.

First, elemental purity and compositional phase purity matter a great deal. The materials here were generally fabricated using 99.99% (or greater) pure feedstocks (metals basis). This purity may be insufficient for high-quality semiconductors, as impurities in the range of 100s of ppm could be detrimental to minority carrier lifetime. Preliminary results suggest that moving to 99.9999% pure feedstocks could yield improved lifetimes. More pernicious, though, is the fact that the rated purity only accounts for metals. Carbon and oxygen are common impurities in feedstock materials like iodine for example, which may come from organic sources, and these are unaccounted for in the purity analysis given by manufacturers. Many of the iodides used here are also hygroscopic, meaning that they may be intercalated with H$_2$O. These oxygen or carbon impurities may impact the minority carrier transport, or even alter the phase of the material synthesized.

Compositional purity is also a common issue in the materials synthesized here. InI grown by solution methods frequently disproportionates to form InI$_3$; BiI$_3$ is hypothesized to contain small quantities of Bi metal; and MBI can have a small
volume fraction of unconverted BiI\textsubscript{3} under certain fabrication conditions. Fabricating a phase-impure sample like this can lead to false negatives, as one is testing a material which is not the target composition. This was seen in initial tests on InI, which showed many regions of very low minority carrier lifetime potentially due to a large fractional content of InI\textsubscript{3}. Especially detrimental for devices are metallic phases or phases with smaller bandgaps than the target phase, as these could be points of faster recombination and may limit minority carrier lifetime.

One route to avoiding some of the effects of phase and elemental impurities is to synthesize bulk crystals from the melt. For many materials, this allows one to target a specific window in the phase diagram, and to hit it reliably. It is also a relatively clean and simple procedure, involving only the feedstock materials sealed in a pure quartz ampoule. The material may be readily purified further by exploiting differences in solubility or vapor pressure between the desired phase and impurities, for example through zone refining. In the case of InI, this phenomenon was exploited successfully to separate the InI from a small fraction of In\textsubscript{2}O\textsubscript{3} (which remained solid) and indium metal, which was immiscible with molten InI. Larger grain materials may also be fabricated with these techniques, reducing the density of grain boundaries and structural defects. This provides a window into the minority carrier transport properties that may be achievable by defect engineering, without having to perform exhaustive optimization on thin films.

However, the range in performance found here does not necessarily imply experimental variation, and may point to important conclusions about the design criteria used here.

### 3.7.1 Revised Design Criteria

Based on the range of lifetimes observed in the present study, most of the original design rules still apply — in particular, materials with the highest dielectric constant and lowest effective masses outperform the other materials tested. However, given that many of the materials tested have not attained the high minority carrier lifetime and mobility of the MAPbI\textsubscript{3} perovskites, alternative design criteria should be
considered.

The first criteria is the symmetry of the crystal structure. From the array of materials calculated above, symmetric crystal structures (e.g., rocksalts, perovskites, or CsCl-type structures) tended to exhibit a higher tendency for direct bandgaps and lower effective masses. Meanwhile, the layered compounds with greater anisotropy in their crystal structure exhibited higher effective masses and flatter valence bands, in particular. This trend is apparent going from InI and SnS, to BiI$_3$ and MBI. The latter materials produce 2D or 0D structures with Coulombic or van der Waals interactions between layers, while the former exhibit some covalent bonding between layer planes — and the difference in hole effective masses between these two groups of materials is over an order of magnitude. This effect is not specific to Bi compounds, but rather to the layered structure; NaBiS$_2$ based on the rocksalt PbS lattice appears to exhibit a direct bandgap and lower effective masses.

The second criteria is the importance of the choice of anion. While the importance of cation s-orbital contribution were discussed, it is important to recognize that 70-90% of the VBM partial DoS comes from anion p-orbitals in these materials. The dispersion of the VBM depends in large part on the hybridization between anion p-orbitals and cation s-orbitals. For BiI$_3$, deep s-orbitals (Bi) and higher energy p-orbitals (I) lead to very little interaction and minimal contributions from Bi to the valence band edge. Perhaps Bi would be better paired with anions with deeper anion orbitals, such as O or S. This is an open area for research and could lead to important insights.

Furthermore, the oxidation state of the defect will affect the type of defects that it tends to form. Given that Bi is in the 3+ charge state, $V_{\text{Bi}}$ can take on multiple charge states including 1− and 3−. Recent theoretical calculations suggest that the 1−/3− charge transition level for $V_{\text{Bi}}$ is quite deep in the bandgap.[84] For a weakly n-type material, these deep, highly charged acceptors could be detrimental to lifetime. Moving towards 1+ and 2+ cations may decrease the likelihood of forming deep hole traps.

Finally, while the present work relates primarily to cation vacancy defects, recent
theory has offered some potential lessons regarding the anion vacancies.[47][105] Shi and Du suggest that shallow anion vacancies arise when the cation dangling bonds that surround the vacancy have minimal overlap or interaction once the anion is removed. This occurs when the anion has a low coordination number (e.g., only 2 in the case of perovskites), and when cation-cation distances are large. This occurs more readily for larger anions (and larger lattice constants). They demonstrate that several selenides, iodides, and selenoiodides with low anion coordination all show shallow anion vacancies.[47][105]. Meanwhile, sulfides such as SnS and PbS demonstrate deep sulfur vacancies,[106][107] and oxides such as ZnO show deep oxygen vacancies.[108] This work may point to larger, less coordinated anions like iodine in the perovskite crystal structure.

What is clear is that the MAPbI$_3$ perovskite offers a very special combination of cation and anion, coupled with crystal structure, that lead to its shallow intrinsic point defects. There are likely very few compounds that hit this exact recipe correctly, but with careful design, hopefully another successful material may be discovered. For shallow cation vacancies, a partially oxidized cation in a low valence state would be a good start — In$^+$, Sn$^{2+}$, Tl$^+$, Pb$^{2+}$, Cu$^+$, or Ag$^+$ have all demonstrated this property in multiple compounds. For shallow anion vacancies, one might look for a disperse CBM formed from heavy cation $p$-orbitals, or to form the conduction band from non-bonding states as in TiO$_2$.[109] Alternatively, one may think about minimizing the potential cation-cation hybridization that occurs when an anion vacancy is formed[47] — by reducing the coordination of the anion (using crystal structures like perovskite), increasing the cation-cation spacing (with large anions like I$^-$ or Br$^-$), and/or insuring that the orientation of the cations’ orbitals produce minimal overlap (for example, avoid 90° bond angles for materials with cation $p$-derived CBMs). In fact, these suggestions for shallow anion vacancies are just as true for shallow cation vacancies — the large cations listed above produce larger anion-anion separation, and if they do interact to form a deep state, the presence of cation $s$ antibonding orbitals at the VBM ensures that this state ends up resonant with the VB, not in the bandgap. Satisfying all or some of these features may require more clever searches in materials
databases based on crystal structure, bond lengths, and coordination numbers, or it may require design of entirely new materials, such as ternaries that creatively use alkali or transition metals to produce certain crystal structures or certain band edge states.

In the end, all of the heuristics discussed above are rules of thumb and principles designed to approximate the effect of defects in materials, and can never replace direct calculations of defects in materials. These calculation should look for shallow defects <0.3 eV from the valence or conduction band for acceptors or donors respectively — and ideally with a lower charge state. Being able to compute the point defects’ charge transition levels and densities (expensive, but possible) and capture cross sections (still very difficult, given the electron-phonon interaction) directly would be superior, but is limited to several weeks per material. The heuristics discussed here may currently be the only tool available to handle searches through tens of thousands of materials, but hopefully the growing power of computers and increasingly sophisticated first-principles techniques will obviate this approach in the coming decade.

3.7.2 Other Practical Considerations

Many of the materials tested exhibit very high resistivity and low background carrier concentrations due to not having (or having compensating) shallow native acceptors and donors. This means that all of their carriers for conduction must come from photoexcitation, otherwise the series resistance of such a cell may be too high. However, if the lifetime is too short, the material will not be able to sustain a sufficiently high injection level. This effect is demonstrated in Fig. 3-20, for a range of effective minority carrier lifetimes from picoseconds to microseconds. For a 1 µm thick film under 1-sun illumination, the injection level of photoexcited carriers in the material is calculated as a function of lifetime. For lifetimes below 1 ns, it is difficult to exceed an injection level of $10^{12}$ cm$^{-3}$. Such low carrier concentrations could lead to a through-thickness series resistance >50 Ω cm$^2$, which is generally too high for an efficient solar cell. A benchmark for a high-performing solar cell is a series resistance below 1 Ω cm$^2$, marked with a dashed red line, and corresponds to achieving a car-
Figure 3-20: Effect of lifetime on device series resistance, for an intrinsic, undoped material. A series resistance of $1 \ \Omega \ \text{cm}^2$ is marked with the dashed red line.

Carrier lifetime in the tens to hundreds of nanoseconds. This explains why the record efficiency perovskite devices do not suffer from high series resistance, but suggests that materials with 1–10 ns lifetimes may be too resistive — moving towards higher lifetimes, thinner absorbers, or extrinsic doping would be necessary to ameliorate this effect.

A final problem is the issue of softness, as many layered materials and those with crystal structures composed of more ionic bonds may have lower yield stresses and could plastically deform more easily. BiI$_3$ is a very soft material with a Vickers Hardness of 12–15.[110] The ease with which one may scratch the material is a liability for shunting and catastrophic failure in thin-film PV cells. In addition, one must evaluate the effect of this softness and the crystal structure’s anisotropy when the material is heated and cooled in traction with its substrate, in relation to dislocation generation (plastic deformation), cracks, and pinholes, all of which could reduce device performance. InI, with its slightly distorted rocksalt structure, exhibited increased hardness over the Bi-halides tested here, suggesting that materials like it may be more robust to scratches and mechanical failure.
Chapter 4  
Finding Appropriate Carrier Selective Contacts

After finding an optimal semiconductor to use as the absorbing layer, capable of producing a large separation in quasi-Fermi levels and capable of moving free charges to the contacts, the device must extract these carriers efficiently and at the maximum possible electrochemical potential difference. This requires finding an optimal pairing of semiconductor and contact material — structurally, chemically, and electronically. For some absorber materials, the search for optimal contact materials represents the most critical research challenge — and often becomes the time-limiting step in novel materials screening.

In thin film devices, especially with non-planar textures, the high surface area to volume ratio makes the surface and interface properties a crucial component of device performance, in particular at heterojunction interfaces responsible for charge separation. The interfaces involve making contact between the absorber semiconductor layer and the front and back contacts, which include a combination of wide bandgap semiconductors and metals. In the majority of thin film heterojunction devices, the front contact includes a transparent conducting oxide such as aluminum doped zinc oxide (Al:ZnO) or indium doped tin oxide (ITO), a buffer or window layer of a semiconductor such as CdS, and metal fingers. For a $p$-type absorber, this set of layers is responsible for collecting the electrons from the $p-n$ junction. The back contact must
be ohmic as it is typically collecting the holes.

In the present chapter, the measurement and design of carrier selective contacts will be illustrated by the example of cuprous oxide, or Cu$_2$O.\footnote{This chapter is reproduced in part from a first-authored manuscript, Ref. [111].} Cu$_2$O is a promising Earth-abundant photovoltaic (PV) absorber, however its technological relevance is limited by low PV conversion efficiencies.[112] In particular, historical cells demonstrate low open-circuit voltages relative to their Shockley-Queisser entitlement of 1.6 V. While low minority-carrier lifetime contributes to underperforming $V_{OC}$, recent work suggests that a dominant $V_{OC}$ loss mechanism is the conduction-band alignment (offset) between Cu$_2$O and its heterojunction partner,[112][113][114][115] herein referred to as the electron-selective contact (ESC). Engineering this offset has led to open-circuit voltages as high as 1.2 V;[116] in fact, the tremendous improvements in $V_{OC}$ captured in Fig. 4-1 were attained largely through optimizing selective contacts, rather than the absorber layer itself. Thus control, measurement, and modeling of the ESC conduction-band alignment is a critical area of research for Cu$_2$O. This method for screening the $V_{OC}$ potential of candidate ESCs generalizes to other $p$-type absorber materials as well.

4.1 Case Study: Cuprous Oxide Band Alignment

4.1.1 Cu$_2$O Sample Fabrication

The search for more optimal ESCs for Cu$_2$O is especially difficult due to its low electron affinity ($\chi = 3.2$ eV); materials with such a low electron affinity are often challenging to dope $n$-type due to self-compensation by intrinsic defects.[125] Several authors have measured negative, or “cliff”-type conduction-band offsets between Cu$_2$O and other materials to explain the cause of low $V_{OC}$, including ZnO (-1.0 to -1.8 eV),[114][115][126][127] In$_2$O$_3$ (-0.83 eV),[128] TiO$_2$ (-0.74 eV),[129] and GaN (-0.23 eV).[126] The present study will examine specifically $n$-type materials deposited by atomic layer deposition (ALD) or pulsed laser deposition on electrochemically de-
Figure 4-1: Open-circuit voltage deficit relative to the bandgap for an array of PV technologies. The Cu$_2$O cells are divided into thin-film (blue circle) and wafer-based (green triangle) cell designs. Data taken from references [113], [120], [121], [122], [123], [124], [116].
posited Cu$_2$O terminated with a stoichiometric Cu$_2$O surface. The ESC materials explored include Zn(O,S), TiO$_2$, Ga$_2$O$_3$, CdS, and (Mg,Zn)O:Ga.

Electronic band offsets are sensitive to grain orientation, surface atomic termination, adsorbed extrinsic species, chemical reactions, and interdiffusion. Prior work suggests that the offset on Cu$_2$O is influenced by the presence of monolayers of CuO at the surface, which may explain the variation in literature reports of band offsets. To control for these effects, all Cu$_2$O surfaces here are (111) terminated and show only the +1 oxidation state of copper as measured by X-ray photoelectron and Auger electron spectroscopy.

For the present study, Cu$_2$O is deposited by a constant-current two-electrode electrochemical deposition from a basic (i.e., alkaline) solution of copper sulfate, lactic acid, and sodium hydroxide; further details available in Ref. [131].

The deposition solution uses hydrated copper sulfate powder (CuSO$_4$ $\cdot$ 5H$_2$O) as the copper ion source, at 0.4 mol/L concentration. This solution is buffered to a higher pH with a 1 mol/L sodium hydroxide NaOH solution. In a more alkaline pH, the Cu$^+$ ion becomes more stable than the Cu$^{2+}$ ion, allowing for deposition of cuprous oxide rather than cupric oxide. In addition, 3 mol/L lactic acid is added to the copper sulfate solution to act as a complexing agent.

The deposition bath includes two electrodes in solution: the counter electrode is a positively biased Pt film, while the substrate is the negatively biased working electrode and is typically a gold film for high conductivity and stability in alkaline pH. The electrodes are placed one inch apart, as shown in Fig. 4-2. A bath pH of 12.5 leads to the highly preferential (111) surface orientation. Unless otherwise noted, a current density of -0.27 mA/cm$^2$ was used. This current density results in pure phase Cu$_2$O at high deposition rates of approximately 1.2 microns per hour. The film is rinsed in DI water (18.6 MΩ), and stored and transferred in a nitrogen-ambient glovebox to prevent surface oxidation to CuO. Films were typically 1–2 microns thick, on a gold substrate.
4.1.2 Selective Contact Deposition

Unless stated otherwise, all depositions of $n$-type materials onto the Cu$_2$O are performed with a substrate temperature of 120°C.

ZnO$_x$S$_y$ and Ga$_2$O$_3$ overlayers are deposited by atomic layer deposition (ALD) with a custom tube furnace ALD reactor. Diethylzinc[132] and bis($\mu$-dimethylamino)tetrakis(dimethylamino)digallium[116] are used for the Zn and Ga precursors, respectively; deionized H$_2$O and 4% H$_2$S in N$_2$ are used for the oxide and sulfide anion precursors.$^2$

ZnO, CdS, and TiO$_2$ overlayers are deposited by ALD using a Beneq TFS200 ALD reactor. The cation precursors used are diethylzinc, dimethylcadmium, and titanium isopropoxide, respectively, while the anion precursors are the same as above. Deposition temperatures were again 120°C except for TiO$_2$ deposited at 150°C.$^3$

A gallium-doped magnesium zinc oxide alloy, (Mg,Zn)O:Ga, is deposited by pulsed laser deposition using two fixed-composition ceramic targets with 21% Mg or 6% Mg, and 1% Ga; the deposition tool is described elsewhere.$[133]$ Depositions were conducted at a chamber pressure of 9 mTorr, with a 99% Ar and 1% O$_2$ gas environment.

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$^2$These layers are deposited by Helen Park and Danny Chua, Harvard University.

$^3$These layers are deposited with the help of Arrelaine Dameron, NREL.
For all samples, several thicknesses of the ESC material were deposited to track the changes in band bending and band offsets as a function of thickness. For the eventual measurements, the thinnest overlayers were typically used, with thicknesses of 1–2 nm.

### 4.2 Modeling of Selective Contact Materials

To determine an optimal conduction-band offset, I simulate the effect of $\Delta E_C$ on $V_{OC}$ and solar cell efficiency. The conduction-band offset is depicted in Fig. 4-3(a); this diagram generalizes to any $p$-type absorber and corresponding $n$-type ESC.

Recall that the $V_{OC}$ is determined by the hole and electron electrochemical potential difference, or quasi-Fermi level separation in the material. This separation may be limited by bulk recombination, which reduces the concentration of free photoexcited carriers, or limited by the electrochemical potential of electrons in the $n$-type ESC.[134] Revisiting the current-superposition model of the solar cell, the recombination current ($J^i_0$) at the heterojunction interface can be modeled as:

$$J^i_0 = S_p N_V \exp \left( \frac{-\phi_{b,0}}{k_B T} \right),$$  \hspace{1cm} (4.1)

where $S_p$ is the hole surface recombination velocity (SRV) at the heterojunction and is proportional to interface defect density and capture cross-section, $N_V$ is the valence band density of states in Cu$_2$O, $\phi_{b,0}$ is the potential barrier for holes at the heterojunction (see Fig. 4-3(a).[135] If this recombination current is the dominant recombination mechanism, the $V_{OC}$ is limited to a maximum of $\phi_{b,0}$, which is determined by the conduction-band offset and donor/acceptor density $N_D/N_A$ ratio between the ESC and Cu$_2$O. Thus, one would expect the $V_{OC}$ to improve with increasing donor density in the buffer ($N_D$), a less cliff-like conduction-band offset, and decreasing SRV.

To revisit the thermodynamic picture of $V_{OC}$ established earlier, choosing a bad electron selective contact with an electron quasi-Fermi level below that in the $p$-type absorber effectively pins the quasi-Fermi level at this lower energy. The $n$-type
material can supply so many electrons at that particular electrochemical potential, that it pins the maximum separation of quasi-Fermi levels, and fundamentally limits the total free energy or $V_{OC}$ that may be extracted from the solar cell. This is a pernicious effect, because it may easily be confused for a reduced bulk quasi-Fermi level separation due to bulk recombination, when really the contacts themselves are at fault.

This can be quantified with a device model of a heterojunction thin-film Cu$_2$O device, produced using the numerical solar cell simulator software SCAPS. Here, the Cu$_2$O is assumed to have a 1 cm$^2$/V/s minority carrier mobility, typical of electrochemically-deposited Cu$_2$O. The Cu$_2$O and n-type partners are modeled with bandgaps of 2.09 eV and 3.3 eV, as well as carrier concentrations of $10^{15}$ cm$^{-3}$ and $10^{16} - 10^{19}$ cm$^{-3}$ respectively. Changing the concentration of neutral, mid-gap interface defects influences the interface recombination velocity, while changing the concentration of neutral mid-gap bulk defects influences the bulk lifetime. As expected, the $V_{OC}$ decreases with increasing SRV, and drops linearly with decreasing conduction-band offset and logarithmically with decreasing ESC donor density (Fig. 4-3(c)) for cliff-type offsets. A thousand-fold increase in bulk lifetime results in minimal change in $V_{OC}$ over this region. This is consistent with the earlier statement that a poor selective contact material can mask the true bulk quasi-Fermi level separa-
tion. Improvements in bulk material quality therefore result in no change in device performance, and potentially experimental false negatives.

For near-zero $\Delta E_C$, the $V_{OC}$ becomes bulk-recombination dominated instead, and is determined by bulk lifetime alone, making it insensitive to changes in $\Delta E_C$ and SRV (Fig. 4-3(b)), as well as ESC donor density (Fig. 4-3(c)). The transition between these bulk-recombination and interface-recombination limits occurs at different offsets depending upon the SRV and ESC doping density. In the extreme case of a defect-free interface (low SRV) and low-lifetime bulk material, a slight cliff can moderately improve the $V_{OC}$ by providing a barrier for electrons in the ESC from diffusing back into the low-lifetime bulk Cu$_2$O and recombining with holes. This effect disappears at higher SRVs.

The same physics are observed across all materials systems, for both the conduction-band offset between an absorber and the $n$-type electron selective contact, as well as the valence-band offset with the $p$-type hole selective contact. A similar SCAPS simulation performed on a tin monosulfide device reveals the same conclusion as above.[139] Tin monosulfide (SnS) is also a $p$-type absorber material, and is paired with a variety of $n$-type electron selective contacts. In this case, the doping level and the conduction band offset are varied over the range of simulations, for a fixed SRV and bulk minority carrier lifetime in Fig. 4-4. For negative conduction band offsets, or cliffs, the $V_{OC}$ and fill factor drop, producing lower efficiency devices. However, improving the conduction band offset to a positive value is not a panacea. A positive offset, or “spike”, tends to block the electrons from being collected at the ESC, and the $J_{SC}$ drops. This knife edge of efficiency vs. conduction band offset is solved by increasing the doping level in the ESC. A more highly doped ESC layer decreases the depletion region in the $n$-type material, and narrows the width of the potential barrier produced by the spike offset. It also increases the electron concentration in the near surface of the $p$-type absorber, even to the point of inverting the majority carrier type. Both of these effects encourage enhanced tunneling and thermionic emission of electrons over the barrier, and transport is no longer impeded (up to a point).  

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[4] Reproduced from second-authored manuscript, Ref. [139]; simulations run by Niall Mangan.
Figure 4-4: (Contact-layer performance space for Zn(O,S) buffer layers in SnS devices with high lifetime: Colormap of simulated efficiency (color intensity) of SnS device with varying conduction band offset between absorber and buffer layer (x-axis) and varying buffer layer carrier concentration (y-axis). This simulation is for a 500 ns lifetime SnS absorber with no optical or recombination losses from the buffer, window or contacting layers. Color indicates high (lighter) and low (darker) efficiency from 0 to 20%. Parameters for the device stack, other than the band offset and buffer layer carrier concentration, are found in the Appendix. Current-voltage behavior and band alignment for points A through E indicated on the counter plot are also shown. The numerically calculated band diagrams show the conduction and valence bands in black, illustrating the respective band offset and band bending between SnS and the buffer layer at the max power point. The electron (red) and hole (blue) quasi-Fermi levels are also illustrated. These band diagrams are zoomed in to the junction and do not show the full thickness of SnS and ITO. Reproduced with permission from Ref. [139].
4.3 Experimental Methods for Measuring Band Alignment

Given that these band offsets are such strong determiners of device performance, it is important to be able to measure them accurately. The valence- and conduction-band offsets are measured through a combination of X-ray photoelectron spectroscopy (XPS), UV-visible spectrophotometry, and spectroscopic ellipsometry, with methods for each technique described herein.

4.3.1 X-ray Photoelectron Spectroscopy

XPS is form of photon-in, electron-out spectroscopy, which is useful for measuring the binding energies of electrons around various atoms near the surface of a sample (typically the top 100 Å). This binding energy can be used to determine the chemical composition, akin to a “fingerprint” for each element — and at higher resolution, fine differences in this binding energy reveal information about the oxidation state and chemical environment. Fig. 4-5 provides a cartoon of the measurement. Deep core levels around an atom have a finite binding energy relative to the vacuum level, and an incoming photon that exceeds this energy can be absorbed to produce a free electron with kinetic energy equal to the difference in photon energy and binding energy (K.E. + B.E. = $h\nu$).

The velocity of the electrons kicked out of the sample corresponds with their kinetic energy, and this difference in velocities allows them to be easily separated using a magnetic field in a hemispherical analyzer. With an accurate measure of the kinetic energy, the known X-ray photon energy then acts as a measuring stick for the binding energies. Typical spectra are seen in Fig. 4-6 for Cu$_2$O and a Cu$_2$O sample with a thin overlayer of ZnS. The core levels of Cu, Zn, O, and S can be identified using their fingerprints, and their relative intensities and energy levels can be used to infer information about concentrations and electronic offsets, respectively.

In the present work XPS is performed with a Kratos AXIS Nova tool (NREL)
Figure 4-5: On the left, the typical geometry for performing XPS is depicted, with incoming photons and outgoing photoelectrons (under high vacuum). On the right, the relationship between kinetic energy and binding energy is displayed schematically.

Figure 4-6: A typical set of XPS spectra shown for Cu$_2$O and a Cu$_2$O sample with a thin overlayer of ZnS. The core levels of Cu, Zn, O, and S can be identified, as well as Auger photoelectrons, and contaminants like C. The maximum binding energy observable is the X-ray photon energy, rendering only the outer core levels accessible by this technique.
and a Thermo Scientific K-Alpha (Harvard CNS), with a photon energy of 1486.6 eV. Samples experienced <10 minutes of ambient air exposure during mounting, then were pumped down to pressures <10\(^{-8}\) mTorr for measurements. The binding energy scale is calibrated before each run by a linear least squares fitting of reference core levels of Cu 2\(p\) (932.7 eV, 952.3 eV), Ag 3\(d\) (368.3 eV, 374.0 eV), Mo 3\(d\) (227.9 eV, 231.1 eV), and Au 4\(f\) (84.0 eV, 87.6 eV), as well as Fermi levels of all four metals (assumed to be 0 eV). In this way, any linear shifts or stretching in the energy axis are accounted for. This is a more robust strategy than relying on adventitious carbon peaks, as these are prone to shift due to chemical bonding, band bending, or charging; freshly sputtered metal surfaces should provide a more consistent calibration.

For survey scans, a pass energy of 200 eV was typically used, while for detailed peak scans 50 eV was used. Dwell times of 50 ms and energy resolutions of 0.05 or 0.1 eV were used for peak scans, and scans were repeated between 5–30 times until the signal-to-noise ratio was sufficiently high. For core peaks of elements in a binary or ternary compound, the XPS signal was typically strong enough to only require a single scan, while the valence band maximum typically required at least 15 scans to properly resolve.

### 4.3.2 Extraction of Band Offsets

The valence band offset ($\Delta E_V$) is determined by the Kraut method through XPS,[140] using core-level offsets from heterojunction samples in the following combinations:

$$\Delta E_V = E^p_V - E^n_V = (E^p_{\text{core}} - E^n_{\text{core}}) - (E^p_{\text{core}} - E^p_V) + (E^n_{\text{core}} - E^n_V), \quad (4.2)$$

where $E_V$ is the valence band maximum of Cu\(_2\)O (\(p\)-type) or the \(n\)-type material, and $E_{\text{core}}$ is a specific core level for the Cu\(_2\)O or \(n\)-type material. The bracketed regions above suggest that three samples are requisite: two bulk, homogeneous films to determine the core level to valence band offsets, and one heterojunction film with a thin overlayer of the ESC on Cu\(_2\)O to determine the core level offsets. ALD ensures conformal overlayer coverage even at these thicknesses. The extraction of all three
terms is demonstrated in Fig. 4-7 for ZnS on Cu$_2$O as an example. The valence band edges are fit with linear extrapolations intersecting with a linear extrapolation of the background. This is a common approximation, when the exact form of the valence band density of states is unknown. This valence band edge is only fit on the bare Cu$_2$O sample and bare ESC sample.

Core levels are fit using the CasaXPS program. Scans are taken over a window ±10 eV around the peaks of interest. The background was fit by choosing a flat region of the spectrum on either side of the peak, and applying a Shirley background subtraction to the region in between. The peaks were then fit with Gaussian or Voigt functions via a Levenberg-Marquardt algorithm with 5–10 iterations.

To extract the conduction-band offset, $\Delta E_C$, add the difference in bandgap of the Cu$_2$O and ESC materials to $\Delta E_V$, as in:

$$\Delta E_C = \Delta E_V + E_G^p - E_G^n.$$  \hspace{1cm} (4.3)

$E_G$ is determined by fitting the absorption coefficient, measured through UV-visible spectrophotometry or spectroscopic ellipsometry. This necessarily assumes that the optical bandgap is identical to the fundamental bandgap (no Moss-Burstein shift), and that the surface bandgap is the same as the bulk bandgap.

Extrapolation of the absorption edge requires accurate knowledge of the absorption coefficient, which is measured from either UV-Vis spectrophotometry, or ellipsometry. In the case of spectrophotometry, the method of extracting absorption coefficient is described in more detail in Chapter 3. In the case of ellipsometry, $\alpha$ is determined from the extracted extinction coefficient by the relation: $\alpha = 4\pi k/\lambda$, where $\lambda$ is the wavelength of light in vacuum.

The absorption coefficient can be used to create plots of $E_{\text{photon}}$ vs. $(\alpha h\nu)^n$ and the absorption edge is fit using linear regions of this curve — assuming the absorption edge $E_G$ occurs where $\alpha$ extrapolates to zero. The exponent used for the y-axis is assumed to be $n = 1/2$ for amorphous or indirect-transition materials, while it is assumed to be $n = 2$ for crystalline, direct-bandgap materials.[141]
Figure 4-7: Routine for $\Delta E_V$ extraction using 2 nm ZnS overlayers, with three samples; (a) band diagram of heterojunction with core-level to valence bands of separate bulk samples, and core-level offset; (b) valence band edges of pure, bulk samples; (c) Cu $2p$ core levels of pure bulk Cu$_2$O and with a thin overlayer; (d) Zn $2p$ core levels of pure bulk ZnS and in a thin overlayer sample. Reproduced with permission from Ref. [111].
Figure 4-8: Extracted parameters for each $n$-type material from XPS and optical bandgap measurements, and the resulting band offsets including error estimates for bandgap $E_G$, $\Delta E_V$, and $\Delta E_C$.

The $n$-type materials in this study are amorphous with the exception of (Mg,Zn)O, pure ZnO, CdS, and pure ZnS as verified by X-ray diffraction (XRD). For amorphous materials, the band edge is fit by extrapolating the linear region of $E_{\text{photon}}$ vs. $(\alpha h\nu)^{1/2}$, and for crystalline materials using the plot of $E_{\text{photon}}$ vs. $(\alpha h\nu)^2$ instead.

For each material evaluated, the valence band offset is determined using the core level offset for an overlayer <2 nm thick. Given a carrier concentration in the overlayer of less than $1 \times 10^{18}$ cm$^{-3}$, this results in a maximum electric field at the heterojunction of less than $5 \times 10^4$ V/cm. This corresponds to a shift in the binding energies of <0.01 eV over a 2 nm distance; thus the effect of band bending is assumed to be minimal over the typical XPS information depth.

### 4.4 Results of Band Offset Measurements

#### 4.4.1 Electron-Selective Contacts on Cu$_2$O

The results of the core level to valence band and core level to Cu $2p$ 3/2 core level offsets are catalogued in Table 4-8 for each $n$-type material.[111]

The bandgap extraction is plotted in Fig. 4-9 for the direct bandgap crystalline $n$-type materials, and in Fig. 4-10 for the amorphous $n$-type materials.[111][116]
Figure 4-9: Optical bandgap extracted for direct bandgap materials (left) ZnO, CdS, ZnS; (right) Ga:(Mg,Zn)O of varying compositions; and (bottom) Ga$_2$O$_3$. All are measured by spectrophotometry, with the exception of CdS and Ga$_2$O$_3$, measured by ellipsometry).[111][116]
Figure 4-10: Optical bandgap extraction for amorphous materials (top) Zn(O,S) of varying [S]/[Zn] ratios taken from spectrophotometry data, and (bottom) TiO$_2$ taken from ellipsometry data.[111]
Figure 4-11: Band energies (in flat-band condition) of $n$-type materials with respect to Cu$_2$O, and their respective error bars. All energies are referenced to the valence band of Cu$_2$O. Reproduced with permission from Ref. [111].

To determine a statistical error bar for $\Delta E_V$ offset measurements, eight identically processed Cu$_2$O samples were measured throughout the course of the experiment. The standard deviations of the core level energies and valence bands extracted from these represent the cumulative effect of fabrication, measurement, calibration, and fitting variation. The valence band of Cu$_2$O was determined to be 0.35 eV relative to the Fermi level, and the offset between the Cu 2$p$ 3/2 core level and the valence band edge was 931.97 eV. The standard deviation of this offset was 0.033 eV. Similarly, the standard deviation of the energy difference from the Cu 2$p$ 3/2 to the O 1$s$ level across all eight samples was found to be 0.023 eV. Assuming that 0.033 eV and 0.023 eV are representative of the standard deviation of core-to-valence band and core-to-core offset measurements respectively, the cumulative standard deviation from all three offsets in equation 4.2 is 0.052 eV. Therefore, a 95% confidence interval is assigned here for all valence band offset measurements to be ±0.10 eV.

Error bars for the bandgaps are determined from selecting different fitting regions and computing the standard error of the least-squares fit line. The error bars in the conduction-band offsets are assumed to be the sum of the bandgap and valence band offset errors.
All of the offsets measured here are plotted together in Fig 4-11. Based on the simulation results in the previous section, for many conventional n-type electron-selective contacts or buffer layers, the band alignment on Cu$_2$O is not favorable for fabricating a high-quality heterojunction. This is demonstrated by the large conduction-band cliff measured for ZnO, TiO$_2$, and CdS.

However, alloying in the ZnO system demonstrates the potential for improving conduction-band alignment, especially when S assumes fractional occupancy on the anion site. Significant bandgap bowing necessitates going to high sulfur contents to achieve good alignment. While pure ZnS demonstrates a prohibitively large spike, intermediate compositions with a [S]/[Zn] ratio > 70% show near-ideal alignment (note here that the ALD Zn(O,S) has a total anion/cation ratio greater than one due to extra hydroxide and oxide incorporation). Attempts to increase the ZnO conduction band via cation substitution are only marginally successful; this explains why alloying with Mg or Sn on the Zn site has been insufficient to make a high-performance heterojunction.

Another promising material is Ga$_2$O$_3$, which offers near ideal electronic alignment. This alignment has led to the record-high open circuit voltages in thermally oxidized (0.8 V) and electrochemically deposited (1.2 V) Cu$_2$O cells. The offset measured in the present study represents an increase over the previous measurement of -0.18±0.16 eV, which is likely due to differences in surface preparation or deposition conditions. This highlights the necessity of direct measurements under device-relevant conditions.

To address interface defect density and SRV, the formation of detrimental surface phases is limited during storage and processing. All bare Cu$_2$O surfaces show no evidence of the CuO phase, which has been identified as a detrimental defect at Cu$_2$O heterojunctions. For sulfides used here, the exposure of a clean Cu$_2$O surface to the H$_2$S sulfur precursor, under typical ALD conditions, resulted in the formation of Cu-S bonds at the surface as evidenced by the presence of S core peaks in XPS. However, it is unclear whether Cu-S bonds form at the interface during sulfide deposition. This is because it is difficult to distinguish between Cu$_2$S
and Cu$_2$O at a buried interface using XPS, given their nearly identical core electron binding energies.

In summary, one promising strategy to improve conduction-band alignment with the low electron affinity of Cu$_2$O involves creating ternary alloys from conventional ESC materials. Alloyning on the anion site with larger isovalent elements pushes the valence-band and conduction-band orbitals up to higher energies. This is demonstrated here with Zn(O,S), which shows an ideal conduction-band offset for sulfur contents $>$70%. Similar improvements alloying with Mg on the cation site are limited by the poor miscibility of (Mg,Zn)O at higher Mg content. The success of this ternary approach also suggests that intermediate compositions of (Zn,Cd)S would also have optimal alignment.

A second approach is to seek unconventional $n$-type buffer layers that may have reduced conductivity, but an intrinsically lower electron affinity. Ga$_2$O$_3$ is demonstrated here as a promising candidate, which explains its role in the highest performing literature devices to date. However, the simulation results suggest that higher carrier concentration is necessary for high-performing devices, thus extrinsic doping of Ga$_2$O$_3$ ($e.g.$, Sn, Ge, F), and Zn(O,S) ($e.g.$, Al, Ga, F) are high-priority areas of research.

4.4.2 Modifying Band Offsets Through Chemical Treatments

As mentioned in the previous section, offsets are not necessarily intrinsic properties of interfaces, and may vary depending upon the fabrication conditions. To test this, several attempts were made to modify the Cu$_2$O/ZnO interface to evaluate the potential for tuning offsets through chemical means. Prior to deposition of ZnO, the Cu$_2$O surface was treated with oxidizing treatments, acidic aqueous treatments, and with a thin layer of a low work-function metal.

For the oxidizing treatments, the film was exposed to ambient air (23.8°C, 59% relative humidity) either on a hot plate at 200°C for 10–30 minutes, or at room temperature for 160 minutes. Alternatively the film was submerged in aqueous 0.02M NaOH (pH = 12.11) for seven minutes, and then rinsed and dried with nitrogen gas.
Figure 4-12: Valence band offsets at the Cu$_2$O interface with ZnO, after varying surface modifications using acidic and basic treatments, as well as low-work function metals.

For acidic treatments, the sample was submerged in lactic acid (pH = 3) as well as a potassium pthalate buffer solution (pH = 4), for seven minutes each, then rinsed and dried with nitrogen gas. Finally, one Cu$_2$O sample was treated with a 2nm layer of Cs metal at the interface, by evaporating Cs$_2$CO$_3$ which decomposes upon heating.

The hypothesis was that oxidizing (basic) and reducing (acidic) treatments would push the band offsets in opposite directions, as has been observed through a variety of studies on ITO.[145] This effect is produced by the modification of the interface or surface dipole through charge transfer to the adsorbed base or acid. In this scenario, basic surface modification could potentially lead to more cliff-type offsets, while acidic surface modification could produce the opposite.

The results of this study are plotted in Fig. 4-12, showing the extracted valence band offset for all surface modifications tried. Identical untreated Cu$_2$O samples deposited on separate days were used as control samples, and to evaluate error bars on the measurement. Indeed, mild surface oxidation did lead to a slightly larger
cliff-type offset, though the change in offset is within the 95% confidence interval and may not be statistically significant. The other treatments also led to an increase in the cliff type offset. In the case of potassium pthalate, XPS revealed a thin surface layer of K that remained at the interface; thus this sample was comparable to the Cs-interlayer sample. The presence of a low work function metal appears to have also induced a more cliff-like offset.

In conclusion, none of the attempted surface modifications appeared to ameliorate the large cliff-type conduction band offset between Cu$_2$O and ZnO, and in fact all treatments led to minimal change. In that regard, the band offsets on Cu$_2$O appear to be relatively insensitive to surface conditions and preparation.

### 4.5 Additional Band Offset Measurement Results

Other emerging PV absorber materials including SnS or Zn$_3$P$_2$ exhibit similarly low electron affinities as Cu$_2$O. The present work points to the challenges in pairing these absorbers with conventional $n$-type buffer layers. However, it also points to the value of developing ternary, tunable buffer layers and unconventional materials that may greatly expand the range of commercially viable PV materials in the future. These tunable buffer layers were also explored for SnS, and several publications have pointed to the importance of the buffer layer band offsets.\[^{146}\][\(^{147}\)]

The same technique described above was also applied to evaluate the precise conduction band offset of the highest-performance Zn(O,S) buffer layer, as well as to determine the optimal [S]:[O] composition ratio in Zn(O,S) to achieve an ideal conduction band offset.\[^{5}\]

Empirically, the optimal buffer layer for SnS was found to be a Zn(O,S) alloy with a 14% ratio of [S]/([O]+[S]), doped with nitrogen to reduce the carrier concentration. In order to model this interface successfully, it is critical to know the exact conduction band offset that this interface produces. 5 nm layers of Zn(O,S):N were deposited onto

\[^{5}\]This content appears in second-authored manuscript, Ref. [139]; other unpublished measurements performed in collaboration with Chuanxi Yang.
Figure 4-13: The extraction of the conduction band offset at the SnS/Zn(O,S) interface through measurement of the core energy levels (a) Zn 2p and (b) Sn 3d, and (c) valence band edges for each sample. (d) The optical bandgap is extracted for Zn(O,S):N with [S]/[Zn] = 0.14. In (e), each of these measurements is translated into an energy band diagram with the relevant numbers included. Reproduced with permission from Ref. [139].

SnS substrates which experienced several minutes of air exposure between depositions. The valence band offsets are extracted using the Kraut method described above, and the conduction band offsets are extracted additionally using the respective layers’ bandgaps.

In Fig. 4-13, the results are plotted for Zn(O,S) with nitrogen doping, and a [S]/[Zn] ratio of 0.14. The conduction band offset is determined to be $-0.38 \pm 0.2$ eV, in part due to the relatively small bandgap of Zn(O,S):N at this composition. The Zn(O,S) system is expected to display significant bandgap bowing,[142] and the bandgap is likely further reduced due to the disordered Zn(O,S) lattice which could produce conduction band tail states.

Given the successful improvement in conduction band offsets on Cu$_2$O through tuning the Zn(O,S) composition, the same should apply to the SnS system as well—this was explored initially through ultraviolet photoelectron spectroscopy on a select set of compositions.[147] A similar study is performed here using XPS on a wider
Figure 4-14: Conduction and valence band energies at the SnS/Zn(O,S) interface referenced to the SnS VBM. The range of compositions measured herein is compared against similar measurements from Ref. [147]. The optimal composition is expected to be at a sulfur concentration of 35–50%.

range of [S]/([O]+[S]) compositions, in the hopes of finding an optimal composition which could improve upon the 14% [S] material.

The results of this search are plotted in Fig. 4-14. A steady increase in the conduction band offset (to more positive energies) is observed across the entire composition range, yielding an optimal [S]/[Zn] composition of 35–50%.

In both the case of Cu$_2$O and SnS, the achievement of optimal conduction band offsets is an important first step, but it is insufficient to produce an optimal heterojunction, as seen in the following sections.

### 4.6 Importance of Interface Defects and Doping

#### 4.6.1 The Challenge of Low Electron Affinities

The importance of simultaneous optimization of the band alignment, reduction in defect density, and maximization of ESC doping density is exemplified by the case of silicon heterojunction with intrinsic thin layer (HIT) cells,[148] which enables these
heterojunction solar cells to exhibit higher $V_{OC}$ than homojunction cells by reducing emitter and interface recombination. The same is true for thin-film heterojunction PV, as evidenced by the theoretical predictions earlier in this chapter. The case of SnS/Zn(O,S) buffer layers illustrates this point well.

After the optimal Zn[O,S] composition was found to be 35–50%, devices were fabricated at these compositions under the assumption that they would show improved conversion efficiencies. Unfortunately, these devices underperformed relative to the 14% composition, in particular showing significantly reduced photocurrent and modest or no improvement in the $V_{OC}$.[139] As a result, the doping densities of the Zn(O,S) layers were explored further.6

Carrier concentrations of thin Zn(O,S) buffer layers were determined through a combination of Hall effect and sheet resistance measurements, on film samples ranging in thickness from 30–100 nm, under dark conditions. This provided a value for the electron mobility in the dark, which is assumed to remain the same under illumination. Then, the sheet resistance was measured on device-thickness films (30–40 nm) using a two-point contact and an electrometer with a 200 GΩ input impedance. Silver paste was applied between the probes and sample surface to reduce the effect of contact resistance. Knowing the resistivity, and the fixed mobility from Hall measurements, allows extraction of the carrier concentration.

The sample is then illuminated with a solar simulator, on a water-cooled stage to prevent heating during the measurement. The resistivity is tracked over time in the light and dark. Fig. 4-15(a) depicts a typical profile of the estimated Zn(O,S) carrier concentration over time with and without the illumination. These results for the nitrogen-doped $[S]/[Zn] = 0.14$ composition are representative of the other samples as well. Fig. 4-15(b) depicts the stabilized carrier concentrations before illumination, one hour into the illumination, and 10 hours after the light has been shut off, for all six films. The films with a sheet resistance greater than 200 GΩ cannot be measured by the electrometer, and therefore have an uncertain upper bound on resistivity and no lower bound on carrier concentration.

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6This work appears in more detail in Ref. [139].
Figure 4-15: (a) The inferred carrier concentration of nitrogen-doped Zn(O,S) with [S]/[Zn]=0.14, determined from sheet resistance measurements as a function of time. Baseline absorber and buffer carrier concentrations are shown for reference. (b) Summary of the stabilized carrier concentrations of each film in the light and dark. There are three different [S]/[Zn] compositions, each fabricated with and without nitrogen doping.[139]

What these results suggest, is that with increasing sulfur composition, the carrier concentration in the buffer (even under illumination) drops dramatically. Beyond 26% [S]/[Zn], the maximum carrier concentration achievable is $10^{16}$ cm$^{-3}$, less than the acceptor concentration present in the SnS absorber. Recalling the simulations in Fig. 4-4, this is the worst case scenario for devices with near-zero or positive conduction band offsets. This parity in carrier concentration maximizes interface recombination by equalizing the hole and electron concentrations at the structural interface, and blocking forward photocurrent with an electronic energy barrier. This explains why improvements in the buffer layer conduction band offset were not sufficient to improve the device efficiency for SnS.

The same challenge appears for Cu$_2$O devices, in which the optimal buffer layer was determined to be Ga$_2$O$_3$. Again, the low electron affinity of Ga$_2$O$_3$ makes it an optimal electron selective contact for Cu$_2$O, but it also makes it a very challenging material to dope effectively. In recent work with Sin Cheng Siah and other colleagues, the reasons for its low doping efficiency were explored for the Ga$_2$O$_3$:Sn system. The conclusion of this work is that low-temperature, amorphous materials tend to show lower dopant activation, and that control of the oxidation state of the dopant
through the reactant chemical potentials could improve activation.[144] It is therefore possible that for both Zn(O,S) and Ga$_2$O$_3$, an optimal buffer layer may yet exist with appropriate conduction band alignment and sufficiently high doping — but will likely require higher temperature growth conditions and alternative device architectures that can accommodate these processing conditions.

### 4.6.2 Interface Stoichiometry and Defects

A final consideration for the optimal selective contact is the role of defects at the interface. In Fig. 4-3, it was demonstrated that higher SRV directly leads to a lower $V_{OC}$. The SRV is itself proportional to the defect or trap density (per unit area) at an interface:

$$ S = N_t \sigma_t v_{th}, $$

(4.4)

The most common determiner of defects at the heterojunction interfaces presented here are lattice mismatch, and the presence of a surface oxide. While it may be very challenging to achieve lattice matching in these systems, the use of an amorphous selective contact appears to improve the passivation of a heterojunction interface by reducing the density of dangling bonds.[113]

More readily tunable, however, is the presence of a surface oxide. In Cu$_2$O devices, this surface oxide comes in the form of CuO, and is harmful for performance. Here, XPS was found to be a useful tool for quantifying the presence of surface oxide, and this was found to negatively impact device efficiency.[120][143] In SnS, on the other hand, the presence of a surface oxide (SnO$_2$ and Sn(O,S)) appears to be beneficial to device performance. It may tie up Sn dangling bonds at the interface, reducing their concentration.[117]

Surface studies and device results on SnS are as yet-to-date inconclusive as to what the optimal interface treatment is, and whether untreated interfaces exhibit Fermi level pinning due to defect states.[149] In this work, all XPS measurements conducted on blank SnS surfaces resulted in a valence band maximum at 0.25 eV relative to the Fermi level, independent of surface treatment, and persisting even
in pump-probe UPS measurements[147] — implying a strong degree of Fermi-level pinning. To investigate this, high-energy XPS measurements were performed at the HiKE beamline at Helmholtz Zentrum Berlin. These measurements were performed on the SnS/ZnO interface, with pure ZnO ($n \approx 10^{19} \text{ cm}^{-3}$) and nitrogen-doped ZnO to reduce the carrier concentration.\footnote{This work was performed in collaboration with Leonard Köhler, who analyzed the XPS data.}

This study concluded that, while the conduction band offset between SnS and ZnO is a large cliff ($\Delta E_C = -0.7 \text{ eV}$), there was still significant band bending produced in the SnS layer. With 4 nm of ZnO deposited on top, the valence band of SnS showed a 0.53 eV shift in energy, and $E_F - E_V = 0.77 \text{ eV}$. However, with thinner and lower-doped Zn(O,S) layers, this band bending disappears. This implies that the overlayers tested to-date were simply too thin or too lowly-doped to result in significant band bending in the SnS.

However, one worrisome conclusion of this study was that during the ALD growth of the ZnO overlayer on SnS, the composition of the surface oxide changed. Whereas an untreated surface shows SnO$_2$ and Sn(O,S) compositions (<1 nm in thickness), the post-ALD surface showed reduced oxide thickness and the presence of a small percentage of Sn metal. Given that the Sn-oxides and Sn metal may influence the band alignment, Fermi level, and surface recombination velocity, this may explain why device performance is sensitive to the oxidation treatment at the surface. Further study on this subject is strongly recommended — as both the case of SnS and Cu$_2$O demonstrate, the properties of the interface are extraordinarily sensitive to fabrication conditions, and in turn can have an outsize impact on device performance.

4.7 Impact on Devices

As mentioned above, the results of these band offset studies have led to significant increases in the $V_{OC}$ of both Cu$_2$O and SnS solar cells. In particular, they led to the production of the record $V_{OC}$ Cu$_2$O/Ga$_2$O$_3$ solar cell, with a $V_{OC}$ of 1.2 V at room temperature. Fig. 4-16 displays the NREL-certified $J - V$ curve of this record $V_{OC}$.
Figure 4-16: The Cu$_2$O/Ga$_2$O$_3$ J-V curve and photovoltaic characteristics under AM1.5 global normal spectral irradiance (ASTM G173, IEC 60904-3 edition 2 at 25°C), measured at NREL.

cell. It is clear that, while the device outperforms previous thin-film Cu$_2$O cells, it has traded the problem of low $V_{OC}$ for the challenge of a low $FF$. This is explained by the low carrier concentration in the Ga$_2$O$_3$ layer, referenced above. This low doping level produces a non-ohmic contact at the ESC/transparent conducting oxide contact — suggesting that there is still a great scientific need for highly $n$-type, low electron affinity, transparent materials for PV applications.

The role that these contacts have played in improving the efficiency of PV materials after many decades of bulk material optimization is perhaps best demonstrated by the way in which contact selection can improve the performance of lower quality absorber layers — for example, sputtered Cu$_2$O solar cells. Sputtering represents a promising technique for high-throughput, inexpensive manufacturing of photovoltaics. To date, however, no commercial PV modules are formed with pure sputtering (no post-deposition treatments) of the absorber layer. In the case of Cu$_2$O photovoltaics, sputtered absorbers have underperformed, achieving maximum $V_{OC}$ of 0.26 V and conversion efficiency of 0.4%.[150] This is often attributed to poor bulk transport properties such as low mobility and low minority carrier lifetime.
Instead, a sputtered cell is fabricated using the optimal Ga$_2$O$_3$ contact. The resulting cell produces a $V_{OC}$ of 1.1 V and efficiency of 2.04%, as seen in Fig. 4-17. The poor EQE relative to that of the record efficiency, electrochemically-deposited cell described above suggests a very short carrier collection length, and it is clear that the Cu$_2$O layer needs improvement. However, finding the right contact material enables this conclusion — where both contact materials and bulk transport properties are suboptimal, it is often too difficult to determine the root causes of low performance.

### 4.8 Summary

In this chapter, I have presented an experimental approach to quantifying the electronic band alignment between two semiconductors, through the use of photoelectron spectroscopy. This allows one to study the energetics and chemical composition of an interface between an absorber layer and selective contact, and assess where losses may be occurring.

By measuring and modeling the interface properties between Cu$_2$O and a number of possible electron-selective contacts, I have shown that the poorly-aligned conven-
tional contact materials such as ZnO may have masked decades of effort to make higher quality Cu$_2$O solar cells. By solving the contact problems for other novel absorbers, we can hope to avoid decades of misdirected research effort towards developing new PV materials.
Chapter 5

All-Electrical Characterization of Recombination

The measurements of the previous two chapters focused largely on quantifying bulk recombination through minority carrier lifetime, and interface recombination through photoelectron spectroscopy. Indeed, quantifying these losses is necessary to understand the performance of novel PV materials. However, the measurements described therein were time consuming and expensive. XPS measurements of band offsets often require days of sample preparation, measurement, and analysis for each overlayer material and thickness, resulting in months of study. Similarly, measurements of minority carrier lifetime often require dedicated samples and expensive measurement apparatus.

On the path to evaluating more PV materials per unit time, it would be of great benefit to reduce the time necessary to quantify recombination losses in PV cells, and their impact on the $V_{OC}$ in order to pick high-priority research areas.

Fortunately, the very information we seek about these different recombination mechanisms lies hidden in plain sight — in the current-voltage or $J$-$V$ curves measured for every cell produced. $J$-$V$ measurements are fast, easily accessible, inexpensive, and low noise, making them an ideal vehicle for translating the months-long experiments described in Chapters 2 and 3 into weeks instead. Yet, while every recombination mechanism leaves its signature on a room-temperature $J$-$V$ curve, these signatures
are not unique, making it difficult to uniquely identify the mechanisms at work. Put another way, there are many ways to make an underperforming solar cell — the goal of characterization should be to figure exactly what has gone wrong.

This chapter discusses how probing solar cells in other dimensions like temperature, light intensity, and wavelength can allow one to more uniquely separate out and identify the loss mechanisms at work. The use of temperature to electrically probe the energetics of a heterojunction PV device has been discussed for a number of different PV absorbers.[151][152][153][154][155] Recently, there have been several efforts to incorporate illumination intensity as well to provide a more complete understanding of the kinetics of recombination in heterojunction PV devices.[156][157][158] Where different recombination mechanisms exhibit different functional dependences on $T$ and illumination $I$, they may then be identified by directly measuring as a function of these bias conditions. The technique will be referred to herein as "$JVTi$", or the measurement of PV cell current density as a function of voltage, temperature, and illumination intensity with the goal of increasing the precision and accuracy of our cell model fitting as a result. This work extends upon the aforementioned references and applies these models to Cu$_2$O solar cells as an example.

5.1 Analytical Modeling of $V_{OC}$

The $V_{OC}$ point offers a great single measure of the quality of a photovoltaic cell, as a measure of the balance in forward photocurrent and various recombination currents (a.k.a. dark or reverse saturation currents). Alternatively, it is a measure of the electrochemical potential difference between electrons and holes, which corresponds to their ability to do positive work and their respective concentrations relative to the density of available electronic states. In addition to simplifying the mathematical modeling, focusing on the $V_{OC}$ also means that the effects of series resistance are mitigated as no current flows in open-circuit.

Modeling this $V_{OC}$ as a function of $T$ and $I$ identifies the functional forms of different recombination mechanisms, allowing us to identify their presence in the
observed data above.\textsuperscript{1} Returning to the electrical engineering model of the solar cell, recall that, at the open-circuit condition, conservation of charge suggests that all photoexcited carriers generated must recombine in the cell. Thus, for multiple recombination rates, $R_i$, the following expression holds:

$$ G = \sum_i R_i = R_{\text{quasi-neutral}} + R_{\text{depletion}} + R_{\text{interface}} + R_{\text{back contact}} + \ldots $$  \hspace{1cm} (5.1)

If the internal quantum efficiency is 100\%, this generation rate $G$, integrated over the full thickness of the absorber, would equal the photocurrent $J_{\text{ph}}$. However, in many non-ideal materials, not all photogenerated carriers produce a forward photocurrent before they recombine. Such recombination is distinct from the voltage-driven recombination currents modeled here. Thus, the balance between photocurrent and recombination at the $V_{\text{OC}}$ point may be expressed as:

$$ J_{\text{ph}} = J^b + J^d + J^i, $$  \hspace{1cm} (5.2)

where $J^b$, $J^d$, and $J^i$ represent bulk quasi-neutral region, depletion region, and heterojunction interface recombination rates respectively. Each recombination rate (in units of $[\text{cm}^{-2}\text{s}^{-1}]$) is related to a recombination current density by the charge of an electron, as $R = qJ$. Each recombination current is depicted schematically in Fig. 5-1. Back contact recombination is not included in the present work given that the device thickness is over five times greater than the diffusion length in Cu$_2$O; thus very few minority carriers are expected to reach the back contact.

Similarly, the $V_{\text{OC}}$ may also be expressed in terms of the separation of quasi-Fermi levels in the device. Adopting a formalism from Grover and Li,\textsuperscript{[156],[157]} this electrochemical potential difference is captured through the non-dimensional $\beta = \sqrt{n_e p_h / n_i^2}$:

$$ V_{\text{OC}} = \frac{k_B T}{q} \ln \left( \frac{n_e p_h}{n_i^2} \right) = \frac{k_B T}{q} \ln(\beta^2). $$  \hspace{1cm} (5.3)

Now, one can express each recombination current above as a function of the non-

\textsuperscript{1}Dr. Niall Mangan assisted with deriving the equations presented in this section.
Figure 5-1: Cartoon of recombination currents by location, depicting bulk, depletion region, and interface recombination in their respective cell regions.

dimensional $\beta$. Beginning with depletion region recombination, recall Shockley-Read-Hall recombination statistics from Eq. 3.2. Assuming that recombination occurs through the worst-case scenario of a midgap trap, the hole and electron occupancies match the intrinsic carrier concentration, and the recombination rate can be greatly simplified. Integrating this recombination over the depletion width thickness $W_d$ gives the following area recombination rate or current density [157]:

$$R^d = \frac{W_d}{\tau_e + \tau_h} n_i \beta$$  \hfill (5.4)

$$J^d = \frac{q W_d}{\tau_e + \tau_h} n_i \beta = J_0^d \beta.$$  \hfill (5.5)

The functional form of this recombination current includes a voltage-independent term ($J_0$) and an exponential voltage term through $\beta$. In similar fashion, the bulk quasi-neutral region recombination may be modeled for a $p$-type material as [157]:

$$R^b = \frac{W_b n_e p_h}{\tau_e N_A}$$  \hfill (5.6)

$$J^b = \frac{q W_b n_i^2}{\tau_e N_A} \beta^2 = J_0^b \beta^2.$$  \hfill (5.7)
Recombination at the interface may be more similar to depletion region or quasi-neutral recombination depending upon where the Fermi level sits at the interface. If the Fermi level is near a band edge, in the case of a type-inverted interface, the recombination rate is relatively simple as it is limited only by the supply of one carrier type. In the case of a mid-gap Fermi level, or non-inverted interface, the recombination rate is limited by the supply of both holes and electrons. First, for the inverted case, assuming a \( p \)-type absorber with a valence band density of states \( N_A^V \):

\[
R^i = S_p \rho = S_h N_A^V \exp \left( \frac{-E_{IF}^G}{k_B T} \right) \beta^2 \tag{5.8}
\]

\[
J^i = q S_p N_A^a \exp \left( \frac{-E_{IF}^G}{k_B T} \right) \beta^2 = J^i_0 \beta^2, \tag{5.9}
\]

where \( S_p \) is the hole surface recombination velocity at the heterojunction between \( \text{Cu}_2\text{O} \) and the ESC layer, and \( E_{IF}^G \) is the interface bandgap. This expression for interface recombination was first described for inverted interfaces by Rothwarf.\[159\]

However, for the non-inverted case, fewer simplifying assumptions can be made. The recombination at the interface is limited by the concentration of both holes from the absorber \( p_{\text{abs}}^h \) and electrons in the ESC \( n_{\text{ESC}}^e \). Expressions for both may be found in Ref. [160], pg. 66. Combining the voltage-dependent expressions for electrons and holes, and their respective surface recombination velocities:

\[
J^{i,n} = \frac{q S_n S_p}{S_p N_A^{\text{abs}} + S_n N_D^{\text{ESC}}} \sqrt{N_A^{\text{abs}} N_V^{\text{abs}} N_D^{\text{ESC}} N_C^{\text{ESC}}} \exp \left( \frac{-E_{IF}^G}{k_B T} \right) \beta = J^{i,n}_0 \beta \tag{5.10}
\]

Taken together, these recombination rates reveal an important distinction. Where one carrier type is in abundant supply and occupies all of the traps, the recombination rate is dependent upon the supply of the minority carrier. The resulting recombination rates are proportional to \( \beta^2 \), and have an ideality factor of 1. Alternatively where the defects sit directly between the hole and electron quasi-Fermi levels and both carriers are readily available, the recombination rate is instead proportional to \( \beta \) and has an ideality factor of 2. This dichotomy offers a convenient grouping into recombination rates with ideality factor 1 (\( J_{0,1} \)), and those with ideality factor 2 (\( J_{0,2} \)).
The resulting current balance from Eq. 5.2 at open-circuit conditions is therefore:

\[ J_{ph} = J_{0,1} \beta^2 + J_{0,2} \beta. \]  (5.11)

This is a simple quadratic equation for \( \beta \); solving for \( \beta \) and plugging it into Eq. 5.3 gives:

\[ V_{OC} = 2 \frac{k_B T}{q} \ln \left( \frac{J_{0,1}}{2J_{0,2}} \left( \sqrt{1 + 4 \frac{J_{ph} J_{0,2}}{J_{0,1}^2}} - 1 \right) \right). \]  (5.12)

Given the complexity of this equation, it can be simplified by considering several different limiting cases. The first of these is the case where \( J_{0,2} \) terms outweigh \( J_{0,1} \) terms, and/or in high injection, such that \( 4 \frac{J_{ph} J_{0,2}}{J_{0,1}^2} \gg 1 \). In this limit, the expression for \( V_{OC} \) simplifies to:

\[ V_{OC} = \frac{k_B T}{q} \ln \left( 4 \frac{J_{ph} J_{0,2}}{J_{0,1}^2} \right). \]  (5.13)

Substituting the recombination current expressions from above gives an expression for the \( V_{OC} \) under the influence of multiple parallel recombination pathways.

More critical to understand, however, is the functional form for the temperature and illumination dependence of \( V_{OC} \). In particular, the local slope of the \( V_{OC} \) about room temperature \( T_R \), provides information about the activation energy of the dominant recombination mechanism:

\[ V_{OC}(T_R) = \frac{E_A}{q} + T_R \frac{dV_{OC}}{dT}|_{T_R}. \]  (5.14)

Here, the extrapolation of \( V_{OC} \) to 0 K is termed the activation energy, \( E_A \).

Solving this expression for the activation energy, where the ideality factor \( n \) may vary as a function of injection level as well, gives:

\[ E_A = (n - 1) \frac{J_0^d E_G^d + J_0^i E_G^{IF}}{J_0^d + J_0^i} + (2 - n) \frac{J_0^b E_G + J_0^i E_G^{IF}}{J_0^b + J_0^i}. \]  (5.15)

Where the interface recombination dominates bulk recombination, regardless of the ideality factor (i.e., \( J_0^i \gg J_0^{b,d} \)), the activation energy reduces to the interface
In summary, the activation energy tells us a great deal about the nature of recombination in a device. If this activation energy is equal to the bandgap, it is indicative of bulk recombination dominating the $V_{OC}$, while if the activation energy is less than the bandgap, it suggests that interface recombination dominates.

Given the complexity of the aforementioned recombination currents, it can be difficult to intuit where the boundary between bulk and interface limited recombination occurs. To visualize the transition between bulk and interface recombination-dominated regions, the activation energy is plotted in Fig. 5-2. The following properties of Cu$_2$O are assumed: a bulk bandgap of 2 eV, $N_A = 10^{14}$ cm$^{-3}$, depletion width of 500 nm, quasi-neutral region width of 2 $\mu$m, and interface gap of 1.6 eV (see Appendix for additional details). The bulk lifetime $\tau_e$ and interface recombination velocity $S_p$ are varied over several orders of magnitude. The activation energy transitions between 1.6 eV and 2.0 eV for interface- and bulk-limited regimes, respectively.

The transition region between interface- and bulk-dominated recombination is not
fixed; in fact, it changes with illumination intensity (generation rate), and for different interface energy gaps. The contours demarcating bulk- and interface-dominated recombination are plotted in Fig. 5-3. Increasing the size of the conduction band offset or decreasing the interface energy gap increases the region of interface-limited activation energy substantially, and for large cliff-type offsets, it is nearly impossible to find a bulk-dominated recombination regime. For smaller interface conduction band offsets, increasing light intensity can increase the region of parameter space in which bulk recombination dominates. If a cell sits in between these limits in parameter space, sweeping the light intensity should show a change in activation energy.

In summary, analytical models of the $V_{OC}$ as a function of temperature and illumination intensity offer a window into the relative strengths of bulk and interface recombination. In the following sections, I will discuss how such measurements can be performed, and demonstrate an example of model fitting on Cu$_2$O solar cells.
5.2 Experimental Setup for Electrical Measurements

$JVTi$ measurements are performed in a cryostat using a solar simulator lamp as the light source. The measurements reported in this chapter were performed using three different cryostat setups: at the National Renewable Energy Laboratory (NREL) in Golden, CO; at the Helmholtz Zentrum Berlin in Berlin, Germany; and in the PV Lab at MIT. The MIT PV Lab experimental setup described here is similar across all tools.

5.2.1 Cryostat Components

To provide cooling power for low-temperature measurements, an ARS 4K cryostat was used. This cryostat cold finger is capable of achieving temperatures as low as 4 K, and as high as 340 K. Cooling is provided by a helium refrigeration cycle, including an expander inside the cold finger, and an external compressor which recompresses the He and dumps the heat to chilled water in a heat exchanger. This water then exchanges heat with tap water in a Neslab water chiller. The components necessary for this measurement are depicted in Fig. 5-4.

Focusing on the cryostat cold finger specifically, the components are shown in an exploded view in Fig. 5-5. A radiation shield and then a vacuum shroud are placed around the sample and cold finger, and the vacuum can is pumped down to pressures.
Figure 5-5: Exploded view of cryostat hardware, including the cold finger with integral expander and ports for He, vacuum, and wires. The radiation shield and vacuum shroud fit concentrically around the cold finger. The sample is mounted at the end of the cold finger, along with multiple temperature sensors and a 50 Ω strip heater for temperature control.

< 1 × 10⁻⁴ Torr. This ensures negligible convection or conduction heat transfer from the ambient air to the cold sample, and minimal radiative heat transfer.

A typical timescale for cooldown under vacuum is plotted in Fig. 5-6. Sensor A is mounted to the end of the cold finger, while sensor B is mounted to the solar cell sample. While sensor A reaches temperatures as low as 6 K, sensor B on the sample is limited to temperatures in the range of 70–80 K, likely due to radiative heat transfer from the vacuum shroud and optical windows, and a finite thermal resistance between the sample and cold finger. At 100 minutes, the solar simulator is turned on. This additional power input of 100 mW/cm² introduces a heating load which raises the sample temperature by 10–15 K.

5.2.2 Mounting of and Electrical Contact to Cells

A variety of techniques are available for anchoring the sample to the cold finger, using custom copper sample mounts. Each sample mount includes a 1/4-28 threaded screw either integral to the mount or separate, making it easy to screw the sample stage into the cold finger.

Fixing the sample down to the copper sample mount is important, as it will be suspended horizontally during operation. Unfortunately most tapes, glues, and organics fail at cryogenic temperatures, or outgas under high vacuum. This restricts the possible materials to metals like copper, thermally conductive electrical insulators
Figure 5-6: Typical cooling curve for the cryostat under normal operation. Sensor A is mounted to the end of the cold finger, while sensor B is mounted to the solar cell sample. At 100 minutes, the solar simulator lamp is turned on which heats the sample above its base temperature in the dark. Cooling to base temperature takes approximately 100 minutes, after which the time constant for temperature stabilization under changing thermal loads is approximately 5 minutes.

such as sapphire, teflon for any plastic components, polyimide tape, and low-volatility adhesives.

To hold the sample in place, one may add a thin layer of glue (GE Varnish recommended) between the copper stage and sample. A low-volatility glue with reasonable thermal conductivity can both help anchor the sample, and eliminate any vacuum gaps between the back of the sample and the copper stage. However, occasionally the glue delaminates from the copper stage at low temperatures, which dramatically worsens the thermal conductance between the sample and the cold finger. An alternative adhesive is a silicone-based grease such as Apezon or Dow Corning vacuum grease. This also maintains reasonable thermal conductivity at low temperature, and because it does not cure like glue, it is tolerant to vibration and thermal expansion mismatches. In both cases, it is difficult to fully clean the adhesive off of the sample when done.

Where the sample has a conductive back contact and front contact, it must be electrically isolated from the cold copper mount. This may be done with a sapphire plate which is electrically insulating but thermally conductive, or alternatively with a thin layer of kapton/polyimide tape. If the sample requires illumination through the substrate (superstrate growth process), it becomes much more difficult to mount
it effectively. A sapphire window inset into a hole in the copper stage allows one to place the illuminated side of the sample in contact with the sapphire while making electrical contact to the other side.

A handful of typical $JVTi$ copper stages are shown in Fig. 5-7, showing a standard configuration as well as one designed for superstrate illumination, and one designed for electrical isolation of the back contact.

Electrical contact to the cell should ideally be made in a 4-point probe configuration, which eliminates the contribution of contact resistance to the measurement by sourcing/sensing current and voltage on different leads. This is especially critical at low temperatures where contact resistances may be higher. There are three simple strategies for making robust electrical connection. The first is to use mechanical clips, cantilevered to provide a spring force to hold the clip in place. These clips can be cut from copper sheet metal and offer the dual purpose of anchoring the sample \emph{via} their spring force, and providing an electrical conduction pathway. However, the large mechanical force coupled with sample vibrations sometimes leads to the clip punching through the contact and shunting the cell. The risk of this may be reduced by including a piece of indium foil between the clip and contact. The second option is to use Au wire-bonding to run a wire from the device contact to a more robust electrical pad off of the device. This limits the risk of punch-through, but is time-intensive and expensive for every sample. A third strategy, used most frequently in this work, is to affix four probe wires to the contacts using colloidal silver paste. The paste acts as a weak adhesive and a conduction pathway, and is easy to apply to each device in a four-point probe configuration.

Lastly, a silicon diode temperature sensor should be placed in direct thermal contact with the sample, to accurately measure the temperature that the sample experiences. With good thermal contact and proximity to the cell being measured, one should be able to observe the small (< 50 mK) resistive heat load produced during a $J$-$V$ sweep on the sample.
Figure 5-7: Custom machined copper stages for performing $JVTi$ measurements. Clockwise from top: a low thermal inertia sample mount for front-contacted cells; a sample mount with an electrically isolated aluminum plate for making electrical contact to the back of a solar cell; and a sample mount with an inset hole and sapphire window for superstrate illumination. Copper clips visible in each image can be used for mechanical attachment or electrical contact.
5.2.3 Illumination Control

Illumination is provided by a Newport/Oriel LCS-100 Solar Simulator, which is a class ABB simulator with a 1.5" diameter uniform output beam. The solar simulator outputs a constant light flux of approximately 1.3 suns at a distance of 12" from the lamp, so variations in light intensity and spectrum can be achieved through neutral density filters.

Reflective neutral density filters from Thorlabs are mounted in a set of two consecutive automated filter wheels; with 10 unique filters, 36 possible illumination intensities are achievable over 4 orders of magnitude in light intensity. To verify that the neutral density filters produce the intensity expected, the light intensity was calibrated with a reference Si solar cell. Fig. 5-8 plots the expected filter optical density vs. the actual optical density achieved, where 0 is equivalent to 1-sun illumination intensity.
5.2.4 Running a Full $JVT_i$ Sweep and Processing Results

$JVT_i$ measurements may be run manually, or through an automated Labview program. The Labview program steps through a set of pre-defined temperatures, and at each temperature runs through a series of different light intensities. As the temperature can easily change upon changing filter wheel settings, the automated code provides a window of time to stabilize the temperature before each measurement to within ±0.5 K of the target temperature. Typically, a scan through a range of temperatures and light intensities may take 3–8 hours total, and can easily be run in a single day or overnight.

The resulting $J-V$ curves taken at each temperature and light intensity are saved in text files, and can be uploaded and processed through MATLAB code (see Appendix). This code allows one to characterize the $J_{SC}$, fill factor and $V_{OC}$ over the range of observation conditions as well as ideality factors, parasitic resistances, and more. An example of the volume of data produced by one cell is plotted in Fig. 5-9.

The hardware and software framework for running these measurements can also easily be applied to photoconductivity, photo-Hall, and optical impedance spectroscopy measurements as well. In the present work, the tool will be used to illustrate solar cell characterization using Cu$_2$O as a test platform.
5.3 Case Study: Cu$_2$O Interface Band Alignment

Thin-film Cu$_2$O heterojunction solar cells are fabricated with the following device stack: Au/Cu$_2$O/ESC/Al:ZnO, where ESC represents one of three different electron selective contacts: zinc oxide (ZnO), amorphous zinc tin oxide (ZTO), and gallium oxide (Ga$_2$O$_3$). The ESC and transparent conducting oxide (Al:ZnO) are both deposited by atomic layer deposition, while the Cu$_2$O is deposited by electrochemical deposition. Deposition conditions are detailed elsewhere;[113] the cell stacks are identical in thickness and deposition conditions, with the only exception being the differing ESCs. This suggests that all variation in electrical performance between these devices can be prescribed to the ESC properties and heterojunction interface.

Fig. 5-10 displays the room-temperature, one-sun $J$-$V$ scans for all three devices, as well as the $V_{OC}$ of each device plotted as a function of temperature. Cell data is taken over five orders of magnitude in light intensity ($10^{-5}$ to 100 suns, or 0.01–100 mW/cm$^2$ in incident light flux), and over the temperature range of 100–320 K. This full data set is presented in Fig. 5-9 for one particular ESC, the Cu$_2$O/ZnO heterojunction. Surface plots of $J_{SC}$ suggest a linear response with respect to illumination intensity.

To fit the $V_{OC}$ and activation energy of these cells, several additional assumptions can be made about the Cu$_2$O devices. First, the depletion region and interface recombination dominate over quasi-neutral region recombination, given that the depletion width in Cu$_2$O is larger than the minority carrier diffusion length.[131] Similarly, the heterojunction interface is not inverted; thus recombination currents in these cells are expected to have an ideality factor of 2. Lastly, the cells are in low injection due to the low minority carrier lifetime. Given those assumptions, the $V_{OC}$ model reduces to:

$$V_{OC} = 2\frac{k_B T}{q} \ln \left(4 \frac{J_{ph}}{J_0^3 + J_0} \right).$$  \hspace{1cm} (5.17)

Again taking the derivative of $V_{OC}$ with respect to $T$ and extrapolating to 0 K yields
the activation energy:

\[ V_{OC}(T \rightarrow 0K) = \frac{J_0^d E_G + J_0^i E_{IF}^G}{J_0^d + J_0^i}. \]  

(5.18)

If interface recombination dominates over the bulk, then this reduces to:

\[ E_A = V_{OC}(T \rightarrow 0K) = E_{IF}^G. \]  

(5.19)

The \( V_{OC} \) extrapolation to sub-bandgap energy levels in Fig. 5-10 would appear to indicate an interface-limited \( V_{OC} \) and, as a result, the interface bandgap. To verify this, the cells are measured over a range of light intensities. Over two orders of magnitude in light intensity, the activation energy of each cell is found to be roughly constant. There is no evidence of a transition in activation energy towards the bandgap energy. This implies that the cells tested are interface recombination-limited, and that \( J^i \) exclusively determines the \( V_{OC} \) in these Cu₂O cells – even for the highest performing devices.

The interface energy gap extracted may be compared to that measured through
Figure 5-11: Plot of activation energy vs. light intensity for all three Cu$_2$O devices in the present study, showing relatively constant activation energy with respect to $G$, and no transition towards the bulk bandgap at 2 eV.

<table>
<thead>
<tr>
<th></th>
<th>Cu$_2$O/ZnO</th>
<th>Cu$_2$O/a-ZTO</th>
<th>Cu$_2$O/Ga$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{IF}^G$ [eV]</td>
<td>0.8 ± 0.2</td>
<td>1.1 ± 0.2</td>
<td>1.8 ± 0.2</td>
</tr>
<tr>
<td>$E_A$ [eV]</td>
<td>0.91 ± 0.03</td>
<td>1.33 ± 0.03</td>
<td>1.82 ± 0.03</td>
</tr>
</tbody>
</table>

Table 5.1: Cu$_2$O interface energy gaps measured by different techniques

photoelectron spectroscopy. In Fig. 5-12, the measured band offsets for the three ESCs employed here are plotted next to one another.[111][113][116] Comparing the interface energy gap extracted from these photoelectron spectroscopy measurements to that measured from $JVTi$ in Table 5.1 suggests a very strong agreement. $JVTi$ measurements of the interface energy gap on these particular cells offer similar accuracy, but higher precision than comparable photoelectron spectroscopy measurements. This implies that $JVTi$ as a technique may be able to substitute for XPS and UPS measurements and offer a significantly faster rate of materials screening in the pursuit of the optimal contact material.
Lastly, given this interface limit where interface recombination is much greater than bulk recombination currents, it is possible to calculate $J_0^i$ directly from the slope of the $V_{OC}$ vs. $T$ plots in Fig. 5-10. In Table 5.2, this analysis is performed for all three $\text{Cu}_2\text{O}$ devices. For a non-inverted interface with ideality factor = 2, and assuming doping densities in the $\text{Cu}_2\text{O}$ and ESC are comparable, the slope can be expressed as:

$$V_{OC} = \frac{E_{\text{IP}}^G}{q} - \frac{2k_B T}{q} \ln \left( \frac{J_{i00}}{J_{ph}} \right) \quad (5.20)$$

$$\text{slope} = -\frac{2k_B}{q} \ln \left( \frac{q^2 S_n S_p}{(S_n + S_p)^2} \cdot \sqrt{N_C N_V} \right) \quad (5.21)$$

Assuming that the $\text{Cu}_2\text{O}$ valence band and ESC conduction band density of states are $1 \times 10^{19}$ and $3 \times 10^{18}$ cm$^{-3}$ respectively, one can extract an effective surface recombination velocity at the interface, $\text{SRV}_{\text{eff}} = \frac{S_n S_p}{S_n + S_p}$. The interface with $\text{Ga}_2\text{O}_3$ is found to have the highest effective SRV based on this analysis. This is expected to be a lower bound on the effective SRV, as a lower ideality factor (some inversion at the interface) would imply a larger SRV at the interface.

Knowing the SRV and the interface energy gap allows us to revisit the limiting
Table 5.2: Extracted surface recombination velocities from Cu$_2$O cells

<table>
<thead>
<tr>
<th>Cell</th>
<th>Slope</th>
<th>SRV$_{eff}$</th>
<th>$\tau_{\text{min}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O/ZnO</td>
<td>1.74 mV/K</td>
<td>$2 \times 10^2$ cm/s</td>
<td>–</td>
</tr>
<tr>
<td>Cu$_2$O/a-ZTO</td>
<td>2.42 mV/K</td>
<td>$1 \times 10^4$ cm/s</td>
<td>5 ps</td>
</tr>
<tr>
<td>Cu$_2$O/Ga$_2$O$_3$</td>
<td>2.72 mV/K</td>
<td>$6 \times 10^4$ cm/s</td>
<td>0.6 ns</td>
</tr>
</tbody>
</table>

Scenarios expressed in Fig. 5-3. The fact that each of these cells appears to be in an interface-limited regime over all light intensities tested would set a lower bound on the bulk minority carrier lifetime. For the poorly aligned interfaces as in ZnO or ZTO, this lower bound is unhelpfully small; a result of the overwhelming effect of high interface recombination. However, the Cu$_2$O/Ga$_2$O$_3$ device offers a more reasonable lower bound on the lifetime of 0.6 ns — if it were lower in this device, the activation energy should have moved closer to the bulk bandgap. While this analysis requires several assumptions, it offers a window into the thresholds for observing other recombination types in Cu$_2$O solar cells. For the highest performing Cu$_2$O/Ga$_2$O$_3$ cell, it also suggests that thin-film Cu$_2$O devices are approaching the point of equal $V_{OC}$ losses from bulk and interface recombination thanks to the extensive interface engineering described in the previous chapters.

5.4 Accounting for Artifacts in $JVT_i$ Measurements

The models expressed above are built for an ideal solar cell, but Cu$_2$O and other cells may be subject to a number of experimental artifacts which violate the assumptions made above. To avoid these pitfalls, several steps are outlined in the following sections.

5.4.1 Effect of Bulk Carrier Freezeout

The first potential artifact to consider is the role of freezeout of bulk acceptors and its impact on cell performance. Cu$_2$O contains relatively deep bulk acceptors with a binding energy of 0.25 eV,[161] in part due to its low static dielectric constant and
relatively high hole effective mass. This means that not all acceptors are ionized at room temperature, and at the lowest measurement temperatures these acceptors would be expected to be completely frozen out. Reducing the effective doping density in the Cu$_2$O will raise the hole quasi-Fermi level in the absorber and thereby reduce the $V_{OC}$; furthermore at complete freezeout the solar cell will begin to act like a resistor.

The hole concentration as a function of temperature and acceptor binding energy can be expressed as:[162]

$$p = \frac{2N_A}{1 + \sqrt{1 + 2N_A \exp \left( \frac{E_b}{k_B T} \right)}}. \quad (5.22)$$

where $E_b$ is the acceptor binding energy. The hole concentration equals the acceptor density in the limit of sufficiently high temperatures or low acceptor binding energies when the argument of the exponential is small. As the open circuit voltage scales with the natural logarithm of $p$, this freezeout carries over into the $V_{OC}$. Fig. 5-13 plots both the effect of deep acceptor binding energies on the activation ratio (inset), as well as the open-circuit voltage and extrapolated $V_{OC}$.

The most important feature to note from these plots is the temperature at which the slope of $V_{OC}$ vs. $T$ changes. For a binding energy of 0.25 eV, this occurs around 200 K. Thus for Cu$_2$O, extrapolating any information from the plot of $dV_{OC}/dT$ must be done above 200 K. Indeed, in Fig. 5-10 it is clear that for all three devices, the $V_{OC}$ stops increasing and flattens or rolls over between 180–200 K. The observation of this freezeout from device characteristics corroborates earlier measurements of a 0.25 eV bulk acceptor binding energy in Cu$_2$O.

At lower temperatures, the extrapolation of $V_{OC}$ to 0 K is impacted by the deeper acceptor energy, and in fact extrapolates to $E_G - E_b/2$ instead of the bandgap. For other materials with deep acceptors or donors, one may observe sub-bandgap extrapolations of $V_{OC}$ from this artifact, which may be confused with interface recombination. Therefore, measurements should be performed above the appropriate transition tem-
Figure 5-13: Plot of $V_{OC}$ vs. $T$ for a number of different acceptor binding energies, showing the change in slope and activation energy associated with freezeout. Inset, the dopant activation ratio is plotted for the same binding energies.
5.4.2 Effect of Parasitic Shunt Conductance

In the equivalent circuit model of a solar cell, voltage may be lost due to reverse saturation (recombination) currents, as well as ohmic shunting pathways. The effect of a shunt on the open circuit voltage is negligible above a certain resistance, however this threshold resistance depends strongly upon the $V_{OC}$. In Fig. 5-14, room temperature cell data are plotted for a random set of 16 solar cells from the same Cu$_2$O/Ga$_2$O$_3$ device library. For shunt resistances below 1000 $\Omega$ cm$^2$, the $V_{OC}$ drops precipitously. This is critical to avoid when measuring and modeling the $V_{OC}$, as such shunting will strongly mask any real trends in the $V_{OC}$ with respect to temperature and illumination intensity.

To determine a lower bound on shunt resistance for performing $JVTi$ measurements, its impact is confirmed through numerical device modeling in SCAPS, in which a baseline Cu$_2$O/Ga$_2$O$_3$ device is simulated over a range of shunt resistances and tem-
peratures. At 300 K, the model of shunt resistance and open-circuit voltage closely matches the data. At higher temperatures (350 K), the lower $V_{OC}$ makes the cell less sensitive to shunting, while at 250 K, the opposite occurs. Thus, a cell which does not appear to be negatively impacted by shunting at room temperature may become limited by the shunt resistance at lower temperatures. In order to properly measure and model Cu$_2$O devices down to 200 K, it is recommended to have a device shunt resistance greater than 2000 $\Omega$ cm$^2$.

5.4.3 Effect of Voltage-Dependent Photocurrent

A final artifact commonly observed in $V_{OC}$ modeling is voltage-dependent photocurrent. Earlier, it was assumed that recombination currents at the $V_{OC}$ point would perfectly balance the forward photocurrent, taken to be equal to the current at short-circuit conditions. However, in depleted absorbers with relatively low mobility-lifetime products, carriers are collected predominantly through drift rather than diffusion. As the bands flatten closer to the $V_{OC}$ this photocurrent will decrease, forcing the device to reach $V_{OC}$ at a lower voltage than anticipated.

In prior work, the voltage-dependent photocurrent at the $V_{OC}$ point was quantified by subtracting the dark and light $J$-$V$ curves.[163] Unfortunately, this process is difficult for Cu$_2$O devices, which have an injection-dependent series resistance that influences the light and dark $J$-$V$ curves differently near the $V_{OC}$ point. Based on voltage-dependent EQE measurements, the photocurrent is expected to be between 80–90% of the short-circuit value at $V_{OC}$, and the impact of this can be estimated through a simple ideal diode model:

$$V_{OC,\text{real}} = V_{OC,\text{measured}} + \delta V_{OC} = \frac{n k_B T}{q} \left[ \ln \left( \frac{J_{ph}(0V)}{J_0} \right) + \ln \left( \frac{J_{ph}(V_{OC})}{J_{ph}(0V)} \right) \right]. \quad (5.23)$$

For a photocurrent ratio of 1.1–1.2 (or 83–90% of full photocurrent at open-circuit), this corresponds to a $\delta V_{OC}$ of 5–9 mV. For $\delta V_{OC}$ to exceed the 30 meV error bars on the present measurements, this photocurrent ratio would have to exceed 2 — in other words, the photocurrent at $V_{OC}$ would be less than 50% of that at short-circuit
5.5 \textit{JVT}i Measurements on Other Materials

With the successful application of this technique to \ce{Cu2O} and in other materials systems in literature, the tool could be applied to a variety of other semiconductors. One candidate material system is PbS quantum dot (QD) photovoltaics.\footnote{Chia-Hao Chuang fabricated these cells and characterized them; results are reported in a co-authored manuscript, Ref. [155]. This section is based on the results in this paper.} Here, the absorber layer is formed by spin-coating a solution of PbS QDs sized such that the absorption edge lies around 1.15 eV. Then, several halide-based ligands are used to passivate the surfaces and render the dots insoluble. Contact layers deposited above and below the PbS QDs result in the following device stack shown in Fig. 5-15(a), with Au and ZnO as the hole and electron contacts, respectively.

Fig. 5-15(b) illustrates a key scientific challenge for PbS QD devices — the \(V_{OC}\) in state of the art devices is 0.56 V, suggesting a \(V_{OC}\) deficit of 0.6 V relative to the bandgap.\cite{155,164} \textit{JVT}i measurements were used to investigate the origin of this \(V_{OC}\) deficit, and the resulting \(V_{OC}\) vs. \(T\) results are plotted in Fig. 5-15(c). The \(V_{OC}\) extrapolated to 0 K gives an activation energy of 0.92 V, well below the bandgap energy. This suggests that the \(V_{OC}\) deficit may be due in part to a lower activation energy for the dominant recombination pathway.

A first candidate for the low \(E_A\) is the PbS/ZnO heterojunction interface, similar to the \ce{Cu2O} case above. However, modification of the band offsets by tuning the contact layer has demonstrated no improvement on the \(V_{OC}\), and band alignment measurements are inconclusive as to the alignment at this interface.

Instead, PL and electroluminescence (EL) measurements suggest an alternative hypothesis. A sub-bandgap emissive peak appears at 0.85 eV in energy, for PL and EL measurements independent of injection level. This result suggests that a band of sub-gap states may exist between 0.8–0.9 eV, well below the expected bandgap. With a sufficient density of states in this defect band, electrons or holes may be supplied for
recombination through the defect band, meaning that the effective activation energy for recombination is in fact around 0.9 eV — which is consistent with the activation energy measured by $JVTi$.

This result suggests an alternative mechanism by which the $V_{OC}$ may be limited in $JVTi$ measurements, if the effective bandgap is lower than that anticipated by bulk absorption measurement. A similar effect is observed in disordered CZT(S,Se) absorber materials, which display a bandgap fluctuation and a lower “effective” bandgap as a result.\[163\]

5.5.1 Next Steps: Utilizing the Rest of the $J-V$ Curve

The examples presented in this chapter show the array of information accessible through the $V_{OC}$, but what to do with the rest of the $J-V$ curve? A wealth of information is carried by this data, but it is often too difficult to develop analytical models to describe it. For example, Fig. 5-16 shows other cell parameters as a function of temperature for an SnS device. The changing fill factor, ideality factor, and $J_{SC}$ are rich with information, all available for free with the right modeling tools to extract it. The following chapter will begin to explore these tools.
Figure 5-16: The $V_{OC}$, $I_{SC}$, $FF$, and ideality factor for a standard SnS solar cell are plotted as a function of temperature.
Chapter 6

Improving Rate of Learning Through Bayesian Inference

In the previous chapter, a tool and analytical framework were described for fitting JVT data, with the goal of understanding the band structure and recombination kinetics of a solar cell using only electrical cell measurements. While the chapter focused only on the $V_{OC}$ point of the solar cell, rich information is available in the rest of the $J-V$ curve, but is unavailable due to both: (a) the simplicity of our analytical cell models, and (b) the complexity of full numerical models and fitting over a wide range of data.

More sophisticated PV cell models are available, which solve the forward problem of: cell and material properties in; device $J-V$ performance out. The goal of this chapter is to drive towards solving the inverse problem: device measurements in; cell and material properties out. By doing this with only cell electrical data, it may be possible to supplant the many dedicated materials properties measurements necessary to model a solar cell, some of which have featured in earlier chapters of this thesis. This is the final step in the progression of faster cycles of learning on new PV materials.

This strategy offers a pathway to substitute computing power for the labor and capital typically associated with measuring a wide range of solar cell materials. Doing so could shorten the time spent characterizing and learning about each device from
months, to weeks, to days, and would allow for a higher number of trials as in the binomial experiment described at the start.

Specifically, this chapter discusses approaches for fitting materials parameters based on cell electrical measurements. This is done using Bayesian inference, a tool for inferring the probability distributions of different materials properties such as bulk minority carrier lifetime based on the relative likelihood of each lifetime producing the resulting cell data. The subsequent examples provide a framework for doing this mathematically, and show some real cell data where the technique is used.

The Bayesian inference approach here requires three pieces. The first is the ability to measure a device over a range of bias conditions (e.g., $V$, $T$, light intensity, and $\lambda$), which was developed in Chapter 5. The second is an accurate system model which can compute the expected solar cell behaviour for any combination of input parameters, and bias conditions. The last component ties these two together — the inference model goes from observations of output, to discover the underlying parameters that fit with the model used.

6.1 Numerical Modeling of Cells

All numerical models of photovoltaic performance are built on a set of partial differential equations describing the journey of electrons and holes through a PV device. These equations include (i) transport of carriers under electrochemical potential gradients, and (ii) generation of carriers by thermal or optical means, and (iii) recombination of free carriers by a variety of processes.

Holes and electrons diffuse under concentration gradients and drift under electric potential gradients, and in turn their movement influences the concentration and potential gradients. This results in a set of coupled differential equations. First, Poisson’s equation provides the relationship between charge density and electric field strength $\vec{E}$. The net charge density may come from the fixed acceptor density $N_A$, fixed donor density $N_D$, as well as free hole density $p$, and free electron density $n$, all
with units of cm⁻³:

\[
\frac{dE}{dx} = \frac{q}{\epsilon_r \epsilon_0} (p(x) - n(x) - N_A(x) + N_D(x)). \quad (6.1)
\]

Second, the transport equations describe the hole and electron currents that result from both drift and diffusion contributions:

\[
J_n = q\mu_n nE + qD_n \frac{dn}{dx} \quad (6.2)
\]

\[
J_p = q\mu_p pE - qD_p \frac{dp}{dx}. \quad (6.3)
\]

The pre-factor to the electric field may be recognized as the conductivity, a product of mobility, carrier density, and the fundamental charge. \(D\) is the carrier diffusivity in cm²/s. Diffusivity and mobility of carriers are related by Einstein’s relationships through the thermal energy (for band conductors, not for dispersive hopping transport):

\[
D_n = \frac{k_B T}{q} \mu_n \quad (6.4)
\]

\[
D_p = \frac{k_B T}{q} \mu_p. \quad (6.5)
\]

This set of equations can be applied to a finite element mesh in one to three dimensions, and describes how carriers move between the finite elements. The final important piece is the source and sink terms for carriers, the balance of which has been used time and again through this thesis:

\[
\frac{dn}{dt} = \frac{1}{q} \frac{dJ_n}{dx} - (U - G) \quad (6.6)
\]

\[
\frac{dp}{dt} = -\frac{1}{q} \frac{dJ_p}{dx} - (U - G). \quad (6.7)
\]

\(G\) is easy to calculate given the absorption coefficient of the material, or preferably the optical constants \(n\) and \(k\), and furthermore \(G\) may be readily tuned through experiment. \(U\), in turn may be modeled as dependent upon the surrounding carrier
concentration. Recalling Chapter 2, for a $p$-type material the recombination can be parametrized by three terms:

$$U = -An - Bnp - Cnp^2.$$  \hfill (6.8)

The result is a set of partial differential equations solved by knowing: (i) fixed properties of the underlying materials like densities of states, bandgaps, and electronic band alignment; (b) Cell-specific properties in each layer of the cell like $G$, $\mu$, $N_A$ and $N_D$, the recombination rate constants $A$, $B$, and $C$; and (iii) the operating voltage and temperature. This complete device model will have several dozen input parameters, 5–10 of which may be unknown.

In lieu of writing software to solve this tricky finite element problem, several pre-existing softwares have been built for this purpose, including SCAPS, PC1D, Sentaurus, AMPS, AFORS-HET, Quokka, or ADEPT.

In the present work, SCAPS[136] is used to model cells given its higher precision for computing interface recombination, while still being relatively simple to use. While it is typically operated as a GUI, it also has scripting capabilities built in, allowing one to call the simulation from another program and have it effectively return a result, as a black-box cell model. The appendix includes pieces of code for controlling SCAPS through Python, with a similar interface also developed for MATLAB.

### 6.2 Bayesian Parameter Estimation

There are many methods of solving the "inverse problem" posed above; including classical statistical approaches and optimization algorithms. These classical parameter estimation approaches generally assume that there is one true value for the underlying parameter, and to find it they seek the model parameter(s) which minimize a statistical estimator like the root mean squared error, for example.

There are several flaws in this approach; for example, the observed data will most certainly carry some noise or uncertainty with it. In addition, there may be multiple
sets of parameters which provide an equivalently good fit to the data, and it would be more accurate to search for a multivariate distribution of parameters, rather than a single point.

A Bayesian framework instead is able to assign a “credibility” to every combination of parameters. This represents a scientist’s belief that a particular set of parameters is the true set, which can be described by a multivariate probability distribution over all possible combinations of model fit parameters. This credibility is modified every time the scientist observes new data, based on their belief in the new data and its uncertainty. In that way, a Bayesian Parameter Estimation routine is truly the scientific method. It answers the question: “what is the probability that my scientific hypothesis is true, given some new evidence I have discovered?”

There are numerous advantages to using a Bayesian approach to estimating underlying parameters, which will become more apparent by the examples in this chapter. It can accommodate new observations, allowing beliefs to change with every subsequent measurement. Classical statistics, on the other hand, must make assumptions about the probability of data that have not been observed (i.e., deciding when ‘enough’ measurements have been taken). Bayesian approaches can also handle uncertainty in the observed data, with the resulting distributions of credibility including the noise distribution of the data. It can handle both random noise related to the precision of an instrument, and systematic uncertainty arising from uncertain calibrations of tools. As a result, it can easily deal with uninteresting nuisance parameters like background noise.

In a Bayesian framework, every set of possible model parameters may be considered as a unique hypothesis. The credibility of each hypothesis, then, is modeled by a probability distribution. Thinking in terms of probability distributions instead of classical statistical estimators allows us to incorporate elements of information theory into the way one views a probability distribution — any two probability distributions may be compared in terms of their information content, for example. Probability distributions also offer a natural way of restricting the region of model space in which we search — more simulations can be performed in the regions of highest probability.
Beyond the benefits of the Bayesian approach to parameter estimation, the underlying math is straightforward. Each hypothesis can be considered independently; here a given hypothesis is referred to as \( H \). Each new piece of evidence is referred to as \( E \). Bayes Rule, the underpinning of all Bayesian methods, can then be stated as follows:

\[
P(H|E) = \frac{P(H)P(E|H)}{P(E)}. \tag{6.9}
\]

In words, each term can be thought of as one piece of the scientific method. \( P(H) \) is the prior probability distribution, or how strongly one believes in a hypothesis being true before doing any experiments. \( P(H|E) \) is the posterior probability distribution that follows after each observation, or how strongly one believes a hypothesis given the results of an experiment. \( P(E|H) \) is the likelihood, specifically the likelihood that the observed result would occur if the parameters hypothesized were true. Simply, if the set of hypotheses would have produced a very different value from what was observed, the ‘likelihood’ \( P(E|H) \) would be small. Lastly, \( P(E) \) can be considered as a normalizing constant — it is the sum of \( P(H)P(E|H) \) over all the possible hypotheses.

As a simple example, consider a diagnostic test for whether a cookie contains nuts. There are two hypotheses — \( H_{\text{nuts}} \) and \( H_{\text{no nuts}} \). One may know beforehand that 20% of all cookies on average contain nuts. This useful piece of background information is the prior, \( P(H_{\text{nuts}}) \), and the sum of priors over both hypotheses must equal 100%. We have a special tool that can analyze cookies for nut content, and 90% of the time that a cookie contains nuts, it returns ‘True’. This is the likelihood of the first hypothesis, \( P(E|H_{\text{nuts}}) \). There is also a risk of false negatives — 15% of the time when the cookie does not contain nuts, it still returns ‘True’. This is the likelihood of the second hypothesis, \( P(E|H_{\text{no nuts}}) \). Summing over the likelihoods of both hypotheses and their priors gives \( P(E) = 30\% \).

Applying Bayes Rule, produces a posterior probability \( P(H_{\text{nuts}}|E) = 60\% \). This step is called “conditioning” the scientist’s beliefs. Note that even though the test has a 90% rate of success, the fact that it produces false negatives as well means that
overall belief in it is lower. This is the nature of Bayesian inference — certainty in any one hypothesis is a product not only of the likelihood for that particular hypothesis, but the likelihoods of all competing hypotheses.

One may continue to make progressive observations and increasingly gain certainty over the result, which is an advantage of Bayesian inference. Most importantly, this sequence is not necessarily temporal; it is just a logic sequence. Ten tests could be performed simultaneously, in different orders, or far apart in time, and they may still be used to sequentially condition beliefs.

With the basic framework set up, the problem of PV device parameter fitting may be recast as a Bayesian problem. Now, our evidence is the observation of a particular cell characteristic, like the open-circuit voltage. The hypotheses are discrete values of an underlying parameter we would like to fit, for example the carrier lifetime. Bayesian parameter inference poses the question: what is credibility or probability distribution of the carrier lifetime, given that I observe a particular $V_{OC} = 0.4$ V:

$$P(\tau|V_{OC} = 0.4\text{V}) = \frac{P(\tau)P(V_{OC} = 0.4|\tau)}{P(V_{OC} = 0.4\text{V})} \quad (6.10)$$

In this manner, one may compute the distribution of belief or credibility over all possible lifetimes, based on a series of measurements. Bayes theorem tells the scientist precisely how much to revise one’s beliefs in the face of new observations.

6.3 Framework for Inferring Materials Properties

As there is rarely an analytical solution to the Bayesian inference problem posed above, it must typically be solved numerically. The pieces for doing so are outlined in the following sections, including: determining prior knowledge about the problem, gathering data, and then computing the posterior probability distribution.\textsuperscript{1}

\textsuperscript{1}Rachel Kurchin and Chris Roat (Google) were consulted in developing this approach.
6.3.1 Formulating Priors

First, I will distinguish between the three types of inputs into the cell model. There are known constants (such as material bandgaps, or densities of states), unknown parameters that should be fit (such as $\tau$, $\mu$, or $\Delta E_C$), and bias conditions (typically $V$, $T$, and light intensity). The unknown parameters, denoted as $\Theta$, have a starting probability distribution $P(\Theta)$. Specifying this prior probability distribution is a subjective step, as the scientist must roughly guess the range of values expected for the parameter of interest. The simplest assumption is that the credibility or probability is uniformly distributed over a particular interval, e.g., the lifetime may be anywhere from 10 ps to 10 ns. This distribution assumes that values within the interval are equally likely, but values outside of it are impossible. A uniform distribution like this makes the problem definition easier, but it can bias the results by presuming a probability of zero for some hypotheses at the start. While defining a prior may seem subjective, it is important to remember that with enough observations, the probabilities contained in the prior are progressively diluted — so even a “wrong” prior will not ruin the parameter estimation. Picking a correct prior, on the other hand, will greatly accelerate the convergence to the final, true posterior distribution with fewer observations.

In Python, a simple approach to preparing the model is to discretize each parameter in $\Theta$ into $M$ divisions, and store these in a dictionary. For $N$ parameters, every combination of discrete parameter values can be then be stored in an $N$ dimensional matrix, where each dimension is of length $M$. A uniform probability distribution over all $M$ divisions in $N$ dimensions would then result in a probability of $1/MN$ for each entry.

6.3.2 Observing and Modeling Current Densities

The response variable for fitting parameters will be the current density, $J$, measured as a function of the three bias conditions. Using the same $JVTi$ measurement tool as described in Chapter 5 produces a 3-dimensional matrix of current densities, where
each dimension represents \( V \), \( T \), and illumination intensity. Each point in this matrix is a unique observation or piece of evidence, and these may be fed in sequentially to condition the probability distribution over all parameters with every new observation. As mentioned before, these observations don’t necessarily need to arrive in any chronological order. They may be measured all at once and saved for later processing, or they may be measured on the fly while the probability distribution is being formed.

Next, to compute a likelihood one must know what current density to expect for every combination of discrete parameters in \( \Theta \) and every discrete bias condition. This is now a \((N + 3)\) dimensional matrix, which can be filled out by running a unique simulation at every point in the matrix. This is by far the most time-intensive step; for SCAPS, simulations may typically take 4–6 seconds to compute the \( J-V \) curve for a given set of parameters. This means realistically being able to run 15,000–20,000 simulations per CPU in a 24-hour period. The number of voltage sweeps required in SCAPS to fill out the matrix of interest, assuming \( M \) discrete divisions for all \( N \) model parameters, and \( Y \) discrete temperatures and light intensities, scales as:

\[
\text{# of simulations} = M^N Y^2.
\] (6.11)

For \( Y = 2 \) and \( M = 10 \), a single CPU would take two full days to fit just four dimensions in \( \Theta \). One strategy for increasing throughput is to parallelize these simulations, as filling out a gridded matrix of simulation results is what computer scientists would call an “embarrassingly parallel” problem. The computations performed in the present work were done on four parallel CPUs on the Google Cloud Compute Engine.

### 6.3.3 Forming Likelihoods and Posterior

The prior steps have produced an \( N \)-dimensional matrix of prior probabilities, a 3-dimensional matrix of observations (or alternatively a long list of observations), and an \((N + 3)\) dimensional matrix of simulated current densities. These are stored in Python as Numpy array objects. The next step is to compute the likelihood of observing each piece of evidence, given each set of model parameters. This requires
knowledge about the uncertainty contained in a given measurement, coming from random noise or error in the measurement apparatus. Assuming that the measured current, $J$, is distributed around the true value $J_{\text{real}}$ with a normal distribution, the standard deviation of this distribution would be $\sigma_J$. The distribution of measured current would produce the following normal distribution:

$$P(J) = \frac{1}{\sigma_J \sqrt{2\pi}} \exp\left(-\frac{(J - J_{\text{real}})^2}{2\sigma_J^2}\right).$$  \hspace{1cm} (6.12)

Therefore, the likelihood of observing any current ($J_{\text{obs}}$) at a particular set of parameters $\Theta$ is simply its probability, or:

$$P(J_{\text{obs}}|\Theta) = \frac{1}{\sigma_J \sqrt{2\pi}} \exp\left(-\frac{(J_{\text{obs}} - J(\Theta))^2}{2\sigma_J^2}\right).$$  \hspace{1cm} (6.13)

Determining an accurate value for $\sigma_J$ requires investigating the uncertainty inherent in currents measured using a digital multimeter (Keithley 4200). The uncertainty in these measured currents due to the multimeter is expected to be $<0.001\%$, however, other sources of uncertainty may propagate through to the measured current. Uncertainties in $T$, $V$, and light intensity $\Phi$ may increase the effective uncertainty in measured current density by the following error propagation:

$$\sigma_J = \sqrt{(\frac{\partial J}{\partial V})^2 \sigma_V^2 + (\frac{\partial J}{\partial T})^2 \sigma_T^2 + (\frac{\partial J}{\partial \Phi})^2 \sigma_\Phi^2.}$$  \hspace{1cm} (6.14)

$\sigma_V$ is also expected to be very small, approximately $10\mu$V from the Keithley digital multimeter, so this term is relatively small. $\sigma_T$ may be approximately 1 K due to the thermal resistance between the sensor and sample, and fluctuations in temperature due to ohmic heating during measurements. While errors in both voltage and temperature may seem small, note that current density is exponentially dependent upon these, so the partial derivative terms can become quite large, particularly in forward bias. Computing these partial derivative terms at all points in observation space would be computationally expensive, but fortunately one can take advantage of a feature of exponentials — their slope at any point is proportional to their magni-
tude. Therefore, knowing the uncertainty at one point in forward bias is sufficient to approximate the uncertainty at other points as well. The final source of error, $\sigma_\Phi$, is by far the largest. With the Class ABB solar simulator used here, the light intensity of the lamp is rated for a temporal stability range of $\pm 3\%$. For the typical current densities measured in the present work, this corresponds to a typical $\sigma_J$ of between 0.5–1.0 mA/cm$^2$.

The likelihood may now be computed element-wise for every set of parameters in the $N$-dimensional matrix, which is mapped over the same values as the prior probability distribution. These two identically-sized matrices may then be multiplied together element-wise, and normalized — as per Eq. 6.9. Python code for performing each of these steps above is available in the appendix.

The process may be repeated for many observations using the posterior distribution from the previous observation as the new prior. This loop of modeling and changing observation conditions is depicted in Fig. 6-1, in the bigger loop of device fabrication. Once devices are fully characterized, these lessons can inform the fabrication of subsequent devices, and the process may repeat.

6.3.4 Markov Chain Monte Carlo Methods

The approach described above is straightforward to apply, but is not an optimal application of Bayesian inference and suffers from an important inefficiency. Not only does it sample discretely, and may therefore miss parts of solution space if the mesh chosen is too sparse, but it also may spend significant time sampling and computing likelihoods in regions of $\Theta$ space which have a very low probability. A more robust method to improve efficiency and accuracy in mapping out the space numerically is a Markov Chain Monte Carlo (MCMC) algorithm.

This approach assumes that there exists a true, optimal probability distribution over $\Theta$. A Markov chain is a process in which every step of the chain depends only upon the current state. What is most important to recognize is that a Markov chain will always converge to a stationary probability distribution, which should be the posterior distribution. Not knowing this distribution \textit{a priori}, it can be built by a Monte
Figure 6-1: Flowchart of device optimization starting with synthesis and measurement, followed by a sub-loop of Bayesian parameter estimation over successive observations.

Carlo process where the code samples randomly from the distribution, computes the expected probability, and uses this new knowledge to update the probability distribution itself. In this way, the choice of where to run simulations is combined with the process of computing the likelihood and posterior. In Chapter 7, this approach will be revisited.

6.4 Test Demonstrations of Bayesian Parameter Estimation

To test the code and approach developed here, parameter estimation is performed on simulation-generated data, in which the underlying parameters are known. This allows for checking and comparison between the Bayesian output and known inputs.

Initial tests were done using an ideal diode model as the system model, and fitting $n$, $J_0$, and $J_{ph}$. Next, the modeling framework was replaced with SCAPS as the simulation, first with a simple GaAs device model. The GaAs device included a 500
nm p-type absorber and 100 nm n-type emitter, with doping densities of $N_A = 5 \times 10^{16}$ cm$^{-3}$ and $N_D = 5 \times 10^{18}$ cm$^{-3}$, respectively. Three parameters were chosen for fitting: the SRH minority carrier lifetime in GaAs, the minority carrier (electron) mobility, and the back surface recombination velocity for electrons. Other constants in this model may be found in the appendix.

Data was generated for a hypothetical GaAs device with a minority carrier lifetime of 5 ns, an electron mobility of 2000 cm$^2$/V/s, and a back $SRV_n = 10$ cm/s. This device was simulated over a voltage range 0–1 V, and temperatures of 290–320 K. The cell “data” produced from these simulations was treated a series of observations on a GaAs cell, and fed into the Bayesian parameter estimation model.

The results of inputting observations at one temperature (300 K) are plotted in Fig. 6-2. The three-dimensional multivariate probability distribution is projected on 1D vectors to show the distribution for each parameter, and on 2D planes to show covariance between each pairing of parameters. This simulation shows high precision for the minority carrier lifetime, finding it at precisely 0.5 ns. However, it shows significantly less precision for the SRV, and at best can only offer an upper limit on the value. What this suggests is that there is very little variation in $J-V$ performance between 10–100 cm/s in SRV; therefore, the $J-V$ curve carries very little information content with respect to SRV. Put another way, the $J-V$ curve offers evidence for too many different hypotheses, making it poor evidence — akin to a crime witness’s description being so vague as to implicate too many potential suspects.

This imprecision is even worse for the minority carrier mobility, which is not surprising for GaAs — for a 500 nm thick base, once the mobility is >300 cm$^2$/V/s, the diffusion length is long enough such that all carriers will be collected and there is no marginal change with increasing mobility.

6.5 Applying Parameter Estimation to SnS

After gaining some confidence in the method on known data sets, the approach can be applied to SnS devices. Real $JVTi$ data was collected on a baseline SnS solar cell
Figure 6-2: Results of Bayesian parameter estimation on a GaAs device at room temperature, after feeding in modeled data as observations. The diagonal subplots represent probability distributions for each parameter, and the off-diagonal plots show the joint probability distribution on two axes, where red in the heat map indicates highest probability, and white is lowest. This particular observation contained high information content for the lifetime, but not for the mobility, for example.
as described in Ref. [17] and presented in Fig. 5-16. Then, particular $J$-$V$ sweeps were selected from this data at 1-sun illumination and temperatures of 270 K, 300 K, and 320 K.

With a set of observations on hand, a cell model was built for SnS with accurate layer thicknesses, doping levels, and optical constants (including front surface reflectance) based on prior measurements and modeling.[139] Four parameters were chosen to be fit: the minority carrier mobility in SnS, the minority carrier lifetime in SnS, the conduction band offset between SnS and Zn(O,S) (the ESC), and the effective SRV at the SnS/Zn(O,S) interface. Uniform priors were assigned to each of these parameters, and 27,000 simulations were run over a 4D grid of discrete values in this parameter space.

The first observation fed into the inference code was at short-circuit conditions, at 300 K, and the resulting posterior distribution is plotted in Fig. 6-3. It is clear that the short-circuit condition constrains the joint distribution of minority carrier lifetime and mobility, but not of the interface properties. These retain fairly uninformed distributions. From the previous chapters, it may be clear now that the only way to get more information on the interface recombination is to go further into forward bias. Inputting the observations for the entire 300 K $J$-$V$ curve results in the posteriors plotted in Fig. 6-4. The nature of the interface recombination begins to appear — either the device must have a small cliff offset and a large SRV, or the converse. A line of constant probability appears in multi-dimensional space. This is closer to the desired answer, but the distributions are still inconclusive. Note that the holes or discontinuities visible in the projected distributions are largely artifacts of the gridded sampling, and disappear with higher resolution sampling.

To condition the distributions further requires changing another variable; in this case, temperature is a natural next step. Full $J$-$V$ curves at 270 K and 320 K are fed in as observations, and the resulting posterior distribution is plotted in Fig. 6-5. The sharpness of the final distributions is stark. While the minority carrier mobility is still not well constrained, the minority carrier lifetime and interface properties are well constrained. A confidence interval for each of these values may be assigned based
on the resolution of the scan performed: $\tau$ is between 23–36 ps, $\Delta E_C$ is -0.25±0.05 eV, and the interface $SRV$ is found to be 400–1000 cm/s.

Remarkably, these values are consistent with lifetimes measured in the range of 20–40 ps in Ref. [20], and conduction band offsets measured to be in the range of -0.38±0.2 eV in Ref. [139]; extracted here with an all electrical measurement.

### 6.5.1 Summary and Outlook

The discovery of accurate materials properties through a Bayesian parameter estimation routine on electrical measurements, in place of longer free-carrier absorption and photoelectron spectroscopy studies, is a very important result. The spectroscopy and analysis that produced this earlier data took weeks or months to perform, using expensive capital equipment. What might be enabled if this labor and capital could be replaced with the computational algorithms and a simpler measurement apparatus?

While this is only one first step in this direction, it is important to note two ongoing trends — the cost of doing science continues to rise, while the cost of computation continues to drop. Examples like the one presented in this chapter suggest that the future of science may lie in increasing automation, without sacrificing the quality of information achievable. This may free up the scientist to attempt more experiments (increase $n$), and brings us towards an accelerated time frame for new materials development.
Figure 6-3: Results of Bayesian parameter estimation on a SnS device at 300 K and short-circuit conditions, showing conditioning on the minority carrier lifetime but not on other variables.
Figure 6-4: Results of Bayesian parameter estimation on a SnS device at 300 K and over the full $J$-$V$ curve, showing conditioning on the interface recombination parameters now.
Figure 6-5: Results of Bayesian parameter estimation on a SnS device at three temperatures, showing conditioning to narrow regions for most parameters.
Chapter 7

Discussion and Conclusions

The examples described in the previous chapters have covered a wide range of materials and tools, and it is helpful to reconnect these threads and review where they may go next. Each tool described in Chapters 3–6 aimed at engineering and characterizing the recombination pathways that limit device efficiency, especially for novel PV absorbers. This included minimizing bulk recombination through defect-tolerant electronic structures for the absorber layer, and minimizing interface recombination through the appropriate selection of carrier selective contacts and their electronic band alignment. Achieving these low recombination rates is critical for maximizing the separation of electron and hole electrochemical potentials in a solar cell, or alternatively, minimizing the magnitude of recombination currents. This approach to minimizing recombination offers the opportunity for achieving a higher $V_{OC}$ — often an underperforming metric for novel PV materials like Cu$_2$O and SnS.

Where things go wrong, and where a large $V_{OC}$ deficit appears, tools such as TCSPC and $JVTi$ measurements provide a window into the location, magnitude, and type of recombination present. Particularly with improved experimental and modeling techniques, they may offer this information much faster than conventional spectroscopic techniques. Looking forward to the next generation of materials to be screened, it is important to consider how we may move faster, more intelligently, and avoid false negatives more diligently in developing novel PV materials.
7.1 Strategies for Improving Screening

While the materials measured in this study did not display lifetimes as high as the hybrid lead halide perovskites, some achieved lifetimes in excess of 1 ns. The trends in lifetime suggest that materials with the highest dielectric constant and lowest effective masses offered the highest performance. However, alternative design criteria and families of materials may be considered with the hopes of finding even more promising absorber candidates.

As discussed in the conclusion of Chapter 3, there may be a number of additional criteria to consider when designing defect-tolerant materials. This included the role of anion coordination number in producing shallow anion vacancies, the role of crystal symmetry in achieving direct bandgaps and low effective masses, and the importance of the organic cation. While there are still many materials in the MaterialsProject.org database that could be used to explore these questions, there may also be relevant empirical strategies.

Firstly, a number of the materials discussed here show layered crystal structures, such as InI and SnS. Alloying with other compounds may allow for the stabilization of the undistorted rocksalt, or other more symmetric crystal structures. The similarity in ionic radius between In$^+$ and K$^+$ (1.32 Å and 1.33 Å), for example, suggests that alloys with the rocksalt KI could change the phase of InI at relatively small [K] concentrations. A similar strategy is now being developed for SnS, alloyed with CaS.[166] For Bi and Sb compounds, there are fewer large isovalent cations, but alloys with La$^{3+}$ or Ce$^{3+}$ may be feasible. A risk inherent in this strategy is spinodal decomposition of the alloy.

Regarding the role of organic cations, there is a great opportunity to explore this space through isostructural Cs-containing compounds. Performing computational or empirical surveys of mixed Cs-In, Cs-Bi, or Cs-Sn compounds could reveal new crystal structures into which organic cations like methylammonium could substitute. Initial efforts in this direction have suggested a family of hybrid sulfide compounds based on Cs$_2$Sb$_8$S$_{13}$.[167] Furthermore, there is a large unexplored space of molecu-
lar anions or superhalogens — ions in the -1 charge state, but with different radii and electronegativities.[168] Examples include (BF$_4$)$^-$, (PF$_6$)$^-$, (AlI$_4$)$^-$, (NO$_2$)$^-$, or (CF$_3$SO$_3$)$^-$. By taking advantage of the range in effective ionic radii, electronegativities, and atomic orbital energies in these superhalogens, one may be able to tune the crystal structure and electronic structure of a Bi-based compound, for example.

Lastly, it may be worthwhile to reconsider partially-oxidized metals like Cu$^+$ and Ag$^+$, with a full $d$-shell that lends antibonding orbital character to the VBM in many Cu-chalcogenides. For example, compounds like CuI have demonstrated shallow cation vacancies.[169] While the bandgaps of the copper and silver halides may be too large for PV applications, ternary copper halides may be able to achieve smaller bandgaps. For example, the potential ternary compound CuBiI$_4$ could share the benefits of a disperse conduction band and shallow anion vacancies from BiI$_3$, with the valence band features and shallow cation vacancies of CuI. Exploring in this space of ternaries and other similar families could yield interesting materials.

Most importantly of all, full point defect calculations should be performed on more materials in this class, to directly test the hypotheses laid out here and further increase the likelihood of discovering a promising material. Where theory is incomplete, or where the role of structural defects cannot be well modeled, direct characterization of defects experimentally may be attempted. This includes temperature-dependent admittance spectroscopy, which has been used successfully to identify defects in chalcogenide thin films,[170] or deep level transient spectroscopy, positron annihilation spectroscopy, and electron paramagnetic resonance spectroscopy. Each technique suffers from its limitations — for the capacitance techniques, for example, they may only detect majority carrier traps due to the much stronger transient capacitance signal.

7.2 Insights on Selecting Optimal Contacts

The results of Chapter 4 and the survey of band alignments in Chapter 2 both suggest that the search for optimal contacts can be very difficult. There are surprisingly few wide-bandgap semiconductors which achieve high-transparency and high doping
densities, in particular for $p$-type materials, and for $n$-type materials with low electron affinities. Out of this small subset, there is a great deal of luck involved if they align well with the conduction band of a proposed absorber material.

Rather than leaving this band alignment to fortune, it may be possible to engineer it through interface modifications. This was attempted in Chapter 4, with minimal success in modifying the ZnO/Cu$_2$O offset. However, using more robust interface treatments that induce more charge transfer at the interface, as well as applying the subsequent layer with a more gentle deposition technique, may improve the chances of modifying the offset. In the field of quantum dot PV, interface engineering through ligand exchange has been shown to shift band edges of PbS QDs by up to 1 eV[171] — the same treatments may be relevant for thin film sulfides and oxides as well.

Another potential approach is to separate out the roles of a selective contact — surface passivation, electronic alignment, and conductivity — by using a stack of layers which each serve one or more of these purposes. A candidate layer stack for this is the metal-insulator-semiconductor (MIS) contact.[172] As depicted in Fig. 7-1, the first insulating layer would be a wide-bandgap, roughly 1 nm thick layer which passivates the surface and unpins the Fermi level, akin to the gate oxide used in all modern transistors. This could be an oxide like alumina, silica, or hafnia, or another wide bandgap insulator like ZnS. The next layer is a thin (<10 nm) metal layer, which is still mostly transmissive, but thick enough to set the Fermi level at the interface due to the high electron concentration. Metals offer a wide range of work functions for tunable contact energies and are easy to fabricate, but depositing them directly on the semiconductor typically results in Fermi-level pinning and high surface recombination velocities.[172] Finding a lattice-matched or amorphous, chemically compatible wide bandgap layer is much simpler if it no longer has to be conductive or at the right conduction band energy — instead, the metal takes this role. To ensure lateral conductivity in the contact, a transparent conducting oxide may then be deposited on the metal, with relatively guaranteed ohmic transport. Such an MIS contact structure could relax the constraints of finding optimal contacts, and allow for relatively quick screening of different metal work functions.
Figure 7-1: Combinatorial contacts through MIS structures. A thin insulating layer provides passivation, and transport occurs by tunneling through to a metal layer on the other side. This metal layer could have a wide range of work functions, allowing for optimal band alignment. With a thin metal layer for transparency, lateral conductivity must be accomplished with a thicker transparent conducting oxide as well.

7.3 Vision for Increased Automation

The $JVTi$ tool and Bayesian parameter estimation shown in previous chapters were developed to be fairly well automated on their own, but the process of transferring data between them is still done manually, and this means that there is a time lag between modeling, taking the data, and performing parameter estimation, which requires significant supervision from the scientist. Increasing the level of automation and reducing the time for each step would free up the scientist to run more experiments and improve the rate of learning.

7.3.1 Active Learning

An example of how this automation could be improved is the use of active learning, a machine learning technique in which the tool performing parameter estimation can actively advise on what data it would like to be fed.

The first step to active learning is in the hardware and software communication. At present, the cell electrical measurements are performed using Labview, and the data is
saved in ASCII files for later analysis. In addition, the SCAPS device simulations are run through a Python interface, and the data is stored in a text-based archive for later reference. Once both are complete, the parameter estimation routine is performed using Python.

Developing an interface between Python and the Labview code which controls the measurement hardware would allow the Bayesian parameter estimation code to directly query the cell. That is, when the code wants to read in observation, it could perform that observation itself rather than waiting for the scientist to do so. Similarly, when the code wants to simulate a new region of parameter space, it could be built with the autonomy to run simulations on-demand, on its own. With both of these pieces, the code could engage in active learning.

In an active learning algorithm, the parameter estimation code would ask: “what observation conditions would give the most additional information about the underlying probability distribution over the parameter space.” This requires quantifying the information content — given that we are constructing probability distributions, this is relatively straightforward. From information theory, the entropy may be used as a proxy for information. That is, entropy can be used to describe the certainty or predictability of a piece of information. Entropy, $H$ can be defined for a discrete probability distribution over the parameters $X$ as:

$$H(X) = -\sum_{i=1}^{n} P(x_i) \ln P(x_i), \quad (7.1)$$

where every $x_i$ is a discrete combination of parameters. The goal of fitting parameters is to minimize the entropy, which would be accomplished by having a probability of 1 for a single set of parameters, and zero for all others.

In this new approach, the parameter estimation tool would first test out the possibility of measuring at several different bias conditions, and evaluate the information content or potential reduction in entropy that these measurements could bring. Then, it would choose the next-best measurement to perform, and would direct the Labview hardware interface to this point. This is expected to dramatically reduce the amount
of data needed, by avoiding measurements which provide redundant information.

### 7.3.2 Improved Modeling

A major barrier to implementing more creative active learning routines, and to exploring higher dimensional fitting, is the cost of performing a simulation. SCAPS takes 2–6 seconds for a typical simulation, which can become very costly already at the scale of 100s of simulations. This may be improved through massive parallelization, or an alternative simulation tool.

One possibility is to develop a simpler PDE solver for the Poisson and continuity equations from Chapter 6. While SCAPS is designed to achieve high accuracy in defect and interface modeling, these extra features may not always be necessary. For example, modeling a SRH defect in SCAPS includes the capture cross section, thermal velocities, occupation probability, charge state, and density. This is useful for accurately modeling injection dependences and behaviour like capacitance, but it may be abstracted into a higher level property like a monomolecular recombination rate constant. Abstracting parameters into a smaller subset is a form of dimensionality reduction. Building a leaner PDE solver around these dimensionally reduced parameters would not be trivial, as these equations are still tricky to solve, but an order of magnitude improvement in simulation time would enable many smarter algorithms.

Beyond speed, it is important to consider how to improve the accuracy and precision of the parameter estimation demonstrated in Chapter 6. The quality of the results depends entirely upon the quality of the model used, and how well it describes the system in question.

One improvement would be to account for systematic errors in the observation conditions, distinct from the random errors described earlier. For example, the device temperature may consistently be 2 K warmer than the temperature sensor reads due to a miscalibration, or the light intensity may consistently be 5% weaker than anticipated due to a damaged optic element. These “nuisance parameters” can easily be accounted for in a Bayesian framework.[165] One would start by assuming that these systematic offsets exist, and then treat them as input parameters in the model, with
their own prior probability distributions. After calculating the posterior distribution, the parameters of interest will have joint probability distributions with the nuisance parameters. In other words, the expected minority carrier lifetime will vary with the expected lamp power offset, for example. Integrating over the nuisance parameter’s probability distribution marginalizes it, and results in an adjusted distribution for the parameters of interest. This new distribution now fully accounts for the possibility of systematic errors in the measurement.

Finally, one may want to consider more than one system model, as opposed to just different sets of parameters in a single model. Incorporating this model uncertainty is straightforward to implement in a Bayesian framework, as each model can be considered as a group of hypotheses, and the evidence for each model may be compared.[173]

7.4 Conclusions

A broad range of techniques have been discussed in the preceding chapters, and while they may appear to tackle disparate problems, the motivation is the same. Materials science is a field which can enable greater health for humans and the environment, but its solutions often take many decades to be reduced to practice and available for consumers. The development of new materials is fraught with scientific hurdles. With phenomena naked to the visible eye and dimensions inaccessible by manual fabrication techniques, the fabrication and characterization of new materials like semiconductors often require expensive tools. The complexity of the devices under investigation makes it difficult to uniquely determine the performance losses, and engineer their improvement. These factors point towards the necessity for tools that can increase the probability of success and reduce the cost per experiment.

In this thesis, the challenges of developing such tools were discussed for novel PV materials, including absorber layers and their respective carrier selective contacts.

First, new theoretical screening criteria were established based on first principles calculations and solid state physics models of PV performance. These insights
were then used to mine materials of interest from an existing database of electronic structure calculations, including compounds with partially oxidized cations such as Bi and In. These compounds were synthesized through three techniques, and photoluminescence measurements suggest that several may exceed 1 ns in minority carrier lifetime.

Next, two tools were developed for assessing the quality of electron and hole selective contacts. The first technique was X-ray photoelectron spectroscopy (XPS), and was used to identify Ga$_2$O$_3$ as an optimal selective contact for Cu$_2$O solar cells. Next, this technique was compared to current-voltage measurements performed as a function of temperature and light intensity, or $JVTi$, revealing the same conclusions as XPS with higher precision, and through a simpler experimental approach.

Finally, a new modeling tool was developed, using this $JVTi$ data to perform Bayesian parameter estimation on SnS solar cells. This analysis corroborated earlier measurements of the performance deficits in SnS, by extracting several fundamental materials properties. The progression from XPS, to $JVTi$ and Bayesian inference suggests a transition from a decades long empirical approach, to a months long measurement approach, and finally to a measurement and modeling approach on the time scale of one day.

Together, these results suggest that modeling and theory can help guide the empirical search for new PV absorbers, as well as their gradual optimization. By decreasing the time involved for this development, we may be able to address the historically slow progress of materials innovation. Problems like climate change cannot wait any longer for solutions, and this mindset must guide the choices we make in the field of PV, and the field of materials discovery at large.
Appendix A

Numerical Cell Models

A.1 Model Set-Up for SCAPS

In SCAPS, before communicating with the program through the command line, the cell properties should be defined initially using the GUI. The baseline operating conditions such as temperatures, voltages, and input spectra are defined on the front panel. Once the cell and operating conditions are defined, the whole setup may be saved as a `.scaps' file. This can now be called and amended on a property-by-property basis using the command line and text scripts, or a Python wrapper. The following materials properties are used for specific materials modeled here.

A.2 Materials Properties

- Cu$_2$O bulk materials properties: see Table A.1, or for more information see Refs. [131] and [174].

- SnS bulk materials properties: see Table A.2; values are obtained from Refs. [139] and [175].

- GaAs materials properties: see Table A.3, values taken primarily from SCAPS documentation.
Table A.1: Cu$_2$O bulk properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>2.07 eV</td>
<td>[55]</td>
</tr>
<tr>
<td>$\chi$</td>
<td>3.2 eV</td>
<td>[127]</td>
</tr>
<tr>
<td>$N_C$</td>
<td>$2.47 \times 10^{19}$ cm$^{-3}$</td>
<td>[176]</td>
</tr>
<tr>
<td>$N_V$</td>
<td>$1.11 \times 10^{19}$ cm$^{-3}$</td>
<td>[176]</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>7.11</td>
<td>[176]</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>1 cm$^2$/V$\cdot$s</td>
<td>[137]</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>1 cm$^2$/V$\cdot$s</td>
<td>[137]</td>
</tr>
<tr>
<td>$N_A$</td>
<td>$1 \times 10^{14}$ cm$^{-3}$</td>
<td>[137]</td>
</tr>
<tr>
<td>$E_{b,A}$</td>
<td>0.25 eV</td>
<td>[161] [177]</td>
</tr>
<tr>
<td>$N_D$</td>
<td>$5 \times 10^{15}$ cm$^{-3}$</td>
<td>[176]</td>
</tr>
<tr>
<td>$E_{b,D}$</td>
<td>1.0 eV</td>
<td></td>
</tr>
</tbody>
</table>

Table A.2: SnS bulk properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>1.1 eV</td>
</tr>
<tr>
<td>$\chi$</td>
<td>3.8 eV</td>
</tr>
<tr>
<td>$N_C$</td>
<td>$1.8 \times 10^{19}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$N_V$</td>
<td>$2 \times 10^{19}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>13.7</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>30 cm$^2$/V$\cdot$s</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>15 cm$^2$/V$\cdot$s</td>
</tr>
<tr>
<td>$N_A$</td>
<td>$2 \times 10^{14} - 5 \times 10^{16}$ cm$^{-3}$</td>
</tr>
</tbody>
</table>

- ZnO materials properties: see Table A.4. This model for ZnO properties was adapted for Zn(O,S) by modifying the bandgap and electron affinity. This is also the baseline for generic $n$-type electron-selective contacts modeled in the present thesis. Values taken from Ref. [139] and SCAPS documentation.
Table A.3: GaAs bulk properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>1.424 eV</td>
</tr>
<tr>
<td>$\chi$</td>
<td>4.07 eV</td>
</tr>
<tr>
<td>$N_C$</td>
<td>$4.7 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$N_V$</td>
<td>$9 \times 10^{18}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>12.9</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>8000 cm$^2$/V·s</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>400 cm$^2$/V·s</td>
</tr>
<tr>
<td>$N_A$</td>
<td>$5 \times 10^{17}$ cm$^{-3}$</td>
</tr>
</tbody>
</table>

Table A.4: ZnO bulk properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>3.3 eV</td>
</tr>
<tr>
<td>$\chi$</td>
<td>4.3 eV</td>
</tr>
<tr>
<td>$N_C$</td>
<td>$2.2 \times 10^{18}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$N_V$</td>
<td>$1.8 \times 10^{19}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>9.0</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>10 cm$^2$/V·s</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>10 cm$^2$/V·s</td>
</tr>
<tr>
<td>$N_D$</td>
<td>$10^{18} - 10^{20}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$E_{b,D}$</td>
<td>0.01 eV</td>
</tr>
</tbody>
</table>
Appendix B

MaterialsProject Code

B.1 Python API and Interface

To run the following code, install Python 2.7 in your favourite environment – I would recommend CygWin for Windows, or the Anaconda distribution for Mac OS or Windows. Be sure to install all dependencies including scientific computing packages and a Fortran compiler; see MaterialsProject.org for details. Then, register with the MaterialsProject to receive your API key, which is an alphanumeric code assigned to you to gain access to the database. You can enter it in the top of the code below to run it. This first piece of code iterates through a list of compounds, checks to see whether they exist, and then extracts electronic structure properties as well as formation enthalpies and crystal structure information. It writes all of this to a big csv or text file.

```python
from pymatgen import MPRester
from pymatgen import matproj
import csv
import numpy

MAPI_KEY = "XXXXXXXXXX"  # Insert your own private key from MaterialsProject here
mpr = MPRester(MAPI_KEY)
```
with open('results_file.csv', 'wb') as csvfile:
    mpwriter = csv.writer(csvfile,
        delimiter=',', quotechar='|', quoting=csv.QUOTE_MINIMAL)
mpwriter.writerow(['ID', 'Formula', 'Point_Group', 'H_F(eV)', 'Bandgap(eV)',
    'Direct?', 's_fraction_VB', 'd_fraction_VB'])

# Choose your desired range of MP IDs to scan through, from 1 to 999999
for num in range(1000, 2000):
    MP_ID = "mp-"+str(num)
    # keep track of time
    if num % 100 == 0:
        print MP_ID

    # check if material exists in database
    mat_check = mpr.get_data(MP_ID)
    if len(mat_check) == 0:
        continue

    # check if material has a bandgap >0.05 eV
    mat_bandgap = mat_check[0]['band_gap']
    if mat_bandgap < 0.05:
        continue

    # check if the material has a bandstructure calculated
    # if not, will get MPRestError
    try:
        mat_bs = mpr.get_bandstructure_by_material_id(MP_ID)
        # gets the band structure
    except matproj.rest.MPRestError:
        continue

    # If everything works up to now, the mat exists, has a good BG and BS
    mat_formula = mat_check[0]["pretty_formula"].encode('ascii', 'ignore')
# gets the formula
mat_point =
    mat_check[0]["spacegroup"]["symbol"].encode('ascii','ignore')
# get point group
mat_form_E = mat_check[0]["formation_energy_per_atom"]
# gets the formation enthalpy
mat_direct = mat_bs.get_band_gap()["direct"]
# boolean True if direct gap

# Pull full DOS object on material
try:
    mat_dos = mpr.get_dos_by_material_id(MP_ID)
    # Get the CB and VB edges, as well as the energy vector
except matproj.rest.MPRestError:
    continue
(cb_dos,vb_dos) = mat_dos.get_cbm_vbm()

e_dos = mat_dos.energies
# Using these, find the index of energies just below the VBM
vbm_index = numpy.argmin(abs(e_dos-vb_dos))
# And index 1 eV below the VBM
v_index = numpy.argmin(abs(e_dos-vb_dos+1))
# Now pull the orbital partial DOS
spd_dos = mat_dos.get_spd_dos()
s_dos = spd_dos['S']
p_dos = spd_dos['P']
d_dos = spd_dos['D']
# get array of partial DOS just below VBM
# get_densities returns an array from DOS object, 601 long
s_v_d = s_dos.get_densities(spin=None)[v_index:vbm_index]
p_v_d = p_dos.get_densities(spin=None)[v_index:vbm_index]
d_v_d = d_dos.get_densities(spin=None)[v_index:vbm_index]
# figure out what fraction of dos is s orbitals in valence band
B.2 Plotting Density of States

This piece of code imports the DoS for compounds of interest, and then plots the partial density of states by atom and orbital.

```python
from pymatgen import MPRester
from pymatgen import matproj
import numpy
import matplotlib.pyplot as plt
from scipy import signal

MAPI_KEY = "XXXXXXXXXX" # Insert your own private key from MaterialsProject here
mpr = MPRester(MAPI_KEY)
# Start with a list of interesting files, either entered here or read in from a text file
interesting_ids = [675531]
#id_file = open('graph_list.txt','r')
#interesting_ids = id_file.readlines()

for num in interesting_ids:
    MP_ID = "mp-"+str(num)
    # keep track of which material
    # if num\%100 == 0:
    print MP_ID
```
# check if material exists in database
mat_check = mpr.get_data(MP_ID)
if len(mat_check) == 0:
    continue
# check if material has a bandgap >0.05 eV
mat_bandgap = mat_check[0]["band_gap"]
if mat_bandgap < 0.05:
    continue
# check if the material has a bandstructure calculated
# if not, will get MPRestError
try:
    mat_bs = mpr.get_bandstructure_by_material_id(MP_ID)
    # gets the band structure
except matproj.rest.MPRestError:
    continue
# If everything works up to now, the material exists, has a good BG and BS
mat_formula = mat_check[0]["pretty_formula"].encode(’ascii’,’ignore’)  # gets the formula
mat_point = mat_check[0]["spacegroup"]["symbol"].encode(’ascii’,’ignore’)  # get space group
mat_point2 =  
    mat_check[0]["spacegroup"]["point_group"].encode(’ascii’,’ignore’)  #get point group
mat_direct = mat_bs.get_band_gap()["direct"]  
    # boolean True if direct gap

# Pull full DOS object on material
try:
    mat_dos = mpr.get_dos_by_material_id(MP_ID)
# Get the CB and VB edges, as well as the energy vector
except matproj.rest.MPRestError:
    continue

(cb_dos, vb_dos) = mat_dos.get_cbm_vbm()

e_dos = mat_dos.energies

# Using these, find the index of energies just below the VBM
vbm_index = numpy.argmin(abs(e_dos - vb_dos))

# And index right at CBM

cbm_index = numpy.argmin(abs(e_dos - cb_dos))

# And index 1 eV below the VBM
v_index = numpy.argmin(abs(e_dos - vb_dos + 1))

# top 100 meV of VBM

full_dos = mat_dos.densities

# Now pull the orbital partial DOS
dos_dict = {}
eledos_dict = {}
tot_dos = numpy.zeros(len(full_dos[full_dos.keys()[0]]))

# Iterate through each element to get elemental DoS
for ele in mat_check[0]['elements']:
    dos_dict[ele] = mat_dos.get_element_spd_dos(ele)
    temp1 = dos_dict[ele]
    for orb, orbdos in temp1.iteritems():
        temp2 = temp1[orb]
        eleedos_dict[ele + str(orb)] = temp2.get_densities(spin=None)
        tot_dos += temp2.get_densities(spin=None)

# DoSes are generally noisy, and you can smooth the data if you wish
smoother = signal.hann(7)
new_e = e_dos-vb_dos

#full_dos2 =
    signal.convolve(full_dos[full_dos.keys()[0]], smoother, mode='same')/sum(smoother)/2
full_dos2 = signal.convolve(tot_dos, smoother, mode='same')/sum(smoother)

top_dos = max(full_dos2[len(tot_dos)/3:len(tot_dos)])*1.2
plt.plot(new_e, full_dos2, color='black')
plt.ylim([0, top_dos])
plt.xlim([-5, 6])
# plt.xlim([-5, cb_dos-vb_dos+6])
plt.xlabel('Energy-VBM [eV]')
plt.ylabel('Density of States [a.u.]')
plt.title(mat_formula + " (" + mat_point + ") " + MP_ID)

thresh = 0.1
all_col =
    ['green', 'dodgerblue', 'red', 'lime', 'mediumblue', 'darkred', 'forestgreen',
     'cyan', 'mediumvioletred']
leg_list = ['Total']
ii = 0
for key, eledos in iter(sorted(eledos_dict.items())):
    if max(eledos[len(tot_dos)/2:]) > thresh*top_dos and "d" not in key:
        smoothed =
            signal.convolve(eledos, smoother, mode='same')/sum(smoother)
        plt.plot(new_e, smoothed, color=all_col[ii])
        leg_list.append(key)
        print new_e[numpy.argmax(eledos)]
        ii+=1

plt.legend(loc=1, labels=leg_list)
plt.savefig("graphs/\mat_formula\_\MP_ID+.pdf",bbox_inches='tight')
plt.clf()

# print new_e[numpy.argmax(tot_dos)]
Appendix C

Bayesian Inference Code

C.1 Python-SCAPS Interface

The following code allows one to send a list of parameters to SCAPS from Python, and return the results back by reading in the text file.

```
import os
import numpy as np
from scipy import interpolate

# Define SCAPS Directory - CHANGE THIS TO YOUR OWN
SCAPSdef = "SnS_base.scaps"
SCAPSfolder = 'C:\Scaps'
SCAPSversion = 'scaps3300.exe'

def runSCAPS(mu_n_l, Nt_SnS_l, EA_ZnOS_l, Nt_i_l, T_l, ill_l, V_max, scapsNum):
    sName = "pythonscript"
    sPath = SCAPSfolder+str(scapsNum)+'\script\'+sName+'.script'
    rName = "pythonresult.txt"
    rPath = SCAPSfolder+str(scapsNum)+'\results\'+rName
    makeScript(sPath,rName,mu_n_l, Nt_SnS_l, EA_ZnOS_l, Nt_i_l, T_l,
```
ill_l,V_max)

order = SCAPSfolder+str(scapsNum)+"\""+SCAPSversion+" "+sName+'.script'

os.system(order)

J_sweep,V_sweep = readSCAPS(rPath)

f = interpolate.interp1d(V_sweep,J_sweep)

os.remove(sPath)

os.remove(rPath)

return f(np.arange(0,V_max+0.02,0.02))

# Write script
def

makeScript(sFile,rFile,mu_n_l,Nt_SnS_l,EA_ZnOS_l,Nt_i_l,T_l,ill_l,V_max):
    script = open(sFile,"w")
    script.write("//Script file made by Python\n")
    # Set quit policy:
    script.write("set quitscript.quitSCAPS\n")
    # Load the problem statement and general settings
    script.write("load allscapssettingsfile "+SCAPSdef+"\n")
    # Set error handling to not go to screen
    script.write("set errorhandling.overwritefile\n")
    # Edit any parameters like this:
    script.write("set layer1.mun \%f\n" \% mu_n_l)
    script.write("set layer1.defect1.Ntotal \%f\n" \% Nt_SnS_l)
    script.write("set layer2.chi \%f\n" \% EA_ZnOS_l)
    script.write("set interface1.IFdefect1.Ntotal \%f\n" \% Nt_i_l)
    # Run a single simulation, and save the i-v vectors:
    script.write("action workingpoint.temperature \%f\n" \% T_l)
    script.write("action iv.startv \%f\n" \% 0.0)
    script.write("action iv.stopv \%f\n" \% V_max)
    script.write("action iv.increment \%f\n" \% 0.02)
    script.write("calculate\n")
    script.write("save results.iv "+rFile+"\n")
script.write("\n")
script.close()
return None

def readSCAPS(rPath):
    # Read in results to .npy
    ii = 0
    simList = list()
    summaryList = list()
    with open(rPath) as f:
        for line in f:
            if 'jtot' in line:
                simList.append(ii)
            elif 'deduced' in line:
                summaryList.append(ii)
            ii +=1
    ii = 0
    dataLines = list()
    for xi,x in enumerate(simList):
        dataLines.extend(range(x+2,summaryList[xi]-1))
    JArray = np.zeros(len(dataLines))
    VArray = np.zeros(len(dataLines))
    ii = 0
    with open(rPath) as f:
        for jj,line in enumerate(f):
            if jj in dataLines:
                floats = [float(x) for x in line.split("\t")]
                JArray[ii] = floats[1]
                VArray[ii] = floats[0]
                ii += 1
    return (JArray,VArray)
C.2 Framework for Inferring Materials Properties

The following code is the overarching framework used for inference. It is used to produce a gridded matrix of SCAPS results, as well as reading in the observations. Together, these are sent to a final function for the Bayesian inference step.

```python
import numpy as np
import math
import time
import bayesInference4 as bi
import bayesPlot4b as bp
import singleSCAPS_SnS as scaps

# What is the name of the device you are looking at?
device = 'SnS_006'
devPath = "C:\Users\REB\Data Processing\"+device
#os.mkdir(devPath) # Need to uncomment this the first time

# Name the python archive of simulated currents: simFile = 'J'
simPath = devPath+"\J"
# Name the python archive of parameter sweeps
paramPath = devPath+"\sweep"
# Name the python archive of prior/posterior probabilities: probFile =
#probPath = devPath+"\prob"
# Where the observations are stored:
obsPath = devPath+"\"+device+".txt"

# Number of cores to use
numCores = 1

params = {
    "mu_n_SnS": [20, 80, 7, 0],
    "Nt_SnS": [1e16, 1e18, 12, 1],
}
```

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"EA_ZnOS": [3.9, 4.3, 9, 0],
"Nt_i": [1e10, 1e14, 12, 1],

biases = {
"T": [320, 320, 1, 0],
"ill": [100, 100, 1, 0],
"V": [0.0, 0.5, 26, 0]
}

# Just to keep track of the order of the dimensions:
dimensionOrder = [
"mu_n_SnS", "Nt_SnS", "EA_ZnOS", "Nt_i", "T", "ill", "V"]

# Figure out the shape of the resulting matrix:
Jshape = np.ones(len(dimensionOrder))
for ii, dim in enumerate(dimensionOrder):
    if ii < len(params):
        Jshape[ii] = params[dim][2]
    else:
        Jshape[ii] = biases[dim][2]

# Make a fake matrix of data with the right size, which we fill later
Jshape = Jshape.astype(int)
Jmat = np.zeros(Jshape)
#np.save(simPath, Jmat)

###_________________Functions__________________###
# Make a dictionary of values to simulate over. Each list is keyed with the
# name of the parameter in question.
def param_dict(limits):
    parameters = limits.keys()
xp = {}
    for param in parameters:
        lim1 = limits[param]
        if lim1[3] > 0.5: #if its 1, its logspace, if 0, its linspace
            xp[param] =
np.logspace(math.log(lim1[0],10),math.log(lim1[1],10),
num=lim1[2])

else:
    xp[param] = np.linspace(lim1[0],lim1[1],num=lim1[2])

return xp

# Function to read in a list of observations:
def obs_read(oPath):
    observed = np.array([])
    with open(oPath) as f:
        for jj,line in enumerate(f):
            if jj == 1:
                floats = [float(x) for x in line.split("\t")]
                observed = floats
            elif jj > 1:
                floats = [float(x) for x in line.split("\t")]
                observed = np.vstack([observed, floats])
    return observed

# This function normalizes a big array to have a cumulative Prob = 1
def normalize(big_array):
    F = big_array.cumsum()[-1]
    return big_array/F

# This just makes a uniform probability distribution over all the parameters
def make_prior(Pshape):
    return normalize(np.ones(Pshape))

def fillMatrix(p,b,J,dim):
    # ["mu_n_SnS", "Nt_SnS", "EA_ZnOS", "Nt_i", "T", "ill", "V"]
    ii = 0
    tot = len(Jmat.flatten())/(len(b["V"])+0.0)
V_max = max(b["V"])

for i1,a1 in enumerate(p["mu_n_SnS"])::
    for i2,a2 in enumerate(p["Nt_SnS"])::
        for i3,a3 in enumerate(p["EA_ZnOS"])::
            print "Finished " + str(ii*100/tot) + "% at " + time.strftime("%I:%M%p")
            for i4,a4 in enumerate(p["Nt_i"])::
                for i5,a5 in enumerate(b["T"])::
                    for i6,a6 in enumerate(b["ill"])::
                        #for i7,a7 in enumerate(b["V"])::
                        J[i1,i2,i3,i4,i5,i6,:] =
                            scaps.runSCAPS(a1,a2,a3,a4,a5,a6,V_max,1)
                        ii+=1

return J

###____________________Main_Body____________________###
# Read in your observations (.txt file, tab separated)
obsList = obs_read(obsPath)
# Make the full vectors for the purposes of plotting and so forth
paramList = param_dict(params)
biasList = param_dict(biases)
np.save(paramPath,[paramList,biasList])
# Go and run simulations! Will save a J.npy file
Jmat = fillMatrix(paramList,biasList,Jmat,dim)
np.save(simPath,Jmat)
# Make a prior probability distribution:
PO = make_prior(Jshape[0:len(params)])
np.save(probPath,PO)
print "Saved prior, starting inference"
# Now order things over to the inference code
bi.posteriors(simPath,probPath,obsList,biasList,Jshape)
C.3 Computing the Likelihood

The following code is the particular function used to compute the likelihood. It requires another mapping function to choose the matrix of modeled currents to match with the same $V, T,$ and $i$ for each observation, as well as computing the associated error in the current measurement.

```python
# This function takes the observed current and the matrix of calculated currents
# and finds the likelihood, assuming an error for the current.

def likelihood(I_meas, I_model, I_error, v1, v2, v3, v4):
    lkl = make_prior(v1, v2, v3, v4)*0
    for x1i, x1 in enumerate(v1):
        for x2i, x2 in enumerate(v2):
            for x3i, x3 in enumerate(v3):
                for x4i, x4 in enumerate(v4):
                    lkl[x1i][x2i][x3i][x4i]=1/1.772/I_error*math.exp(-(I_meas-
                                                  I_model[x1i][x2i][x3i][x4i])**2/2/I_error**2)

    return lkl
```
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