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Band structure engineering for solar energy applications: ZnO$_{1-x}$Se$_x$ films and devices

By

Marie Annette Mayer

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Engineering - Materials Sciences and Engineering in the Graduate Division of the University of California, Berkeley

Committee in charge:
Professor Eugene E. Haller, Chair
Doctor Wladyslaw Walukiewicz
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Abstract

Engineering ZnO for solar energy applications:
Fabrication and characterization of ZnO$_{1-x}$Se$_x$ and related devices

by

Marie Annette Mayer

Doctor of Philosophy in Engineering-Materials Sciences and Engineering

University of California, Berkeley

Professor Eugene E. Haller, Chair

New technologies motivate the development of new semiconducting materials, for which structural, electrical and chemical properties are not well understood. In addition to new materials systems, there are huge opportunities for new applications, especially in solar energy conversion. In this dissertation I explore the role of band structure engineering of semiconducting oxides for solar energy. Due to the abundance and electrochemical stability of oxides, the appropriate modification could make them appealing for applications in both photovoltaics and photoelectrochemical hydrogen production. This dissertation describes the design, synthesis and evaluation of the alloy ZnO$_{1-x}$Se$_x$ for these purposes. I review several methods of band structure engineering including strain, quantum confinement and alloying. A detailed description of the band anticrossing (BAC) model for highly mismatched alloys is provided, including the derivation of the BAC model as well as recent work and potential applications.

Thin film ZnO$_x$Se$_{1-x}$ samples are grown by pulsed laser deposition (PLD). I describe in detail the effect of growth conditions (temperature, pressure and laser fluence) on the chemistry, structure and optoelectronic properties of ZnO$_x$Se$_{1-x}$. The films are grown using different combinations of PLD conditions and characterized with a variety of techniques. Phase pure films with low roughness and high crystallinity were obtained at temperatures below 450°C, pressures less than 10$^{-4}$ Torr and laser fluences on the order of 1.5 J/cm$^2$. Electrical conduction was still observed despite heavy concentrations of grain boundaries.

The band structure of ZnO$_{1-x}$Se$_x$ is then examined in detail. The bulk electron affinity of a ZnO thin film was measured to be 4.5 eV by pinning the Fermi level with native defects. This is explained in the framework of the amphoteric defect model. A shift in the ZnO$_{1-x}$Se$_x$ valence band edge with x is observed using synchrotron x-ray absorption and emission spectroscopy. Measurement of the optical absorption coefficient, $\alpha$, shows a significant red shift as well as an increase in the low energy density of states with x. Fitting $\alpha$ revealed that the initial Se defect level is located 0.9 eV above the valence band edge and the coupling strength of the interaction is 1.2 eV. Optical reflection data are good agreement with the absorption onset at 2 eV. Taking the derivative of this data reveals experimental observation of the matrix-like band at higher energies.
ZnO$_{1-x}$Se$_x$ is explicitly evaluated for photoelectrochemical applications. An introduction to semiconductor electrochemistry is followed by flat band, photocurrent, and spectrally resolved photocurrent measurements. The flat band measurements are in excellent agreement with the measurements of the ZnO electron affinity using bulk methods, but show that the conduction band edge of ZnO$_{1-x}$Se$_x$ is too low for spontaneous water splitting. Measurements of the incident photon to current conversion efficiency (IPCE) indicated that photons with energies greater than 2 eV excite carriers that do conduct and induce chemical reactions. Tandem ZnO$_{1-x}$Se$_x$/Si devices are made with a natural Ohmic contact between the p-Si and n-ZnO$_{1-x}$Se$_x$. Electrochemical testing proves that the presence of the tandem photovoltaic provides an overpotential of ~0.5 V to electrons enabling the reduction of H$^+$ in solution.

Finally, the carrier scattering and recombination lifetimes in ZnO$_{1-x}$Se$_x$ are considered. Resistivity, Hall effect and Seebeck coefficient measurements are used to probe the scattering lifetime, while the recombination lifetime is investigated using photoluminescence spectroscopy. Electrochemical photocurrent measurements in light and dark are a function of the product of both lifetimes. Results indicate that significant scattering in the lateral direction does not prohibit the photoelectrochemical device from operating, but defects from high fluence growth are extremely detrimental to the recombination lifetime. A textured or otherwise irregular crystal that does not function well for a device designed for transport in one direction might be perfectly operational when the current flow is perpendicular.

The final chapter provides perspective on the future of ZnO$_{1-x}$Se$_x$ in scientific research and obstacles to overcome before industrial applications are possible. Perspective on sustainable hydrogen production is given. The optimist can see a value for nearly all renewable energy technologies in a variety of value-driven applications.
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Chapter 1: An Introduction

1.1 Semiconductors: Yesterday, today and tomorrow

Our history as humans can be classified by the engineering of materials. Early humans living in the Stone Age were motivated by survival and built a civilization based on rocks. As our ability to utilize heat increased, the low melting point of bronze led to a new class of cast tools and weapons – the so-called Bronze Age. During the Iron Age, mankind began to literally forge a civilization. In the 1800s, parallel to the industrial revolution, we began to engineer the iron by adding small amounts of carbon to improve strength. That was the birth of steel, the material supporting everything from civil engineering feats to high temperature engines and beyond. Within the last 300 years we have christened the scientific field of “metallurgy”. Built on a fundamental understanding of chemical and structure properties of metals, it has taken us today to cleverly designed, highly engineered alloys of aluminum that enable flight or titanium with lightweight strength. Of course, this short summary is unfair to the long, rich history of materials science, but it demonstrates that the character of civilization itself is closely tied to the development of metallurgical materials.

There is an analogous story, although less referenced by historians and archeologists, of electronic materials and their influence in our world. One might divide the story into the Stone Age, the Silicon Age and a third age, which is yet to be named. The Stone Age gave us radios and radar, the Silicon Age enabled computers, and the third age is defined by our ability to design semiconductors materials for specific applications. This dissertation describes in detail recent work on band gap engineering for solar applications, which, like today’s high tech metal alloys, allows us to tailor semiconductors precisely for a specific application. However, a glimpse into the history of electronic materials science provides context for the significance of this work.

It is fair to say that the first electronic materials were metals such as the zinc or silver in early batteries made by Volta in 1800 or even the iron in Benjamin Franklin’s kite-born key. There were also insulators, or dielectrics, which enabled the storing of static charge in Leyden Jars. The first semiconductor was chronicled by Michael Faraday in 1833 when he noted that the resistivity of silver sulfide decreased with temperature, an effect opposite to that of most metals. It was soon discovered that semiconductors could act as rectifiers when Ferdinand Braun probed a lead sulfide crystal with a thin metal wire in 1876, making a “cat’s whisker” or point contact diode. These were later patented by Jagadis Bose (no relation to the sound corporation) and employed in crystal radios, which could operate without external power. While these were and continue to be exploited by hobbyists, semiconductors were secondary to vacuum tubes until World War II, when it was discovered that semiconductors could be used as radar detectors and receivers.

Until this point, semiconductor science was effectively in the “Stone Age”, where devices were made of unprocessed materials (or “dirt” in the words of the physicist Wolfgang Pauli) that demonstrated semiconducting behavior when picked up from the ground. In the 1930s,
theorists were frustrated with semiconductor physics because material samples varied too greatly to develop reasonable theories that accurately explained semiconducting behavior.

Major advances in semiconductor technology stem from work at Bell Telephone Labs. Russel Ohl had a long term interest in silicon since he had made sensitive cat’s whisker detectors in the 1920s. While working on the purification of silicon, Ohl accidentally created a bar that was purified over only half of the length. He noticed a significant photo-generated voltage, discovering the first p-n junction. This discovery kicked off further exploration of Si as a semiconductor material that could be controlled better than cuprous oxide or selenium. On December 16th, 1947, John Bardeen and Walter Brittain demonstrated the first point contact transistor, or solid state amplifier, out of germanium that had been highly purified at Purdue University. Afterward, William Shockley conceived the idea of a junction transistor, relying on p- and n-doped semiconductor regions. Planar IC circuits became the focus of Fairchild Semiconductor, which was spun off by 8 frustrated employees at Shockley Semiconductor Laboratory. The “traitorous eight” included Jack Kilby of Texas Instruments and Intel’s Robert Noyce and Gordon Moore. The computer could not be what it is today without transistors, and now they are used ubiquitously in everything from phones and computers to cars and toys. According to estimates for 2011, more than 1 billion transistors are produced annually per person worldwide! Semiconductors today also appear as lasers, lighting, solar cells, and on satellites for photovoltaic power and radiation detection.

However, nearly all of these devices were made of silicon or germanium until recent years. While great materials science elucidated the behavior of these materials and devised methods of purification and synthesis, Si and Ge are not perfect for all applications. Electronics applications such as cell phones have driven development of semiconductors with higher mobilities which led to appearance of GaAs-based devices. Group III-Nitride-based devices are now being commercialized for high efficiency lighting, roughly 20 years after the original fabrication of a blue light emitting diode by Shuji Nakamura. Recently CdTe, GaInP and Cu(In,Ga)Se2 (CIGS) have appeared in manufactured solar cells, but we still use a very limited portion of available semiconducting materials. We are barely at the beginning of the third era of semiconductors, following the Silicon Age. We are designing materials (or materials systems) to be ideal for specific application. To get from theory to practicality, it is imperative to understand structural, electrical and chemical properties of non-traditional semiconductors. The fundamentals learned in Si and Ge can be extended to unique systems. In addition to exploring new materials, there could be huge opportunity for new applications away from traditional devices (especially those relying on electrochemistry). The motivation behind our engineering today is not radios, radar or microelectronics, but an energy revolution.

### 1.2 Semiconductors and the energy revolution

It has become clear for a variety of reasons that is truly a necessary global challenge to prioritize clean, sustainable sources of energy. Perhaps the most compelling is the preservation of our planet. While the role of humans in global warming is surprisingly still a heavily debated topic, it is clear that many of our current energy sources pollute water, land and air. Furthermore, there is a finite amount of fossil fuels in the earth, especially oil that forms over millions of years. And, if someone is not concerned about the environment or running out of fuel, there are always political reasons to push for clean energy. In the 2012 State of the Union Address, President Barack Obama said, “But with only 2 percent of the world's oil reserves, oil
isn't enough. This country needs an all-out, all-of-the-above strategy that develops every available source of American energy - a strategy that's cleaner, cheaper, and full of new jobs." Secure and reliable sources of energy are critical for both the United States and countries struggling to stand on their own.

While wind, hydropower, and geothermal power all have their advantages, solar energy and semiconductor research are a natural duo because semiconductors generate power from photons. The area required to meet U.S. or worldwide energy needs is relatively small, as seen in Figure 1.1, reminding us that there is far more capacity in sunlight than fossil fuels. Sunlight can do useful work in 4 distinct processes: photosynthetic, photothermal, photovoltaic (PV) and photoelectrochemical. The original mechanism of solar energy conversion is photosynthesis in plants, which converts sunlight and CO$_2$ to chemical fuels in the form of sugars. Photothermal conversion relies upon sunlight to provide heat, which can be combined with turbine technology. Photovoltaics, which are at record production and distribution, are known to convert sunlight into electrical energy. Significant recent effort has also being made to use photogenerated carriers to supply energy for chemical processes, or photoelectrochemical fuel production. This process is especially important for transportation and storage of solar energy as fuel.

![Figure 1.1 Area required in order to meet U.S. energy need with photovoltaics, 2011.](image)

Calculation originally by John Turner; redone by author using 2011 U.S. Department of Energy data.

1.3 Semiconductors for photovoltaics

Unlike fossil fuel energy, the market for photovoltaics (or cost of output power) is determined by the initial cost of a PV system. For reference, analysis predicts that if solar energy is less than $2/watt ($3/watt), PV energy will provide 30% (11%) of U.S. energy consumption. A reduction in the cost of the arrays encourages investment in solar power either by developers or consumers. Either overcapacity (low demand) or reduced raw materials cost for the same output power can drive the price down, although only the latter is sustainable in the long term for manufacturers.
Thus, semiconductor PV research is motivated either by making the solar cell more efficient and/or reducing the cost of materials feedstock – such as less material or more abundant elements. A semiconductor to be used for solar energy must maximize both absorption of sunlight (or output current) and output voltage. These properties are not independent; a single semiconductor solar cell is fundamentally limited by its band gap according to the Schokley-Queisser limit\textsuperscript{18}. If the band gap is too small, the output voltage is small, and if the gap is too big, few photons are absorbed and the current is limited.

Approaches for achieving high efficiency solar cells include utilizing a multijunction solar cell or introducing an intermediate band in a single junction cell. A multijunction cell (Figure 1.2) typically relies on individual p-n cells in tandem to convert different narrow ranges of photons, which requires that the band gaps of the cells be selected for optimum coverage of the solar spectrum. Although these cells can reach nearly 44\%\textsuperscript{19}, the current is limited by the least effective layer, and strict materials requirements often lead to complex, expensive technology including several different elements, three different dopants and two or more tunnel junctions\textsuperscript{20}. These cells are manufactured and included on spacecraft today, and current commercial efforts for terrestrial use are underway. In the second approach, the intermediate band can serve as a “stepping stone” for below-band-gap photons to transfer electrons from the valence band to the conduction band. This increases the number of carriers generated in a single band gap cell and the resulting output current, yet the voltage remains as large as the overall band gap\textsuperscript{21}. Although this concept was proposed in the early 1990’s, there were no practical demonstrations until last year\textsuperscript{22}. Both of these cells reduce losses caused by phonon relaxation.

![Figure 1.2 Schematic of a triple junction tandem solar cell, courtesy of Becca Jones-Albertus.\textsuperscript{23}](image)

While development of high efficiency cells is certainly a reasonable approach to reducing the dollar per watt cost of solar power, they also require a rather significant infrastructure which has, to date, kept concentrated photovoltaics (CPV) from being economical. Instead, Si-based solar cells (with just under 20\% efficiency\textsuperscript{24}) have dominated the market. Thin film technologies made of CdTe and CIGS are also available for purchase, but receive criticism for relying on toxic (Cd) or rare/byproduct (Te, In) elements. The ideal solar cell material would be nontoxic, require little processing or purification and be made of abundant elements, all of which reduce the price of the final product. By these standards, oxides are excellent candidates. However, the material still must have appropriate optical (band gap) and electrical (doping and mobility)
properties to function as a solar cell. By nature, oxides have wide band gaps (hence their white color and use in sun screen), but in this dissertation we design, synthesize and characterize the optical and electrical properties of ZnO$_{1-x}$Se$_x$, a narrow gap oxide.

1.4 Semiconductors for photoelectrochemical applications

PV technology is continuously improving, but commercial systems will always face a question: what happens when the sun is not shining? Additionally, most transportation cannot efficiently take advantage of the equivalent of 1.3 trillion barrels of oil produced annually by the sun$^{25}$ because of surface area and/or weight constraints. There is clearly great opportunity for battery technology. Electric cars charged by solar energy are a clean source of transportation (and commercially available today). However, our current lifestyles depend on being able to carry fuel and refuel in minutes rather than recharge over hours. Hydrogen (or other photoelectrochemically-produced fuel) made from sunlight and water or CO$_2$ is a suitable alternative to fossil fuel that requires little restructuring of our social habits.

\[\text{Figure 1.3 The cost of hydrogen based on the electricity prices alone; no capital, operating, or maintenance costs are included in the calculation. HHV, higher heating value. From J. Turner.}^{26}\]

Splitting water into gaseous hydrogen and oxygen components with direct current, or electrolysis, was first performed in 1800$^4$. Today, fuel cells can extract stored energy from hydrogen, while hydrogen is already transported for use in fossil fuel refineries$^{26}$. The U.S. Congress even formed a special committee in 1975 to discuss the possibilities for large scale hydrogen replacement of fossil fuels$^{27}$. However, it is still not clear how to produce clean hydrogen economically. Any electrons produced by clean methods (wind, solar, geothermal etc.) are able to produce clean hydrogen, but, to date, the cost of a clean power system and a catalysis system is prohibitively high for a large scale fuel source$^{26}$. This is illustrated in Figure 1.3, which shows the ideal cost of a clean hydrogen electrolyzer compared to available technologies in 2004. A certain output of hydrogen/hour must be maintained to make photoelectrochemical hydrogen production and economical decision. As the initial cost of the system increases, so does the rate of output required to actually make money. A commercial electrolyzer typically operates at about 1 A/cm$^2$, which requires a voltage of 1.8-2V for such high current once overpotentials are accounted for. In opposition to these economics, “the energy efficiency of
electrolysis is defined as the electrochemical potential of hydrogen divided by the voltage required for operation.” Since the thermodynamic requirement for the water splitting reaction is 1.23 volts, this makes efficiencies (1.23 divided by operating voltage) of 62-68% possible.

Current electrolyzer technology sacrifices efficiency in exchange for high output rates to pay back the cost of expensive platinum-based catalysts. In order to operate near the thermodynamic potential for water splitting (and thus take advantage of solar energy), cheaper catalyst materials/initial systems must be developed. Replacing the solar cell and electrolyzer with an integrated system for direct photoelectrolysis immediately eliminates at least two costs: (1) it eliminates the cost of top contacts, metallizations, coatings etc. and (2) a p-n junction is no longer necessary, which also enables the use of materials systems where p-n junctions are difficult to form. While a PV cell electrically wired to a catalyst may become economically viable as solar technology and catalysis improves, there is certainly exploration to be done on materials for a monolithic reactor. The description of such a system is provided in section 5.1.2.

1.5 This Dissertation

There are seven chapters in this dissertation. The first is the introduction which puts the design and engineering of semiconductors into historical context. It provides a framework of solar based energy and therefore the requirements for solar materials intended for these applications. The second chapter introduces the concept of band gap engineering, an important contributor to semiconductor design. I discuss the effects of both physical structure and chemical composition (alloying) on the band gap. A specific class of alloys, so-called highly mismatched alloys and are described within the framework of the band anticrossing model.

The remaining chapters emphasize specific cases of solar materials fundamentals, design and engineering. Chapter 3 is an in-depth description of the properties of ZnO$_{1-x}$Se$_x$ grown by pulsed laser deposition—including structural, chemical, electrical transport and optical attributes. In Chapter 4, the electronic structure of the alloy is modeled and described within the framework of the band anticrossing model. The band gap of ZnO, 3.3 eV, can be reduced by nearly 1 eV with less than 10% replacement of O anions with Se. In Chapter 5, I present a brief review of semiconductor electrochemistry and photoelectrochemical measurements followed by an analysis of these alloys for use as the absorber layer in a photoelectrochemical cell. By tailoring the band structure of an oxide, we can make a stable material with poor absorption utilize a larger portion of the solar spectrum. I show significant improvement in low wavelength photocurrent with the addition of Se to ZnO and suggest methods for optimization of carrier extraction. Chapter 6 describes the optical and electronic advantages and challenges inherent to devices made from highly mismatched alloys. Finally, Chapter 7 provides a broad overview of the impact of this work as well as an outlook for the future of solar-based fuels.
Chapter 2: Band structure engineering

2.1 Semiconductor bands and band gaps

The “band gap” defines the transition between the highest occupied state and the lowest unoccupied state. In most semiconductors, this is the energy difference between the top of the valence band and the bottom of the conduction band. It can be easily observed through a material’s interactions with light, through absorption or emission. Both the increase of light absorption as a function of energy and the energy of the emitted light gives the material band gap.

![Diagram of GaAs band structure](image)

An in-depth discussion of band structure is beyond the scope of this thesis, but, in general, there are two models used for the derivation of a semiconductor band gap. In either case, the valence bands and conduction bands are the corresponding momentum (k) space description of a real space arrangement of atoms (often, but not always, crystals). The definition of k space is convenient to discuss the interaction of the solid with electromagnetic waves (light), acoustic vibrations and electrons. The first gap derivation is a quantum mechanical calculation of the complete band structure, as shown in Figure 2.1a. The so-called nearly free electron model treats each atom in the crystal structure as a potential (Bloch’s theorem) and calculates the allowed energy states of an electron in the crystal. The band gap is then the minimum distance between the conduction band and the valence band. Figure 2.1a shows a direct band gap, where the conduction band minimum and the valence band maximum are at the same value of k. Alternatively, a material with an indirect gap requires that an electron undergo a change in
momentum in addition to energy in order to transition. The second derivation of a band gap relies on molecular orbital theory\textsuperscript{31}. Most semiconductors have some degree of covalent bonding, so the atomic $s$ and $p$ orbitals hybridize into $sp^3$ orbitals. These in turn form bonding (low energy) and antibonding (high energy) states between neighboring atoms. The effectively infinite number of atoms in a crystal results in the spread of overlapping orbital energies into bands because of the Pauli Exclusion Principle. As shown in Figure 2.1b, these bands are the valence and conduction bands, respectively. A detailed description band structure can be found in a number of textbooks, including those by Rockett\textsuperscript{29}, Kittel\textsuperscript{32} and Yu and Cardona\textsuperscript{30}.

### 2.2 Structural band gap engineering

Based on the relation of atoms and band structure, it follows that altering the physical lattice in some form would affect the band structure. Perhaps the simplest demonstration of this is applying hydrostatic stress to the crystal. Compressing a solid decreases the physical lattice spacing, while tensile stress increases the lattice spacing. At first approximation, a smaller lattice spacing leads to a larger band (direct) gap because the difference between the bonding and antibonding orbital (Figure 2.1b) is dependent upon the square of the interatomic distance. A narrowing of the band gap can actually occur in indirect materials because the large dispersion in the conduction band causes high momentum band minima to shift downward with strain.\textsuperscript{29} Thin film scientists often grow thin films epitaxially on substrates (with <5% larger or smaller lattice spacing) in order to strain the material. The final lattice spacing between atoms in the film is either smaller or larger than in a bulk crystal\textsuperscript{33}. Accurate prediction of the band gap as a function of anisotropic lattice strain requires a comprehensive calculation. This type of calculation has been performed for the band gap decrease demonstrated by a strained Si layer on a relaxed Si-Ge substrate\textsuperscript{34}.

![Figure 2.2 Emitting CdSe nanoparticles of varying size, from http://nanocluster.mit.edu/ Photography by Felice Frankel.](image)

A second method of altering the band structure of a material is to use quantum confinement. As materials are made smaller, they can approach a size on the order of the electron wavelength at which the quantum nature of the system pervades. This can occur in two (semiconductor quantum well), one (nanowire), or zero (quantum dot) dimensions. As has been demonstrated with quantum dot growth, reducing the system dimension(s) can increase the apparent “band gap”. In this case, it is inappropriate to use bands for the $k$ space description within the well because electron transitions occur between discrete states rather than bands of states. To a first approximation, these states can be derived through quantum mechanics by treating the nanoparticle as a quantum potential with the 1-D, time-independent Schrodinger equation\textsuperscript{35}. The result is that the lowest possible energy transition is larger than transitions in the bulk material. Figure 2.2 shows CdSe dots which emit at different energies. As the size
decreases further, the well narrows, and the resulting confinement and splitting increases. It is worth noting that layered quantum well structures are often used in heterostructure lasers as a method of confining carriers in a narrow real space region\textsuperscript{29}. In this case, the quantum well material is chosen to have a narrower gap than the surrounding bulk material through a separate method of band gap engineering, often alloying.

2.3 Chemical band gap engineering

Perhaps the most well-known method of band gap engineering is alloying. In the simple case, two semiconductors are mixed, and the resulting band gap lies between the two original band gaps as a function of the alloy composition. In most cases, it can be assumed that the composition is a linear function of the alloy lattice parameter. This is illustrated in Figure 2.3. Heterostructure devices (lasers\textsuperscript{36}, light emitting diodes\textsuperscript{8}, solar cells\textsuperscript{20}) made from III-V materials rely heavily on this type of engineering for quantum wells, 2-D electron gases and tuning the band gap to obtain exact emission or absorption energies. When a direct gap semiconductor is alloyed with an indirect gap semiconductor, the band gap is a linear function of the compositions of the endpoint materials. In some cases, there is a slight bowing to the linear band gap change. This bowing is usually empirically measured rather than calculated a priori. It is related to changes in both the lattice potential and the electron potential that are the inputs to the Schrodinger equation for the calculation of a band structure, such as the one in Figure 2.1a.\textsuperscript{29} In general, the larger the bowing, the greater the miscibility gap when x is on the order of 0.5. However, the extreme bowing observed in so-called highly mismatched alloys (HMAs) such as GaN\textsubscript{1-x}As\textsubscript{x} can be treated differently. This scenario will be discussed in Section 2.2.

![Figure 2.3 Band gap as a function of lattice constant. Lattice constant is linear with composition. From http://gorgia.no-ip.com/phd/html/thesis/phd_html/node4.html](http://gorgia.no-ip.com/phd/html/thesis/phd_html/node4.html)

The III-nitride alloy system has proven to be of special interest within the last 20 years. Band gaps ranging from 0.7 eV (InN) to 6.1 eV (AlN) make group III-Nitride alloys an attractive choice for numerous applications including photovoltaics, light emitting diodes and lasers\textsuperscript{37,38}. 
The original blue laser was fabricated in In$_{1-x}$Ga$_x$N and today (in 2012) such devices are produced by several companies. The large span of the nitride system band gap allows the possibility of a multijunction solar cell within a single alloy system. Finite element analysis has shown that incorporation of a graded In$_{1-x}$Ga$_x$N section increases cell efficiency$^{39}$. However, the prospects for any optoelectronic devices requiring low band gap nitrides have been deterred by the presence of a highly conducting n-type layer on all InN surfaces such that contacting the p-type bulk has proven unachievable in samples with more than 37% In.$^{40}$

There are two more cases of band gap changes through alloying that must be included for completeness. The first is “alloy ordering”. Typically, ternary alloys are assumed to be random, such that in an alloy AB$_{1-x}$C$_x$, B and C are interchanged randomly. However, under specific growth conditions, a super lattice can form. This alloy ordering can reduce the band gap compared to the random mixture by 10-100 meV.$^{41-43}$ Additionally, quaternary alloys are synthesized frequently, especially as thin film growth techniques continue to be developed$^{44,45}$. A general trend is that the difficulties of synthesis increase as the number of elements increase, and therefore thin film alloys with greater than three elements require molecular beam epitaxy for synthesis. Ternary alloys band gap gradients generally result from either a change in the conduction band or a change in the valence band. Quaternary and quinary alloys allow for adjustment of both the conduction and the valence bands, which is a valuable tool in semiconductor heterostructures. They also can be used to control the lattice parameter. The author is familiar with at least one proprietary quinary alloy in commercial development.

2.4 Highly mismatched alloys and band anticrossing

At small values of $x$, highly mismatched alloys (HMAs), such as AB$_{1-x}$C$_x$, are an AB semiconductor matrix. A small percentage of C replaces an isovalent atom B, where B and C necessarily have different electronegativities. Traditional dopants in semiconductors are typically classified as either shallow or deep level dopants, both of which have wave functions that interact with the periodic potential of the host lattice.$^{47}$ Shallow level dopants have single wave functions highly correlated with the host wave functions; hence the energy level of the dopant within the gap is determined primarily by the host according to the hydrogenic model$^{29,47,48}$. As a rule of thumb, shallow levels have a ground state within 10s of meV from the host band edges. Conversely, deep level dopants have wave functions highly delocalized in k space and do not track with the host bands. In small concentrations, these levels remain independent of the host bands and act as traps within the band gaps of the semiconductors$^{48,49}$.

In large concentrations, resonant impurities, or defects with energies that overlap states in the band, can actually interact strongly with the nearby host band. These impurities can be highly mismatched isovalent impurities or, in certain cases$^{50}$, deep level dopants. In the simplest case of an impurity level interacting with the conduction band, this can be treated as a band anticrossing (BAC) interaction of two initial states, the localized impurity state and the highly delocalized band state$^{51}$. The Hamiltonian for such a system can be expressed as$^{51}$:

$$
\begin{bmatrix}
E_x^c - E(k) & C\sqrt{x} \\
C\sqrt{x} & E^d + \Gamma_d - E(k)
\end{bmatrix} = 0
$$

(2.1)

where C is an empirically determined coupling parameter, $x$ is the concentration of the impurity (in terms of percentage), $\Gamma_d$ is a broadening parameter, $E(k)$ is the dispersion relation of the
band and $E^d$ is the impurity energy level. The result of this mixing is a splitting into two sub-bands given by:

$$E_x(k) = \frac{1}{2}(E_{Se} + E(k)) \pm \sqrt{(E(k) - E_{Se})^2 + 4C^2x}$$  \hspace{1cm} (2.2)

where, in this conduction band model, $E_+(k)$ is the mostly delocalized conduction-band-derived state and $E_-(k)$ is the mostly localized impurity-band-derived state. The model has been successfully used to analyze the interaction of localized isovalent impurity states with the conduction band$^{52,53}$. The bands as predicted by the BAC model are shown in Figure 2.4 for a highly mismatched alloy of GaN$_{0.05}$As$_{0.95}$.

However, the problem becomes more complex in the case of defect states that lie near the valence band. Here, a complete description of the final states requires that the 3 valence band states (heavy hole, light hole and spin-orbit split off band) mix with the p-like states of the impurity state resulting in a 12x12 Hamiltonian matrix. This system has been theoretically treated in detail for both highly mismatched alloys as well as Ga$_{1-x}$Mn$_x$As by K. Alberi et al.$^{49,54,55}$ Valence band anticrossing (VBAC) occurs in systems where the substitutional atom is much less electronegative than the matrix atom. This is the case for GaN$_{1-x}$As$_x$ and GaAs$_{1-x}$Sb$_x$, for which the calculated$^{49}$ valence band structure is shown in Figure 2.5. It has been shown that this structure can also be approximated by using a 2x2 Hamiltonian or a single defect and a single valence band$^{50}$.

![Figure 2.4 Conduction sub-band dispersion relations as predicted by the BAC model. (Figure courtesy of K. Alberi)](image)

While it has been known that the endpoints ($x<0.1$) could be treated by the band anticrossing model, the assumption of dilute impurity states with non-interacting wave functions does not necessarily apply to midrange alloy compositions. Until 2009, a theoretical interpolation of HMA systems across the midrange compositions was used to show the potential for band gaps much less than either of the end point materials. Such materials have proven difficult to synthesize due to a large miscibility gap. Despite these challenges, researchers have recently synthesized GaN$_{1-x}$As$_x$ across the entire composition range using low temperature molecular beam epitaxy$^{56}$. The midrange alloy compositions were amorphous. The band gaps of all compositions as measured by optical absorption and photoreflectivity are compared to the
theoretical calculation show surprisingly good agreement with the BAC model despite the assumption of dilute impurities. This system demonstrates that midrange HMA compositions can be achieved, opening up a new range of band gaps in nearly any alloy system.

Figure 2.5 Valence sub-band dispersion relations of GaSb$_{0.04}$As$_{0.96}$ (Figure courtesy of K. Alberi)

Figure 2.6 Dependence of the optical band gap energy on the value of $x$ for crystalline and amorphous GaN$_{1-x}$As$_x$ alloys. Calculated composition dependences of the band gap of GaN$_{1-x}$As$_x$ alloys based on the BAC and virtual crystal approximation. (Figure courtesy of Kin Man Yu.)

Finally, it is important to mention that the band in an HMA material can be used in one of two ways, depending on the location of the Fermi level. For a Fermi level located within the defect-derived band, the band acts as an intermediate band (IB) within a larger band gap. The half-full IB can serve as a stepping stone for two lower energy photons to excite one electron to the conduction band; this process is known as “two-photon absorption”. This type of structure (GaAs$_{1-x}$N$_x$ with $x$~0.02) has been used to demonstrate the first IB solar cell$^{22}$. In such a device, the short circuit current is increased through the utilization of low energy photons, but the open circuit voltage is determined by the larger band gap. For the composition used by Lopez et al., the N-derived intermediate band (IB) is 1.1 eV above the valence band and the valence band is
1.9 eV from the matrix-like conduction band. An Al\textsubscript{1-x}Ga\textsubscript{x}As blocking layer isolated the IB from the charge collecting contacts in order to maintain a large open circuit voltage.

In the second case of BAC material, the doping in the material is such that the Fermi level is located within the gap, rather than within the band. This results in an effective narrowing of the band gap since the gap between the highest filled and lowest unoccupied states has decreased. In a VBAC material, an n-type material would set the Fermi level well above a localized defect band derived from anticrossing with the valence band. Thus the localized band would effectively become the valence band, allowing for absorption of lower energy photons or emission of lower energy light.
Chapter 3: Synthesis of the highly mismatched oxide alloy ZnO$_{1-x}$Se$_x$

3.1 Oxides for solar applications

The technological advance of commercial Si solar cells toward theoretical efficiencies$^{18}$ drives a constant search for the next generation of photovoltaic absorber materials. Several thin film absorber materials have already entered the market, including Cu(In,Ga)Se$_2$ and CdTe, but these require the use of toxic or potentially rare elements. Photoelectrochemical applications are sensitive to band edge alignment with hydrogen and oxygen evolution potentials and therefore require even finer tuning beyond narrowing or widening of the band gap.$^{25}$ Additionally, materials to be used in a photoelectrochemical cell must be stable in solution. Search for materials satisfying these stringent conditions requires the synthesis of a wide variety of unconventional alloys. The concern about the presence of toxic/rare elements in large scale distribution of solar power as well as stability has led to a recent surge of interest in oxides for solar energy applications.$^{57,58}$ Yet the fact remains that oxide band gaps are too wide to absorb visible light which hinders their usefulness in solar energy conversion.

Band gap engineering of these highly attractive oxide materials could make them accessible to photoelectrochemical and solar cell applications. As described in Chapter 2, substitution of a small fraction of the anion atoms with an isovalent element of distinctly different electronegativity and/or size leads to a dramatic rearrangement of the energy band structure of compound semiconductor alloys. ZnO$_{1-x}$Se$_x$ is the analogous II-VI compound to the III-V material GaN$_{1-x}$As$_x$, an extensively studied and well understood highly mismatched alloy (HMA). Thus, it was expected (and will be proven in later chapters) that the ZnO band gap can be analogously reduced by replacing a small percentage of oxygen with selenium anions. In ZnO, a small amount of Se (which has an electronegativity of 2.55 compared to the oxygen value of 3.44) forms localized states at 0.9 eV above the valence band, as will be shown in Chapter 4. An anticrossing interaction of these localized states with the valence band of the ZnO matrix results in the formation of two bands: (1) a narrow band with high effective mass and slightly delocalized character and (2) a valence-like band of delocalized states. The width and density of states of the impurity band is a function of the Se content. The high electron affinity of ZnO causes the films to be n-type and hence both bands are expected to be fully occupied. Thus, the effective band gap, or transition from highest occupied state to lowest unoccupied state, is between the narrow Se derived band and the conduction band, which for a film with Se content $x=0.1$ is roughly 2 eV.$^{59}$

3.2 Pulsed laser deposition of ZnO$_{1-x}$Se$_x$

Although in this work we focus on ZnO-based compounds, oxide-based ternary alloys have been synthesized in a variety of contexts with a range of results.$^{60-63}$ The effects of growth
conditions (or techniques) are far from established, especially since ideal growth conditions deviate from those optimized for binary oxides. Thin film structure and chemistry are dramatically affected by the growth conditions which in turn determine the optoelectronic and electrochemical behavior of films. Because these materials are tailored for specific purposes, it is important that they are synthesized exactly as designed because slight changes in composition can completely alter the band structure.

The difficulty of synthesizing ZnO$_{1-x}$Se$_x$ can be understood by considering the ionic radii and vapor pressures of the elements present. The atomic radius of Zn is 134 pm. The wurtzite crystal structure describes a two element compound isomorphous to a hexagonal close packed structure where half of the tetrahedral holes are occupied. The space for an interstitial atom, $r_{\text{interstitial}}$, is $0.225 r_{\text{large}}$. For Zn atoms, this predicts that an interstitial atom is only 30 pm. In fact the ionic radius of oxygen is 66 pm, which is twice as large as the interstitial slot. The Zn atoms can separate to accommodate this atom due to energy gained from the ionic bond. However, the ionic radius of Se is 120 pm, which is twice as large as oxygen’s radius and four times as large as the interstitial spacing! Thus, one can see that it is difficult to replace the oxygen atom with such a large atom. If all of the atoms are thermodynamically able to rearrange, it is unlikely that the Se will stay in the film at all. However, as will be shown in later sections, low temperature growth under non-equilibrium conditions can form the structure as designed.

ZnO-alloy samples were grown with pulsed laser deposition (PLD) on polished c-plane sapphire. PLD is an obvious choice for a HMA oxide material due to the potential for both stoichiometric transfer of target materials to the substrate and non-equilibrium growth conditions. The technique offers a wide range of controls for fine tuning the material. A schematic of a PLD growth system is shown in Figure 3.1a. After the optics are aligned and the target and substrate installed, the chamber is evacuated ($< 10^{-4}$ Torr) with a dry scroll (roughing) pump followed by a cryogenic pump. A high energy pulsed laser (248 nm KrF excimer laser) is focused through a window onto a pressed powder target of appropriate composition. The spot shape is typically set by a metal aperture to be either round or rectangular (the shape of the initial laser pulse). In our case, the laser spot the image of a rectangular aperture focused onto the target. The spot size can be measured by a single pulse onto fax paper* that is affixed to the target while the chamber is open to set up for growth (Figure 3.1b inset). A clearly imaged spot without ‘hot spots’, or laser energy variation, is critical to ensure repeatable film growth with controllable fluence, or energy per area. We accomplished this with a long (~10 meter) beam path length and high quality UV mirrors and lenses.

The large electric field of the laser impinging upon the target removes electrons from the bulk material. The motion of these electrons heats the near-surface material, vaporizing it to a plasma plume, which was photographed by the author and is shown in Figure 3.1b. This overall process is known as ablation. A suitable film substrate is affixed to a heater such that the plasma plume is normal to the substrate surface. The plasma then deposits the ablated particles onto the film surface. Table 3.1 lists the tunable parameters to optimize film growth, as well as the effects.

For the growth of ZnO$_{1-x}$Se$_x$, rotated cold-pressed powder targets with varying compositions of ZnO and ZnSe were used. For clarity we discuss in this chapter only samples grown from an 8% (atomic percent) ZnSe, 92% ZnO target. It is also important to note that the surface of the target affects the final composition of the films. Ablation during growth leaves the

* Unlike typing paper, fax paper is burned by the laser and thus captures an image of the laser spot. The flash of the UV laser can be viewed (with eye protecting) on typical white printing paper, but no image is recorded.
target surface Se-rich (to the eye, the surface appears metallic), such that the composition of the ablated surface of the target was found to be 18% Se compared to the 8% Se of the bulk target material. To maintain target composition, PLD targets were sanded to remove damage after each growth.

![Figure 3.1 a. Schematic of PLD chamber, courtesy of Erin Ford. b. Image of a PLD plume recorded by the author through the window of a chamber located in the Ramesh laboratory at UC Berkeley. White inset shows a life-sized, focused laser spot recorded with fax paper at the PLD target (5/24/2011).](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect on film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature</td>
<td>Film nucleation and atom motion on the surface. The higher the temperature, the higher the nucleation density and atom motion. The temperature can also affect the phase in cases where multiple phases are possible or the composition in certain alloys.</td>
</tr>
<tr>
<td>Chamber background pressure/composition</td>
<td>For oxide growth, a low oxygen background pressure is often used to maintain stoichiometry. The pressure reduces the energy of particles within the plume, so lower pressure also can lead to more damage. Finally, lower O₂ background increases the number of oxygen vacancies in a film.</td>
</tr>
<tr>
<td>Laser fluence</td>
<td>If the laser fluence is too low, material will not transfer stoichiometrically or at all. If it is too high, target material will transfer in clumps.</td>
</tr>
<tr>
<td>Laser pulse rate</td>
<td>Generally a lower pulse rate allows more time for atom motion on the surface and less defective films are obtained.</td>
</tr>
<tr>
<td>Distance between target and substrate</td>
<td>Ideally, the substrate should be positioned at the focus of the ablated plume to ensure proper stoichiometric transfer. The plume is adjusted by the laser energy, so the position of the target can be adjusted (if possible) to meet these conditions.</td>
</tr>
<tr>
<td>Target composition</td>
<td>Film composition.</td>
</tr>
<tr>
<td>Substrate material</td>
<td>The crystallography of the substrate will affect to what degree the film is epitaxial. In the case of low (&lt;2%) mismatch between the bulk parameters of the material to be grown and the substrate, an epitaxial film can be obtained and the strain can be controlled. Large mismatch can lead to high defect concentrations in epitaxial films.</td>
</tr>
</tbody>
</table>

_Table 3.1. PLD growth parameters & effects_
The samples studied in this thesis were grown in two different PLD chambers, one located in the Ramesh laboratory at UC Berkeley and one located in the Mao lab at Lawrence Berkeley National Laboratory. The Ramesh chamber was evacuated with a cryogenic pump and reached a background pressure of $6.2 \times 10^{-6}$ Torr, while the Mao chamber was evacuated with a turbo pump and reached a background pressure of $\sim 1 \times 10^{-5}$ Torr. The samples discussed in this chapter were grown in the Ramesh chamber, which could not access pressures between $6.5 \times 10^{-6}$ Torr and $1 \times 10^{-4}$ Torr. In all cases, the PLD chamber was pumped down to the background pressure and backfilled with oxygen when specified; otherwise the growth occurred under base pressure conditions. After growth, samples were cooled at a constant rate in the growth atmosphere. The pulse frequency for all depositions was 5 Hz; pulse frequency appeared to have limited effect on the final samples. Substrates were mounted with silver paint or paste to a substrate heater where temperature was controlled and read by two thermocouples. The target to substrate distance was 5 cm. Fluence was calculated based on a rectangular laser spot size of 0.03 cm$^2$, and KrF laser energy was measured at the target prior to growth with a power meter. Growth parameters of the samples are described in Table 3.2. ZnO reference samples were grown in the same chamber under similar conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Growth Temperature</th>
<th>Laser Fluence (J/cm$^2$)</th>
<th>O$_2$ pressure (mTorr)</th>
<th>RBS Se Composition (%Se/O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZOS18</td>
<td>400</td>
<td>4.4</td>
<td>base</td>
<td>6</td>
</tr>
<tr>
<td>ZOS19</td>
<td>450</td>
<td>4.4</td>
<td>base</td>
<td>4.5</td>
</tr>
<tr>
<td>ZOS20</td>
<td>500</td>
<td>4.4</td>
<td>base</td>
<td>2</td>
</tr>
<tr>
<td>ZOS21</td>
<td>300</td>
<td>4.4</td>
<td>base</td>
<td>6</td>
</tr>
<tr>
<td>ZOS22</td>
<td>350</td>
<td>4.4</td>
<td>base</td>
<td>7.4</td>
</tr>
<tr>
<td>ZOS23</td>
<td>550</td>
<td>4.4</td>
<td>base</td>
<td>1.4</td>
</tr>
<tr>
<td>ZOS24</td>
<td>400</td>
<td>3.4</td>
<td>base</td>
<td>5</td>
</tr>
<tr>
<td>ZOS25</td>
<td>400</td>
<td>2.4</td>
<td>base</td>
<td>7.6</td>
</tr>
<tr>
<td>ZOS26</td>
<td>400</td>
<td>1.4</td>
<td>base</td>
<td>7</td>
</tr>
<tr>
<td>ZOS27</td>
<td>400</td>
<td>4.4</td>
<td>16</td>
<td>0.25</td>
</tr>
<tr>
<td>ZOS28</td>
<td>400</td>
<td>4.4</td>
<td>0.1</td>
<td>1.6</td>
</tr>
<tr>
<td>ZOS32</td>
<td>400</td>
<td>4</td>
<td>base</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table 3.2. ZnO$_{1-x}$Se$_x$ samples discussed in Chapter 3.

### 3.3 Characterization techniques used in this chapter

X-ray diffraction (XRD) measurements were taken in a thin film setup using copper K-alpha radiation in order to determine the orientation of the PLD oxide films. With the help of Dr. Kin Man Yu, the film thicknesses and compositions were determined by Rutherford backscattering spectrometry (RBS) with a 3.04 MeV He$^+$ beam at a backscattering angle of 168$^\circ$ and using the Rutherford Universal Manipulation Program$^{67}$ or SIMNRA$^{68}$ to model the data. Additional compositional information was determined using energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM). EDS measurements provide chemical information about samples by relying on the detection of the energies of electrons excited by the incident electron beam. Atomic force microscope (AFM) measurements were taken on a Digital Instruments (Bruker) Nanoscope in tapping mode.

Electrical measurements were carried out using “pressed-on” In contacts in the van der Pauw configuration and a 0.6 T magnetic field for Hall effect measurements. Thermopower
measurements were taken to probe the carrier concentrations of films where the Hall effect was unreliable. The thermopower apparatus has been described in detail elsewhere. Photoluminescence (PL) measurements were performed at room temperature using a 325 nm HeCd 50mW laser as an excitation source and a Hamamatsu R928 photomultiplier tube as a signal detector. Spectra were normalized to the instrument function as measured with a calibration lamp. Optical transmission was measured using a Perkin–Elmer Lambda 950 spectrophotometer. Raman spectroscopy measurements were performed using the 488 nm line of an Ar⁺ laser with a camera lens for collection of the scattered light. The collected light was passed through a triple spectrometer to be detected by a CCD camera. The setup is located in the Ager laboratory at Lawrence Berkeley National Laboratory.

### 3.4 Effects of growth on the structural and chemical properties

Growth conditions determined the structure and chemistry of the final films. Here we examine the impact of temperature, laser fluence and pressure on the growth of ZnO_{1-x}Se_x materials so as to define the parameter space under which phase pure material can be grown. Within this space, the grower can tune certain properties to optimize optical or electrical properties as needed.

The temperature controlled the chemistry and structure of the alloy thin films (ZOS18-23) in three aspects: alloy composition (x), crystalline texturing and phase homogeneity. This set of films was grown at base pressure using a fluence of 4.4 J/cm² and are pictured in Figure 3.2. The substrate temperature ranged from 300-550°C. There is a clear increase in visible light absorption for those samples grown at lower temperatures.

![Figure 3.2. (From left to right) PLD samples of ZnO_{1-x}Se_x grown at 300, 350, 400, 450, 500, and 550°C on sapphire substrates at a fluence of 4.4 J/cm².](image)

X-ray diffraction (XRD) measurements probed the crystallinity of the ZnO_{1-x}Se_x films. Figure 3.3a shows that only the 0002 diffraction peak is present in the XRD patterns from all ZnO_{1-x}Se_x thin films, while Figure 3.3b shows the film composition as a function of growth temperature. Despite the 16.8% lattice mismatch between Al₂O₃ and ZnO, the ZnO_{1-x}Se_x films grew in the 0001 (c-plane) preferred direction established by the 0006 sapphire substrate. This was confirmed by transmission electron microscopy, which is discussed in Section 6.2. The height of the film peak compared to the substrate peak indicates that decreasing the temperature decreased the film crystallinity and texturing.

However, despite aligning the grain orientation, higher temperature growth also led to phase separation. There is evidence for the presence of two phases in the XRD data: peaks for films grown above 450°C could only be fit using two Gaussian distributions. At higher temperatures, with additional energy present for atom migration, the films segregated into a ZnO_{1-x}Se_x phase and a small amount of a pure ZnO phase. We confirmed the identity of these phases using room temperature ZnO band edge PL at 3.3eV, which is present only in the samples which show two peaks in XRD (Figure 3.4).

Simultaneously, as is immediately apparent from Figure 3.3b, increasing the substrate temperature during growth decreased the amount of Se incorporated into the ZnO matrix. At
low temperatures (400°C or below), the ZnO$_{1-x}$Se$_x$ transferred with good stoichiometry from the target to the substrate. However, since the Se vapor pressure is significantly higher than that of Zn, at higher growth temperatures it is expected that Se would be more easily desorbed during deposition. For example, at 550°C, the Se vapor pressure increases to 0.1 Torr, two orders of magnitude higher than the Zn vapor pressure. It was independently determined that increasing the amount of Se increased the amount of texturing (or in-plane rotation of the grains) in the films using synchrotron x-ray absorption measurements (Section 4.3). The influence of Se on crystallinity was independently confirmed with transmission electron microscopy (TEM) and synchrotron x-ray absorption measurements.

Figure 3.3. a. XRD for ZnO$_{1-x}$Se$_x$ samples grown at a series of temperatures, log scale, arbitrary units. Red lines indicate total Gaussian fit, green lines indicate separate peaks which add to form the final fit where necessary. The sapphire 0006 peak is at 41.8°. B. Composition as a function of growth temperature for several ZnO$_{1-x}$Se$_x$ samples. True composition was measured with RBS and EDS, while XRD includes effects of crystallinity.

It is interesting to note that while RBS and EDS measurements of the composition were in excellent agreement regarding the composition of the films, compositions extracted using Vegard’s law$^{21}$ ($x_{ZnO}=0.521$ nm) and the XRD peak positions tended to be consistently 4% higher. This discrepancy could be due to a systematic deviation from Vegard’s law or the presence of compressive strain due to oxygen vacancies in the a-plane of the ZnO$_{1-x}$Se$_x$ films. A highly defective but Se-free ZnO film grown in the same chamber under the same conditions demonstrated that tensile strain in these films can account for a +3% error in the determination of the Se composition in these oxide alloys. Therefore, effects of strain should be taken into account when determining absolute composition from XRD even in polycrystalline films.

I next address the effect of growing ZnO$_{1-x}$Se$_x$ films under different atmospheres. Films for this test were grown at 400°C with a laser fluence of 4.4 J/cm$^2$. The most obvious influence of adding O$_2$ to the growth environment was the reduction of Se incorporation. The presence of oxygen could have impeded stoichiometric transfer of the target to the film. Growths with oxygen pressures greater than 20 mTorr yielded ZnO films with no detectable Se content. This suggests that incorporation of Se is efficiently suppressed by O$_2$ overpressure. This effect could be utilized to vary the film composition in the growth of ternary oxide alloys.
Figure 3.4. Photoluminescence spectra for a series of ZnO$_{1-x}$Se$_x$ samples grown at several temperatures, as well as a reference sample of pure ZnO. Samples grown below 450°C show only system background.

However, even within the limited range of attainable growth pressures in which Se could be incorporated, high growth pressures (>5mTorr) led to amorphous films (by XRD) and rougher surfaces. Figure 3.5 shows 1 micron square AFM images of films grown at O$_2$ overpressure of 2x10$^{-6}$ Torr, 0.1 mTorr and 16 mTorr (ZOS18, ZOS28, and ZOS27). The smoothest surface occurred in the film grown at an intermediate pressure, 0.1 mTorr (with only 1.6% Se), which is in good agreement with studies on pure ZnO$^{72}$. Choopun et al. attributed the optimal smoothness to a transition between three growth modes. Although we did not observe faceting in the ternary alloy, high interfacial energy and atom desorption causes steps to form during at low pressure (<10$^{-4}$ Torr) growth which introduced roughness in the final film. Intermediate pressures resulted in small nucleation islands and smooth films. Films grown at high pressures form by large island nucleation and result in rougher films with increased texturing.$^{72,73}$ It is possible that the slow nucleation at lower pressures actually decreases the potential for phase separation, as the higher pressure films (ZOS28 and 27) contained a pure ZnO phase, as evidenced by ZnO band edge PL.

Figure 3.5. 1 micron square AFM topography data for 3 ZnO$_{1-x}$Se$_x$ samples grown at varying O$_2$ pressures (from left to right) 6x10$^{-6}$ torr, 1x10$^{-4}$ torr and 1.6x10$^{-3}$ torr. The z scale is 8 nm.
The study on the variation of laser fluence revealed that the fluence used for target ablation affected the final structure of the films. A series of samples was grown at base pressure and 400°C while the laser fluence varied from 1-4.4 J/cm². The full width half max (FWHM) of the XRD peaks from the films grown at low fluences (1-2 J/cm²) is roughly half that of films grown at higher fluences, decreasing from 0.97 to 0.36 degrees. Studies of the growth of undoped ZnO report a similar effect and attribute it to an increase in the grain size. Additionally, in the ternary alloy films, the narrowing of the FWHM suggests that lower fluences produce films with more uniform Se distribution across the film.

Growths using lower laser fluence also resulted in smoother surfaces. Representative one micron surface profiles taken by AFM are shown in Figure 3.6 (ZOS18, ZOS24-26). The z range of the sample grown at 1.1 J/cm² is 2 nm, roughly half of the samples grown at 4.4 J/cm² fluence. Significant variations in surface topography are present in the samples grown at larger fluences but are far less frequent in the lower fluence samples. The implication is that the larger fluences transfer the alloy material in clumps from the target, causing boulders and likely significant composition fluctuations and defects in the films.

![AFM Surface Profiles](image)

**Figure 3.6.** Topographic line scans from AFM topography data for 4 ZnO₁ₓSeₓ samples grown with different laser fluences, indicating smoother surfaces at lower fluences.

### 3.5 Effects of growth on the electrical properties

Electrical transport in ZnO₁ₓSeₓ (or oxide alloys in general) is of great concern for any potential applications such as photovoltaic or photoelectrochemical devices. Our goal here is to present how the physical structure of low temperature grown oxides affects the transport.

Resistivity, Hall effect measurements and thermopower of the samples were recorded. For films grown using a fluence of 4.4 J/cm² without the addition of O₂ and at temperatures at/or below 400°C, the resistivity of the samples was constant (Figure 3.7a). Films grown with the same laser energy and pressure but at temperatures above 450°C had dramatically increased resistivities, doubling in value compared to those grown at low temperatures. The presence of phase inhomogeneities in the films grown at high temperature is most likely responsible for the increase of the resistivity. Hall effect measurements were reliable and quite consistent in films grown at or below 450°C. The n-type carrier concentrations were 6-7x10¹⁹ cm⁻³ with mobilities
ranging from 13-20 cm²/Vs. Since thermopower depends on the carrier concentration it is often used to characterize films in which it is difficult to measure Hall effect\textsuperscript{75}. The thermopower ranged from -60 to -80 μV/K in the low temperature-grown samples indicating small variation in the electron concentration. Apparently, in ZnO\textsubscript{1-x}Se\textsubscript{x} alloys grown at low pressures, the growth temperature had little effect on the carrier concentration and mobility, provided that it was low enough to obtain single phase material.

Figure 3.7 (b) shows the dependence of the resistivity on the growth fluence for samples grown at 400°C. For films grown at O\textsubscript{2} pressures above background, electrical measurements were unreliable due to phase separation in the films, so we do not consider these in further analysis. As seen in Figure 3.7 (b), increasing the laser fluence led to a dramatic reduction of the resistivity. When a lower laser fluence was used during growth, Hall effect could not be measured in these polycrystalline alloy films for reasons which will be discussed below.

Figure 3.7. a. Resistivity as a function of substrate temperature for a constant fluence of 4.4 J/cm\textsuperscript{2}. b. Resistivity as a function of laser fluence for the substrate temperature of 400 C during growth.

On the other hand, as shown in Figure 3.8, the value of thermopower, which is inversely related to carrier concentration (Section 6.3), decreased with increasing laser fluence during the growth indicating that the change in the resistivity of the samples grown at different fluences (Figure 3.7b) can be attributed to changes in electron concentration. Therefore, the lower carrier concentration in ZnO\textsubscript{1-x}Se\textsubscript{x} films grown with low laser fluences, makes these films more desirable for applications requiring a large depletion width for the separation of optically-generated carriers. This will be discussed in more detail in Chapter 6.

Because these films were not single crystals, it is important to consider the role of grain boundaries in electrical transport. The Hall effect in polycrystalline materials has been thoroughly described by Orton and Powell\textsuperscript{76}. While a detailed description is beyond the scope of this dissertation, we observed a thermally activated mobility in polycrystals that is related to carrier transport over a Schottky-like barrier which occurs as the carriers move between grain boundaries. This is especially surprising because the mobility in bulk Si is significantly higher than that of bulk ZnO; for an electron concentration of 10\textsuperscript{17} cm\textsuperscript{-3} (10\textsuperscript{19} cm\textsuperscript{-3}), the mobility in bulk Si is 900 cm\textsuperscript{2}/Vs (100 cm\textsuperscript{2}/Vs) and 200 cm\textsuperscript{2}/Vs (60 cm\textsuperscript{2}/Vs) in bulk ZnO\textsuperscript{77}. In general, the
heights of the barriers at grain boundaries that limit the mobility are determined by the pinning of the energy bands at the boundaries.

The relatively high mobilities of our polycrystalline films can be understood in the framework of the amphoteric defect model. It has been established that the energy of the surface Fermi level (E\text{FS}), or the average energy of native defects, is located at 4.9 eV below the vacuum level\textsuperscript{1}. Because the bands of semiconductors vary with respect to vacuum and therefore E\text{FS}, band bending on the surfaces of different semiconductors also varies dramatically. In Si, E\text{FS} is midgap, pinning the surface of the material to be nearly intrinsic\textsuperscript{78}. Conversely, in ZnO as well as in O-rich ZnO\textsubscript{1-x}Se\textsubscript{x}, E\text{FS} is close to the bottom of the conduction band, resulting in a preference for formation of donor-like defects and small energy barriers at surfaces, interfaces and grain boundaries. Therefore a combination of the small barriers and a large electron concentration facilitate charge transfer between grains resulting in relatively high electron mobilities.

Figure 3.8. Thermopower for samples grown with different laser fluences during growth.

### 3.6 Effects of growth on optical properties

The growth conditions and structure also affected the optical properties of ZnO\textsubscript{1-x}Se\textsubscript{x} alloy films. Chapter 4 describes in detail how the addition of Se to ZnO alters the band structure\textsuperscript{59}, but here it is interesting to note how the growth parameters affect the optical properties. In several cases, the structural effects discussed above can be observed (i.e., phase separation).

As the temperature influences the amount of Se incorporation, it also significantly affects the location of the absorption edge. This is shown in Figure 3.9. For samples grown at or below 400°C, the absorption resulting from the transitions from the Se-derived band to the conduction band edge was constant at ~2.2eV because of the almost constant Se concentration. The low energy absorption became less pronounced due to both decreasing Se content and the presence of a pure ZnO phase in samples grown at higher temperatures. This is consistent with the previously reported results and analysis of the optical absorption (Sections 4.4-5)\textsuperscript{59}. The absorption coefficient of ZnO grown under similar conditions is shown for comparison. We saw little effect on the optical absorption or transmission in samples grown with different fluences.
This is in good agreement with the almost constant Se content in these samples. We do not observe an energy independent, defect induced reduction in transmission in any samples, as was previously reported in ZnO grown with high laser fluences\textsuperscript{74}.

![Graph](image)

Figure 3.9. The absorption edge of ZnO\textsubscript{1-x}Se\textsubscript{x} blue shifts as a function of temperature due to reduced Se incorporation. Legend refers to growth temperature in °C.

### 3.7 Vibrational modes in ZnO\textsubscript{1-x}Se\textsubscript{x}

Raman spectra were recorded on the phase pure films as another method of observing the film structure. The ability of vibrational spectroscopy to identify trace compounds has made it popular in criminal forensics\textsuperscript{79}, as well as the chemical and phase identifications undertaken by the author. While Raman spectroscopy could be (and has been) the subject of a number of doctoral dissertations\textsuperscript{80}, in this thesis it was used predominantly to look for pure Se inclusions. Incident laser light can be scattered from a material either elastically (Rayleigh scattering) or inelastically, which is known as Raman scattering. The most common inelastic interaction with a crystal is by the creation or annihilation of phonons. (In Raman scattering, the incident radiation either induces quantized vibrations (phonons) or absorbs phonons.) The former slightly reduces the energy of the detected light, which is known as a Stokes shift, while the latter increases the energy, causing an anti-Stokes shift. Each material/crystal structure has its own signature phonon vibrations, making non-destructive Raman spectroscopy especially powerful for identifying all phases and compounds present in a sample—even those at low concentrations\textsuperscript{30,80}. As in classical oscillators, optical phonons can be classified into transverse and longitudinal. In ionic crystals, the longitudinal and transverse modes of vibration show different frequencies because they actually have different restoring forces which break degeneracy\textsuperscript{80}.

Representative Raman spectra on ZnO\textsubscript{1-x}Se\textsubscript{x} samples grown at different temperatures are shown in Figure 3.10. The sapphire substrates have a strong Raman signal and are responsible for the tall sharp peaks denoted with black arrows. The most important observation of the Raman spectroscopy study was that no pure Se phases were observed through any method, including TEM and Raman spectroscopy. As demonstrated in phase segregated TiO\textsubscript{2-x}Se\textsubscript{x}, Se
clusters or nanoclusters would result in a Raman peak at the vibrational frequency for Se, is 272 cm\(^{-1}\). The lack of peak confirms that light scattering off of Se inclusions was not the cause of low energy optical responses.

The ZnO\(_{1-x}\)Se\(_x\) film peaks are labeled with red, blue and dashed gray arrows. It is immediately apparent that they are broad, due to compositional variation as well as disorder in the films. The breakdown of the translational symmetry is also apparent through the presence of the disorder-activated peak at 280 cm\(^{-1}\), which is a silent mode in perfectly crystalline ZnO. The longitudinal (LO) and transverse optical (TO) modes of ZnO are typically found to be at 574 and 378 cm\(^{-1}\), respectively. These spectra are taken in the backscattering configuration impinging on the c plane. In such configuration, the Raman allowed modes are the LO mode vibrating along the c axis and the non-polar \(E_{2h}\). In fact, in non-resonant conditions, the \(E_{2h}\) mode is the most prominent in ZnO; however, its frequency lies in the sapphire signal region (432 cm\(^{-1}\)), and thus could not be discerned. It is also noteworthy that in non-resonant conditions, the LO mode should be much less intense than the \(E_{2h}\). In this case, we observe a resonant LO feature, which is consistent with the band gap reduction obtained by the presence of Se.

Figure 3.10. Measured Raman spectra for ZnO\(_{1-x}\)Se\(_x\) samples grown at different temperatures

The LO mode appears as the broad peak near 565 cm\(^{-1}\) (red arrow), which is shifted to lower frequencies due to the presence of Se in the lattice. The band near 220 cm\(^{-1}\) is believed to be the localized vibrational mode (LVM) of ZnSe.

This behavior was explored in more detail by fitting each of these peaks (or groups of peaks) with Lorentzian functions, as demonstrated in Figure 3.11. The peak maxima (data points) are reported as a function of Se content for the ZnO LO peak (Figure 3.12a) and the ZnSe-derived peak (Figure 3.12b). Just as the band gap of a semiconductor \(AB_{1-x}C_x\) changes with x, the frequencies of the phonon modes also shift since the reduced mass of the vibrating atom changes. In two mode behavior (occurring in most semiconductor alloys), two sets of
phonon modes appear that are close to the vibrational frequencies of the two endpoint compounds.

From a classical point of view, an oscillator frequency can be deduced from Hooke’s Law. In the case of the TO mode, a squared dependence can be assumed because of Hooke’s law:

\[ \omega = \sqrt{\frac{k}{\mu}} \]  

(3.1)

where \( \omega \) is the vibrational frequency, \( k \) is the spring constant (unique to the material) and \( \mu \) is the effective mass of the vibrating atoms (AB), derived from the masses of the individual elements:

\[ \mu_{AB} = \frac{1}{\frac{1}{m_A} + \frac{1}{m_B}} \]  

(3.2)

As a vague approximation, one can think of an impurity mode as if one oscillator (ZnSe) has been transferred to another medium (ZnO). In other words, while the vibrating atoms are Zn and Se, the spring constant would come basically from the ZnO lattice. Thus, the impurity mode of a ZnSe pair in ZnO could be calculated from:

\[ \omega_{imp} \approx \sqrt{\frac{k_{host \_ lattice}}{\mu_{impurity}}} = \omega_{host} \sqrt{\frac{\mu_{host}}{\mu_{impurity}}} \]  

(3.3)

One might think of this case as if a spring is being transferred to another medium. The transition of the LO mode, on the other hand, can be calculated from the Lyddane-Sachs-Teller relationship:

\[ \frac{\varepsilon_0}{\varepsilon_\infty} = \frac{\omega_{LO}^2}{\omega_{\Gamma O}^2} \]  

(3.4)

where \( \varepsilon_0 \) and \( \varepsilon_\infty \) are the low frequency and high frequency dielectric constants and the \( \omega \) terms are the vibrational frequencies of the end points.

Figure 3.11 Lorentzian fitting of Raman peaks. Each individual Raman peak is shown in blue, while the total fit for each cluster is shown in red.
This is the basis for the calculation shown in Figure 3.12a for the ZnO-like phonon mode, assuming a LO mode of 573 cm\(^{-1}\) for ZnO, a ZnO localized vibrational mode of 333 cm\(^{-1}\) and 251 cm\(^{-1}\) for ZnSe. There is good agreement with the measured data in this case. The same calculations for both the TO and LO modes are shown in Figure 3.12b for the ZnSe-rich phonon mode assuming LO and TO frequencies in ZnSe to be 251 and 200 cm\(^{-1}\), respectively\(^8\). In this case, the calculation deviates significantly from the measured peak locations. This could be related to the difficulty of fitting broad peaks or the presence of any additional convoluted phase peaks. Additionally, the endpoint vibrational frequencies are not well established for wurtzite ZnSe since this is a difficult material phase to obtain. Despite these complications, a clear alloying trend is still observed.

![Figure 3.12. a. Measured Raman peaks (data points) compared to a calculation of the two mode Raman ZnO-like LO peak as a function of composition. b. Measured Raman peaks (data points) compared to a calculation of the two mode Raman ZnSe-like LO (blue) and TO (purple) peaks as a function of x, obtained by RBS.](image)

### 3.8 Summary

The growth of ternary oxides is a developing and exciting field due to the many applications that could benefit. Here we have shown connections between growth conditions and material structure and chemistry. The properties of an oxide ternary alloy film are quite different than their binary oxide counterparts when grown under the same conditions. Highly mismatched oxide alloys must be grown at lower temperatures than typically reported for the binary oxide in order to incorporate the third element and prevent phase separation, which leads to lower crystallinity than that obtained in binary compounds. Low pressures are ideal for incorporation of elements with high vapor pressures; low laser fluences in PLD lead to smoother films. With these constraints, the crystal structure is textured rather than epitaxial on most readily available substrates.

Because of high electron affinities, grain boundaries do not reduce the mobility as severely in naturally occurring n-type oxides as in traditional group IV or III-V semiconductors.
As a result, ternary oxides do not need to be grown as single crystals in order to be useful for optoelectronic applications. This allows for low temperature growth with minimal processing or novel substrate choices, even for carefully tailored materials with unique optoelectronic properties.
Chapter 4: Electronic structure of ZnO$_{1-x}$Se$_x$

4.1 Relevance and goals of understanding the electronic structure

Heterojunction solar devices depend heavily on not only the separation between the conduction and the valence band, but upon the absolute location of these bands with respect to the vacuum level (which is directly references with respect to the standard hydrogen electrode, which will be discussed in Chapter 5). The semiconductor electron affinity determines the amount of band bending at the surface of a material, the behavior of native defects in the material, as well as the Schottky or Ohmic nature of a contact to an external circuit. Additionally, photoelectrochemical applications require that the band edges be known with respect to the oxygen and hydrogen redox potentials. The information reported in this chapter is all determined using ex situ measurements outside of the electrochemical cell and will be compared to measurements taken using in situ electrochemical techniques in Chapter 5. In general, there is good agreement between the methods. This work provides guidance to the experimentalist when selecting and interpreting measurements.

The electron affinity of ZnO has been reported to range from values of 4.2 eV to 6 eV using several techniques, including the Kelvin method and ultraviolet photoelectron spectroscopy. Furthermore, many of these techniques are surface sensitive and the orientation of the exposed crystal plane can changed the measured value of surface sensitive techniques by at least 1 eV. While this is useful fundamentally, a specific value is important for any optoelectronic applications. Therefore, I measured the band alignment of undoped ZnO as a starting point for electronic band observations.

Once the absolute band edges are known, one can consider how to adjust the bands (band gap) of ZnO through the introduction of isovalent states. As discussed in Section 2.4, the replacement of a small percentage of oxygen anions with Se in ZnO is expected to cause a valence band anticrossing interaction. The energy band structure of such highly mismatched alloys (HMAs) forms according to an anticrossing interaction between localized states of the substitutional minority anions and extended states of the host conduction or valence band. The strength of the interaction depends on the location of the localized states with respect to the band edges and the strength of the coupling between localized and extended states. In this chapter we identify the location of the localized Se states and the strength of the coupling between the two states. X-ray absorption and emission spectroscopy verify that the valence band is in fact affected by the introduction of Se, while optical absorption is using to quantitatively identify these parameters. By knowing these parameters, the composition of ZnO$_{1-x}$Se$_x$ can be tuned to the specific needs of a given application.
4.2 The electron affinity of ZnO found using the Fermi stabilization energy

The locations of the semiconductor band edges are key parameters determining suitability of a semiconductor material for solar water splitting. Here I present a measurement of the absolute band edge positions of ZnO relying on the pinning of the Fermi level by native defects.

4.2.1 The amphoteric defect model

According to the amphoteric defect model\textsuperscript{1,93}, the position of the Fermi energy is linked to the changing character (donor or acceptor) of the native defects, such as vacancies or antisites, depending on the location of the Fermi energy. In other words, an ‘amphoteric’ defect can behave as either a donor or acceptor depending upon the location of the Fermi level. In the case of ZnO, one might write reactions for native defects as:

\begin{align}
V_{Zn}^{-2} + O_O & \leftrightarrow O_{Zn}^{+4} + V_{O}^{+2} \\
ZnO^{-4} + V_{Zn}^{-2} & \leftrightarrow V_{O}^{+2} + Zn_{Zn}
\end{align}

(4.1)

(4.2)

Here the letter V refers to a vacancy and the subscript to the site in the original lattice. The charges come from the II-VI natures of the atoms on the periodic table. A positively-charged defect acts as a donor while a negatively-charged defect acts as acceptor. Considering an oxygen vacancy, for example, the oxygen present in the lattice typically binds electrons from neighboring Zn atoms strongly. Since an oxygen vacancy is the absence of an electronegative atom, the same electrons are now free to move within the lattice.

The Fermi level for which these two reactions are in equilibrium is known as the Fermi stabilization energy, \( E_{FS} \). Not unlike Le Chatelier’s principle for chemical reactions\textsuperscript{94}, the amphoteric defects tend to compensate the original doping of the semiconductor\textsuperscript{1}. As an example, if the Fermi level is slightly above (n-type) \( E_{FS} \), any created defects will rearrange to form donors and the equations will shift to the left. Alternatively, removing a Zn atom from the lattice would form a Zn vacancy, but in a p-type sample the lattice would rearrange to form an oxygen vacancy and oxygen antisite. When the Fermi level is equal to \( E_{FS} \) these two reactions (Equations 4.1 and 4.2) are at equilibrium. This is also observable graphically. The energetics and resulting Fermi level are illustrated in Figure 4.1 for GaAs, for which equations similar to 4.1 and 4.2 have been written\textsuperscript{93}.

The nature of a defect’s wave function determines the strength of the interaction with either the nearby band or the entire wave function. A shallow defect, such as phosphorus or boron in silicon, is highly delocalized in real space but localized in \( k \) space and derives its character almost entirely from the conduction or valence band\textsuperscript{47}. Conversely, native defects are delocalized in \( k \) space and their character is derived from a convolution with the entirety of the semiconductor band structure. Because the overall band structures of most semiconductors are similar, \( E_{FS} \) is roughly universal and located at 4.9 eV below the vacuum level.\textsuperscript{23} The Fermi stabilization level is also known as the charge neutrality level\textsuperscript{95}. Theoretical researchers have attributed this type of behavior to the presence of hydrogen in films, although this is difficult to prove experimentally due to the difficult-to-detect prevalence of hydrogen in all materials\textsuperscript{96}. There have also been other attempts to blame this universal pinning on metal-induced gap states\textsuperscript{97}, although this explanation is unsatisfactory for bulk point defects or non-metallized

\textsuperscript{†}To directly apply Le Chatelier’s principle, one might add 8 electrons to the right sides of Equations 4.1 and 4.2 and think of n-type material as material with excess electrons. This is satisfactory as long as one realizes that the addition of electrons to a system has balanced charge, since one physically cannot add electrons without the attached ion. Necessarily, the addition of electrons will not cause the formation of native defects. Conversely, one can remove a Zn ion without the affiliated electron.
surfaces. Despite alternative semantics, it is well established that the introduction of native defects, either through dangling bonds or point defects, does in fact pin the Fermi energy at 4.9 eV below the vacuum level.

Figure 4.1. Defect formation energies of simple vacancies \( V_{Ga}, V_{As} \) and related defects in GaAs. The numbers at the curves represent the net charge transferred from the Fermi sea to the defects. The diagram maximum corresponds to the Fermi stabilization energy, \( E_{FS} \) in GaAs. From 1.

### 4.2.2 Measuring electron affinity using stabilization of the Fermi level

Previously, particle irradiation has been used to introduce point defects into semiconductors as a method to determine the location of the band edges by pinning the bulk Fermi level at \( E_{FS} \). Assuming parabolic bands, the band edges relative to the Fermi level can be calculated from the measured carrier concentration and using the equation:

\[
n_F = N_c \int_0^\infty \frac{x^{1/2} e^{-x}}{1 + \exp \left[ \frac{x - E_F}{k_B T} \right]} \, dx.
\]

where \( N_c \) is the effective density of states in the conduction band, \( x \) is unitless energy and \( k_B \) is the Boltzmann constant. Knowledge of the CBE and VBE with respect to \( E_{FS} \) combined with the known value of \( E_{FS} \) at 4.9 eV allows for the determination of the actual band edge positions with respect to the vacuum level.

In order to measure \( E_{FS} \) with respect to the ZnO band edges, we irradiated PLD-grown (Section 2.3) ZnO films using Ne\(^+\) ions with energies of 150 and 50 keV to ensure constant damage through 200-nm-thick films. As can be observed in Figure 4.2, the saturation electron concentration in ZnO was \( 5 \times 10^{18} \) cm\(^{-3} \), which is equivalent to \( E_{FS} \) at only 0.04 eV above the conduction band edge. Therefore, we concluded that the conduction band edge of ZnO is 4.95 eV below the vacuum level. Later in this work we show that this value is also in excellent agreement with values measured electrochemically. This method cannot be used on ZnO\(_{1-x}\)Se\(_x\) films due to the low electron mobility of the films, especially after irradiation, making the electron concentration obtained by Hall effect unreliable.
4.3 Band Edge measurements using synchrotron x-ray spectroscopies

When an x-ray impinges upon a material, it gives energy to one of the material’s electrons in one of three basic ways\textsuperscript{100}, as depicted in Figure 4.3. In x-ray photoelectron spectroscopy (XPS), a well-known chemical analysis technique, there is enough energy to actually eject the electron from the material according to the photoelectric effect\textsuperscript{101}. The measured kinetic energy of the ionized ‘photoelectron’ equals the initial x-ray energy minus the binding energy of the electron and the work function of the material. The binding energy reflects the initial chemical environment of the element from which the electron was released.
X-ray absorption spectroscopy (XAS) and soft x-ray emission spectroscopy (SXE), on the other hand, rely on lower x-ray energies such that the electron is excited from a bound state but not ejected from the material. XAS is similar to optical absorption, where an incident x-ray excites a core hole into the conduction band but, since x-rays are more energetic, can probe the entire conduction band density of states. The detector measures x-rays that did not pass through the material in transmission mode or the resulting fluorescence (secondary x-rays) from the absorption event. XAS spectra contain additional information because XAS relies on core electrons rather than valence electrons (such as in optical absorption). Therefore, unique chemical information about bonding or molecular orientation in each element can be extracted from XAS data because the excited core electron was originally associated with a single atom rather than the many atoms that share valence electrons. This feature is exploited in x-ray fine absorption spectroscopy (XAFS), which is beyond the scope of this dissertation.

SXE, conversely, measures the partially occupied states (or valence states) of the material. An incident x-ray leaves behind a core hole. When an electron relaxes to fill it, an x-ray is emitted. The core hole can be anywhere from the top of the valence band or below so the spectrum reflects the entire density of states of the valence band. In this case, the measurement detects the emitted x-ray. Together, XAS and SXE directly probe the partial density of states of the conduction band and valence band, respectively. SXE and XAS spectra provide a direct measurement of the relative energy positions of the VBE and CBE in semiconductor materials.

In order to directly measure the band edge position shifts with the introduction of Se, we used the combination of SXE and x-ray absorption XAS spectroscopies. The oxygen K-edge at around 530 eV was investigated at room temperature at the Advanced Light Source (ALS) on Beamline 8.0.1. XAS was detected with the total fluorescence yield detection mode, and SXE was measured using the Tennessee/Tulane grating spectrometer with a total energy resolution of 0.6 eV. An elastic emission peak in the SXE spectra found near threshold excitation was used for calibration of the SXE detector energy to the XAS monochromator energy. For the curves shown in Figure 4.4, the sample polar angle was set at 45° to the synchrotron beam. The excitation energy was then tuned to the onset of the CB and the resultant SXE due to electronic transitions from the upper VB to the O K-shell was recorded with a wavelength-dispersive detector. The SXE spectra are scaled such that second order Zn L₃ and L₂ emission peaks at 505 and 516 eV, respectively, are at constant height. The XAS spectra are normalized to a unitary step height from below threshold to far above (~570 eV). The relative intensity scaling between SXE and XAS spectra is arbitrary.

Figure 4.4 shows SXE and XAS spectra for ZnO and ZnO₀.⁹₁Se₀.⁰₉. The main figure shows a wide energy range, while the inset focuses on the highest occupied (effective valence band) and lowest unoccupied states (conduction band). Measured films had Se content up to 28% and I observed little change in the onset of the XAS spectra, aside from slight broadening as the disorder in the films increased. Conversely, the SXE spectra thresholds showed a slight broadening and monotonic energy shift to the right with Se concentration. This is consistent with the hybridization of a localized Se level and the ZnO valence band. A linear extrapolation of the ZnO SXE leading edge and XAS threshold provided estimates of the VB maximum and CB minimum to be 528.9 and 530.2 eV, consistent with a bulk ZnO band gap of 3.3 eV. Alternatively, the high energy tail in the VB spectra for 28% Se extends almost to 528 eV, which is consistent with a shift of the valence band edge to the Se-derived band at ~1 eV above the VB.

‡ with the assistance of Dr. Jonathan Denlinger
maximum of the ZnO matrix, as shown in Fig. 4.9. The different SXE threshold lineshapes confirm the VBAC upward shift of the valence band obtained from a theoretical interpretation of the optical absorption coefficient\textsuperscript{59}.

![Figure 4.4. XES and XAS data. The inset shows the full spectrum, while the large portion of the figure is a close up of the near band edge region.](image)

One also notices the replacement of sharp features by smooth profiles within the XAS spectra as $x$ increases. This behavior is attributed to an increase in disorder as a function of the film selenium content\textsuperscript{56}. For $x>0.17$, the long-range periodicity of the film structures deteriorated, reflecting the transition from textured to amorphous films. This is exhibited in Figure 4.5.

![Figure 4.5. XAS for several values of $x$ in ZnO$_{1-x}$Se$_x$ showing that crystal symmetry breaks down at higher $x$ values.](image)
### 4.4 The optical absorption coefficient

Optical absorption spectroscopy measurements are perhaps the most straightforward way to gain information about the band gap (Section 2.1) of a semiconductor. When a photon ultraviolet (UV) or visible (vis) light impinges on a semiconductor, one of three processes occurs: reflection, transmission, or absorption. Reflection will be treated in Section 4.6. The physics behind these interactions is rich and extensively treated mathematically. This dissertation intends to provide enough detail for the reader to understand the experiments, but refers them elsewhere for detailed mathematical derivations. An excellent description of the mathematical and physical interpretation of the optical responses of semiconductors has been provided by Yu and Cardona in Chapter 6 of their textbook.

The majority of below-band gap light is transmitted through the material because these photons cannot provide ample energy for the electrons near the top of the valence band to reach the lowest unoccupied states at the bottom of the conduction band. There are exceptions to this rule when intermediate states in the gap (usually caused by defects) contribute to excitation of the photon, or in the case of “virtual state” light. These are not eigenfunctions, but have lifetimes derived from the uncertainty principle and have been observed with high intensity incident light.

![Figure 4.6. Measured absorption coefficient (α) for a direct band gap GaN thin film.](image)

Photons with energy greater than the band gap are absorbed through the excitation of an electron from the valence band to the conduction band. The absorption coefficient, or optical penetration depth, of a material is defined by Beer’s Law:

\[
I = I_0 e^{-\alpha t}
\]

(4.4)

where \(I_0\) is the incident light of a given wavelength, \(\alpha\) is the absorption coefficient in units of inverse thickness, and \(t\) is the film thickness. \(I\) is the intensity of the light that was not absorbed by the sample, which is the photons that are transmitted or reflected. The software for the Perkin-Lambda 950 spectrometer used for absorption data in this dissertation was written using the chemistry convention for absorbance, \(A\); therefore, the optical absorption coefficient is:

\[
\alpha(\omega) = \frac{A_{\text{measured}}(\omega) \ln(10)}{t}
\]

(4.5)
Comparing the incident light intensity to the measured transmission and reflection gives an accurate value of the absorbed light. The absorption coefficient is directly proportional to the imaginary portion of the index of refraction and shows a sharp increase at the semiconductor band edge:

$$\alpha = \frac{4\pi \text{Im}(\tilde{n})}{\lambda_0}$$

where $\lambda_0$ is the light wavelength in vacuum and $\tilde{n}$ is the index of refraction. Figure 4.6 shows the absorption coefficient of GaN, which has a direct band gap of 3.4 eV. As was discussed in Section 2.1, the exact mechanism for this transition is dependent upon the direct or indirect nature of the band gap.

The absorption coefficients of ZnO$_{1-x}$Se$_x$ films were measured in order to determine the effect of Se dopants on the ZnO band structure. Absorption spectra from five representative films are shown in Figure 4.7. All measured films of pure ZnO showed a sharp onset at 3.3 eV, consistent with literature band gap values of ZnO. The below band gap oscillations are due to Fabry-Perot effects within the smooth-surfaced thin films (Section 4.6). Alternatively, as is seen in Figure 4.7, films of ZnO$_{1-x}$Se$_x$ with $x > 0$ showed a sharp red shift in the absorption onset to roughly 2 eV. Additionally, the absorption onset is gradual, not immediate as in the ZnO case which is a result of the VBAC band structure. Increasing the Se content in the films increased the absorption coefficient at lower energies. This dramatic shift in the onset and shape of the absorption edge indicates the complex nature of the band edges in ZnO$_{1-x}$Se$_x$ alloys and is consistent with a VBAC band structure as shown in Figures 2.6 and 2.7. This will be discussed in detail in the next section.

Figure 4.7. Measured absorption coefficient (α) for several ZnO$_{1-x}$Se$_x$ films with varying values of x.

4.5 Theoretical determination of the ZnO$_{1-x}$Se$_x$ dispersion relation

The absorption coefficient, at first approximation, is a direct measurement of the semiconductor density of states because electrons can only be absorbed from the relatively flat
valence band into available states in the conduction band. For semiconductor with parabolic bands (most group IV, III-V and II-V semiconductors), the density of states, $g(E)$, can be written as:
\[
g(E) = 2\left(\frac{2\pi m^* k_B T}{\hbar^2}\right)^{3/2} E^{1/2}
\] (4.7)
where $m^*$ is the effective mass of electron (hole) in the conduction (valence band), $k_B$ is Boltzmann’s constant ($8.617\times10^{-5}$ eV/K), $\hbar$ is Planck’s constant ($4.135\times10^{-15}$ eV·s) and $E$ is energy. Therefore the absorption coefficient is proportional to $E^{1/2}$ and the absorption coefficient squared vs. wavelength can be linearly fit to extract the band gap of a material. A quantitative treatment requires use of a “joint density of states” $g_{\text{spec}}$, in which case each energetic transition allowed between the valence band and conduction band is counted. The general expression for the joint density of states can be written as
\[
g_{\text{band}}^\text{spec}(\hbar\omega) = \sum_k \delta(E_{\text{final}}(k) - E_{\text{initial}}(k) - \hbar\omega)
\] (4.8)
where, for each possible transition, $E_{\text{final}}$ is the final energy state of the electron (typically located within the conduction band), $E_{\text{initial}}$ is the initial state of the electron (typically within the valence band) and $\hbar\omega$ is the energy of the incident photon. The use of a delta function requires that the value of the joint density of states is zero unless $\hbar\omega$ is exactly equal to a possible transition at a given value of $k$. This reflects the physical requirement that a photon can only be absorbed if, at any value of $k$, there exists a transition such that the energy difference between the initial and final state is exactly equal to the energy of the incident photon. Summing over all values of $\hbar\omega$ counts all possible transitions between the occupied band and the unoccupied band and gives the joint density of states. Typically, this summation becomes an integral over $k$ space in calculations.

However, in the case of n-type ZnO$_{1-x}$Se$_x$, we know from SXE measurements that the low energy transitions are from the top of the defect-like band to the bottom of the conduction band. The defect-like band has a unique, non-parabolic dispersion relationship (Figure 2.4, 2.5). The complete mathematical formulation of such valence band anticrossing (VBAC) systems has been described elsewhere. Here I adopt a simplified version of VBAC. We ignore spin effects and separate the remaining 6x6 problem into 3 simple 2x2 problems. A similar approach has been used previously to consider VBAC in GaMn$_{1-x}$As$_x$ alloys. The dispersion relations for each of the 2x2 problems are given by the solutions of the BAC equation:
\[
E_{\pm}(k) = \frac{1}{2} \left( E_{\text{Se}} + E(k) \right) \pm \sqrt{(E(k) - E_{\text{Se}})^2 + 4C^2x}
\] (4.9)
where $E_{\text{Se}}$ is the energy of localized Se level above the valence band, $E(k)$ is the matrix valence band dispersion, $C$ is the coupling constant and $x$ is the Se composition. $E(k)$ is considered to be parabolic such that
\[
E(k) = \frac{\hbar^2}{2m} k^2
\] (4.10)

Additionally, because the p-like states of elemental Se have a relatively large spin orbit splitting energy of 0.37 eV, an optical transition from the spin orbit band to the conduction band has to be considered as well. Therefore, to evaluate the absorption coefficient in ZnO$_{1-x}$Se$_x$ alloys we consider optical transitions from three valence bands: the Se derived impurity band to conduction band ($E_+(k)$), Se spin orbit split band to conduction band ($E_{+\text{SO}}(k)$) and the ZnO matrix-like band to conduction band ($E(k)$).
Final consideration is given to the physical nature of these bands. In order to account for broadening in the bands inherent to the BAC model and arising from localized composition fluctuations, we convolve the energy dependent joint optical density of states with a Gaussian function at each value of $k$. Additionally, only delocalized carriers are expected to contribute to the optical absorption.

With these assumptions, Eq. 4.8 can then be used in order to obtain the joint density of states. Hence, the expression for the joint density of states determining optical absorption for a single valence-like band ($E_v(k)$) to the conduction band can be written as an integral over the wavevector $k$:

$$g_s(h\omega) = \frac{1}{4\Delta \pi^2} \left( \theta \right)^2 \exp \left( \frac{h\omega - [E_v(k) - E_c(k)]}{\Delta} \right) k^2 dk$$  \hspace{1cm} (4.11)

where $E_c(k)$ is the conduction band dispersion relationship (Equation 4.10 with opposite sign), and the first factor under the integral represents the fraction of the delocalized states that contribute to the interband transitions where $\theta$ is defined as:

$$\theta(k) = Tan^{-1} \left( \frac{2Cx^{1/2}}{E(k) - E_{Se}} \right)$$  \hspace{1cm} (4.12)

where $\Delta$ is the broadening parameter.

The expression for the total absorption coefficient includes all three transitions,

$$\alpha(h\omega) = \alpha_0 \left( \frac{2}{3} g_v(h\omega) + \frac{1}{3} g_w(h\omega) + g_o(h\omega) \right).$$  \hspace{1cm} (4.13)

where the transitions are weighted with the degeneracy factors and $\alpha_0$ is a scaling constant. The fits of Equation 4.13 to the experimental data are shown in Fig 4.8 as dashed lines. Each individual contribution to the absorption specified in Equation 4.12 can be seen in the inset. A very good agreement with the experiment is obtained by a single set of the VBAC parameters: the coupling constant, $C = 1.2$ eV and the localized Se level, $E_{Se} = 0.9$ eV above the valence band. These two parameters ($C$ and $E_{Se}$) were varied throughout the calculation algorithm and were set by fitting all compositions of samples simultaneously. The broadening parameter $\Delta$ ranged from 0.15-0.25 eV for the highest impurity band and between 0.4 and 0.55 eV for the lowest matrix-like band. The Mathematica code used for this procedure can be found in Appendix D. The final calculated dispersion relation for a ZnO$_{0.95}$Se$_{0.05}$ sample is provided in Figure 4.9.

Combining the determined $E_{Se}$ and the valence band coupling constant with the previously reported oxygen impurity level, $E_o$, in ZnSe and the conduction band coupling constant, the composition dependence of the conduction and valence band edges as well as the band gap can calculated. This is presented for all values of $x$ in Figure 4.10. BAC calculations reveal that the large reduction of the band gap of O-rich and Se-rich ZnO$_{1-x}$Se$_x$ HMs arises mainly from the upward movement of the valence band and the downward movement of the conduction band, respectively.

As has been shown above, the full description of the absorption coefficient of the nonparabolic bands in ZnO$_{1-x}$Se$_x$ alloys requires detailed calculations using the VBAC model. However, at small k values ($<5\times10^6$ cm$^{-1}$), the dispersion relation for the impurity band, $E_v(k)$, can be approximated by a parabolic dependence and therefore for low absorption values, $\alpha(h\omega) < 2\times10^4$ cm$^{-1}$, extrapolation of $\alpha(h\omega)^2$ to zero absorption is expected to give an approximate value of the band gap. The red data points shown in Figure 4.10 were obtained using this simplified
procedure. A reasonably good agreement with the VBAC calculated band gap validates usefulness of this method of the band gap determination. As observed experimentally and explained theoretically, it is possible to significantly reduce the band gap of a stable oxide in a controlled fashion as dictated by the BAC model.

Figure 4.8. Measured absorption data for five ZnO$_{1-x}$Se$_x$ films (symbols) and theoretical fits based on the VBAC model. Additional films were measured and fit but are not shown here to maintain clarity. The coupling constant, $C$, is 1.2 eV and the value of $E_{\text{Se}}$ is 0.9 eV above the valence band. Oscillations below the band edge result from Fabry-Perot interference. The inset shows the total absorption for the 4.6% Se sample separated into the absorption contributions from each band.

Figure 4.9. Calculated band structure of ZnO$_{0.95}$Se$_{0.05}$ approximating the valence band and impurity band each as a single band rather than derived from three $p$ states.
Figure 4.10. Band gap as a function of composition for the ZnO$_{1-x}$Se$_x$ system as calculated from the BAC model (blue solid line), while the inset shows the calculated band edges. The red circles were extracted linearly from absorption data in this work while the orange circles are from ref. 111. The abrupt reduction of the band gap at low Se contents is associated with the appearance of the Se derived E$_\sigma$(k) band at energy higher 0.9 eV above the valence band.

4.6 Optical reflectivity

Reflection occurs at low levels across the entire UV-Vis range in most semiconductors but has a strong critical point at the band gap edge. Reflection, $R$, is a function of the complex index of refraction, $\tilde{n}$, which is wavelength dependent:

$$R(\omega) = \left| \frac{\tilde{n}(\omega) - 1}{\tilde{n}(\omega) + 1} \right|^2$$  \hspace{1cm} (4.14)

The index of refraction is also equivalent to the square root of the dielectric function, $\varepsilon(\omega)$, which is the fundamental property of a semiconductor that determines the semiconductor’s response to the electromagnetic polarization (incident light). Because the imaginary portion of the dielectric function is directly sensitive to carrier transitions from occupied to empty states, a critical point occurs at the band gap which is then, according to Eq. 4.14, also apparent in the reflection. At energies below the band gap, the reflection can be approximated as a constant. Additionally, Fabry-Perot oscillations can be observed in thin films, which result from light reflection off of the front and back surfaces of the films. The oscillations can be removed from experimental absorption data by measuring reflected light ($I_R$) and subtracting it from the transmitted light ($I_T$) in order to obtain the absorption. This can be expressed as:

$$I_A = \frac{I_T}{100 - I_R}$$  \hspace{1cm} (4.15)

These are emphasized in band structures with sharp transitions. Finally, any scattering due to surface roughness is a form of reflection. Regardless of the source, experimental UV-Vis spectroscopy should include consideration of reflected light when obtaining quantitative values.

Additionally, the optical reflection of ZnO$_{1-x}$Se$_x$ was measured. The reflection replicates the structure of the index of refraction. In general, the index of refraction depends upon the derivative of the absorption coefficient according to $^{105}$.
\[
n(E) - 1 = CP \int_0^\infty \frac{1}{(E')^2 - E^2} \frac{d\alpha(E')}{dE'} dE'
\]  
(4.14)

where \(P\) represents the Cauchy principal value of the integral and \(E\) is energy. It is important to understand from Equation 4.14 that the index of refraction exhibits a structure whenever \(d\alpha(E)/dE\) goes through a maximum or minimum, which would occur with the onset or drop off of strong absorption. By this logic, the reflection would show structure at the band gap edge. To graphically demonstrate this, \(d\alpha(E)/dE\) is scaled and shown (blue dashed curve) along with \(\alpha(E)\) and a measurement of reflection for the same ZnO sample in Figure 4.11. There is a strong inflection point in \(d\alpha(E)/dE\) exactly at the absorption edge, 3.3 eV. Careful examination of the reflection measurement shows a disruption in the oscillations at the same point, indicating that the index of refraction is altered significantly. This is the energy of a strong transition, which in this case we know to be the band gap.

These measurements were also taken on ZnO\(_{1-x}\)Se\(_x\) samples. Two representative samples with \(x=0.06\) (ZOS18 and ZOS26) are shown in the same format in Figure 4.12. The gradual absorption onset is observed, but the derivative of the absorption coefficient shows distinct peaks below band gap. These do not appear in ZnO, even when heavy concentrations of oxygen vacancies are present. Therefore, the author attributes the large feature immediately below the band gap to the Se-derived defect level. The onset of the low energy feature is close to 2 eV, as found by the theoretical model (Section 4.5).

![Figure 4.11. The derivative \(d\alpha(E)/dE\) is scaled and shown (blue dashed line) along with \(\alpha(E)\) (black line) and a measurement of reflection (red line) for the same ZnO sample.](attachment:figure411.png)

The reflection data are also depicted. The damping of the reflection oscillations is gradual, rather than abrupt as in the ZnO samples. Due to both broadening from the quantum mechanical uncertainty principle in the BAC picture and composition fluctuations, there is a spread in the density of states between the defect-like and matrix-like bands. Thus, the absorption onset and the inflection points in the index of refraction are both gradual in these films. However, the most defined critical point of the reflection data occurs at 3.7-4.0 eV, which
is much larger than the ZnO band gap. This is evidence that the anticrossing interaction not only introduces a localized state above the valence band, but the valence band shifts to slightly lower energies, which can be seen in Figure 4.9. This is the first experimental observation of the matrix-derived band in VBAC.

![Graph showing energy levels](image)

*Figure 4.12. The derivative $da(E)/dE$ is scaled and shown (blue dashed line) along with $a(E)$ (black line) and a measurement of reflection (red line) for two ZnO$_{0.94}$Se$_{0.06}$ samples. ZOS18, grown with a fluence of 4.4 J/cm$^2$ is on the left and ZOS26, grown with a laser fluence of 1.4 J/cm$^2$, on the right.*

### 4.7 Summary

It is apparent that the band structure of ZnO can be significantly altered through the introduction of small percentages of the element Se. Here I presented a method of measuring the electron affinity of ZnO to be 4.95 eV by relying on the amphoteric nature of point defects. SXE and XAS were used to determine that Se introduces a defect level that interacts with the valence band forming bands with enough delocalized character for significant transport. The exact nature of these bands was analyzed in depth by relying on optical absorption and reflection data. The band gap of ZnO of 3.3 eV can be reduced to approximately 2 eV by replacing less than 10% of the oxygen atoms with selenium atoms, although the density of states near the band gap minimum is smaller than that of a direct band gap semiconductor with parabolic bands. The ability of ZnO$_{1-x}$Sex to absorb visible light, and thus a larger portion of the solar spectrum, opens up a number of interesting applications for this material. Additionally, as will be discussed in Section 7.2, the upward shift of the valence band is an opportunity to obtain reliable doping in p-type ZnO, which is notoriously difficult to obtain.
Chapter 5: Photoelectrochemical evaluation of ZnO$_{1-x}$Se$_x$

5.1 Semiconductor electrochemistry

As discussed in Section 1.4, there is potential for semiconductors to be used in photoelectrochemical fuel production. Semiconductor electrochemistry is a science of interfaces: the voltage drops across them and the charge transport between them. While the greatest challenges awaiting the semiconductor electrochemist require materials science, learning to shift between the isolated lexicons of physics and electrochemistry is a close second. In some cases, the vocabulary is completely unknown to one field, or, even worse, the definition of the same word is dramatically different! In this section and the appropriate appendices, I will review the basics of semiconductor electrochemistry, particularly those that are prohibitive for conversations between electrochemists and semiconductor physicists. The remainder of this chapter describes the characterization and evaluation of ZnO$_{1-x}$Se$_x$ as an electrode for photoelectrochemical applications.

5.1.1 The electrochemical cell

While there are numerous geometries that will not be discussed here, a basic electrochemical cell consists of a cathode, an anode, a solution and the associated collection of interfaces. The reduction reaction, in which the reactant gains an electron, occurs at the cathode, while an oxidation reaction, or loss of electrons, occurs at the anode. The electrons travel from the cathode to the anode through an external connection and the charge transfer is balanced by the movement of ions in solution. Appendix C contains helpful mnemonic devices. In a typical semiconductor test setup, the semiconductor is either the anode or the cathode, while a highly catalytic metal, such as platinum or carbon black, is the other electrode. Since the reaction of interest occurs at the semiconductor, it is known as the ‘working electrode’, while the platinum is referred to as the ‘counter electrode’. A third electrode, the ‘reference electrode’, is often introduced into an electrochemical system to eliminate any unknown interface voltage drops in the measurements. This allows measured voltages to be compared to a universal standard rather than only considered as floating values in a given electrochemical cell.$^{112}$

The most interesting interface in a semiconductor electrochemical cell is considered to be that between the working electrode and the electrolyte. Even without current flow, at any interface between conductors or semiconductors, charge will be exchanged such that the average energy of electrons on both sides of the system is equal. For example, the work function ($\Phi$) of zinc is smaller than that of platinum (unoccupied states of lower energy exist in the Pt), so a junction between these two materials would result in electrons transferring from the Zn to the Pt, shown in the schematic of Figure 5.1. At equilibrium, the work function of a material is also the electrochemical potential, $\eta$, (equivalent to the Fermi level). Similarly, an electrolyte has an electrochemical potential based on the average energies of ionic species in solution. The
Gaussian shapes of the ion energy distributions originate from harmonic oscillations of the solvation of ions on the surface\textsuperscript{113}. These fluctuations arise from thermal fluctuations of solvent dipoles, polarizations and complex formations\textsuperscript{114}. Since the Pt work function is less than the average energy of the solution, electrons would be transferred from the solution to the Pt at a water-Pt junction (Figure 5.1). Electrons transfer to and from ions according to equilibrium reactions. The specific ions in the electrolyte determine the equilibrium reactions within the solution and thus the electrochemical potential.\textsuperscript{115,116}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{charge_transfer.png}
\caption{Charge transfer in a metal-metal junction and a metal-aqueous junction before equilibrating. The $y$ axis is energy. Grey areas are filled states.}
\end{figure}

Charge transfer also occurs when a semiconductor is in contact with an aqueous solution. The n-type semiconductor shown in Figure 5.2 has a Fermi level greater than the electrochemical potential of the solution. Therefore, electrons transfer to H\textsuperscript{+} ions until the Fermi level stabilizes, at which point electron transfer remains at equilibrium. Just as in a p-n junction\textsuperscript{117}, the positively charged donors in the semiconductor are fixed space charge in the lattice and the bands bend upward at the surface. A typical\textsuperscript{8} p-type semiconductor in solution has bands bent downward (opposite to Figure 5.2) and charge transfers in the opposite direction to reach equilibrium. Charge accumulates in an insulating solid only as a result of adsorbed ions but, in metals, the accumulated charge actually is the result of electron transfer. The fixed charge on a semiconductor surface is derived from a combination of these occurrences, as well as the presence of any surface defects. To emphasize, the band bending of a semiconductor in solution is due to two kinds of “surface states”\textsuperscript{**}: (1) dangling bonds or solid state defects and (2) adsorbed aqueous ions that can inject or extract electrons from solution. Finally, the Fermi level of the counter electrode must also equilibrate with the semiconductor and electrolyte.\textsuperscript{114,115}

Electrochemistry is a powerful tool because externally applying a potential controls the behavior (accumulation, depletion, inversion etc.) of the space charge region, but no solid state junction is required.

As a result of coulombic interactions, a layer of fixed charge is also present in the electrolyte at the semiconductor or metal surface. Oppositely-charged aqueous ions arrange themselves in a thin (~1 nm) layer in response to this charged layer within the solid surface. For

\textsuperscript{8} P-type InN, which is beyond the scope of this thesis, has a large electron affinity and therefore behaves very differently. The same is true for CdO and InAs, although to a lesser extent.

\textsuperscript{**} (1) is the typical definition for a solid state physicist; (2) is the definition to an electrochemist.
example, at the electron-depleted surface of n-type semiconductor, cations arrange themselves on the semiconductor surface. The adsorption is a function of pH. Coupled with the fixed charge in the solid, this is known as the Helmholtz double layer. The most notable effect of the Helmholtz layer is the introduction of a capacitance to the system. In fact, the dielectric constant of such a layer is higher than that of most oxides, allowing electrolytic gating to be used where an oxide dielectric would suffer from breakdown or fail to passivate surface states.

Figure 5.2 An n-type semiconductor in contact with an aqueous electrolyte, water, before and after equilibration. The solid blue line in the semiconductor is the Fermi level, η is the chemical potential. Grey areas are filled states.

As a result of the charge accumulation, any solid-liquid interface causes a voltage drop. The number of interfaces combined with the natural fluctuations in an electrochemical system make potentials difficult to quantify in a two electrode system. Including a reference electrode in the circuit eliminates this problem. An ideal reference electrode is one that maintains a constant potential regardless of its surroundings. This is accomplished by having a surplus of species contributing to a reaction at a fast rate. For example, in the Ag/AgCl electrode, bulk silver is coated in AgCl and immersed in a chloride (Cl\(^{-}\))-rich solution. The reaction for this system is:

\[ \text{AgCl}_{(s)} + e^{-} \leftrightarrow \text{Ag}_{(s)} + \text{Cl}^{-}_{(aq)} \]  

(5.1)

This reaction has very fast kinetics such that it, when at equilibrium, cannot be interrupted under normal cell operating conditions, and thus the reference electrode maintains constant potential.

The voltage associated with one reference electrode reaction can be referenced to other electrodes or to the standard hydrogen electrode, which is 0 at 4.5 eV below the vacuum level at a pH of zero. These each provide a different scale, all with units of (e)V. Conversion between them is provided in Table 5.1. The vacuum scale is usually written as “# below the vacuum level” or simply “- #”. It is important to note that electrochemical scales are usually written such that the values become more positive as the reader moves down the page. This is convenient so that the voltage axis in a I/V sweep corresponds directly to the electrochemical scale, provided that the positive direction is defined as the anodic direction. Being able to choose an appropriate measurement scale and to shift fluently between scales are valuable skills to both solve semiconductor electrochemistry problems and to communicate properly across (and even within) disciplines!

Measurements in an electrochemical system are typically made using a potentiostat, which has become the generic name of a voltage/current source with multimeter capabilities. The electronics in a potentiostat can sweep voltage/current, fix the voltage of a system
(potentiostatic hold) or fix the current of a system (galvanic hold). What makes a potentiostat especially unique is that the applied voltage can be between two electrodes (i.e., the working electrode and the counter electrode) while the measured voltage is between two others (i.e., the working electrode and the reference electrode). This is possible with the use of an operational amplifier, which uses two inputs (one controlled by the potentiostat and one the output of the operational amplifier) to set the output\textsuperscript{112}. More details can be found on the Gamry company website\textsuperscript{120} or in textbooks\textsuperscript{112,121}.

Although not directly applied in this dissertation, a potentiostat can also be used for impedance spectroscopy, which allows a user to measure the impedance of a system as a function of frequency or applied bias. The data can be fit using a model of the electrochemical system constructed from circuit elements in order to extract information about the materials of interest. When the circuit elements can be treated as capacitors, analytical models can be applied to extract information about semiconductors, including doping and band alignment. This is the basis for a Mott-Schottky interpretation of a semiconductor electrochemical cell, which is described in Appendix B. A detailed treatment of the extensive capabilities of impedance spectroscopy can be found in a number of sources\textsuperscript{112,122}. One last word of caution to physicists embarking in electrochemistry: the natural fluctuations within the electrochemical system cause more variation than typically found with solid state devices, so precision within 0.1-0.2 V is often excellent for semiconductor electrochemistry!

<table>
<thead>
<tr>
<th></th>
<th>Natural Hydrogen Electrode (NHE) (V)</th>
<th>Vacuum level (eV)</th>
<th>Standard Calomel Electrode (SCE) (V)</th>
<th>Ag/AgCl Electrode (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHE (V)</td>
<td>-(e NHE+4.5 eV)</td>
<td>NHE-0.242V</td>
<td>NHE-0.197V</td>
<td></td>
</tr>
<tr>
<td>Vacuum (eV)</td>
<td>-(Vac+4.5 V)/e</td>
<td>-(Vac-4.258 V)/e</td>
<td>-(Vac-4.303 V)/e</td>
<td></td>
</tr>
<tr>
<td>SCE (V)</td>
<td>SCE+0.242 V</td>
<td>-(e SCE+4.742 eV)</td>
<td>SCE+0.045</td>
<td></td>
</tr>
<tr>
<td>Ag/AgCl (V)</td>
<td>AgCl+0.197V</td>
<td>-(e AgCl+4.697 eV)</td>
<td>AgCl-0.045</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1 Conversions between different absolute scales\textsuperscript{115}. The user should look at the row of the scale they have and the column of the scale they want.

5.1.2 Semiconductor photoelectrochemistry

The previous section described an electrochemical cell in equilibrium. The goal of photoelectrochemistry is to extract photo-generated electrical carriers to do useful chemical work directly. As in a solar cell, illuminating the semiconductor generates electron hole pairs and generates two quasi Fermi levels\textsuperscript{117} within the semiconductor. Under open circuit conditions, the carriers accumulate at the interface. The excess holes cause the bands to flatten slightly. This is depicted in Figure 5.3\textsuperscript{25}. Eventually, the open circuit voltage (with respect to the reference) as a function of illumination intensity will saturate; this is the basis for an illuminated open circuit flat band potential measurement (Section 5.2).
Figure 5.3 An n-type semiconductor electrochemical cell at equilibrium (a) and under above band gap irradiation (b). \(E_F\) is Fermi level, \(H^+/H_2\) and \(O_2/H_2O\) denotes the hydrogen and oxygen evolution redox potential. \(V_B\) is the built in potential. \(U_{FB}\) is the flat band potential, discussed in Section 5.2. In b, \(h\nu\) denotes a photon that generates an electron hole pair. The Fermi level splits into two quasi-Fermi levels. The distance between them is the photo-generated voltage, \(V_{ph}\). From Bak et al.\textsuperscript{25}.

When the semiconductor is illuminated and connected to the counter electrode, current flows spontaneously if the electrons and holes are able to transfer spontaneously into the oxygen and hydrogen redox potentials. This is the case if the semiconductor bands straddle the redox potentials. However, if this is not the case, applying an anodic (cathodic) bias for an n-type (p-type) semiconductor system allows the holes (electrons) to transfer directly into the solution. This splits the Fermi level between the semiconductor electrode and the metal counter electrode, as shown in Figure 5.4. In general, anodic bias results in a depletion region at the n-type semiconductor-electrolyte interface; electrons are extracted through the bulk to the counter electrode where they react in an oxidation reaction. Conversely, a cathodic bias bends the semiconductor bands downward and reduction occurs at the surface of the semiconductor. In n-type (p-type) materials, there is no cathodic (anodic) photoresponse because current flow in this direction originates from majority carriers.\textsuperscript{25,115} The magnitude of the current is determined by both catalytic activity and the applied potential. The reader is referred to Appendix A for more detail on catalysis. The rate of reaction can also be increased by choosing an electrolyte where the reduction and oxygen reactions have fast kinetics. This is a suitable option for experiments measuring characteristics of the semiconductor itself rather than the occurrence/rate of a specific light-driven reaction.
5.1.3 Water splitting with photons

As described in Section 1.4, there are interesting applications for a photoelectrochemical cell that is capable of spontaneously producing fuel when illuminated with solar radiation. For the sake of clarity, this dissertation focuses on the production of hydrogen fuel, although the electrochemical reduction of carbon dioxide to methane (or other similar reactions) is also a possible source of fuel. The requirements for all systems are analogous, but the specific electrode energy requirements are determined by the actual energies of the redox couple for a given reaction.

In general, two electrode measurements are analogous to photovoltaic characterization techniques. Under these conditions, the solar-to-hydrogen efficiency (STH) can be calculated as:

\[
\text{STH} = \frac{\text{mmol} \text{H}_2}{\text{s}} \times \frac{237 \text{ kJ}}{\text{mol}} \times \frac{\text{W}}{\text{cm}^2} \times \frac{\text{Area}}{\text{cm}^2}
\]

In words, the efficiency is the rate of hydrogen gas produced multiplied by the change in Gibbs free energy per mole of hydrogen divided by the incident power density and sample area. A gas chromatograph or mass spectrometer can be used to accurately measure the moles of hydrogen produced. However, if such instrumentation is not available, it is generally acceptable to assume that Faradaic current in the absence of any sacrificial reagents is due to the production of hydrogen gas. In this case, Equation 5.2 can be rewritten as:

\[
\text{STH} = \frac{I_{\text{SC}} \times 1.23 \text{ V} \times \eta_F}{P_{\text{total}} \times \text{Area} \times \text{cm}^2}
\]

The Faradaic efficiency is often approximated as 1, although the most accurate reports to STH would measure it directly with a gas chromatograph. \( I_{\text{SC}} \) is the short circuit current of the system; 1.23 V is the thermodynamic potential required for hydrogen and oxygen evolution.
Equations 5.2 and 5.3 should only be used without applied bias. More details on water splitting efficiency can be found in Chen et al., Bolton et al., and Khaselev et al.

Three electrode measurements, as described in Section 5.1.1, are especially useful when there is no spontaneous hydrogen or oxygen evolution under illumination. The three electrode configuration is also valuable to characterize the electrode itself or to explore a specific half reaction but not to evaluate a photoelectrode under operating conditions.

Figure 5.5 Electrochemical cell setup for water splitting.

A schematic of a photoelectrochemical cell for evaluating an n-type semiconductor is shown (Figure 5.5) with an n-type semiconductor photoanode and a Pt anode. Both electrodes are immersed in electrolyte, which for hydrogen production would be water or a slightly acidic/basic solution to increase conductivity. Hydrogen reduction always occurs at the cathode and the oxygen-producing oxidation reaction occurs at the anode. When illuminated by sunlight, optically-excited electrons diffuse to the bulk of the n-type semiconductor, while the minority carrier holes travel to the semiconductor-electrolyte interface. At the semiconductor-electrolyte surface, the holes oxidize water to O₂:

\[
2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+ \quad \text{(acidic solution) (5.4)}
\]
\[
2\text{OH}^- + 4\text{h}^+ \rightarrow \text{O}_2 + 2\text{H}^+ \quad \text{(basic solution) (5.5)}
\]

The electrons at the cathode reduce the hydrogen contained in water molecules according to:

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad \text{(acidic solution) (5.6)}
\]
\[
2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(basic solution) (5.7)}
\]

A commercial monolithic photoelectrochemical (PEC) cell could have two functional parts: an energy absorber/converter and a catalyst deposited on the photoactive layer. A deposited catalyst increases the rate of the desired photoelectrochemical reaction; more detail can be found in Appendix A. There are three energetic requirements for the energy absorber: (1) it must have a band gap suitable to absorb sunlight, (2) the bands must be wide enough to straddle the H₂ and O₂ reduction and oxidation reactions (Figure 5.6) and (3) the material must be resistant to corrosion. Just as the reduction reaction of H⁺ ions to H₂ gas can be represented as an electron acceptor energy within the gap, a corrosion reaction can be represented as an oxidation (reduction) energy level, or hole (electron) acceptor. Oxidation can dislodge metal ions from the semiconductor surface (Equation 5.8), while reduction of the semiconductor can
result in the formation of a thin layer of metal on the semiconductor surface (Equation 5.7). These reactions could be as follows for a metal, M, and any counter ion, X:

\[ MX + zh^+ + \text{solvent} \rightarrow M^{z+} + X \]  
\[ MX + ze^- + \text{solvent} \rightarrow M + X^{z-} \] (5.8) (5.9)

To prevent corrosion, these reactions must be thermodynamically less favorable than the hydrogen and oxygen evolution reactions and preferably at energy levels not located in the gap at all. It is important to note that no single material fulfills all three of these requirements. Oxides that typically withstand corrosion have band gaps too wide for significant absorption\(^{13}\), while III-V semiconductors can be highly efficient but unstable over time\(^{28,126}\).

![Figure 5.6 Schematic of ideal water splitting band alignment](image)

### 5.1.4 Experimental setup

The potentiostat used for this dissertation was a Gamry Reference 600 model. The Gamry Virtual Front Panel Labview software was used for potentiostatic and galvanostatic holds, while current-voltage sweeps and open circuit potential measurements were performed using the Gamry Framework software.

Our semiconductor electrochemical setup was specifically designed so that the surface of the semiconductor was exposed to solution, but the pressed-on In contact was isolated from the liquid. This was accomplished using a silicone o-ring (O-rings West) on photoelectrochemical semiconductor anodes. The o-ring was placed on the top of the sample. A glass beaker with a drilled hole (area of 0.0831 cm\(^2\)) compressed the o-ring using clamps formed by rubber bands. The cell is shown in a three electrode configuration. The alligator clips in the photo connect the counter, working and reference electrodes to the potentiostat. For two electrode measurements, the reference electrode is removed from the solution and the white clip is connected to the counter electrode clip.

Unless otherwise noted, the electrolyte used was a pH 9 phosphate buffer (Hydrion) chosen based on the reported stability of ZnO in pH 8-12\(^{127}\). The solution was purged with nitrogen for any experiments requiring charge transfer for the semiconductor to the solution. A 300 W Xenon lamp was used as simulated sunlight with an IR glass filter and UV-reflecting Al mirror (Thor labs). The physical setup is shown and labeled in Figure 5.7 in the room light and under photoelectrochemical operating conditions. No catalysts were used.
5.2 Characterizing ZnO\textsubscript{1-x}Se\textsubscript{x} band edges

As illustrated in Figure 5.8, the valence bands of common oxide photoanodes lie almost 2 eV below the water oxidation potential, but the conduction band edge is close to the hydrogen reduction potential\textsuperscript{25,96}. In particular, ZnO has a conduction band edge close to the hydrogen reduction potential (- 4.5 eV relative to vacuum). ZnO is known to be stable in pH 8-12\textsuperscript{127,128}, but is totally inactive in visible light due to a 3.3 eV band gap\textsuperscript{129}. Therefore it remains appealing to be able to narrow the band gap of ZnO in a controlled fashion by shifting the valence band upward, which, as was shown in Chapter 4, is exactly the case for alloying small percentages of ZnSe with ZnO. Several groups have previously explored ZnO or ZnO/GaN-based systems for photoelectrochemical water splitting, although these results relied primarily on UV excitation\textsuperscript{130-132}.

As discussed in Section 5.1.3, the location of the semiconductor band edges with respect to vacuum is critical to its use in a successful photoelectrode. Electrochemists typically refer to the flat band potential, \( V_{FB} \), which is defined as the absolute value of the Fermi level with respect to the reference electrode when the semiconductor bands are completely flattened. In addition to the \textit{ex situ} methods discussed in Sections 4.2 and 4.3, the flat band potential of a semiconductor can be measured electrochemically in three different ways: illuminated open circuit potential (IOCP)\textsuperscript{133}, photocurrent onset\textsuperscript{134} and using a Mott-Schottky plot of capacitance vs. voltage (Appendix B). Each method requires a specific set of approximations and has different
advantages and disadvantages which will be discussed. Previous measurements on other semiconducting systems suggest that these relationships persist as a function of pH.\textsuperscript{135}

![Figure 5.8 Band edge alignments of several oxides considered for use in photoelectrochemical cells. Si is shown in comparison.](image)

Measuring the IOCP is the simplest method of band edge measurement to implement. This technique is based on the band physics described in Section 5.1.2. In this measurement, the semiconductor bands are intentionally flattened by illuminating the samples with high intensity, above band gap light. Under these open circuit conditions, photoexcited carriers near the interface accumulate to oppose the built in electric field, flattening the semiconductor bands. The measured IOCP is then the sample Fermi level with respect to the reference electrode. The primary assumption for this measurement is that the bands are basically flat under IOCP conditions and not pinned by surface defects that cannot be controlled by the electrolyte. Depending upon the role of surface states and radiative recombination, this approximation could report a band edge position that is 100-200 meV lower than the actual value. However, no complex circuit models or kinetics are introduced.\textsuperscript{124,133,134}

First, the open circuit potential of the sample in the dark was measured, and then the sample was exposed to a high intensity, white Xenon lamp.\textsuperscript{133} IOCP measurements were recorded using the open circuit potential function in the Framework software for a Gamry Reference 600 potentiostat. A measurement of the change in open circuit voltage between light and dark conditions is shown in Figure 5.9. As it can be seen, for n-type samples, the open circuit potential (OCP) becomes more negative with light. The transient present when the light is turned off is due to desorption/adsorption of ions from the surface which occurs on a long time scale compared to solid state physics measurements. The sample should not be left illuminated for long times (>15 seconds) to avoid formation of oxide/hydroxides from the surface of the sample. For each measured sample, the power of the lamp was increased until the IOCP saturated at the reported value.
The ‘x’s in Figure 5.10 represent the raw IOCP data as measured in this fashion. However, since the IOCP is a measurement of the sample Fermi level rather than the actual band edge, the results should be corrected for the difference in the Fermi energy in the samples with carrier concentrations ranging from \( n=10^{17} \text{ cm}^{-3} \) to \( 3\times10^{20} \text{ cm}^{-3} \). Using Equation 4.3, the Fermi level was found to extend from 0.1 eV below the conduction band edge for \( n=10^{17} \text{ cm}^{-3} \) to 0.5 eV above the conduction band edge for \( n=3\times10^{20} \text{ cm}^{-3} \), confirming that the usual approximation that the conduction band edge is equivalent to the IOCP in n-type semiconductors\(^{124}\) is not valid. The squares in Figure 5.10 mark the actual conduction band edges for the ZnO\( _{1-x} \)Se\( _x \) samples after accounting for the energy difference between the Fermi level and the conduction band edge.

For comparison, I also measured the flat band potential using the photocurrent onset method. Again, this method is based upon the band bending described in Section 5.1.2. Upon immersion in electrolyte, most n-type semiconductor bands bend upward at the surface. The bands are flattened as the voltage is swept from more negative voltages through \( V_{FB} \) to anodic (positive) voltages. At voltages immediately above \( V_{FB} \), electrons are easily transferred to the electrolyte and current flow is observed. Because of catalytic inefficiency, the chemical reaction requires an overpotential so this measurement is expected to report slightly lower conduction band edges (with respect to the vacuum level).\(^{133}\) Anodic three electrode current-voltage curves in the light (Figure 5.13) were measured using the Gamry Framework software from the dark open circuit potential. Using the method described by Butler\(^{134}\), the photocurrent onset was obtained by a linear fit of the photocurrent squared as a function of voltage vs. the reference. It is interesting to note that these values roughly corresponded to an onset threshold of 1 \( \mu \text{A/cm}^2 \) in this material system.

The measured photocurrent onsets are shown as red squares in Figure 5.10. They were consistently found to be on the order of 0.2 eV below those measured by the IOCP method, as expected when kinetics were taken into account, but indicate the same qualitative trend as a function of Se content. It is interesting to note that the data presented in Figure 5.10 is from...
samples grown in two different PLD chambers over the course of 3 years. The trend remains consistent as a function of composition.

Figure 5.10 Flat band measurements using open circuit potential and photocurrent onset measurements.

Mott-Schottky (M-S) measurements are not reported for these samples because the assumption of two capacitors, the semiconductor depletion width and the Helmholtz double layer, did not appear to be accurate in this system. This could be due to a high concentration of defects at the surface or the presence of unaccounted for capacitances. From the author’s experience, Mott-Schottky plots work well typically in highly crystalline semiconductors with carrier concentrations between $10^{16}$ cm$^{-3}$ and $10^{18}$ cm$^{-3}$. A good rule of thumb is that the M-S method may not be reliable on samples where making an Ohmic contact to the semiconductor can be done only with mechanical contact. More on the M-S method can be found in Appendix B.

The conduction band edge measured by the IOCP method shows excellent agreement (within 0.2 eV) with the measurements of the ZnO conduction band edge (CBE) using the Fermi stabilization by irradiation method, as shown in Figure 5.11. It is notable this agreement is not achieved if the location of the Fermi level in relation to the band edges is not accounted for in the flat band measurement. In general, the CBE of these ZnO$_{1-x}$Se$_x$ alloys is about 0.5 eV too low to spontaneously split water. However, in addition to the upward shift of the valance band edge, there is also a slight upward shift of the CBE with Se content. This can be attributed to the CBE

†† Other methods of making Ohmic contacts to semiconductors include alloyed contacts, tunnel junction contacts made by increased doping at the surface through implantation or growth and/or mechanically rubbing In/Ga alloy, Sn/Zn alloy or liquid Ga gently into the semiconductor surface. (E.E. Haller, University of California at Berkeley, 2008)
shift in the alloy as a function of $x$. The CBE of ZnO is 4.95 eV in ZnO and 3.7 eV in ZnSe relative to the vacuum level.

5.3 Photocurrent production of ZnO$_{1-x}$Se$_x$

5.3.1 Spectral dependent photocurrent

As described in Chapter 4, there is clearly a dramatic restructuring of the band edges as ZnSe is added to ZnO. These states can participate in absorption. However, for any solar application it is important that the excited photocarriers are not only absorbed, but also extracted from a device. We observed photocurrent in ZnO$_{1-x}$Se$_x$ ($x<0.15$) at wavelengths well below the ZnO bandgap using incident photon to current conversion efficiency (IPCE)$^{124}$. Measurement of the IPCE verifies that photons in the visible spectrum can excite extractable carriers. This measurement is identical to the external quantum efficiency$^{123,136}$ of a solar cell when a two electrode electrochemical cell is used. However, IPCE is often reported for materials which cannot split water spontaneously, in which case an external bias must be supplied by the potentiostat using the three electrode configuration. Here the absolute value of the IPCE is a function of the external bias and can no longer be universally compared to other systems. Finally, IPCE measurements are an excellent opportunity to use electrolytes with redox couples that have high turnover rates, provided that the color of the solution does not interfere with light transmission. (Methyl viologen is a popular sacrificial reagent, but the solution is colored violet.)

IPCE was done using a three electrode electrochemical cell with a semiconductor working electrode, platinum foil counter electrode and a Ag/AgCl reference electrode in a pH 9
phosphate Hydrion buffer electrolyte. A 150 W xenon lamp served as the excitation source; the lamp spectrum was removed from the final spectra with a silicon reference diode according to

\[ IPCE(\lambda) = \frac{I_{\text{electrochemical cell}(\lambda)}}{I_{\text{reference diode}(\lambda)} F_{\text{mirror}(\lambda)}} EQE_{\text{reference diode}(\lambda)} \]  

where \( F_{\text{mirror}} \) is the reflectivity of the mirror (Figure 5.7) as a function of wavelength, and \( I_{\text{electrochemical cell}} \) was measured with the potentiostat (described below). The current of the reference diode was measured in the setup while the EQE of the reference diode was provided by the manufacturer for calibration. The light passed through a monochromator with a 600 g/mm grating and 2 nm slit width. Light exiting the monochromator was chopped at 155 Hz and passed through a 578 nm long pass filter at wavelengths greater than 600 nm to eliminate second harmonics from high energy white light. A bias ensured adequate band bending for charge carrier extraction.

An anodic potentiostatic hold was applied to the working electrode using the Gamry Virtual Front Panel software. A Stanford Research Lock-in amplifier was connected to the current readout (±3V) of a Gamry Reference 600 potentiostat and controlled through a custom Labview program. Specific details regarding the electronics of this system are of interest to any experimentalist interested in repeating such measurements with the Reference 600 output. Possible current/voltage (I/E) conversion ranges on the Gamry Reference 600 are 600 mA, 60 mA, 6 mA, 6 μA, 0.6 μA, 60 nA, 6 nA, 600 pA, 60 pA, 6 pA and 0.6 pA. The appropriate I/E range on the potentiostat must be chosen to read a given value of current; this should be the lowest I/E range that can still measure current over the entire range of photon energies. Necessarily, a single I/E range must be used for an entire IPCE spectrum. The electronics were designed such that in a given I/E range, i.e., 60 mA, the actual current was linearly converted to voltages that were relayed to the lock-in amplifier and once again reported as a current to the computer. For example, at the 60 mA sensitivity setting, a measurement of 60 mA would read 3V, 30 mA would read 1.5 V and so on from the Reference 600 to the lock-in amplifier. Samples with higher current flow would need to be measured at larger current ranges. A simple case of two samples can be considered to demonstrate the complications of this arrangement: Sample A has a peak current of 55 mA while Sample B has a peak current of 75 mA. In reality, they are only 20 mA different, but the reported voltage for Sample A is 2.75 V and only 0.375 V for Sample B. Therefore, the signal to noise ratio is roughly nine times larger for Sample A, even though the net output current was less! The specific potential used for the reported curves (anodic 1.5 V with respect to Ag/AgCl) to be reported was chosen because the signal to noise ratio was roughly equivalent in all samples. Although the magnitude of photocurrent for each sample was different, all samples showed current in the middle to upper portion of the I/E range. Applying anodic potentials of 0.5 V and 1 V produced qualitatively identical results but with varying contributions from system noise. As will be discussed in Section 5.3.2, the absolute magnitude of the current was not a function of any single sample property and therefore the curves were normalized.

The normalized IPCE measurements for four samples are shown in Figure 5.12. There was a monotonic redshift with ZnO$_{1-x}$Se$_x$ in the photocurrent onset from 3.3 eV in pure ZnO to 1.8 eV in the ZnO$_{0.87}$Se$_{0.13}$ sample. The increase in the relative low energy density of states with as a function of Se content was also apparent. Additionally, in the x=0.07 and x=0.13 samples, a second current onset after a plateau was observed at about 3.3 eV, roughly where the matrix-like band is expected from the band anticrossing model (Figure 4.9). These measurements confirm that the Se-derived band does in fact contribute to photocurrent production at longer wavelengths and that the highly mismatched alloy is able to use a larger portion of the solar spectrum than the
unaltered oxide. The spectra were normalized to their maxima for objective comparison of the influence of Se composition on the spectrally dependent behavior, since the magnitude of the photocurrent is influenced by the electron mobility independently of Se content.

5.3.2 Effect of mobility on current extraction

It is known that the absolute magnitude of the broadband photocurrent depends on the sample mobilities\cite{137} and carrier recombination rate as well as band gap of a photoelectrochemical material. In many cases, including this one, the first two of these properties are either directly or indirectly dependent variables, making it difficult to separate the effect of each of them on the photocurrent.

The dark current and the photocurrent using a white light source was recorded as a function of applied bias for ZnO$_{1-x}$Se$_x$ photoanodes. The results for several samples with different Se compositions and mobilities using a three electrode cell are shown in Figure 5.13. The ZnO reference sample measured here had a mobility of 23 cm$^2$/Vs and showed a lower photoresponse than the ZnO$_{1-x}$Se$_x$ alloys. The largest photoresponse and greatest fill factor was observed in a ZnO$_{0.87}$Se$_{0.13}$ sample with a mobility of 6 cm$^2$/Vs. However, the photocurrent response was not only a function of Se content; the second best performing sample had x=0.09 and mobility of 24 cm$^2$/Vs, which caused it to outperform the x=0.16 sample with a mobility of only 5 cm$^2$/Vs. This higher mobility sample also outperformed a sample of nearly identical composition (x=0.08) with a mobility only half as large. Depending on the PLD growth conditions, a wide variety of mobilities within ZnO thin films have been reported ranging from 1 to up to 150 cm$^2$/Vs\cite{138}. The ZnO reference samples used in this study had mobilities ranging from 5-50 cm/Vs, while the ZnO$_{1-x}$Se$_x$ alloy mobilities ranged from 2-20 cm$^2$/Vs. Additionally, application of an oxygen catalyst to the semiconductor surface would increase the overall carrier transfer to the solution and enhance the absolute photocurrent.
The geometry of a photoelectrochemical device is favorable to materials grown at low temperatures or on a variety of substrates. A textured polycrystalline film can be thought of as an array of aligned nanowires pressed together, such that carriers travel through the length of the grain (film thickness) more easily than between grains (laterally through the film). In these cases, the mobility is anisotropic such that carriers can flow through the thickness of the films easily, but encounter thermal barriers at grain boundaries affecting the charge transport in the plane of the film \(^{76}\). This topic is explored in Chapter 6.

### 5.4 Tandem ZnO\(_{1-x}\)Se\(_x\) devices on Si

#### 5.4.1 Composite systems

Certain challenges, especially band alignment, can be overcome through clever geometries or designs of composite systems. A single semiconductor-electrolyte junction, or Single gap device, such as is described in Section 5.1.2 requires two photons to make a single molecule of hydrogen. This configuration has been characterized as a S2 device\(^{139}\). Although there is a 1:1 photon to H relationship, a S2 device is difficult to make for the reasons described in Section 5.1.3.

One attempt to improve an S2 device has included using a thin oxide coating to prevent the corrosion of a highly efficient active layer. I tested this geometry using p-GaP and several 10-15 nm oxide coatings deposited by PLD. The band diagrams of such a configuration (as calculated and fabricated are shown in Figure 5.14. Among other oxides, TiO\(_2\) and Al\(_2\)O\(_3\) were considered for different reasons. In p-type semiconductors (and in general), holes are responsible for corrosion reactions. According to the calculation, the TiO\(_2\) should block holes from entering solution which would to promote electron reactions and prevent corrosion reactions. Alternatively, a thick layer of Al\(_2\)O\(_3\) would block both electrons and holes from
entering solution, but a thin layer would allow carriers to tunnel. Because electrons can tunnel more efficiently, this geometry would again promote reduction reactions and prevent oxidative corrosion reactions. Unfortunately, the experimental results of this study remain inconclusive because continuous films could not be produced using pulsed laser deposition. Recently another group has shown that continuous oxide films grown by atomic layer deposition can indeed protect semiconductor electrodes, although did not confirm the mechanism \[^{128}\]. Similar protection was reported for MoS\(_2\) coatings on MoO\(_3\) nanowires under hydrogen-producing conditions in the dark \[^{140}\].

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**Figure 5.14** Band structure calculations using SIMwindows for oxide protection of p-type GaP with TiO\(_2\) (left) and Al\(_2\)O\(_3\) (right).

An alternative to S\(_2\) devices are so-called D\(_4\) \[^{139}\] devices. These devices are Dual bandgap devices that use 4 electrons to produce a single hydrogen molecule. Two possible configurations for this type of device have been suggested, one that is a tandem electrode, not unlike a tandem solar cell, and the other that combines two materials with different band gaps to act as separate anodes and cathodes. The first (known as a Turner cell) uses a photovoltaic cell in series with the photoelectrochemically active layer to provide the excess voltage required to drive the hydrogen (oxygen) evolution reaction by connecting an n-type (p-type) layer through an Ohmic contact, typically a tunnel junction, to a p-n (n-p) junction \[^{28}\]. The original Turner cell, which reached 12\% efficiency before corroding severely, was a p-type In\(_{1-x}\)Ga\(_x\)P cathode on a GaAs solar cell fabricated by MOCVD \[^{28}\]. A highly doped n\(^+\)/p\(^+\) tunnel junction was grown between the two materials. The band diagram for such a tandem device with an n-type photoanode is shown in Figure 5.15. In the second configuration, a single n-layer connected to a single p-layer, such that the p-layer would drive the cathodic hydrogen reduction and oxygen evolution would occur at the n-type photoanode. \[^{139}\] This configuration is informally called a 'z-scheme' \[^{141}\] device and has been promoted extensively by the Lewis and Atwater groups at Caltech University.

\[^{128}\] The term z-scheme originates from the alignment of the p-type and n-type semiconductor bands. The shape can be envisioned by covering the n-Si portion of figure 9, although the pictured carrier transport and counter electrode become irrelevant.
5.4.2 Opportunities for p-Si and n-oxide composite systems

Based on Sections 4.2 and 5.2, the electron affinity of ZnO and ZnO$_{1-x}$Se$_x$ with small values of x is $\sim$4.95 eV, locating the CBE of these materials below the hydrogen reduction potential at 4.5 eV. This prevents the alloy from functioning as a photoanode of a S2 device for the spontaneous production of hydrogen and oxygen. However, this oxide is an ideal candidate for a dual band gap device that uses 4 photons in a so-called D4 device$^{139}$. Despite being inappropriate for a S2 device, Si has been shown to be a good choice for a D4 photocathode$^{141}$ due to its cathodic durability, appropriate band alignment and ease of manufacture. However, a suitable oxide for the anode remains to be found.

The band positions in Figure 5.8 show that the energetic values of bottom of the ZnO valence band and the top of the Si conduction band are close. Therefore, if the n-type oxide alloy is grown directly on a Si p-type layer, an electron in the ZnO conduction band can easily recombine with an excited hole in the Si valence band while the remaining hole and electron can be transferred to solution to evolve products. This is apparent in Figure 5.15 as well. By changing the Se composition in ZnO$_{1-x}$Se$_x$, one can narrow the band gap of the oxide through dramatic adjustment of the valence band and minimal shift of the conduction band.

5.4.3 p-Silicon/n-ZnO$_{1-x}$Se$_x$ device fabrication

The results reported on D4 devices in this dissertation are from layers of ZnO$_{1-x}$Se$_x$ grown on p-n junctions of (111)Si$^{142}$ wafers. From the 111 direction, the diamond lattice appears roughly hexagonal. The structural and electrical properties of ZnO$_{1-x}$Se$_x$ films on Si were first evaluated by growing films on intrinsic Si. These were found to be similar to films grown on sapphire. As depicted in Figure 5.16, XRD of both types of layers indicated diffraction only from the 0002 ZnO, with shift on the order of the experimental error (±0.1 degrees on a powder diffraction setup).
Figure 5.16 The 0002 peak of ZnO$_{1-x}$Se$_x$ grown on sapphire and silicon. ZnO is shown for comparison.

ZnO$_{1-x}$Se$_x$ films grown on conductive (3.5x10$^{-3}$ $\Omega$cm) p-type Si were used to test the Ohmic contact between the film and p-type Si. Figure 5.17 shows that for currents up to 20 mA/cm$^2$, the contact between the oxide film and Si diode was near Ohmic (linear fit $R^2=0.98$) with overall contact resistances ranging from 40-80 Ohm/cm$^2$. Although this is larger than optimized tunnel junction resistances, the bulk oxide and bulk Si as well as nonideal Si back contacts made of InGa alloy contributed to this high resistance. There remains opportunity to improve the oxide/Si interface.

Figure 5.17. Current voltage measurements across an n-type ZnO$_{1-x}$Se$_x$ on p-type junction. Linear behavior indicates an Ohmic contact.

Si p-n junctions were fabricated from Si(111) wafers by the following process: a lightly doped n-type Si wafer (n~10$^{16}$ cm$^{-3}$) was B$^+$ implanted at 33 keV with $1x10^{15}$ cm$^{-2}$ ions on the top to form a p-n junction. The back of the wafer was separately implanted with P$^+$, $1x10^{15}$ cm$^{-2}$
ions at 33 keV to form the n-type back contact. The implant profiles used are given in Figure 5.18.

![Graph](image)

*Figure 5.18 (Left) Implant profile for P in Si (photovoltaic cell back contact). (Right) Implant profile for B in Si (p dopant for p-n junction) as modeled in SRIM. Plots courtesy of Holland Smith.*

The implanted wafer was annealed at 940°C for 20 seconds to activate the dopants. The backs were vapor etched with HF before the evaporation of Pd/Au back contacts. The front surface of the diodes were protected with black Apiezon wax, then the diodes were immersed in HNO₃:HF (20:1) for 30 seconds. This was found to be necessary to eliminate edge leakage in the diodes along cleavage surfaces. After the slow etch, the wax was removed from the surface with warm xylenes and the surface was cleaned with a one minute oxygen plasma clean in a PlasmaPreenII-862. All Si-grown samples were HF vapor etched for 1 minute immediately before deposition.

Several silicon p-n junctions were processed one step further in order to add Al/Ag front contacts for photovoltaic evaluation (due to the presence of the metal these were not used for oxide growth). The I/V characteristics of a fabricated Si solar cell are compared to those of a commercial Si solar cell in Figure 5.19. The fill factor of the commercial cell was much higher (67% vs. 27%), with a short circuit current nearly 10 times greater than currents measured in the fabricated cells. Power conversion efficiencies of these solar cells were found to depend on the contact placement, but open circuit voltages (V_{OC}) on the order of 0.3 V were obtained under 1 sun. The measured V_{OC} was reduced to 0.2V when the incident lamp light first passed through a orange 550nm filter in order to simulate the operating conditions of the solar cell as the bottom section of the tandem ZnO₁₋ₓSeₓ/Si device. The short circuit current with the filter was 68% of that without the filter. We expect the Si solar cells in the ZnO₁₋ₓSeₓ device to have slightly better carrier extraction since the ZnO₁₋ₓSeₓ film would provide complete surface coverage instead of only a metal grid contact. Despite their flaws, the fabricated Si solar cells were excellent proof-of-concept devices and comparison to a commercial cell optimistically suggests an obvious route to improve the overall tandem device.
Figure 5.19 (Left) Commercial Si solar I/V data taken in the dark and under illumination. (Right) I/V characteristic for a Si diode fabricated by the author according to the procedure in the text.

5.4.4 Photoelectrochemical device results

Finally, I measured the performance of tandem photoelectrochemical devices fabricated by growing ZnO$_{1-x}$Se$_x$ films on top of such Si solar cells. As the data points in Figure 5.10 show, the use of these rudimentary Si diodes as substrates for an oxide alloy shifts the flat band potential by 0.3-0.4 V toward spontaneous hydrogen evolution. This is in good agreement with the expected open circuit potential (Section 5.4.1). I also saw a 0.5 V shift in the photocurrent onset potential for devices grown on silicon instead of sapphire. No such change was observed in ZnO$_{1-x}$Se$_x$ samples grown on intrinsic or p-type silicon.

The results of a two electrode IV measurement between the ZnO$_{0.01}$Se$_{0.09}$ semiconductor working anode and the platinum counter electrode are shown in Figure 5.20. The photocurrent onset in the 2 electrode configuration for the ZnO$_{1-x}$Se$_x$ on sapphire reference was near zero, even more so than expected from flat band measurements. The discrepancy may be due to evolution of undesirable products instead of hydrogen/oxygen evolution that could be eliminated by including an oxygen evaluation catalyst. Regardless, the presence of an underlying Si p-n junction shifted the photocurrent onset 0.5 volts negative, suggesting that the photoelectrochemical cell was able to output power in addition to perform a chemical reaction. My Si (111) photovoltaic diodes had significant variation and low output power compared to commercially-available Si solar cells, due mainly to non-optimized doping and processing. By using commercial-grade Si solar cells, the flat band voltage should easily surpass the hydrogen evolution potential.
Figure 5.20. Illuminated 2 Electrode current vs. voltage curve in light for a ZnO$_{1-x}$Se$_x$ film on a silicon p-n junction compared to the same material grown on sapphire as a reference.

5.5 Summary

Photoelectrochemistry holds great promise for future energy storage opportunities. For now, however, there exist significant materials challenges in order to obtain functional photoelectrodes that can withstand long term operation. In this chapter, I have presented evidence that ZnO$_{1-x}$Se$_x$ is a promising photoanode material that, when combined with a silicon cathode in a D4 device, could be a step toward a materials solution. Together, Chapters 4 and 5 indicate that there are different measurement techniques available which deliver similar information, provided that the experimentalist includes appropriate assumptions for interpretation. This methodology can be applied to any materials system.
Chapter 6: A tale of two $\tau$'s

6.1 Motivation

Optoelectronic devices either use light to make electrical carriers (photovoltaic devices) or use electrical energy to make light. These processes are determined by the interaction of light and electric fields with a given material, which are likewise influenced by the structure. In this chapter, I synthesize electrical, optical, photoelectrochemical and structural information in order to identify the challenges and advantages of using ZnO$_{1-x}$Se$_x$ films for photoactive devices. This analysis can be extended to other highly mismatched alloy systems.

One way of analyzing the optoelectronic behavior of a material is to consider two specific carrier lifetimes that need to be optimized in optoelectronic devices, both of which are usually represented simply by “$\tau$”.

§§ The first is the recombination lifetime, denoted here as $\tau_r$, which is the length of time that a photo-generated carrier (photocarrier) exists before recombination. The recombination can either be radiative, or non-radiative by one of several mechanisms, and measurement of the recombination lifetime requires either excitation with or detection of emitted light. In general, only the recombination lifetime of the minority carrier is of interest in an optoelectronic device. The second $\tau$ is the scattering lifetime, $\tau_s$, which is the amount of time that a carrier can travel through a crystal before being scattered by one of many processes. Long scattering lifetimes of both majority and minority carriers are important for effective carrier extraction/injection. Each of these lifetimes will be addressed experimentally for the case of ZnO$_{1-x}$Se$_x$. In either case, a small value of $\tau$ limits the number of photoexcited carriers that can be extracted from a photovoltaic device (although small values of $\tau_r$ can enhance light emitting devices). Due to the linear relationship between $\tau_s$ and $\mu$, maximization of the product $\tau_s\tau_r$ is also recognized as optimization of the “$\mu\tau_r$” product, especially in semiconductors being developed for radiation detection.

6.2 Scattering in crystals

Most experimentalists make the approximation that the carrier concentration, mobility and resistivity measured in one crystal direction are indistinguishable from that measured in another direction. In practice, electrical measurements (such as I-V and Hall effect) are often measured interchangeably in any crystal direction. Therefore, in an optoelectronic device the expectations are, generally, that the photo-generated carriers (photocarriers) can be swept out to any two contacts conveniently placed independently of the crystal structure. However, when the transport in a material is anisotropic, especially dramatically so, it is critical that the geometry of a fabricated device corresponds to the ideal direction.

From a theoretical standpoint, the assumption of an isotropic mobility is incorrect because, in a perfect crystal, the mobility of a carrier in a semiconductor is limited by the

§§ Much to the chagrin of an interested graduate student!
effective mass of that carrier. The effective mass varies with the crystal direction because the semiconductor band structure is ellipsoidal in three dimensions; hence the effective mass is sometimes reported as \( m_L^* \) and \( m_T^* \) to denote the longitudinal and transverse directions. A detailed study of this effect in Si was completed by Martin Green\textsuperscript{144}. The effective mass, \( m^* \), directly determines the mobility, \( \mu \), according to:

\[
\mu = \frac{e \tau_s}{m^*}
\]

(6.1)

where \( \tau_s \) is the scattering lifetime of the carrier. As a result, the mobility is also anisotropic with crystal direction. This behavior has been directly observed in ordered alloys using an optical microscope coupled to a scanning electron microscope\textsuperscript{43}. These are important observations and cannot be ignored in specific situations, especially in highly-ordered materials. However, for most applications, the effective mass of an electron can be simplified to a single mass for the density of states in the conduction band. Equivalently, the effective mass of a hole is dependent upon the density of states in the light hole, heavy hole and “split-off” valence bands.

As a result, the assumption of an isotropic effective mass is usually sufficient for semiconductor transport measurements. As Equation 6.1 indicates, the mobility is dependent upon scattering mechanisms present in the semiconductor\textsuperscript{30}, and often \( \tau_s \) limits the mobility much more than the effective mass. Carriers are most often scattered by phonons or impurities. Phonon scattering, which increases as a function of temperature, is a nearly elastic process when the energy of the phonon is low compared to the carrier\textsuperscript{47}. In such a process, the collision alters the direction of the carrier momentum but not the magnitude. Ionized impurity scattering is a coulombic process, requiring the scattering interaction to be proportional to \( Z^2 \) (\( Z \) being the charge of the ion). Neutral impurity scattering is a weak process but prevalent in doped semiconductors with low compensation. More detail on these mechanisms have been provided by Haller and McCluskey\textsuperscript{47}. Scattering mechanisms can also include grain boundaries and dislocations, among others. It is important to note that many of these mechanisms are independent of the crystal symmetry, but depend heavily on defects in the crystal.

### 6.3 Transport and scattering time

Standard electrical semiconductor characterization techniques were performed on the films in a lateral configuration, or across the top surface, of ZnO\(_{1-x}\)Se\(_x\) films grown in two different PLD chambers. Pressed-on In contacts in the Van der Pauw configuration provided Ohmic contacts. The resistivities of all Se films with \( x < 0.2 \) were measured. In addition to the data shown in Chapter 3 that pertains to various growth conditions, a plot of the measured resistivity as a function of \( x \) is shown in Figure 6.1. There is a roughly logarithmic dependence of the resistivity on the Se concentration, \( x \). While the exact mechanism of this behavior is not obvious, it appears to be related to a decrease in carrier concentration rather than mobility based on Figure 6.2.

Hall effect measurements were attempted on all of these films as well. The measurable carrier concentrations and mobilities are shown in Figure 6.2. The concentration appears to be roughly correlated with the Se concentration, \( x \). A reasonable hypothesis for this behavior is that the Se added to the films occupies oxygen vacancies or prevents zinc interstitials, both of which have been identified as native defects responsible for n-type native defects in zinc oxide\textsuperscript{129}. This is advantageous for use of the material in optoelectronic devices, since a lower (~\(10^{17} \text{ cm}^{-3}\)) carrier concentration results in a larger depletion width. The depletion width for the larger carrier concentrations of ~\(10^{19} \text{ cm}^{-3}\) is less than the thickness required to absorb all incident light.
Thus, a larger depletion width causes more electron hole pairs to be separated. Conversely, the mobility is fairly constant across the range of compositions, at least up to close to 12%. While these are both qualitative statements, a plot such as Figure 6.2 suggests that the mobility, or scattering lifetime, can be optimized separately from the Se composition. This is ideal. If, in ZnO$_{1-x}$Se$_x$ films, reducing the band gap also increased the scattering these materials would be difficult to utilize. In that case, it would be difficult to extract carriers from the films with the most desirable band gaps for solar applications.

Nevertheless, there remains a subset of films for which measuring the Hall effect was unreliable and which needs to be addressed. Typically, low mobility, high concentration films have small Hall voltages. The Hall voltage (in the y direction) can be written as

$$V_H = \frac{J_x B_z}{e n w_x}$$  \hspace{1cm} (6.2)

Where $J_x$ is the applied current, $B_z$ is the applied magnetic field, $n$ is the net electron (or hole) concentration and $e$ is the charge of an electron (hole). The result of equation 6.2 is that large carrier concentrations result in small Hall voltages. Additionally, the definition of low mobility carriers are those that respond weakly to an electric field.

![Figure 6.1 Resistivity measured laterally in ZnO$_{1-x}$Se$_x$ thin films as a function of x.](image)

This trend in electrical properties was pursued further by measuring the thermopower (Seebeck coefficient) of these materials. These results were provided in Figure 3.8, and show that the thermopower increased from -60 to -340 μV/K as the laser fluence used for growth was decreased from 4.4 to 1.4 J/cm$^2$. Because the thermopower is inversely proportional to the carrier concentration, this data suggests that the films grown at low fluence (“low fluence films”) had fewer free electrons compared to those films grown at higher temperatures (“high fluence films”). A calculation of the ZnO$_{1-x}$Se$_x$ thermopower considering only elastic scattering ($r=1$) and a parabolic conduction band is shown in Figure 6.3. The thermopower, $S$, was calculated according to$^{50}$. 

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where $g(E)$ is the parabolic density of states as defined by equation 4.7, $E_F$ is the Fermi level, $e$ is the charge on an electron, $T$ is temperature and $F(E)$ is the Fermi distribution function:

$$F(E) = \frac{1}{\exp\left(\frac{E - E_F}{kT}\right) + 1}.$$  


Assuming that thermopower is quantitatively proportional to carrier concentration in these polycrystalline films, the calculation suggests that the carrier concentration decreases from $6 \times 10^{19}$ cm$^{-3}$ in the films grown at high fluences to less than $10^{18}$ cm$^{-3}$ carriers in the low fluence films. While there is insufficient data to confirm the accuracy of this calculation, it provides insight into the qualitative behavior of the carrier concentrations in these films.

Surprisingly, based on Chapter 3, the films grown at low laser fluences were the same films that had unstable Hall voltages and apparently low carrier concentrations. As Figure 3.7 indicates, they did have somewhat larger resistivities. However, they showed strong diffraction peaks and the full width half max became 2.7 times wider as the laser fluence was increased from 1.4 J/cm$^2$ to 4.4 J/cm$^2$. Additionally, the measured AFM topography (Figure 3.6) was significantly smoother in the films grown at low fluences. Generally, these structural trends are indicative of films with fewer defects and therefore fewer scattering centers (high mobility). With no other information, one might expect the opposite of the experimental observations: that the Hall voltages would be larger and therefore easier to measure.
Figure 6.3 Theoretical calculation of the ZnO$_{1-x}$Se$_x$ thermopower using Equation 6.3. Triangle data points are experimental data.

However, examination of the structure of ZnO$_{1-x}$Se$_x$ reveals another potential scattering mechanism. Transmission electron microscopy (TEM) images of a film are shown in Figure 6.4. The columnar structure is visible in cross section (right), while the plane view of the film is shown on the left. Small (~10 nm) hexagonal grains are visible from this angle, as expected from the presence of the 0002 diffraction peak. As discussed in Chapter 3, these grain boundaries scatter carriers and reduce $\tau_s$. In materials with large carrier concentrations, the boundaries at the grains do not cause large barriers, in opposition to a material like Si where the dangling bonds at the grain boundaries form Schottky-like barriers. In addition, the conduction band edge of ZnO is located right at the average energy of native defects so the observed reduction in carrier concentration is not expected to increase the thermal barrier. Any shift of the conduction band should be insignificant in these materials (Section 5.2 and 4.5). While it is possible that $\tau_s$ is affected by grain boundary scattering, more TEM images would be helpful to confirm this effect.
6.4 Photoluminescence

Photoluminescence measurements probe the recombination lifetime, $\tau_r$, of photocarriers within a semiconductor. The materials used in solar cells need to have long carrier lifetimes so that the carriers can be separated, usually by the built in electric field, before recombining. This can be expressed as $^{117}$:

$$L = \sqrt{D\tau_r},$$  \hspace{1cm} (6.5)

where $L$ is the carrier diffusion length before recombination and $D$ is the diffusivity of the carrier, which is a material property. There are both radiative and non-radiative mechanisms of recombination; the total decay rate ($1/\tau$) is equal to the sum of the radiative and non-radiative rates. In the best solar cells, radiative recombination is the process that causes the open circuit voltage of a solar cell to be less than the band gap$^{136}$. An unavoidable mechanism of non-radiative recombination is Auger recombination, in which an excited carrier transfers energy equivalent to the band gap to another carrier in the form of kinetic energy. This mechanism is important in solar cells with a high carrier density because there are frequent interactions between carriers. However, the most detrimental type of non-radiative recombination can be reduced through materials engineering; this is due to mid-gap trap states in $k$ space caused by defects in the semiconductor material.$^{19,47,136}$ The extended states in $k$ space provide an easy route to recombination for excited electrons in the conduction band. Non-radiative recombination plays an ever larger role as the solid structure deviates from a perfect, pure crystal due to the presence of defects, grains or voids$^{30}$. A highly defective material might result in no radiative recombination of carriers at all, but instead promote cascading recombine only through...
defect states***. This would lead to a shorter lifetime and separation of fewer electron hole pairs. (Not surprisingly, the same physical defects often lead to a reduction of $\tau_s$, as discussed in Section 6.2.)

Photoluminescence (PL) spectroscopy is a method of detecting the radiative recombination in a semiconductor as a function of energy. The most obvious application of PL in semiconductor materials science is to observe the separation of the bands in direct gap materials and/or the presence of optically active defect states, because PL results as carriers relax from excited state to filled states. In semiconductor systems, this is most often from the conduction band (or a bound exciton) to the valence band or defect states located within the gap. For a system with a single emitter, or a homogeneous system, the lifetime of the carrier is a Fourier transform of the Lorentzian distribution of the emitted energy. Following the Heisenberg uncertainty principle, the width of the PL emitted by a single quantum dot is a direct function of $1/\tau_r$.\textsuperscript{146} A heterogenous system includes many emitters with necessarily slightly different environments. In this case, the Lorentzian shape transitions to the Gaussian distributions measured in thin film semiconductors.\textsuperscript{147} Broadening in these distributions can originate from a decrease in the carrier lifetime as well, but also due to the nature of more states contributing to the emission. Materials effects that also need to be considered include alloy variation, interface roughness, and tailing in the density of states (carrier localization)\textsuperscript{111,149} among others.

PL spectra of ZnO\textsubscript{1-x}Se\textsubscript{x} were taken to investigate radiative recombination and to probe the lifetime of films grown under low temperature conditions. Photoluminescence (PL) measurements were performed at room temperature using a 325 nm HeCd 50mW laser as an excitation source and a Hamamatsu R928 photomultiplier tube as a signal detector. No measurements were taken below 360 nm (3.54 eV) because of interference by the laser light. This was an important limitation because, as it will be shown, the ZnO\textsubscript{1-x}Se\textsubscript{x} samples appear to have transitions at higher energies. Spectra were normalized to the instrument function as measured with a calibration lamp.\textsuperscript{†††} For low temperature measurements, the samples were cooled to ~15 K inside of an evacuated cryostat cooled by a cold finger with a helium refrigerator. Measurements of PL from a ZnO reference sample grown under similar conditions as the ZnO\textsubscript{1-x}Se\textsubscript{x} samples are shown in Figure 6.5. Reference samples showed exceptionally strong PL, especially at low temperatures. The band edge emission, 3.28 eV at room temperature and 3.35 eV at low temperature, is in good agreement with all other measurements (Chapters 4 and 5) as well as PL results reported in the literature\textsuperscript{138}. The large shoulder can be attributed to bound excitons and an Urbach tail in the density of states\textsuperscript{150}. The broad defect PL is strong and agrees well with spectra reported in the literature. This part of the spectrum has been attributed to zinc and oxygen vacancies, though debate about the origin of the emission energy continues\textsuperscript{129}. Independent room temperature time resolved photoluminescence measurements\textsuperscript{‡‡‡} on a similar ZnO sample indicated that the lifetime was on the order of 20 ps.

PL from ZnO\textsubscript{1-x}Se\textsubscript{x} samples was also measured. As shown in Chapter 3, none of the single-phase ZnO\textsubscript{1-x}Se\textsubscript{x} samples indicated strong band edge PL at room temperature, although defect PL was apparent. PL measured at room temperature and ~15 K for two single phase samples grown with different laser fluences is shown in Figure 6.6. As discussed in Chapter 3 and Section 6.3, the high fluence samples had a larger number of structural defects. At room

\footnotesize

*** Discrete defect levels can also promote radiative recombination, but even this type of defect-mediated radiation reduces $\tau_s$ in a semiconductor.

††† By Karen Bustillo

‡‡‡ Taken by Robert Broesler, 2010
temperature, the sample grown at high fluence indicated no luminescence. The low fluence sample showed the expected ZnO defect PL, but no PL from transitions between the conduction band and the valence band.

In both cases, the low temperature PL was quite different. Two broad peaks were observed in the sample grown at high fluence, one of which required a two-Gaussian fit. The peak at roughly 3.34 eV is attributed to the transition between the conduction band and the matrix-like band, while the 3.0 eV peak is likely related to transitions between the conduction band and the Se-derived band. However, these peaks are difficult to quantify due to both the 360 nm cutoff of the system as well as the broadening of the peak that is also observed in materials with impurity bands formed by a Mott transition. Transitions between the conduction band and the native defect level were also observed at low temperatures. The transition from the matrix-like band to the conduction band is distinct compared to that observed in the sample grown at high fluence. However, the PL intensity appears to peak at energies higher than the measurable range; thus it can only be said that the largest transition is at an energy greater than 3.44 eV. It is likely that this transition is between the conduction band and the matrix-like valence band. There is another broad transition peaking at 2.96 eV. Although the onset of this peak is at 2.6 eV, it is still at slightly higher energy than might be expected for a transition between the conduction band and the defect level based on optical absorption data measurements (Chapter 4) and IPCE measurements (Section 5.3.1). This could be due to one or more possibilities: the transitions at low energies are too weak to be measured by this PL configuration or the presence of ZnO defects interferes with the radiative recombination at lower energies. It is notable that the defect PL in this sample at low temperatures is actually weaker than at room temperature.
Figure 6.6 Photoluminescence of two ZnO$_{1-x}$Se$_x$ samples grown at different laser fluences. The PL was taken at both room temperature and ~15K. The peaks found by fitting with Gaussians are labeled with arrows matching the curves.

It is clear that the radiative recombination of ZnO$_{1-x}$Se$_x$ samples increases at low temperatures. Furthermore, the PL in the samples grown at high fluences is quite different than is observed in the samples grown at low fluences. While the low fluence sample had defect PL at room temperature as well as band edge PL at low temperature, the high fluence sample only showed broad PL at low temperatures. This behavior suggests that the ratio of radiative to non-radiative recombination is higher in the sample grown with lower laser fluence. This is in good agreement with the structural integrity of the film. Although there are several complications with estimating $\tau_r$ from PL data in thin films, it is quite possible that the minority carrier lifetime in this sample is also longer. Finally, the band edge peak appears to shift to a slightly higher energy despite the cutoff by the laser energy. This suggests that the matrix-like band and the Se-derived band are less convoluted, or approach the theoretically predicted band structure (Section 4.5) more so than the sample grown at higher fluence.

A possible origin for these defect states can be observed in the AFM topography shown in Figure 3.6. The surfaces of the high fluence films were much rougher. At higher laser fluences, more material is expected to transfer in a single pulse. These clusters may not have time to fully ionize before their kinetic energy allows them to reach the surface. The term for this effect is bouldering, which is often associated with high fluence growth. Additionally, the high energy of the laser could cause the transferred material to adhere strongly to the surface rather than move and nucleate across the substrate, leading to a more disordered film. The combination of these effects would be responsible for the observed roughness, although AFM did not explicitly reveal exceptionally large boulders on the surface of the high fluence films.
The numerous structural defects likely induce states in the gap between the matrix-derived and Se-derived bands. These states not only enhance non-radiative recombination but broaden the observed luminescence. It is reasonable to attribute the reduced $\tau_r$ in high fluence films to these effects remaining from the growth process.

Indeed, several of these interpretations are only hypotheses. In fact, this is the first photoluminescence to be observed in a sample with a VBAC band structure\textsuperscript{151}. Further study of the emission of ZnO$_{1-x}$Se$_x$ aimed at achieving more conclusive results is underway by a collaborator using a UV laser for excitation. However, an important qualitative conclusion is that growing ZnO$_{1-x}$Se$_x$ at lower PLD fluences allows for longer radiative recombination lifetimes, which is favorable for solar device performance.

### 6.5 Photocurrent

Hall effect and lateral resistivity measurements suggest that $\tau_s$ is decreased by growing ZnO$_{1-x}$Se$_x$ at lower fluence, but photoluminescence measurements indicate that $\tau_r$ is actually increased in the same films. Although no quantitative values were obtained, this relationship is inconvenient for the development of solar materials. However, an optimal product of the two $\tau$'s is more important for photocarrier extraction than the effect of either $\tau$ independently.

Photocurrent measurements detect the effect of $\tau_r$ and $\tau_s$ convoluted together. Specifically, chopped-light current-voltage curves\textsuperscript{152,153} are an excellent method to observe the photoresponse of a given sample, both as a function of time and as a function of voltage. This compact data form also allows for an uncluttered comparison of more than one sample on the same plot, as long as the measurements are normalized by sample area. I take advantage of semiconductor band bending induced by an electrochemical contact, as described in Section 5.1.4. The current through the junction is measured as a function of voltage applied between the semiconductor and the reference electrode. For n-type semiconductors, the Faradaic charge transfer, or current, is measured as a function of voltage. During the scan, the light is blocked and unblocked, which results in the step function appearance.

Chopped light IV curves for samples grown with different laser fluences are shown in Figure 6.7. The voltage scans were measured at 20 mV/sec with a 5 mV step size and the light blocked manually with a solid shutter. Photocurrent was extracted through an In front contact that was isolated from the solution. For potentials below 1 V, the current was negligible when the light was off. By comparing the samples grown at different laser fluences, it is apparent that the photocurrent production monotonically increases as a function of the laser fluence used during growth. For example, the difference between the current with the light on versus off in the blue curve (1.4 J/cm$^2$) is much larger than in the black curve (4.4 J/cm$^2$). This is true regardless of the length of time that the light was applied. The presence of transients does not affect the fact that more photocurrent can be produced in samples that were grown using lower laser fluence.

It is well established that some, but not all, electrodes exhibit large transients in the current as a function of time in chopped light IV curves. For example, in the author’s experience, III-V semiconductors such as GaP do not usually show any transient behavior\textsuperscript{126}. The initial rise in the photocurrent is the peak value, which then decreases due to carrier recombination by one of three mechanisms (in n-type semiconductors): hole accumulation at the surface, electron accumulation in the bulk or trapping of the carriers at surface states. Hole accumulation in the bulk can be confirmed if cathodic transients are also observed when the light is turned off. The
region of interest in these curves is expanded in Figure 6.8. There are small cathodic transients circled in green, indicating that hole accumulation is partially responsible for the transient behavior, but not completely. Recombination via surface states is determined by applied potential rather than the light intensity. The transients in Figure 6.7 are fairly constant as a function of potential, suggesting that surface states do not play an important role.

![Figure 6.7 Chopped light IV curves for ZnO$_{1-x}$Se$_x$ samples grown at different laser fluences during pulsed laser deposition.](image)

Therefore, the expectation is that these transients are actually due to poor transport of electrons in the bulk. The transients do increase in the samples grown at lower fluence, which is in agreement with low mobilities inferred from the inability to measure reliable Hall effect data (Section 6.3). However, the effect of both $\tau_r$ and $\tau_s$ to the produced photocurrent can be further understood through the expression for photocurrent developed for photovoltaics$^{123}$:

$$I_L = eAG(L_h + W)$$

(6.6)

where $A$ is the device area, $G$ is the generation rate of carriers, $L_h$ is the diffusion length before the minority carrier recombines, and $W$ is the depletion width. $L_h$ can be expressed in terms of Equation 6.5. The Einstein relationship$^{117}$ is

$$D_h = \frac{\mu_h kT}{e}$$

(6.7)

where $D_h$ is the diffusivity of the hole, a material property. Combining Equations 6.1, 6.5 and 6.6 leads to the following relationship:

$$L_h = \frac{\sqrt{\tau_r kT}}{m^* - \tau_s}$$

(6.8)

where all of the symbols have the same meaning as before. Examining Equations 6.6 and 6.8 shows that the generated photocurrent is proportional to the square root of the product of $\tau_s$ and $\tau_r$. 

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This is the proof that, as alluded to before, optimizing the product $\tau_s\tau_r$ is more important than optimizing either $\tau$ at the expense of the other. Thus, even if $\tau_s$ is smaller in the low fluence films, as is indicated by large transients and low mobility, $\tau_r$ seems to be large enough to compensate. This suggests that the defects limiting each $\tau$ are not the same. As explained in Section 6.4, it is likely that “bouldering” during growth is responsible for the recombination lifetime, $\tau_r$, limitations. The scattering lifetime in the lateral direction could be a function of grain boundaries in the film. In nitride alloys, which are also very ionic, dislocations are not typically responsible for reduction of the recombination lifetime \(^{154}\) and could explain the lack of correlation between $\tau_r$ and $\tau_s$.

Figure 6.8 Close up of the low current regime for chopped light IV curves for ZnO\(_{1-x}\)Se\(_x\) samples (Figure 6.6) grown at different laser fluences during pulsed laser deposition. Green circles denote cathodic transients.

6.6 Summary

Electrical transport and photoluminescence measurements were taken in order to probe $\tau_s$ and $\tau_r$ in ZnO\(_{1-x}\)Se\(_x\) film independently, while photocurrent measurements examine the effect of both together. It seems that $\tau_s$ is optimal in films grown at higher laser fluences while $\tau_r$ is superior in films grown at lower laser fluences. It is reasonable to conclude that $\tau_r$ can be increased through a reduction of “bouldering” effects during growth. Although $\tau_s$ in these low laser fluence films is too small for effective Hall measurements, it is sufficient for carrier extraction in photocurrent measurements. Thus, because the product $\tau_s\tau_r$ determines the device operation, the low fluence films had superior performance.

It is also interesting to consider geometrical effects of transport in the system. Light emission is insensitive to the crystal geometry. However, techniques with contacts in the Van der Pauw configuration such as resistivity and Hall effect rely entirely on lateral carrier transport across the films, or in the $a$-plane of the wurtzite structure. Conversely, photocurrent measurements with back contacts give rise to carrier transport through the thickness of the film, or along the $c$-direction of the wurtzite structure. In this case, one might consider each of the
hexagons imaged in the plan view (Figure 6.4) as a nanowire. The film can then be treated as an array of nanowires with no interior space. This configuration would explain enhanced transport in the c-plane compared to the a-plane. The photocurrent measurements reported in this dissertation were taken with a single front contact, as the films were grown on insulating sapphire. Despite the contact configuration, the photocurrent generated near the contact at least required minimal lateral transport, thus causing this measurement to approach a $\tau_s$ determined by scattering in the c-direction, which need not be isotropic with that observed in the a-plane direction. Consequently in-plane measurements of transport properties may not be relevant for many potential device applications of such materials.

Further studies of this phenomenon that combine the techniques in this chapter with TEM images would prove to be interesting work and illuminating for operation of devices made from $\text{ZnO}_{1-x}\text{Se}_x$ alloys. These types of studies would also be applicable to similar semiconducting materials with structures that greatly deviate from perfect crystals.
Chapter 7: Outlook

7.1 Review

Band structure engineering is a powerful tool to tailor semiconductors for specific needs. Today, semiconductor devices are designed around material properties. Solar efficiencies are limited by band gaps of manufacturable semiconducting materials. Transistors and computer chips are limited by the mobility of silicon\textsuperscript{155}. Nitride blue- and green-light emitters suffer because the alloy compositions with the appropriate band gaps can (to date) be synthesized only with large numbers of dislocations\textsuperscript{156}.

As our base of knowledge about semiconductor materials properties grows, we not only understand material limitations but learn how to find solutions to inconvenient properties. With an optimistic mindset, one can imagine a world where interdisciplinary engineers dream up a device structure to fulfill some application, then synthesize the material to meet device requirements. This is not to say that we are yet at this stage, but it is at least a goal for the future.

In this context, this dissertation provides a roadmap for undertaking such a challenge. The goal was to narrow the band gap of an oxide such that it would respond to photons in the visible portion of the solar spectrum. Proper materials engineering begins with an understanding of the concepts behind the device to be constructed. Chapter 2 provided background information on methods of band gap engineering, while Section 5.1 served as introduction to semiconductor electrochemistry. A material, ZnO\textsubscript{1-x}Se\textsubscript{x} was theoretically designed based upon integration of semiconductor band physics and electrochemistry.

The next step was to choose an appropriate method of synthesis. In general, highly mismatched alloys are difficult to synthesize; this is potentially the primary challenge hindering perfect customization of semiconductors. For initial growth of ZnO\textsubscript{1-x}Se\textsubscript{x}, the most appropriate method was to use pulsed laser deposition in order to control composition in a non-equilibrium material. It is true that PLD is not practicable for large area film growth. Further development of this material for large scale energy applications must consider alternative growth methods include sputtering, chemical vapor deposition\textsuperscript{29} or evaporation. There will definitely be challenges in achieving the desired compositions, but potentially a Se-rich environment or growth source could compensate for evaporated Se. Chapter 3 demonstrates that there is a small window in which phase pure material of high structurally quality can be obtained. This was heavily dependent upon the PLD substrate temperature, background pressure and laser fluence. ZnO\textsubscript{1-x}Se\textsubscript{x} films were seen to grow along the c-direction of the hexagonal sapphire substrate lattice. Because the films have large electronegativities, defects led to free electrons. High carrier concentrations actually improved transport in films containing large concentrations of grain boundaries, but also led to narrow depletion widths.

The band structure of ZnO\textsubscript{1-x}Se\textsubscript{x} films was characterized in Chapter 4. In order to reduce the discrepancy amid literature values, the electron affinity of ZnO was measured using a bulk technique. Next, the movement of the valence band edge was directly observed with x-ray absorption and emission spectroscopies. The exact band structure was determined by modeling
the optical absorption coefficient, the results of which were in excellent agreement with measured reflectivity data. Together these findings confirmed that the theoretical prediction of valence band anticrossing when Se is introduced into ZnO is indeed accurate. With this method, the 3.3 eV band gap of ZnO is narrowed to absorb photons on the order of 2 eV.

The material was then evaluated and tested in an electrochemical environment. Flat band measurements confirmed that the ZnO$_{1-x}$Se$_x$ conduction band is too low to split water into hydrogen and oxygen spontaneously. However, spectrally dependent measurements confirm that the low energy photons do actually produce photocurrent in ZnO$_{1-x}$Se$_x$ ($x>0$). ZnO$_{1-x}$Se$_x$ alloys are an excellent choice for an oxide/silicon tandem water splitting device due to the natural alignment between the Si valence band and the ZnO$_{1-x}$Se$_x$ conduction band. Thus, carrier recombination in a tandem device can easily occur at this junction without the growth of complicated structures. Initial results from ZnO$_{1-x}$Se$_x$ layers grown on Si diodes indicated that (1) this natural Ohmic junction does work and (2) the extra voltage from the Si provides enough extra potential to the electron that spontaneous hydrogen and oxygen evolution can occur.

Finally, the carrier scattering and recombination lifetimes in ZnO$_{1-x}$Se$_x$ were considered. Apparently significant scattering in the lateral direction does not prohibit the photoelectrochemical device from operating. This may be due to geometrical effects or a longer recombination lifetime, but is most likely an effect of both. Thus, a textured or otherwise irregular crystal that does not function well for a device requiring for transport in one direction might be perfectly operational if redesigned for perpendicular current flow in the material.

7.2 Challenges and future work

Despite the overall success of this initial work, there remain interesting scientific pursuits to be explored and challenges to be overcome before ZnO$_{1-x}$Se$_x$ or other highly mismatched oxide alloys can be commercialized.

The first of these challenges is the synthesis of such materials. They are often grown with low temperature molecular beam epitaxy (MBE) in order to trap a large atom (such as Se) in place of a smaller atom (such as oxygen). MBE is both difficult to scale and limited by thermodynamics. Additionally, the low temperature growth is known to lead to disrupted crystal structures. Pulsed laser deposition (PLD) is a second suitable technique, as shown in this work, since the composition can be moderated through both the target and the atmosphere. PLD growth of films in a slightly Se-rich or O-rich environment ($10^{-5}$-$10^{-4}$ Torr) would allow for further optimization of film properties. Additionally, this ought to reduce the ubiquitous oxygen vacancies responsible for such high carrier concentrations. This methodology would also facilitate growth of these materials with sputtering or evaporation, which typically do not incorporate the isovalent ion in significant concentrations. It is likely that pursuit of this angle will require customizing a growth chamber to obtain background pressures with such accuracy, as well as to accommodate the safety precautions required for evaporated selenium or gaseous H$_2$Se. However, a variation on this type of apparatus has already been built for sulfidizing of oxides, so it is certainly achievable.

A second interesting synthesis challenge is the incorporation of nitrogen into ZnO$_{1-x}$Se$_x$ films. ZnO has been notoriously difficult to dope p-type and even more difficult to maintain as p-type material that is stable over several days. This is due both to the large electron affinity that causes native defects to compensate any p-type dopants, as well as the nonexistence of suitable p-type dopant species. Obtaining high quality p-type ZnO would enable commercial
transparent bipolar switching devices or other clever applications of a transparent p-n junction. Incorporating the ZnO$_{1-x}$Se$_x$ into the p-n structure could either enable a transparent device or a device absorbing in the visible depending upon the thickness of the alloy layer. In any case, successful p-type doping of a ZnO-based material would be an enormous scientific breakthrough!

The most successful reports of p-type ZnO have relied upon nitrogen doping. Despite nitrogen being the ‘industry leader’, it is still ineffective because it is a deep acceptor in ZnO with an ionization energy of 1.3 eV above the valence band\textsuperscript{157,158}. In this work, it has been shown that replacing several percent of oxygen atoms with selenium atoms raises the valence band by roughly 1 eV. In this case, the acceptor ionization energy is reduced to only 300 meV, which is only twice as deep as the well-established acceptor Mg in GaN. This is illustrated in Figure 7.1. The physical incorporation of N into the ZnO$_{1-x}$Se$_x$ is not trivial however. Besides the necessary quenching of n-type native defects, it will also require either a modification of the deposition chamber or significant post processing to incorporate the atoms into the lattice. The strong triple bond in an N$_2$ molecule makes it difficult to separate into individual N atoms. Typical methods of incorporating N during growth include the use of ammonia or a nitrogen plasma. The ablation plume in PLD may be able to split N$_2$ molecules for doping, but this has not been proven yet. Post processing techniques could include ion implantation followed by an anneal with a capping layer or in a nitrogen/ammonia environment. Ammonizing of the PLD target prior to growth may be a third option.

![Figure 7.1](image)

\textit{Figure 7.1 The acceptor level of nitrogen is much shallower in ZnO$_{1-x}$Se$_x$ than in undoped ZnO.}

The final interesting synthesis problem would be to grow ZnO$_{1-x}$S$_x$ or ZnO$_{1-x}$Te$_x$ and evaluate the shift in the valence band structure. Based on the ionization energies of S, Se, and Te, smaller percentages of Te should effect a greater change in the band gap. An example of this was calculated roughly based upon the atomic ionization energies and is shown in Figure 7.2. The same challenges of incorporating a large atom exist for the Te case, which is the motivation...
for exploring the S case. Previous studies suggest that ZnO$_{1-x}$S$_x$ is easier to synthesize, so one might be able to achieve longer recombination/scattering lifetimes in this material.

![Figure 7.2](image.png)

*Figure 7.2 Calculated values of ZnO$_{1-x}$E$_x$ where E is any element isovalent to oxygen. The rough calculation is done for 5% of oxygen replaced and based on the atomic ionization energies.*

Another area of interest to explore in ZnO$_{1-x}$Se$_x$ alloys is that of its use in actual hydrogen-producing devices. This material was designed to modify the optical properties of ZnO without affecting its stability over long term operation. While the ZnO$_{1-x}$Se$_x$ samples remain stable through several repeated tests as described in Chapter 5, the material’s resistance to corrosion over long term operation is extremely important to understand. This could be done with a galvanostatic hold, where the total charge passed through the device was counted and compared between samples. In this case, a profilometer, SEM, XPS or AFM could be used to look for etching after the measurement. Alternatively, a potentiostatic hold at an overpotential large enough to induce current flow would show a decrease in current over time as the material degraded. Finally, an *in situ* technique such as Raman spectroscopy could provide information as to the corrosion reactions occurring. This insight is the first step to prevention of corrosion.

For long term stability testing, or if hydrogen production is being measured explicitly, a catalyst should be present on the surface of the film. This could be electrodeposited platinum or a specific oxygen catalyst, such as the one developed by the Nocera group. Without the catalyst, carriers cannot be transferred to the solution at a reasonable rate. In this case, they will react to form oxides or corrosion products that are not thermodynamically favorable. Additionally, ZnO$_{1-x}$Se$_x$ films can be grown on commercial silicon devices. A tandem configuration using a diode with high $V_{OC}$ and $I_{SC}$ would increase spontaneous hydrogen production.
7.3 Sustainable hydrogen

Scientific presentations about renewable energy technologies often end with the inevitable questions from the audience: “Will this technology ever work? What about the problem X? Isn’t technology Y a better choice?” Sustainable fuel production almost always draws these thoughts and I would like to end by addressing these questions.

The answer to the first question is that, yes, hydrogen can be sustainably produced. Today, we could hook up 3 commercial silicon solar cells in series to supply ~2.1 V. At this voltage, the current provided to two platinum electrodes immersed in water would be enough to split water – using only photons from the sun. This is not done regularly today is, as mentioned in Chapter 1, because platinum is too expensive to use for large area electrodes. High quality Si solar cells are also expensive, and the overall cost of the system is prohibitively high. Furthermore, we have no infrastructure in place to utilize clean hydrogen with fuel cells – no filling stations, no hydrogen transport and few consumer fuel cells. We regularly move hydrogen through the southern United States for use in the fossil fuel industry, so we are definitely capable of building pipelines and storage centers to safely move hydrogen. Hydrogen in motorist vehicles has been shown to be safe, if not safer than gasoline. This is illustrated in Figure 7.3. Fuel cell technology continues to develop, but cannot reasonably be deployed in cars until filling stations are available. This is a “chicken or the egg” problem, since no industrialist will be interested in building hydrogen filling stations until there are cars that need hydrogen. In short, technologically hydrogen production, transportation and fueling are possible. But, with today’s technology and gasoline as the major competitor to hydrogen, there is no economic drive for the hydrogen economy.

![Image](H2_Gasoline.png)

*Figure 7.3 The effect of fuel ignition in a gasoline-power vehicle compared to fuel ignition in a hydrogen powered vehicle. From Dr. John Turner, National Renewable Energy Laboratory.*

This also is an answer to the second point of the critic: there are several problems to be solved before a clean hydrogen economy can become a reality. A monolithic device, as discussed in Section 1.4, is not a technologically feasible solution today because no such device has been shown to operate efficiently over long periods of time. This makes it an excellent topic for academic research! According to Dr. John Turner’s at the National Renewable Energy Laboratory, our primary objective as researchers is to reach 20% efficiency (or at least 10%). This perspective is based on a Department of Energy-commissioned technoeconomic analysis.
To obtain these values, the absorber layer must have a band gap below 2 eV. Several excellent semiconductor choices for light absorbers with the appropriate band gap already exist. These include GaInP\textsuperscript{28}, GaPN\textsuperscript{126} and InGaN\textsuperscript{135}. Although the 2 eV achieved in ZnO\textsubscript{1-x}Se\textsubscript{x} is remarkable improvement for an oxide, the use of these material is still several generations out.

With this in mind, perhaps the most critical portion of the device to be improved is the catalyst. Because platinum and other noble metals are so expensive, catalysts for oxygen and hydrogen production (or CO\textsubscript{2} reduction) are crucial to reduce the initial investment in a hydrogen producing system. Good catalysts can be coupled to photovoltaics even if a suitable, stable absorber can never be marketed. Conversely, without a catalyst, a stable absorber is still not useful for a monolithic photoelectrochemical device. Furthermore, an ideal catalyst would quickly transfer all electrons from the semiconductor surface to solution reactions and prevent corrosion. In the case of an improved but still imperfect catalyst, the semiconductor electrodes can be coated with thin protective layers. With these ideas in mind, future photoelectrochemical device development ought to be directed toward catalyst development and optimization of integrated (catalyst + absorbers at both electrodes).

The final concern from the hypothetical cynic is perhaps the most frustrating to the researcher: another clean technology is perceived to be a better choice than a hydrogen economy. For a given application, clean hydrogen fuel may not be the appropriate choice. Similarly, for another application photovoltaic, thermoelectric, wind power, hydropower, nuclear power, geothermal or fossil fuels may not be the right choice. No company expects their product to meet the needs of every consumer, thus it makes no sense that an energy producing technology should fulfill all power needs. Investing all research efforts in a single technology is unreasonable. As universities continue to understand and develop ideas in parallel, new applications for each will continue to emerge and move to industry. For clean technologies to flourish amidst a world driven by fossil fuels, creativity needs to transpire both in laboratories and in clever business models that foster the value of discoveries. Sustainable energy resources and methods of conservation must continue to develop to foster political relations, environmental health or if only because the last SUV on the road will run out of gasoline one day.

To end, I revisit the words of Jules Verne. Verne wrote about air, underwater and space travel before they were anything but science fiction. The time has come for his perceptions of energy resources to become as commonplace as air travel. In his 1874 novel The Mysterious Island\textsuperscript{163} his marooned pioneers redevelop their civilization. In the midst of survival, the engineer muses that,

"Yes, my friends, I believe that water will one day serve as our fuel, that the hydrogen and oxygen which compose it will supply an inexhaustible source of heat and light. I believe that when the coal mines have been exhausted, we will both heat and be heated with water. Water is the coal of the future."
Appendix A: Overpotential & catalysis

A.1 Overpotential

Extra voltage to drive a reaction, beyond the thermodynamic requirement, is called “overpotential”. This is the reason that, although the hydrogen and oxygen evolution redox potentials are separated by a mere 1.23 V, the reaction usually requires upwards of 1.8 V to proceed. A Volt is a Joule/Coulomb, which defines the amount of energy that a single electron has on average. Each electron has some chance of transferring to a nearby H\(^+\) ion, but increasing the energy of each average electron increases the chances of the completed reaction. As far as I can tell, an analogous situation is a group of lemmings standing on the edge of the cliff. If they move from foot to foot, eventually one or two will fall off the edge. However, if they all bounce at maximum energy many more are guaranteed to “transfer” into space.

In mathematical terms, the overpotential is described by the Tafel equation:\(^{112}\)

\[
\Delta V = \frac{d \log i_{\text{rate}}}{dV} \log \left(\frac{i}{i_0}\right)
\]

\[(A.1)\]

The differential term refers to the slope of a Tafel plot, which shows the reaction rate (current) on a natural log scale vs. the voltage. As can be observed in Figure A.1, there should be a linear relationship. The exchange current, \(i_0\), is the reaction rate at equilibrium or how fast electrons move in both directions when there is no net change in the reaction (Pt has the largest exchange current, hence why it is a spectacular catalyst.).

![Figure A.1 Schematic of a Tafel plot. The reduction reaction is in blue; the oxidation reaction is in red. The exchange current is denoted as “\(i_n\)”](image)
Graphically, this is the intersection of the oxidation and reduction exchange currents as a function of voltage. The slopes deviate from linear near the exchange current because the total current is composed of both oxidation and reduction reactions. The transfer coefficient is a rate constant representing the kinetics of the reaction. The result of the Tafel equation is that when greater overpotentials are used, the current becomes larger because the reaction is attempting to push electrons faster in one direction. 112

Although technically separate from catalytic activity, it is worth noting that there are also Ohmic losses in a semiconductor photoelectrochemical system. These also require application of a voltage higher than expected from thermodynamic limits. Although confusing lexicon, this is a second use of the word overpotential.25

A.2 Rate

The ‘turnover rate’ describes the rate of reaction; a good catalyst is said to have a high turnover rate. Catalytic activity for a given reaction on a given material can be explained with the Sabatier principle. This principle states that the “stickiness” of the reactants and products to the catalyst substrate should be “just right” (analogous to Goldilocks’s preferences at the home of the three bears). If the interaction is too weak, the reactants will not be in one another’s presence long enough to react. If the bond is too tight, the reactants will poison the surface of the substrate and not react with one another at all. This is best shown as a “volcano plot”, of which an example is given in Figure A.2. The Gibbs free energy ($\Delta G_H$) is a measurement of the “stickiness” of a given catalyst material for H reactants. The largest current density, or catalytic activity, is observed in the elements with middling values of $\Delta G_H$. Platinum, palladium and rhodium and iridium show the highest activity, explaining why these rare elements are so often used for catalytic processes (and consequently, why replacing the catalytic convertor in a car is so costly!).

Figure A.2 Volcano plot of the exchange current density for hydrogen production as a function of the DFT-
calculated Gibbs free energy of adsorbed atomic hydrogen for several materials. From 2

In metals, the value of $\Delta G_H$ is closely related to the work function. However, in other materials, *a priori* knowledge of $\Delta G_H$ is difficult to know, with theoretical calculations leading the way to the design of new materials 164. Significant work has been produced over the last few years to study new materials for catalysts that do not require noble metals. MoS$_2$ has been shown to have excellent catalytic activity which is geometrically dependent 2,165, NiO has shown good activity 166 and researchers have developed a cobalt-phosphate oxygen catalyst 159.
Appendix B. Electrochemical capacitance and the Mott-Schottky technique

Electrochemical capacitance voltage profiling (ECV) is a combination of traditional semiconductor characterization techniques and electrochemistry. It is a capacitance measurement of the space charge in the semiconductor made with one electrolytic contact and one Ohmic metal contact, which is also referred to as the Mott-Schottky (M-S) technique. However, for simplicity, this discussion will begin with an ideal metal-semiconductor contact to represent the electrolytic contact.

An ideal n-type semiconductor with a flat band and thus no surface states will equilibrate with a metal Schottky contact according to figure B.1. The depletion region, which is where the energy bands of the semiconductor bend, is formed when electrons flow from the semiconductor to the metal and leave positive space charge, Q, behind. Mathematically, this can be represented as:

$$Q = eN A w_d(V_d)$$  \hspace{1cm} (B.1)

where $e$ is the charge on an electron, $N$ is the space charge in the semiconductor which is typically assumed to be equivalent to the free carrier concentration, $A$ is the area of the junction, $w_d(V_d)$ is the length of the depletion layer as a function of $V_d$, the built in bias. It is established that for a semiconductor junction, the capacitance caused by this space charge, $C=dQ/dV$, is equivalent to:

$$C = \frac{\varepsilon \varepsilon_0 A}{w_d}.$$  \hspace{1cm} (B.2)
Equation B.2 shows that flattening the bands removes the space charge region and increases the capacitance of the junction to infinity. The derivative with respect to $V_d$ and rearranging gives

$$N = \left( -\frac{1}{2} e \varepsilon \varepsilon_0 A^2 \frac{dC^{-2}}{dV_d} \right)^{-1}$$  \hspace{1cm} (B.3)

which is another form of equation 2.1. However, in this case, it can be seen that plotting $1/C^2$ as a function of the voltage should generate a straight line with a slope linearly related to the carrier concentration if $N$ is constant. Similarly, the intercept on the voltage axis is the flat band potential of the semiconductor where there is no bending to the band.

In ECV profiling, several assumptions are made to apply this same equation to an electrolytic semiconductor contact, where the electrolyte is typically a high pH or low pH solution. They are as follows:

1. The Fermi level of the electrolyte is equivalent to the electrochemical potential of the solution which is due to the reduction and oxidation couples present in solution, and is analogous to the metal Fermi level.$^{112}$
2. Any resistance due to the solution is negligible or can be removed experimentally through the use of a reference electrode. The reference electrode contains a chemical reaction which occurs at a constant voltage vs. the standard hydrogen electrode, which, in addition to allowing calculation of the solution resistance, allows the voltage at the working electrode to be known precisely with respect to this scale.$^{112}$
3. The capacitance of the wires or contacts is also negligible or experimentally removed.
4. The capacitance of the system is frequency independent over a finite range of frequencies.
5. No Faradaic reactions (charge transfer or current flow) occur at the measurement potentials.
6. The semiconductor and the Helmholtz double layer in solution are the only two capacitors in the system.

Such a measurement can be taken with a 3 electrode setup including the semiconductor electrode, a reference electrode and a counter electrode such as Pt. $V_d$ is swept from the working electrode to the semiconductor. At each value of $V_d$, an alternating voltage is applied to measure the real and imaginary portions of the impedance. From this, the capacitance of the junction can be extracted and converted to $1/C^2$, from which the doping concentration can be determined. The x-intercept of the linear fit can be taken as the flat band potential, provided that assumptions 1-5 are true. A sample plot is shown in Figure B.2.

Of course not all cases behave ideally, if any do at all$^{114}$. A typical semiconductor has surface states which contribute another source of charge. Charge due to defects can be frequency dependent and observed as the slope changes as a function of AC frequency, in which case $N$ does not exactly equate to the free carriers in the sample. This measurement also relies on having little to no leakage current in the junction. Some of these effects can be extracted through modeling of the data using a series (semiconductor capacitor in series with solution or intrinsic resistance), parallel (semiconductor capacitor in parallel with solution or intrinsic resistance) or 3-term model (semiconductor capacitor in series and in parallel with resistors). These models typically account sufficiently well for any series or leakage resistance.

The profiling method used to determine the dopant concentration as a function of depth$^{50,168}$ takes advantage of the standard M-S technique described above. However, after the
first measurement, a calibrated system is used to apply a voltage in the etching direction appropriate for the sample type in order to remove material. For a p-type sample, this means that electrons flow away from the SC-electrolyte interface, so the etching bias is applied from the semiconductor to the counter electrode. The opposite is true for a n-type semiconductor, where etching is also facilitated by light.

Figure B.2. Mott-Schottky plot taken at 1500Hz for a n-GaP sample
Appendix C: Reduction and Oxidation

Two effective (although perhaps facetious) mnemonic devices to remember the difference between reduction and oxidation are:

1. “LEO says GER” (Losing Electrons is Oxidation and Gaining Electrons is Reduction)

![GER!]

Figure C.1 “LEO says GER” (Losing Electrons is Oxidation and Gaining Electrons is Reduction) and a “RED CAT and AN OX” (REDuction occurs at the CAThode and OXidation occurs at the Anode). Image from www.free-predator-pic.com

2. Remembering a “RED CAT and AN OX” (REDuction occurs at the CAThode and OXidation occurs at the ANode). The electrons travel from the cathode to the anode through an external connection and the charge transfer is balanced by the movement of ions in solution.

![Mnemonics]

Figure C.2 Picturing two mnemonic devices: a “RED CAT and AN OX” (REDuction occurs at the CAThode and OXidation occurs at the Anode). http://fineartamerica.com/featured/red-cat-ingrid-torjesen.html and http://www.clker.com/clipart-cartoon-gnu.html
Appendix D: Quintessential Mathematica programs used in this Dissertation

These programs were written in Mathematica 7.0.

**D.1 Calculation of two mode Raman (Section 3.6)**

**Phonon mode calculation for Highly mismatched alloys**
(*) This program was written by Esther Alarcon Llado and modified by Marie Mayer, January 2012. *)

**Setting up things - Units and constants**

*General startup*

Here's a couple commands that Joel always puts at the start of my Mathematica programs. The first one clears all the variables. The second command suppresses the error messages that are generated when two similarly-spelled variables are defined.

ClearAll["Global`*"];
Off[General::spell, General::spell1];

Now load the packages. I'm using Mathematica 7 right now, so there may be some differences compared to JA version (6).

Needs["PlotLegends`"] (* This was PlotLegend, a legacy package, in earlier versions *)
<<Units ` (* S.B. units package, in which a bunch of constants and units are defined*)

plotSettingsEA = {ImageSize -> Large, PlotStyle -> {Thick, PointSize[0.02]}, Frame -> True, GridLines -> Automatic, GridLinesStyle -> Directive[LightGray], FrameStyle -> Directive[Thick, Bold, 18], AxesStyle -> Directive[Thin, Bold, 18], LabelStyle -> Directive[Bold, 18]};
SetOptions[Plot, BaseStyle -> {FontFamily -> "Helvetica",FontSize -> 18}];
SetOptions[ListPlot, BaseStyle -> {FontFamily -> "Helvetica",FontSize -> 18}];
SetOptions[ListLogPlot, BaseStyle -> {FontFamily -> "Helvetica",FontSize -> 18}];

**Parameters**

**Massess**

\[ \mu_{\text{Zn}} = 65.41; \]
\[ \mu_{\text{O}} = 15.999; \]
\[ \mu_{\text{Se}} = 78.96; \]

**Binary 1: ZnO**

\[ \omega_{\text{A1LO}} = 573; \]
\[ \omega_{\text{A1TO}} = 378; \]
(*where is this number from?*)
\[ \epsilon_{\text{par}} = 3.72; \]
\[ \omega_{\text{E1LO}} = 590; \]
\[ \omega_{\text{E1TO}} = 410; \]
\[ \epsilon_{\text{perp}} = 3.68; \]

\[ \omega_{1A} = \omega_{\text{A1LO}}; \]
\[ \omega_{1A} = \omega_{\text{A1TO}}; \]
\[ \epsilon_{1A} = \epsilon_{\text{par}}; \]
\[ \mu_{1A} = 1/(1/\mu_{\text{Zn}} + 1/\mu_{\text{O}}); \]

**Binary 2: ZnSe**

\[ \omega_{\text{A1LO}} = 251; \]
\[ \omega_{\text{A1TO}} = 200; \]
$epar = 3.76;\\n\omega E1LO = 255;\\n\omega E1TO = 204;\\n\epsilon_{perp} = 3.76;\\n\omega_L = \omega A1LO;\\n\omega_T = \omega A1TO;\\ne_B = e_{par}; (* from cubic, extrapolation from e0/e_{inf} = LO2/TO2 *)\\n\mu_B = 1/(1/\mu_Zn + 1/\mu_{Se});\\n\\n\omega_{impA} = \omega_T Sqrt[\mu_B/\mu_A]\\n\omega_{impB} = \omega_T Sqrt[\mu_A/\mu_B] - 3\\n333.645\\n223.588\\n\\nCalculation\\n\\n\Omega_A = \omega A^2 - \omega T^2;\\n\Omega_B = \omega B^2 - \omega T^2;\\n\\nTOA[x_] := Sqrt[\omega T A^2*(1-x) + x \omega_{impA}^2];\\nTOB[x_] := Sqrt[\omega_{impB}^2*(1-x) + x \omega T B^2];\\n\\nEa[x_] := TOA[x]^2 + (1.0 - x) * \Omega A;\\nEb[x_] := TOB[x]^2 + (x \Omega B);\\nV_{ab}[x_] := ((x*(1.0 - x) * \Omega A * \Omega B));\\nE_{ab}[x_] := 0.5 * (Ea[x] + Eb[x]);\\nD_{ab}[x_] := 0.5 * (Ea[x] - Eb[x]);\\ndis[x_] := Sqrt[(D_{ab}[x] + V_{ab}[x])];\\n\\nLOM[x_] := Sqrt[E_{ab}[x] + dis[x]];\\nLOm[x_] := Sqrt[(E_{ab}[x] - dis[x])];\\n\\ntheoryplot = Plot[{LOM[x]}, {x, 0, 0.15}, Evaluate[plotSettingsEA], PlotLabel -> "ZnO-like modes", FrameLabel -> {"O content", "Raman shift (cm\(^{-1}\))"}];\\nPlot[{LOM[x], TOB[x]}, {x, 0, 0.1}, Evaluate[plotSettingsEA], PlotLabel -> "ZnSe-like modes", FrameLabel -> {"O content", "Raman shift (cm\(^{-1}\))"}];\\n\\nComparison\\nexpLOZnO = {{0.02, 565.1}, {0.044, 564.67}, {0.06, 560}, {0.074, 559.4}, {0.06, 564.67}};\\nShow[Plot[{LOM[x]}, {x, 0, 0.15}, Evaluate[plotSettingsEA], PlotLabel -> "ZnO-like modes", FrameLabel -> {"Se content", "Raman shift (cm\(^{-1}\))")}], ListPlot[expLOZnO, PlotStyle -> PointSize[0.03], Evaluate[plotSettingsEA]], AspectRatio -> 1];\\nexp269 = {{0.02, 269.1}, {0.044, 264.6}, {0.06, 265}, {0.074, 263.4}};\\nListPlot[exp269, PlotStyle -> PointSize[0.03], Evaluate[plotSettingsEA]];\\nexp220 = {{0.02, 222.3}, {0.06, 216.9}, {0.06, 219.48}, {0.074, 214.8}};\\nListPlot[exp220, PlotStyle -> PointSize[0.03], Evaluate[plotSettingsEA]];
Show[Plot[{LOm[x], TOB[x]}, {x, 0, 0.4}, Evaluate[plotSettingsEA], PlotLabel -> "ZnSe-like modes", FrameLabel -> {"Se content", "Raman shift (cm^{-1})"}, PlotStyle -> {Thick, Thick, Thick}], ListPlot[exp220, PlotStyle -> PointSize[0.03], Evaluate[plotSettingsEA]], PlotRange -> {{0, 0.4}, {210, 230}}, AspectRatio -> 1]

Show[Plot[{LOM[x], LOm[x], TOB[x]}, {x, 0, 0.15}, Evaluate[plotSettingsEA], PlotLabel -> "ZnO-like modes", FrameLabel -> {"O content", "Raman shift (cm^{-1})"}], ListPlot[expLOZnO, PlotStyle -> PointSize[0.01], Evaluate[plotSettingsEA]], ListPlot[exp220, PlotStyle -> PointSize[0.01], Evaluate[plotSettingsEA]], PlotRange -> {{0, 15}, {200, 600}}, AspectRatio -> 1/2]
D.2 Calculation of the Fermi level (Section 4.2.2, 5.2)

(*Iterative calculation of the Fermi level in an n-type material, assuming a parabolic conduction band. Program was originally written by Becca Jones-Albertus for a nonparabolic conduction band prior to 2007, and modified by Marie Mayer in 2010.*)

"Constants";
chg = 4.806 10^-10; (* electron charge, esu or [erg-cm]^0.5 *)
hbar = 1.0546 10^-27; (* erg-s *)
h = 6.626 10^-27; (* erg-s *)
kb = 8.617 10^-5; (* Boltzmann constant, eV/K *)
me = 9.11 10^-28; (* electron rest mass, grams *)
lightspeed = 3 10^10; (* cm/s *)
everg = 1.602 10^-12; (* conversion from eV to erg *)
T = 300; (* temperature, Kelvin *)

"Variables to alter":
Eg = 3.2; (* fundamental band gap, in eV, for fitting *)
mc = .27; (*effective mass in CB*)
ntable = {2.54 10^19, 2.01 10^19, 8.98 10^18, 7.75 10^18, 4.39 10^18, 3.85 10^18, 4.02 10^18, 3.31 10^18};

(* Finding the Fermi energy from n *)
elow = 0; (* low guess for Fermi energy, in eV *)
ainc = 0.50; (* energy difference between high and low guesses, in eV *)
ehigh = elow + ainc; (* high guess, in eV *)

(*+9Solve[z kb T ==hbar^2 k^2/2/me - Eg everg/2+Sqrt[(Eg everg)^2/4+Eg everg hbar^2 k^2/2/me/kb],k];*)(*Commented out so I don't have to wait everytime*)
(* solving the nonparabolic dispersion relation for k *)
kfn[z_] = Sqrt[(Eg everg me)/hbar^2 + (Eg everg me)/(hbar^-1)/(hbar^-mc) Sqrt[(Eg everg hbar^- mc^-e (Eg everg mc+Eg everg mc^-4 kb mc T z)]]; (* nonparabolic wavevector that includes the free electron term *)

nequation[e_, limit_] := Re[1/3/Pi^2 NIntegrate[(Exp[x - e/(kbev T)]/(1 + Exp[x - e/(kbev T)])^2) kfn[x]^3, {x, 0, limit}];
nlow = nequation[elow, 600];
nhigh = nequation[ehigh, 600]; (* back calculations of n based on elow and ehigh *)

(* Finding the Fermi energy from n *)
elow = 0; (* low guess for Fermi energy, in eV *)
ainc = 0.50; (* energy difference between high and low guesses, in eV *)
ehigh = elow + ainc; (* high guess, in eV *)

(*+9Solve[z kb T ==hbar^2 k^2/2/me - Eg everg/2+Sqrt[(Eg everg)^2/4+Eg everg hbar^2 k^2/2/me/kb],k];*)(*Commented out so I don't have to wait everytime*)
(* solving the nonparabolic dispersion relation for k *)
kfn[z_] = Sqrt[(Eg everg me)/hbar^2 + (Eg everg me)/(hbar^-1)/(hbar^-mc) Sqrt[(Eg everg hbar^- mc^-e (Eg everg mc+Eg everg mc^-4 kb mc T z)]]; (* nonparabolic wavevector that includes the free electron term *)

nequation[e_, limit_] := Re[1/3/Pi^2 NIntegrate[(Exp[x - e/(kbev T)]/(1 + Exp[x - e/(kbev T)])^2) kfn[x]^3, {x, 0, limit}];
nlow = nequation[elow, 600];
nhigh = nequation[ehigh, 600]; (* back calculations of n based on elow and ehigh *)

(* Loop to adjust Ef guesses until nlow and nhigh converge to the electron concentration *)
For[dd = 1, dd < 40, dd++,
  nlow = nequation[elow, 400];
  nhigh = nequation[ehigh, 600];
  Eftable = {};
]
nhigh=nexpression[ehigh,400];

/* End loop to find Fermi energy from n */
Ef=(elow+ehigh)/2 + Eg-Eg;
AppendTo[Eftable,Ef];/* Fermi energy referenced to the conduction band edge, in eV */

/* End loop to find Fermi energy from n */

ListPlot[Eftable, PlotRange→{0,10},{0,.2}]

(*Calculate the Fermi wave vector if desired.*)
k[n_]:=\{(par\}{(3\pi^2 n)^{1/3}}
VB[n_, mhole_]:=(\hbar^*k[n])/(2mhole)

kftable=Table[(ntable[[i]]*3*\pi^2)^{1/3}, {i, 1, Length[ntable]}]
Table[(\hbar^2 kftable[[i]]^2/2/me-Eg eVerg/2+Sqrt[(Eg eVerg)^2/4+Eg eVerg^2 \hbar^2 kftable[[i]]^2/2/mc/me])*1/eVerg, {i, 1, Length[ntable]}]
D.3 Theoretical modeling of the absorption (Section 4.5)

(*Written by Marie Mayer to calculate theoretical absorption with the BAC model and compare to data. 5-21-10*)
<<Units`
<<PhysicalConstants`
(*Defining constants*)
Ese=-.9; (*Se defect level above VB*)
SO=0.35; (*spin orbit splitting for Se*)
ESeSO=Ese+SO; (*SeSO defect level above VB*)

me=ElectronMass;
mstar=.5; (*The effective mass is assumed constant for this model—this ought to be the effective hole mass*)
\hbar=PlanckConstantReduced/(Joule Second);
meff=mstar*me;
\hbarovermeff=Convert[\hbar/(Joule Second)/(2me*mstar),
ElectronVolt*(Centimeter)]/(ElectronVolt/(Centimeter))^2; (*For VB*)
\hbarovermeffCB=Convert[\hbar/(Joule Second)/(2me*.27),
ElectronVolt*(Centimeter)]/(ElectronVolt/(Centimeter))^2; (*Include CB effective mass*)
EgZnO=3.2; (*For CB*)

(*Defining energy relationships*)
Energy[k_]=k \hbarovermeff ; (*Valence band*)
Ec[k_]=(EgZnO+k \hbarovermeffCB ); (*Conduction band*)
Eplus[k_, cc_, x_, ESe_]=-1/2*((ESe+Energy[k])+Sqrt[(Energy[k] -ESe)^2+4cc^2 x]) ; (*These minus signs invert the whole picture so that it looks normal but also account for the imaginary roots of the spectral density of states later*)
Eminus[k_, cc_, x_, ESe_]=-1/2*((ESe+Energy[k])^-Sqrt[(Energy[k] -ESe)^2+4cc^2 x]);
EplusSO[k_, cc_, x_, ESeSO_]=-1/2*((ESeSO+EnergySOVB[k])+Sqrt[(EnergySOVB[k] -ESeSO)^2+4cc^2 x]); (*These minus signs invert the whole picture so that it looks normal but also account for the imaginary roots of the spectral density of states later*)
EminusSO[k_, cc_, x_, ESeSO_]=-1/2*((ESeSO+EnergySOVB[k])^-Sqrt[(EnergySOVB[k] -ESeSO)^2+4cc^2 x]);

(*Solve[En==1/2*((ESe+Energy[k])+Sqrt[(Energy[k] -ESe)^2+4cc^2 xx] ), k]*)
Plot[{Eminus[0,cc,.09, Ese],Eplus[0,cc,.09, Ese],EminusSO[0,cc,.09, EseSO],EplusSO[0,cc,.09, EseSO]},{cc,.01,7}, PlotRange->{{0,5},{-1.2,2}}, PlotStyle->{Red, Blue}, AxesLabel->"coupling constant","Band edge at k=0"][*looking at coupling constant effect*]

(*Plot of band structure*)
Plot[{Eplus[k, 1.7,.09,Ese],Eminus[k,1.7,.09, Ese],EplusSO[k,1.7,.09, EseSO],EminusSO[k,1.7,.09, EseSO], Ec[k]},{k,-8*10^7,8*10^7}, AxesLabel->"k", "E[k]", PlotRange->{-8*10^7,8*10^7},{-2,4}],PlotStyle->{Directive[Thick,Red], Directive[Thick,Blue], Directive[Thick,Red, Dashed],Directive[Thick,Blue, Dashed],Directive[Thick,Purple]},LabelStyle->Directive[FontFamily->"Helvetica", 16],Frame->True] (*The bands are all in "normal" directions because of the
signs that I forced onto the Eplus/Eminus formulas. Dashed lines are split off. (*)


\[ \Theta[k_, cc_, x_, ESe_] = \arctan\left(\frac{2cc (x)}{\text{Energy}[k] - ESe}\right); \]

(*Calculate angle to alter use in wave function. Energy[k] is in the original formula as e1 - e2 but here I need that as a function of k because I want to look at the whole band, not just a single k value*) (*by chosen convention, Psi2 is the impurity*)

\[ P_{\text{local minus}}[k_, cc_, x_, ESe_] = \cos\left(\frac{\Theta[k, cc, x, ESe]}{2}\right); \]

\[ P_{\text{delocal minus}}[k_, cc_, x_, ESe_] = \left(-\sin\left(\frac{\Theta[k, cc, x, ESe]}{2}\right)\right); \]

\[ P_{\text{delocal plus}}[k_, cc_, x_, ESe_] = \cos\left(\frac{\Theta[k, cc, x, ESe]}{2}\right); \]

(*ok i think i straightened these out since they were wrong for the thermopower*)

\[ P_{\text{local plus}}[k_, cc_, x_, ESe_] = \sin\left(\frac{\Theta[k, cc, x, ESe]}{2}\right); \]

\[ \text{kvector}[\text{energy2}_2, cc_, x_, ESe_] = \sqrt{\frac{\text{ESe}}{\text{energy2}}} \sqrt{\frac{\text{energy2}}{\text{cc}^2 \text{x}}}; \]

(*Doublechecking that my definition of k is still true by looking at half k vs. E*)

\[ \text{dos plus SO}[\text{energy2}_2, cc_, x_, ESeSO_, del_] = \frac{1}{4\pi} \text{NIntegrate}[\text{Pdelocalplus}[\text{kvector}[\text{h}, cc, x, ESe], cc, x, ESe]*\text{gauss}[\text{h}, \text{Ec}[k] - \text{EplusSO}[k, cc, x, ESeSO], del]*k', \{k, -10^7, 10^7\}]; \]

\[ \text{dos minus SO}[\text{energy2}_2, cc_, x_, ESeSO_, del_] = \frac{1}{4\pi} \text{NIntegrate}[\text{Pdelocalminus}[\text{kvector}[\text{h}, cc, x, ESeSO], cc, x, ESeSO]*\text{gauss}[\text{h}, \text{Ec}[k] - \text{EminusSO}[k, cc, x, ESeSO], del]*k', \{k, -10^7, 10^7\}]; \]

\[ \text{gauss}[\text{x}, \text{center}, \text{del}] = \frac{\text{Exp}[-((\text{x}-\text{center})/\text{del})^2]}{(\text{del} \sqrt{\pi})}; \]

(*not a true gaussian formula*)

\[ \text{dos plus}[\text{h}, cc_, x_, ESe_, del_] = \frac{1}{4\pi} \text{NIntegrate}[\text{Pdelocalplus}[\text{kvector}[\text{h}, cc, x, ESe], cc, x, ESe]*\text{gauss}[\text{h}, \text{Ec}[k] - \text{Eplus}[k, cc, x, ESe], del]*k', \{k, -10^7, 10^7\}]; \]

\[ \text{dos minus}[\text{h}, cc_, x_, ESe_, del_] = \frac{1}{4\pi} \text{NIntegrate}[\text{Pdelocalminus}[\text{kvector}[\text{h}, cc, x, ESe], cc, x, ESe]*\text{gauss}[\text{h}, \text{Ec}[k] - \text{Eminus}[k, cc, x, ESe], del]*k', \{k, -10^7, 10^7\}]; \]
(*Make sure you make Ec a function of x if you want it to change with composition*)

(*looking at different dos*)
alpha[\alpha,cc_,x_, alpha0_, ESe_, ESeSO_, delplus_, delminus_]:=alpha0 (dosplus[\alpha,cc,x,ESe, delplus]+2/3 dosminus[\alpha,cc,x,ESe, delminus]+1/3 dosminusSO[\alpha,cc, x, ESeSO, delminus]) (*Absorption coefficient based on both bands absorbing at all energies greater than the band*)

(*Reads in a data file to fit. It is in the form wavelength, absorption coefficient (already bkgrnd subtracted). This is for a 0.09% sample. This is sample 031210a*)
SetDirectory["C:\Documents and Settings\Marie\My Documents\Berkeley documents\ZnOSi\Absorption\aprildata\4-5-10"];
dataxy1=ReadList["121009aadj.txt",{Number, Number}]; (*wavelength, alpha*)
energy1=Table[1240/dataxy1[[b,1]],{b,1,Length[dataxy1]}];
alphal=Table[dataxy1[[b,1]],{b,1,Length[dataxy1]}];
calculation=Table[{\alpha, Chop[alpha[\alpha,1.2,.046,1,Ese, EseSO, .4, .25]},{\alpha,1.5,6,.1}];
Export["121009aadjFIT.csv",calculation] (*Exports your calculation to make pretty graph later*)
121009aadjFIT.csv
ListPlot[{calculation}, Joined->{True,False}, PlotRange->{[0,6],[0,2 10^3]}]
SetDirectory["C:\Documents and Settings\Marie\My Documents\Berkeley documents\ZnOSi\Figures"];
ListPlot[{Table[{energy1[[i]],alphal[[i]]},{i,1,Length[energy1]}],Table[{calculation[[i,1]], 1.1 10^-7*calculation[[i,2]]},{i,1,Length[calculation]}]}, Joined->{False, True, True}, PlotRange->{[1.5,3.5],[0,2 10^3]},FrameLabel->{"Energy (eV)", "\alpha"}, PlotStyle->[Directive[Blue,PointSize[.01]], Directive[Thick,Red], Directive[Thick,Black, Dashed], Directive[Darker[Green], Directive[Purple]], Frame->True,LabelStyle->Directive[FontFamily->"Helvetica", 20]] (*rafit from another file, 4-28-10-012710fit-2*) (*Scaling paramater changed here*)

Export["121009aabsfitsml.pdf",%,ImageSize->{800,800}]
121009aabsfitsml.pdf

1.5 2.0 2.5 3.0 3.5
0 50000 100000 150000 200000
Energy eV

Export["121009aabsfitsml.pdf",%,ImageSize->{800,800}]
121009aabsfitsml.pdf
D.4 Thermopower calculation (Section 6.3)

(*Written by Marie Mayer, March 2012 to qualitatively investigate the relationship of thermopower to carrier concentration in ZnO1-xSex*)

<<PhysicalConstants`
<<Units` me=ElectronMass; mstar=.2; x=.038; (*Composition of thermopower sample*)

h=PlanckConstantReduced; lightspeed=3*10^8 Meter/Second; (*Mnconc=x*2.2*10^22; *)(*NUmber of Mn impurity states to start*)

kbev=Convert[BoltzmannConstant, ElectronVolt/Kelvin]/ElectronVolt*Kelvin; T=300;

gamma=0.050; (*eV*)
(*Define a general dispersion relationship.*)

hbarovermeff=Convert[h^2/(2me*mstar), ElectronVolt*(Centimeter)^2] (*This is the constant for k as a function of energy*)

constant=Convert[(Sqrt[2]*meff)/(pi*3),1/(ElectronVolt^(3/2)*Centimeter)] (*This is the constant for the density of states*)

Energy[k_]:=k^2 *hbarovermeff
(*Determine Fermi function*)
Fermi[energy_, Efermi_, Temp_]:=1/(Exp[(energy-Efermi)/(kbev Temp)]+1)

DirFermi[energy2_, ef_, Temp_]:=1/(Exp[(Eminus[energy2]-Efermi)/(kbev Temp)]+1)*

(*Here I take the derivative of F(E)*)

D[Fermi[energy2, ef, Temp, energy2] = (11604.5 ef energy2 Temp)/(1+(11604.5 ef energy2 Temp)^2 Temp))

DirFermi[energy2_, ef_, Temp_]:=1/(1+(11604.5 ef energy2 Temp kbev)^2 Temp kbev)

dos[energy_]:=constant*energy^(1/2)

Plot[dos[r],{r,-1,1}]

p[fermien_]:=Re[NIntegrate[Fermi[energy2, fermien, T]*dos[energy2],{energy2,0,2.59}])

S[ef_, r_, temp_]:=NIntegrate[(energy2-ef)*dos[energy2]*DirFermi[energy2, ef, temp]^2, {energy2, 0, 2.59}, PrecisionGoal=8]/(temp*NIntegrate[(dos[energy2])*DirFermi[energy2, ef, temp]^2, {energy2, 0,2.59}, PrecisionGoal=8])

Plot[S[ef, -2, 300]*10^7,{ef,-.2,.6}]

offset=0;
ListLogLinearPlot[Table[{p[ef], S[ef, 1.5, T]*10^6}, {ef, -.25, 1, .05}], {6 10^13, 60}, {2.3 10^14, 41}, {5.7 10^15, 51}], Joined -> {True, False, False, False}, FrameLabel -> {"n (cm^3)", "RT Thermopower (\mu V/K)"}, PlotMarkers -> {"", "\[FilledCircle]"}, PlotStyle -> {Directive[Red, Thick], Directive[Black, PointSize[.01]], Directive[Black, PointSize[.015]], Directive[Red, PointSize[.01]]}, LabelStyle -> Directive[FontFamily -> "Helvetica", 20], GridLines -> {{10^17, 10^18, 10^19, 10^20}, {60, 155, 413, 340}}, GridLinesStyle -> Directive[Gray, Thin, Dashed], Frame -> True]

(*r=3/2 is for ionized impurities*)
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B. Ellis, personal communcation with M. A. Mayer (Hayward, CA, 2012).
T. F. Jaramillo, personal communication with M. Mayer (Stanford, CA, 2012).
Bryan Ellis, Marie Mayer, Gary Shambat, Tomas Sarmiento, Eugene E. Haller, James S. Harris, and J. Vuckovic, Nature Photonics 5, 297-300 (2011).
Further Reading

The following publications are on material related to the work described in this dissertation.


17. Marie Mayer, Kin Man Yu, Eugene Haller and Wladek Walukiewicz, "Tuning structural, electrical and optical properties of oxide alloys: ZnO$_{1-x}$Se$_x$" accepted to Journal of Applied Physics

16. Gary Shambat, Bryan Ellis, Jan Petykiewicz, Marie A. Mayer, Arka Majumdar, Tomas Sarmiento, James Harris, Eugene E. Haller, and Jelena Vuckovic, “Electrically driven photonic crystal nanocavity devices” in press


