(In, Al) co-doped zinc oxide as a novel material system for quantum-well multilayer thermoelectrics

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(In, Al) co-doped ZnO as a Novel Material System for Quantum-Well Multilayer Thermoelectrics

by

Sean Teehan

A Dissertation
Submitted to the University at Albany, State University of New York
In Partial Fulfillment of The Requirements for the Degree of Doctor of Philosophy

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I dedicate this work to my fiancé Randi Lee, my son Jackson Riley, and my parents. Without their continuous support, love and encouragement, I could not achieve this.
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Abstract

Waste heat recovery from low efficiency industrial processes requires high performance thermoelectric materials to meet challenging requirements. The efficiency such a device is quantified by the dimensionless figure of merit $ZT=S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature and $\kappa$ is the thermal conductivity. For practical applications these devices are only cost-effective if the $ZT$ is higher than 2.

Theoretically it has been proven that by engineering nanostructures with lower dimensionality one can significantly increase $ZT$. A superlattice, or a system of 2-dimensional multilayer quantum wells has previously shown the potential to be used for thermoelectric structures. However, the use of conventional materials within these structures has only allowed this at low temperatures and has utilized cross-plane transport. This study focuses on both high temperature range operation and the in-plane transport properties of such structures, which benefit from both quantum confinement and an enhancement in density of states near $E_F$. The n-type structures are fabricated by alternately sputtering barrier and well materials of Al-doped ZnO (AZO) and indium co-doped AZO, respectively. Samples investigated consist of 50 periods with targeted layer thicknesses of 10nm, which results in sufficient sampling material as well as quantum well effects. The indium doping level within the quantum well was controlled by varying the target power, and ultimately results in a 3x improvement in power factor ($S^2\sigma$) over the parent bulk materials. The film characterization was
determined by X-ray reflectometry, transmission electron microscopy, X-ray
diffraction, auger electron spectroscopy, as well as other relevant techniques.

In addition, process optimization was performed on material parameters such
as layer thickness, interface roughness, and band-gap offset which all play a major
role in determining the thermoelectric performance. Within this study we
theoretically and experimentally have developed correlations between each of
these material parameters and its overall effect on thermoelectric performance.
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Chapter 1

Introduction

Within the last decade the concern for new alternative energy sources has become one of the biggest concerns of both individuals and governments alike for two simple reasons. The first is that none of our major current energy sources are renewable, and the second is that these energy sources pollute the environment.

1.1. Research Motivation

1.1.1. Energy Crisis

Crude oil reserves are a limited energy source which has taken millions of years to develop from trapped organics at certain pressures and temperatures below the earth’s surface. Over the past 50 years, international energy consumption has grown at increasing rates, stimulated by cheap fossil fuels and increased rates of industrialization in North America, Europe and Japan.\(^1\) The total primary energy demand has increased an average of 2\% annually since 1970. In 2007, BP’s Statistical Review of World Energy was published, and stated that with current demand the world has enough reserves to provide us with 40 years of energy generation. However, the prediction for the next 50 years introduces a more complex addition which includes the rapid growth of energy consumption in developing countries such as India and China, which account for 1/3 of the world’s population.
In Fig. 1 it is observed how there exists an exponentially increasing demand for oil due to the industrial growth in developing countries, such as China and India, which account for a large percentage of the world population. In this chart MTOE, is millions of tons of oil equivalent. In addition, the supply is forecasted to peak in around 2015 where thereafter will be a deficiency of oil available for the consumer. On a per capita basis, the amount of oil used has been approximately level, at about 4.6 barrels per person, between 1982 and 2006. Based on this scenario, the forecast is that the amount of oil available per person is will decrease from approximately 2.5 to 2.0 barrels per person, by 2030.

As a result if we do not eliminate the global oil dependency the result will be an international catastrophe with rising food prices, recession, and ultimately an
economic depression. This is the reason for the increased interest in harvesting of renewable energies.

Energy harvesting is the process by which energy is captured from the environment and stored in a form which can be put to use, and renewable energies are energies derived from resources that are regenerative and cannot be depleted. These two techniques must be combined in order to overcome the problem of renewable sources being intermittent in nature. Typical renewable energies are generated from natural resources such as sunlight, wind, rain, tides, and geothermal heat. Available storage options for renewable energy sources include batteries, hydrogen fuel cells, thermal mass, and pumped-storage hydro systems. In the REN21 Renewables 2011 Global Status Report, it was published that despite continuing economic recession and incentive cuts, in 2010 the renewable energy market supplied an estimate 16% of the global final energy consumption. It is now estimated that the renewable capacity now comprises about a quarter of the total global power generating capacity. The initial costs can be high, but can are recoverable over the life of the system.

1.1.2. Environmental Impact

It is known that there are many harmful outcomes which result from the process of converting fossil fuels to energy. Some of these include air pollution, water pollution, and accumulation of solid waste. For this reason there has been an increased interest in the search for a sustainable energy source, which by
definition is a source of energy that will meet the needs of the present without compromising the ability of future generations to meet their needs.

The main environmental issue currently facing today’s society is the increased levels of greenhouse gases and the effect is has on global warming. These gases (carbon dioxide, methane, nitrous oxide and ozone) have a "greenhouse effect" by which they let in light, but keep heat from escaping, similar to the walls in a greenhouse.

Fig. 2: Total carbon emissions from various sources of energy processes.

As we can see here in Fig. 2 the total carbon emissions from fossil fuels has increased exponentially within the last century. This increase coincides with the increasing production and usage of fossil fuels.
Along with global warming and the “greenhouse effect”, this past year one of larger environmental disasters occurred with BP’s gulf coast oil spill. The spill stemmed from a sea-floor oil gusher that resulted from the April 20, 2010 Deepwater Horizon drilling rig explosion. The explosion killed 11 platform workers and injured 17 others. On July 15, the leak was stopped by capping the gushing wellhead after releasing about 4.9 million barrels (780×10³ m³) of crude oil. As a result, the spill is causing extensive damage to marine and wildlife habitats as well as the Gulf’s fishing and tourism industries. It is theorized that the immediate need for drilling has led to limited time for review and development of the plans which resulted in poor designs and regulations.

The United States has a renewable energy resource that can reduce the carbon emissions that threatens our planet, the dependence on the foreign oil that threatens national security, and the energy costs that threaten wallets. It does not pollute like coal and petroleum, and does not depend on the weather like solar and wind power. In addition, it does not raise concern like nuclear plants, and it does not take a decade to build. The miracle source is known as increasing energy efficiency, which is a relatively easy concept; wasting less energy.

1.1.3. Energy Inefficiency

Most of today’s energy producing processes has 60 to 70% energy efficiency, resulting in an energy loss of 30-40% to waste heat. The transportation industry accounts for the largest amount of energy usage and greenhouse gas emissions. As we can see from the Fig. 3, which is the energy flow diagram for a typical
automobile engine which only receives roughly 30\% of the total energy produced through gasoline combustion. The remaining 70\% of the energy is lost to exhaust gases, coolant, and friction.

Currently, the consumer demands more electrical power on the engine due to enhanced performance, emission controls, and comforts such as on-star, navigation, telematics, etc which has led to even more decreased levels of fuel efficiency. In addition to low fuel efficiency we have also seen an international call for reduced emissions. These requirements are beyond the capabilities of the current generators and require supplemental electrical generation.

An average of 383 million gallons of gasoline is used per day in the U.S. This corresponds to daily consumer spending of nearly $1.4 billion not counting the environmental cost of this consumption rate (U.S. Energy Administration Corporation, 2011). Assuming a decrease of 10\%, the daily savings of 38 million gallons of gasoline could be achieved or $100 million per day in consumer spending. A reduction in gasoline consumption of this magnitude would also remove 70 million kg of CO$_2$ from being emitted into the atmosphere per day (Office of Transportation, 2005).
Fig. 3: Energy usage diagram for a typical internal combustion automobile engine.

In addition to the transportation sector, large scale waste heat recovery of industrial and power generation processes is also an area of interest for waste heat recovery due to process inefficiencies. This sector would benefit from both lower energy costs as well as a reduction in fossil fuel pollution. Fig. 4 shows the breakdown of a variety of industrial processes and the percentage of waste heat that they produce. For near term applications in the US alone, between 0.9 and 2.8 TWh of electricity could be regenerated.
Modern high-performance chips operate at multi gigahertz frequency, such as microprocessors, which consume larger amounts of power as indicated in Fig. 5. This rate of increase has been following Moore’s law since the mid 1960’s. The power density is increasing due to an increase in operation frequency and the leakage power is also increasing due to the technology scaling and increasing operation temperature. Like other energy flows a substantial part of the power consumed is also translated into heat. This heat creates a large temperature gradient between the die surface and environment and is known as the hot-spot. This can result in chip failure if not designed with appropriate heat removal mechanisms.

Fig. 4: Chart of estimated waste heat recovery for major industrial processes.
1.2. Introduction to Thermoelectrics

The term thermoelectricity refers to the phenomena in which a temperature gradient creates an electrical potential, or an electrical potential creates a temperature gradient. The three main types of thermoelectric effects are known as the Peltier, Seebeck, and Thompson effects.

The Peltier effect is the principal effect concerned with thermoelectric refrigeration or thermoelectric cooling (TEC). This effect is interfacial and transports heat between two different conductors, from one junction to another, when an electric current passes through the closed loop circuit, as shown in Fig. 6. The Peltier effect is linear with respect to current, which is in contrast to irreversible Joule heat, which is quadratic with respect to current. The rate at
which heat is absorbed is proportional to the current and depends on the nature of the two materials comprising the junction. Ultimately, the Peltier effect is where an electric current induces a temperature gradient.

The Seebeck effect is used for thermoelectric electrical generation (TEG) and occurs when two dissimilar conductors are joined at two points that are maintained at different temperatures. An electromotive force will develop over the closed loop that can be measured by inserting a voltmeter into the loop; it is also known as the thermocouple voltage.\(^3\) The Seebeck effect for materials A and B, is interfacial and arises when charge carriers in a conductor are exposed to a temperature gradient within the conductor. The hotter electrons generated from the extra external heat will then diffuse to the cold end thru the concentration gradient. This in turn produces an electric flow of current that lasts as long as there is a temperature difference along the conductor. Fig. 6 depicts both the Peltier and Seebeck effects as functional flow diagrams.

![Fig. 6: Functional diagrams for the Peltier and Seebeck effects.](image-url)
Fig. 7: Schematic and image of a thermoelectric module consisting of an array of p-n junction pairs.

Also noteworthy is the Thomson effect, which is a bulk effect that transports heat within a current carrying material at one temperature to the same material at a different temperature (i.e. in a material with a temperature gradient). Phonons and electrons act as the two modes of heat transfer and this effect can be thought of as the evolution/absorption of heat in a conducting material whenever a current traverses that material with a temperature gradient, thereby transporting electrons of one temperature to a zone with electrons at another temperature. Thomson heat, just like Peltier heat, is reversible and is in addition to any irreversible Joule heat.

A conventional thermoelectric module is typically comprised of an array of p- and n-type semiconductor material pairs that are oriented in series electrically, but in parallel thermally, as shown in Fig. 7. A high conductivity metal such as copper is typically used to electrically connect the semiconductor pillars and complete the electric circuit. This circuit is usually sandwiched between two
ceramic substrates that are electrically insulated but thermally conductive, such as AlN.

The use of thermoelectric modules offers solutions to various markets and in some cases maybe the ONLY solution. Some of the more significant advantages of thermoelectric modules include:

- **No Moving Parts**: Works without any moving parts so are virtually maintenance free.

- **Small Size & Weight**: In comparison to other energy sources, TE devices are much smaller can be easily meet strict application requirements.

- **High Reliability**: Due to the solid state construction of these devices, the lifetime is usually > 200,000 hours of operation.

- **Quit Operation**: Unlike most mechanical energy systems, TE devices are acoustically silent.

- **Environmental Stability**: TE’s can be used in extreme environments, such as zero gravity, for aerospace applications.

- **Environmental Friendly**: Do not use or generate gases of any kind.

In addition to the above advantages, a TE device is also capable of combining its usage with that of other energy sources, such as fossil, nuclear, and solar.

1.3. Driving Forces and Currents

As previously discussed, the thermal and electrical currents are coupled in conducting solids by the Seebeck effect. The Seebeck effect though is only one example of the more general phenomena of physical driving forces coupling with
multiple currents, as described by the thermodynamics of irreversible processes. This section follows the derivations introduced by Cadoff and Miller.\textsuperscript{4} In general, the driving forces $X_k$ such as pressure, concentration, temperature and electrical and magnetic potential gradients produce currents such as diffusion, thermal, spin, and electrical currents $J_i$ via equation (1), where the $L_{ik}$ are kinetic transport coefficients;

$$J_i = \sum_k L_{ik} X_k$$  \hspace{1cm} (1)

In the specific case of TE materials, there are two such driving forces: a temperature gradient and an electrical potential, both of which drive the thermal and electrical currents. In order to make the appropriate choices of forces and currents we begin with the following observation: at its thermodynamic equilibrium, systems total entropy is a maximum with respect to the system properties, i.e., temperature, electrical charge, etc. Then by denoting $y_i$ when the system is at equilibrium, and $y'_i$ when it is not, the deviation of these non-equilibrium values is $Y_i = y'_i - y_i$. By definition then, $Y_i$ is zero at equilibrium and the entropy $S$ is also a maximum at equilibrium. Therefore the change in entropy from equilibrium is expressed here; where $g_{ik}$ are the specific Gibbs functions.

$$\Delta S = -\frac{1}{2} \sum_{ik} g_{ik} Y_i Y_k$$  \hspace{1cm} (2)
With the currents of our system being simply the time derivatives of the respective properties:

\[ J_i = \dot{Y}_i \]  

(3)

The driving forces are then calculated in the following manner:

\[ \chi_i = \frac{\partial (\Delta s)}{\partial Y_i} \]  

(4)

\[ \chi_i = -\sum_k g_{ik} Y_k \]  

(5)

And then by multiplying equations (3) and (5), we get;

\[ \sum_i J_i \chi_i = \frac{d(\Delta s)}{dt} \]  

(6)

Therefore, in order to discover the driving forces and currents of a given system, one can write an expression for the change of the systems entropy with time in terms of the systems properties. In regards to thermoelectric systems, there are three points at which entropy is produced: the hot and cold ends at the two junctions of the materials, and the resistive load. We denote the cold end temperature \( T_c \) by “A”, hot end temperature \( T_c + \Delta T \) by “B”, and the resistive load by “C”. Thus we have;

\[ \Delta s = \Delta s_A + \Delta s_B + \Delta s_C \]  

(7)
The Gibbs equation then tells us that for given entropy ($\Delta s$) at temperature $T$ with a voltage $\Delta V$ and charge $q$, there is an associated energy $\Delta U$;

$$\Delta U = T\Delta S - q\Delta V \quad (8)$$

Thus for our thermoelectric system, with $T=T_c$ we may rewrite Eq. (7) as:

$$\Delta S = -\frac{\Delta U}{T} + \frac{\Delta U}{T + \Delta T} - \frac{q\Delta V}{T} \quad (9)$$

The resistive load possesses a voltage $\Delta V$ by virtue of the Seebeck effect, and we assume that it is at the same temperature, $T_c$. The reason for the negative sign in the term on the right is due to the fact that energy is being lost by the cold end, whereas energy is entering the hot end. Taking the derivative of Eq. (9) with respect to time, and assuming the temperature different $\Delta T$ and voltage $\Delta V$ are maintained across the system, we have;

$$\frac{d(\Delta S)}{dt} = \frac{dU}{dt} \left( \frac{1}{T} \right) + \frac{dU}{dt} \left( \frac{1}{T + \Delta T} \right) - \frac{dq}{dt} \left( \frac{\Delta V}{T} \right) \quad (10)$$

Then by multiplying the first two terms on the right hand side by $(T+\Delta T)/(T+\Delta T)$ and $T/T$, and simplifying, we obtain;
\[
\frac{d(\Delta s)}{dt} = -\frac{dU}{dt} \left( \frac{\Delta T}{T^2} \right) - \frac{dq}{dt} \left( \frac{\Delta V}{T} \right)
\]  

(11)

Now using this equation we can easily identify the driving forces and currents in the thermoelectric system as follows;

\[
\chi_q = -\frac{\Delta T}{T^2}
\]  

(12)

\[
\chi_2 = -\frac{\Delta V}{T}
\]  

(13)

\[
J_1 = \frac{dU}{dt}
\]  

(14)

\[
J_2 = \frac{dq}{dt}
\]  

(15)

Where the “1” subscript refers to the thermal properties and the “2” subscript refers to the electrical properties. Now Eq. (1) can be written as;

\[
\begin{pmatrix}
\frac{dU}{dt} \\
\frac{dq}{dt}
\end{pmatrix} = \begin{pmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{pmatrix} \begin{pmatrix}
\frac{\Delta T}{T^2} \\
-\frac{\Delta V}{T}
\end{pmatrix}
\]  

(16)

Here the two diagonal elements $L_{11}$ and $L_{22}$ of the matrix $L$ are related to the thermal and electrical conductivities, respectively, and the off-diagonal elements are related to the cross-coupling of heat and electricity.
1.4. Device and Material Efficiency

The efficiency $\eta$ of a device that generates an electrical power $P$ via an input of energy $Q$ is defined:

$$\eta = \frac{P}{Q}$$

(17)

In order to calculate the efficiency of a given thermoelectric device, we must then express $P$ and $Q$ in terms of the relevant device properties. The power is simply related to the Seebeck coefficient ($S$) and temperature gradient ($\Delta T$), generated across a resistive load of resistance $R$:

$$P = \frac{(S\Delta T)^2}{4R}$$

(18)

The factor of $\frac{1}{4}$ is due to the fact that for best performance, precisely one half of the Seebeck voltage is distributed across the resistive load, and the other half is distributed across the rest of the device, which has the same resistance $R$ as the load. To then calculate $Q$ in terms of meaningful quantities, we must perform an energy balance at the hot end of the TE device. First, there is the heat flow $Q_F$ from the hot to the cold end, which can be calculated by Fourier’s Law of Heat Conduction. Second, there is Joule heat $Q_J$, generated by the finite resistances of the two conductors, half of which flows across the load. Third and final, there is the heat $Q_P$ generated by the Peltier effect due to the current generated by the Seebeck effect. On the other hand the complementary is the Seebeck effect,
which is simply the conversion of an electrical current to a heat flux within a material as explained earlier. These three terms are expressed as follows, wherein $A_n$ and $A_p$, $l_n$ and $l_p$, $\rho_n$ and $\rho_p$, $\kappa_n$ and $\kappa_p$ are the cross-sectional areas, lengths, electrical resistivities, and thermal conductivities of the n and p-type conductors, respectively:

$$Q_F = \left( \kappa_n \frac{A_n}{l_n} + \kappa_p \frac{A_p}{l_p} \right) \Delta T$$  \hspace{1cm} (19)

$$Q_J = \frac{1}{2} I^2 \left( \rho_n \frac{l_n}{A_n} + \rho_p \frac{l_p}{A_p} \right)$$  \hspace{1cm} (20)

$$Q_p = SIT_h$$  \hspace{1cm} (21)

Thus, the total heat input $Q$ at the hot end of the TE device is:

$$Q = Q_F - Q_J + Q_p$$  \hspace{1cm} (22)

$$Q = \left( \kappa_n \frac{A_n}{l_n} + \kappa_p \frac{A_p}{l_p} \right) \Delta T - \frac{1}{2} I^2 \left( \rho_n \frac{l_n}{A_n} + \rho_p \frac{l_p}{A_p} \right) + SIT_h$$  \hspace{1cm} (23)

The current $I$, is simply the Seebeck voltage ($S\Delta T$) divided by the total resistance $2R$ of the device, which follows Ohm’s law.

$$I = \frac{S\Delta T}{2R}$$  \hspace{1cm} (24)
Now, expressing $\eta$ in terms of $P$ and $Q$ via equations (18 and 23), we arrive at Eq. (26) for the efficiency of a thermoelectric device with a geometry expressed in Eq. (27).

$$\eta = \frac{\Delta T}{2T_h - \frac{\Delta T}{2} + 4\left(\left(\kappa_n \rho_n\right)^{1/2} + \left(\kappa_p \rho_p\right)^{1/2}\right)^2}$$

$$\frac{A_n l_p}{A_p l_n} = \frac{\rho_n \kappa_p}{\rho_p \kappa_n}$$

By separating out all of the material dependent properties into one dimensionless figure variable $Z$ we get;

$$\eta = \frac{\Delta T}{2T_h - \frac{\Delta T}{2} + 4\frac{Z}{S^2}}$$

$$Z = \frac{S^2}{\left(\left(\kappa_n \rho_n\right)^{1/2} + \left(\kappa_p \rho_p\right)^{1/2}\right)^2}$$

This value $Z$ is known as the Figure of Merit for TE materials and it is the measurement of the material efficiency. By further simplifying $Z$ for the individual material components of both the n and p type materials at a certain temperature we get;
\[ ZT = \frac{S^2 T}{\kappa \rho} \]  

(30)

1.5. Current Limitations

As we can see from Eq. (30), for a material to have a high \( ZT \), one requires a high thermoelectric power factor \((S^2/\rho)\), and a low thermal conductivity. However, it is difficult to improve \( ZT \) in actual systems for the following reasons.

First, the main limiting factor of bulk materials is the Wiedemann-Franz Law.\(^5\) This law states that \((\rho \kappa)\), the electrical resistivity times the thermal conductivity is proportionality constant. This inverse relationship means that as either property is increased the other will directly decrease. The second reason is the direct relationship between \( S \) and \( \rho \), where, an increase in the Seebeck coefficient will simultaneously lead to an increase in the electrical resistivity. These relationships have been theoretically predicted and confirmed for most bulk materials, as seen in Fig. 8. The best bulk TE materials are heavily doped semiconductors. Insulators have poor electrical conductivity and metals have low Seebeck coefficients. However, in semiconductors, the thermal conductivity has contributions from both electrons \((\kappa_e)\) and phonons \((\kappa_p)\).
Conventional TE materials that have been developed until the 1990s have been selected by these previous guiding principals and are typically intermetallic compounds and alloys with covalent bonding characteristics (for higher mobility), and that consist of heavy elements (for lowering $\kappa_p$).

Fig. 9 is a trend chart showing various thermoelectric materials systems and their corresponding operating temperature ranges. Also included in this chart are the required temperature ranges for many of the inefficient energy conversion systems used today.

For near-room temperature applications, such as refrigeration and waste heat recovery up to 500K, Bi$_2$Te$_3$ alloys have proved to have the highest figure of merit for both n- and p-type systems. Bi$_2$Te$_3$ was first investigated as a material of great TE promise in the 1950s. It was quickly realized that alloys Sb$_2$Te$_3$ and Bi$_2$Se$_3$ allowed for the fine tuning of the carrier concentration alongside a
reduction in lattice thermal conductivity. The electronic transport properties and detailed defect chemistry of these alloys are now well understood thanks to extensive studies of single and polycrystalline materials. The peak $ZT$ values for these materials range from 0.8 to 1.1.

For mid-temperature power generation (500-900K), materials based on group-IV tellurides are typically used, such as PbTe, GeTe or SnTe. The peak $ZT$ in optimized n-type materials is about 0.8. Again, a tuning of the carrier concentration alters the temperature where $ZT$ peaks.9,10

Successful, high-temperature (>900K) thermoelectric generators have typically used silicon-germanium alloys for both n- and p-type legs. The $ZT$ of these materials is fairly low, especially for the p-type material, because of the relatively high lattice thermal conductivity of the diamond structure.11,12

The best performing material previously mentioned achieves a $ZT \approx 1$ with a heat source at 525K and a heat sink at room temperature, which corresponds to only 10% efficiency of heat to energy conversion. In addition, these materials are incapable of wide-scale commercialization because of further shortcomings such as poor durability at high temperature in air, low abundance and high cost of the comprising elements, and high toxicity.
Fig 9: Waste heat and operating temperature ranges for various TE materials.
Chapter 2

A Nanoengineering Approach to Thermoelectrics

This chapter will discuss both the limitations and theoretical mechanisms for improving material efficiency of thermoelectric materials. In addition, the latter sections will discuss state-of-the-art results from recently published studies on TE material performance that has been shared among the international thermoelectric communities.

2.1. Low Dimensionality

Thermoelectric technology is entirely solid-state, and therefore the TE systems are quite simple compared to conventional mechanical systems; however, this simplicity comes at a price. This price is the complexity of the energy conversion problem being shifted to the solid-state physics aspects of the materials themselves. Energy transport in nanostructures differs significantly from macrostructures because of classical and quantum size effects on energy carriers.

The use of lower dimensional systems for thermoelectric applications is of interest because they can provide: (1) an opportunity to reduce the phonon thermal conductivity (2) a method for enhancing the Seebeck coefficient, by altering the electron density of states, and (3) an opportunity for increasing carrier
mobility when quantum confinement conditions are satisfied. We will now discuss each of these in further detail.

2.1.1. Thermal Transport

It was recognized in the 1990’s that low-dimensional materials, such as quantum wells, superlattices, quantum wires, and quantum dots offer new ways to manipulate the electron and phonon properties of a given material. In the regime where quantum effects are dominant, the energy spectra of electrons and phonons can be controlled via altering the size of the structures, which leads to new ways to increase $ZT$. In this regime, the low-dimensional structures can be considered new materials, despite the fact they consist of the same atomic structures as their parent materials. Although the parent materials are typically simple materials with well-known properties, the low-dimensional structures are amenable to a certain degree of analysis, prediction, and optimization. Even when quantum size effects are not dominant, it is still possible to utilize classical size effects to alter the material properties. This brings us to our first advancement; the exploitation of interface and boundaries to reduce thermal conductivity without too high a loss in mobility. This arises because the phonon mean free path $l_p$ is limited by $d$, and the electron mean free path $l_e$ is less so, where $d$ is the dimensions of the structure. Obviously this requires that $l_p \approx d \geq l_e$ holds.

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thermal conductivity (2) a method for enhancing the Seebeck coefficient, by altering the electron density of states, and (3) an opportunity for increasing carrier mobility when quantum confinement conditions are satisfied. We will now discuss each of these in further detail.

Our first method of improvement utilizes classical size effects and works even when the quantum size effects are not dominant. The mechanism behind reducing the thermal conductivity without too high a loss in mobility is the exploitation of interface and boundaries. This arises because the phonon mean free path $l_p$ is limited by $d$, and the electron mean free path $l_e$ is less so, where $d$ is the dimensions of the structure. Obviously for this case $l_p \approx d \geq l_e$ holds true.

2.1.2. Electrical Transport

The Seebeck coefficient in low-dimensional systems at a given carrier concentration is expected to be enhanced over that of a 3D system, for two reasons: size-quantization effects and electron energy filtering. To explain this we refer to the Mott relation for the Seebeck coefficient. We can associate an electrical conductivity $\sigma(E)$ to the electrons that fill the energy levels between $E$ and $E+dE$, irrespective of the mechanism that limits $\sigma(E)$. The total electrical conductivity is the integral of this over the entire energy range, moderated by the Fermi distribution function $f_o(E)$. By integration of parts, the total conductivity is then

$$\sigma = \int_0^\infty \sigma(E) \left( -\frac{df_o(E)}{dE} \right) dE.$$ (31)
Cutler and Mott then derived the Seebeck coefficient in this formalism to be the differential form of the Mott relation

$$S = \frac{k_B}{q} \frac{1}{\sigma} \int_0^\infty \sigma(E) \left( \frac{E - E_{F}}{k_B T} \right) \left( \frac{\partial f_0(E)}{\partial E} \right) dE. \quad (32)$$

In systems in which the Fermi statistics are degenerate, such as metals and degenerately doped semiconductors, Eq. (32) simplifies to the better known form of the Mott relation

$$S = \frac{\pi^2}{3} \frac{k_B}{q} k_B T \left( \frac{d[\ln(\sigma(E))]}{dE} \right) \bigg|_{E=E_F} \quad (33)$$

This equation holds when conduction is thru the band states, localized states, hopping and/or other mechanisms. In the particular case of band conduction, the differential conductivity can be expressed by the product of the density of carriers $n(E)$, which is a function of the density of states $g(E)$, and their differential mobility $\mu(E)$ or relaxation time $\tau(E)$:

$$\sigma(E) = n(E)e\mu(E) = g(E)f_0(E)e^2 \frac{\tau(E)}{m^*}. \quad (34)$$

Where $e$ is the free electron charge, and $m^*$ is the effective mass. Using equations (32 or 33) it is evident that any mechanism that enhances the energy-
dependence of the conductivity will therefore enhance the Seebeck coefficient. Therefore, there are two ways to enhance $\sigma(E)/dE$, namely by enhancing either $dn(E)/dE$ or $d\mu(E)/dE$.

Increasing $dn(E)/dE$ can be achieved by enhancing the dependence of the density of states on energy, $dg(E)/dE$. The size-quantization effect does this for us in low-dimensional structures. Shown here is a plot of the energy dependence of the density of states for 3, 2, 1, and 0D structures. These results come from a dispersion relation $E(k)$, in which electrons have a momentum $k$ along 3, 2, or 1 axes of the crystal in 3, 2, or 1D, with a set of fixed quantum numbers (1, 2, 3…) along directions in which the motion is constrained. It is evident that the sharp maxima in $g(E)$ for quantum wires will result in a strong increase in the Seebeck coefficient via Eqs. (32) or (33). This theory was first discussed by Hicks and Dresselhaus and is summarized in Fig. 10. Both quantitative calculations and experimental results of this effect have since been verified.

![Energy dependence of the electronic density of states in 3, 2, 1, and 0-dimensional structures.](image)

Fig. 10: Energy dependence of the electronic density of states in 3, 2, 1, and 0-dimensional structures.
An increase in the energy-dependence of the mobility $d\mu(E)/dE$ can result from increasing the scattering times energy dependence, $d\tau(E)/dE$, by preferentially scattering electrons depending on their energy: this is known as electron energy filtering. In conventional semiconductors with parabolic bands, it is customary to ascribe a power-law dependence for the relation time;

$$\tau = \tau_0 E^{\frac{\tau-1}{2}}$$

(34)

The origin of this formula is as follows; the relaxation time is the inverse of the scattering probability, which is in turn determined by two factors: a) the density of initial and final states, which for 3D solids is the factor $E^{1/2}$, and b) the probability matrix element which, very schematically, gives rise to the factor $E^\tau$, where, $\tau$ is the scattering exponent approximated for various scattering mechanisms as: $\tau=0$ for scattering of electrons on acoustic phonons, $\tau=1/2$ for scattering of electrons on neutral impurities, and $\tau=2$ for scattering of electrons on ionized impurities. It has been recognized since early days of semiconductor thermoelectric technology that an increase in $\tau$ would be beneficial, and obviously therefore ionized impurity scattering would influence that. Unfortunately, many counter-doping of alloyed bulk materials has resulted in a decrease in mobility as well.
2.1.3. Figure of Merit

By using a semi-classical theory based on the Boltzmann equations, Hicks et al. predicted that a 2D semiconductor will have at least a three-fold higher $ZT$ than one with 3D behavior.\textsuperscript{15} In a follow-up paper they calculated a further improvement for a 1D material, as shown in Fig. 11.

![Diagram](image.png)

Fig. 11: Theoretical dependence of $ZT$ for 2D (quantum wells) and 1D (nanowires) on structural dimensions.
2.2. State of the Art Materials

As was just discussed, there is currently a renewed interest in thermoelectric materials which has been motivated by the realization that complexity at multiple length scales can lead to new mechanisms for high $ZT$. We will now discuss some of the most promising state-of-the-art materials currently begin investigated. These material systems can be broken down into two groups, the first being complex alloying in order to obtain structures with nanoscale effects such as “rattling atoms” or disordering, and the second is fabricating nanostructures in order to induce quantization size effects as was just discussed, i.e. quantum wells, nanowires, etc..

2.2.1. Complex Alloying

The potential to reduce thermal conductivity through disorder within the unit cell is particularly large in structures containing void spaces. Skutterudites, such as CoSb$_3$, contain corner-sharing CoSb$_6$ octahedra. These tilted octahedral create voice spaces that may be filled with rattling atoms. For skutterudites containing elements with low electronegativity differences such as CoSb$_3$ and IrSb$_3$, there is a high degree of covalent bonding, which enables high carrier mobility and therefore good electron-crystal properties. However, this in theory also leads to high lattice thermal conductivities, and thus the challenge is to reduce the lattice thermal conductivity. By doping CoSb$_3$ within the void area both increases the carrier concentrations and reduces thermal conductivity through electron-phonon
interactions. A clear correlation has been found between size and vibrational motion of the specific filling atom to the decrease in thermal conductivity.\textsuperscript{16}

One good characteristic of nearly all thermoelectric materials is valence balance, which is the charge balance of the chemical valences of all the atoms. This is required whether the bonding is ionic or covalent. Valence balance enables the separation of electron energy bands needed to form a bandgap. Complex Zintl compounds have recently emerged as a new class of thermoelectrics because they can form quite complex crystal structures.\textsuperscript{17} A Zintl compound contains a valence-balanced combination of both ionically and covalently bonded atoms. The mostly ionic cations donate electrons to the covalently bound anionic species. The covalent bonding allows higher mobility of the charge-carriers than that which could be found in purely ionic materials. The combination of the bonding types leads to complex structures with the possibility of multiple structural units within the same structure. One example is Yb\textsubscript{14}MnSb\textsubscript{11}, which contains \([\text{MnSb}_4]^{0}\) tetrahedral, polyatomic \([\text{Sb}_3]^{7-}\) anions, as well as isolated \(\text{Sb}^{3+}\) anions and \(\text{Yb}^{2+}\) cations. This structural complexity enables extremely low lattice thermal conductivity, and in combination with large Seebeck coefficient and high electrical conductivity results in a \(ZT\) of \(\sim 1.0\) at 900°C.\textsuperscript{18} This is nearly twice that of p-type SiGe which has been used as the choice material for NASA spacecraft generators.

Just earlier this year in 2012, a Rensselaer Polytechnic Institute research group led by Prof. Ganapati Ramanath developed a new wet-chemical method for fabricating sulphur-doped pnictogen chalcogenide nanoplates in a low-cost
microwave achieving $ZT > 1$ at room temperature. This fabrication method used a combination of sub-atomic-per-cent doping and nanostructuring. The resultant materials had $ZT$ values 25--250% higher than their non-nanostructured bulk counterparts. This method of bottom-up fabrication of nanostructures within bulk materials is currently patent pending.

Oxides typically have low mobility and high lattice thermal conductivity, due to the high electronegativity of oxygen and the strong bonding of light atoms. Metal oxides are ionic compounds consisting of metal cations and oxygen anions that are alternately placed with Coulombic attraction interactions between them. Since the metal-oxygen bonds are largely polarized, the conducting electrons tend to localize on the positively charged metal cations. Moreover, overlapping of atomic orbitals between the atoms is smaller than that with covalent bonds. The characteristics have lead to carrier mobility 2-3 orders of magnitude lower than Si and similar compounds. For these reasons metal oxides were completely disregarded for TE materials until the early 1990s.

To change the transport mechanisms of the metal oxide materials and thus the material properties can occur in two ways. First, the localized characters of the electronic carriers in oxides can be exploited when the carriers with large effective masses can be doped, thereby creating large $S$ and high $\sigma$ simultaneously; such as with layered cobalt oxides and Ti-based oxides. The second approach may be to reduce the ionicity of the metal-oxygen bonds in oxides in order to increase the carrier mobility. ZnO-based thermoelectric materials have been known to do both.
Zinc oxide is a wide band gap semiconductor with a direct band gap of 3.2 - 3.5eV. Zinc has a relatively large electronegativity as a metal, resulting in the less polarized Zn-O bond compared to other metal-oxygen bonds. Moreover, although the ratio of the ionic radii of Zn$^{2+}$ and O$^{2-}$ geometrically requires 6-fold coordination of O$^{2-}$ around Zn$^{2+}$, Zn$^{2+}$ prefers 4-fold coordination in reality, and hence ZnO crystallizes into the wurzite structure consisting of apex-sharing ZnO$_4$ tetrahedra, the packing density of ions being much less than that of the closest packing. According to this coordination structure, the orbitals of valence electrons of Zn in ZnO can be regarded as sp$^3$ hybrid similar to that of C in organic compounds, suggesting a large covalency of chemical bonds and thus a high mobility which is required for thermoelectric performance. This peculiar coordination structure as an oxide also restricts the elements and their solubility limits for substitution at the Zn sites in ZnO. This material system is the focus of this work and will be discussed in depth in the following sections.

2.2.2. Nanostructures

As previously discussed the incorporation of nanostructures allows different mechanisms to improve $ZT$ in both the in-plane and cross-plane directions. Along the in-plane direction, quantum size effects including sharp changes in the density of states and reduction in phonon thermal conductivity through interface scattering. Along the cross-plane direction the key idea is to use interfaces for reflecting phonons while transmitting electrons together with electron energy filtering, etc. These mechanisms have been explored through a few systems with
reasonably high levels of $ZT$ to start with, including $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$, PbTe/PbSe, and Si/SiGe.

So far the largest enhancement in $ZT$ of a V-VI superlattice has been found to arise in the cross-plane direction with the major gain coming from the thermal conductivity reduction. In this work Venkatasubramanian reported a $ZT$ of 2.4 at room temperature for a p-type $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattice with a period of 6nm.$^{20}$

For high temperature operation Si and SiGe have been identified as promising materials due to their promising bulk thermoelectric properties as well as their ability to vary material properties with doping.$^{21}$ In addition, they have the capability of monolithic integration into Si-based electronic devices.$^{22}$ Current applications for these structures are quantum cascade lasers, and p-type metal-oxide-semiconductor field effect transistors. These fabricated superlattices of n-type Si/SiGe have previously demonstrated $ZT$ values of 1.1 using low Ge content within the quantum well, but similar p-type structures have yet to reach 0.6. Two remaining issues are observed interdiffusion at elevated temperatures, and that without proper packaging the material oxidation in atmosphere will result in an increase in film resistivity, which typically occurs anywhere >800°C.

In addition, Si/SiC structures have been proposed for to be used in place of the Si/SiGe structures due to the feasibility of raw carbon compared go germanium.$^{23}$ In addition, SiC has also been used within the IC industry as a both a high mobility, highly thermally stable Si-based material.
Chapter 3

Thermoelectric Design and Material Selection

In this section we will discuss the proposed nanostructural design of the samples, and proposed and benefits. In addition, we will discuss in-depth the methodology used in choosing the ZnO-based material system as our baseline crystal.

3.1. Quantum Wells

Based on Section 2.1 this work describes a low dimensional approach using quantum wells to influence our material properties, which in theory will result in promising TE properties. The quantum well structure was chosen for one main reason: it is a stepping stone moving forward to lower dimensional structures which currently provides simple scalability and an ease of implementation into the current market compared to both 1D and 0D structures. These 1D and 0D structures, such as nanowires and quantum dots require very complex methods of measurement and fabrication which currently need more understanding and in-depth investigation.

A quantum well (QW) is a potential well that confines particles, which were originally free to move in three dimensions, to two dimensions. This well is formed between two materials: The first material being the active layer is the
quantum well, and the second material with a band-gap offset act as the barrier layer. The effects of quantum confinement take place when the quantum well thickness becomes comparable at the de Broglie wavelength of the carriers. Using the QW structure allows an increase in the density of states which results in an increase in the Seebeck coefficient, while at the same time lowering the resistivity due to the quantum confinement of the carriers. The periodic interface between the layers reduces the thermal conductivity by straining the lattices which directly results in defect formation, and increases the phonon scattering.23

Because of their quasi-two dimensional nature, electrons in quantum wells have a density of states as a function of energy that has distinct steps, versus a square root dependence that is found in bulk materials. Additionally, the effective mass of holes in the valence band is changed to more closely match that of electrons in the conduction band. These two factors, together with the reduced amount of active material in quantum wells, have leads to better performance in optical devices such as laser diodes. As a result quantum wells are currently widely used in diode lasers, including red lasers for DVDs and laser pointers, infra-red lasers in fiber optic transmitters, or in blue lasers. They are also used to make HEMTs (High Electron Mobility Transistors), which are used in low-noise electronics.

If we consider two semiconductors, with bandgaps $E_{g,\text{barrier}}$ and $E_{g,\text{well}}$, if the band alignment is straddled then we obtain the band diagram shown in Fig 12. If LQW is small then size quantization occurs and the resultant emission energy of the QW is different than either of the bandgap energies of the two semiconductors.
3.2. Material Selection

In order to select an appropriate material system for the QW structure we needed to look at the following material selection criteria;

- The lattice mismatch between the barrier material and the quantum well.
- The required deposition temperature of the material in order to achieve high quality polycrystalline films w/out influencing dopant interdiffusion.
- The ability of doping in the barrier and well in order to obtain optimum band gap energy for a certain operating temperature range.
- And most importantly promising known thermoelectric material properties of the bulk material system.

Based on literature review and a high temperature operating temperature as the focus the ZnO-based host material was chosen. It can be easily deposited in
many different ways ranging from sputtering to sol-gel deposition to atomic layer deposition, which will be further discussed in later sections. The raw materials are both feasible and environmentally friendly as compared to the conventionally used TE materials. In addition, literature has shown this material system has emerged as one of the leading bulk n-type metal oxide materials as shown in Fig. 13. Other notable performs are n-type SrTiO$_3$/SrO superlattices, and p-type Bi$_2$Sr$_2$Co$_2$O$_y$ 1-dimensional whiskers.

Fig. 13: A timeline for the highest ZT of oxide thermoelectric materials.

The binary, direct semiconductor ZnO crystallizes into the wurtzite structure. ZnO is highly ionic, with a Zn cation bonded to four oxygen anions in a tetragonal
configuration. The wurtzite crystal structure is depicted in a ball and stick representation here in Fig. 14. The primitive unit cell is depicted by the dark lines in the center. The crystal structure lacks an inversion center; therefore, wurtzite ZnO exhibits a crystallographic polarity along the c-axis. The stacking of alternating Zn- and O-layers along the c-axis is thus clearly visible in Fig. 14, with the blue dots marking the oxygen, and red zinc lattice sites. This stacking causes a positive and negative net charge on alternating surface planes. Certain material properties like etching, growth kinetics, defect incorporation, and piezoelectricity depend on this crystal orientation.

![Crystal structure of wurtzite ZnO](image)

Fig. 14: Crystal structure of wurtzite ZnO. The blue and red dots mark the oxygen and zinc lattice sites, respectively. Viewing is along the a-axis.

It is known that undoped ZnO films have n-type properties due to intrinsic defects such as oxygen vacancies or Zn interstitials. However, due to poor thermal stability and degraded electrical conductivity at higher temperatures,
doping methods are necessary for better stability and adjustment of transport properties. n-type ZnO can easily be obtained by doping with group III elements such as Al, Ga, or In. These elements incorporate readily on the Zn-lattice site and form shallow effective mass donors. It has been shown that it is possible to obtain highly conductive ZnO thin films with electron concentrations $>10^{20}$ cm$^{-3}$.

To date, Al doping has been the focus of this related research due to its smaller ionic radius easing the site substitution into the Zn lattice site, and to-date has obtained some of the best n-type bulk oxide TE measurements. Previous literature shows that due to the solubility limits of Al into the ZnO matrix, a doping of 2 atomic % Al results in the largest $ZT$ of 0.3 at 1273K.$^{24}$ Since, two mechanisms of improvement have been the introduction of nanovoid structures into densely sintered Al-doped ZnO (AZO), as well as co-doping with additional impurities.$^{25,26}$ Fig. 15 below is a plot of $ZT$ vs. temperature for various ZnO films co-doped with Al and Ga. As we observe there is a minimal level of doping which proves optimum in terms of TE performance. In support of this result, the study showed a serious degradation in electrical conductivity for samples with >4% Ga doping, which can be attributed to the samples being highly porous. This possibility of this occurring is much more probable for sintering of mixed powders vs. high vacuum thin film deposition as we will discuss in further sections.
In addition to Al-doped ZnO, In and Ga doped ZnO films have also been investigated for use as transparent conducting oxides. This doping mechanism is referred to as aliovalent substitution as the new impurity ion is of a different oxidation state as the original ion (Zn), which forces either Zn oxidation or the formation of ion vacancies. As previously mentioned, Al doping is simple because the ionic radius being much smaller than that of In, and Ga. However, relevant thermodynamic, shown in Table 1, indicates that the free energy heat of formation of Al$_2$O$_3$ is lower than that of both In and Ga, suggesting that Al$_2$O$_3$ has a very high reactivity with oxygen and will phase transition into its native oxide much easier than the latter two.
Table 1: The ionic radius, electronegativity, and the enthalpy heats of formation data for some oxides.

<table>
<thead>
<tr>
<th>Element</th>
<th>r(Å)</th>
<th>χ</th>
<th>Oxide</th>
<th>ΔH°f(kJ/mol)</th>
<th>ΔEg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.18</td>
<td>1.61</td>
<td>Al₂O₃</td>
<td>-1675.7</td>
<td>8.06</td>
</tr>
<tr>
<td>Ga</td>
<td>1.36</td>
<td>1.81</td>
<td>Ga₂O₃</td>
<td>-1089.1</td>
<td>4.5</td>
</tr>
<tr>
<td>In</td>
<td>1.56</td>
<td>1.78</td>
<td>In₂O₃</td>
<td>-925.8</td>
<td>3.21</td>
</tr>
<tr>
<td>Zn</td>
<td>1.42</td>
<td>1.65</td>
<td>ZnO</td>
<td>-348</td>
<td>3.73</td>
</tr>
</tbody>
</table>

In this regard, for high temperature thermoelectric operation indium is an attractive dopant for n-type ZnO, as it has less reactivity and greater resistivity to oxidation. In the case of oxides, this natural behavior is illustrated by a typical reaction such as:

\[
\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}
\]

\[
E_g(\text{Fe}_2\text{O}_3) = 2.1 \text{eV} \rightarrow E_g(\text{Al}_2\text{O}_3) = 8.06 \text{eV}
\]

\[
\Delta H°f(\text{Fe}_2\text{O}_3) = -822.2 \text{kJ/mol} \rightarrow \Delta H°f(\text{Al}_2\text{O}_3) = -1675.7 \text{kJ/mol}
\]

where, \(E_g\) is the optical band gap, and \(\Delta H°f\) is the formation enthalpy. Indeed many of the chemical reactions occur in order to form compounds with a large optical gap. While at the same time, such a chemical evolution involves an increase in the enthalpy energy. This formation of ZnO to an alloy with a secondary oxide is unfavorable in regards to thermoelectric properties. An
obvious conclusion is that one can establish a correlation between thermodynamic properties and optical band gaps. For the materials related to our study, Table 1, provides each preferred dopants ionic radius, electronegativity, and both the enthalpy heat of formation and Gibbs energy of formation for the corresponding oxide.

In addition to indium’s resistance to oxidation as a dopant, the larger radius size will ultimately allow increased solubility within the ZnO lattice. With the Al-doped ZnO having shrunk the lattice and created compressive stresses due to the smaller Al radius, the Zn will have an opposite impact and create tensile stresses to counteract those of the Al impurities. This will in turn lead to the ability to have increased carriers w/out the degradation of the crystal.

3.3. Multilayer Quantum Well Structures

A superlattice can be described as a structure consisting of multiple alternating periods of layers <20nm thick. The structures investigated in this work are just that, yet, we will refer to our structures as multilayer QW structures. The reasoning for this is that in our application we wish to exploit the in-plane transport, where heat and current flow parallel to the substrate, as shown in Fig. 16. This is in contrary to conventional superlattices, which take advantage of the cross-plane transport as superlattices.\textsuperscript{27}
Fig. 16: A representative diagram of the in-plane approach to a multilayer QW thermoelectric structure.

Using this in-plane approach to the multilayer technology we can obtain larger temperature gradients across the material due to large distances (~cm) between hot and cold side, which is roughly 4 orders of magnitude greater than when using cross-plane transport (~µm). This increased distance between heat source and heat sink allows for a lower heat flux, \( q_x = \frac{\kappa \Delta T}{x} \), where \( \Delta T \) is the temperature differential and \( x \) is the distance. In parallel we plan to utilize the structural QW effect to increase the thermoelectric power factor by methods explained previously.
Chapter 4

Material Characterization and Transport Measurements

For our study, sample texture, composition, and microstructure were all analyzed using several techniques. In addition, transport measurements were taken both on-site and off-site by a third party contributor for verification purposes. The details of all methods used will now be explained in further detail.

4.1. Material Characterization

Analysis of texture and identification of structural phases of the as-deposited films were performed using X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM). The sample microstructure in terms of layer periodicity and thickness was measured using X-ray reflectivity (XRR), and confirmed with transmission electron microscopy (TEM).

The overall material crystallinity, as well as phase identification, was analyzed with XRD. These scans were carried out on a Scintag X-ray diffractometer equipped with a Cu Kα X-ray source and a horizontal wide-angle four-axis goniometer, with stepping motors that allowed independent or coupled theta/2-theta axes motion. All of the deposited films were scanned from 20 to 80°. The collected XRD measurements were then compared to reference patterns from
the standard Joint Committee for Powder Diffraction Standards (JCPDS) powder diffraction file (PDF).

In order to obtain an accurate and reliable X-ray analysis one needs to verify a smooth contaminant free sample surface. In order to verify similar surface morphologies among samples we obtained AFM measurements. A Veeco Dimension 3100 Scanning Probe Microscope was used with a sharp silicon probe that is ideal for tapping mode at 42N/m and 320kHz. In addition, top-down and cross sectional morphologies were imaged with a Leo 1550 Schottky source SEM. An accelerating voltage of 10kV was used to obtain the images within this work.

X-ray reflectivity is commonly used method to study the interface structure and morphology of superlattices. The specular reflectivity is a measure of the average electron density profile of the superlattice and can be used to determine the interdiffusion and average roughness of the interfaces. The most common used approach to calculate the low-angle profile is the recursive application, where the layers are assumed to be continuous media of constant electron density. This calculation includes effects of multiple scattering, absorption, refraction, and surface and substrate reflections. This method of simulation was applied to the XRR analysis performed here at CNSE. The XRR profiles were obtained using a Bruker D8 Discover diffractometer with CuKα radiation from a sealed X-ray tube operating at 40kV and 40mA. The X-ray line source was conditioned using a parabolic graded multilayer mirror and a V-groove Ge channel cut crystal monochromator. Incident and receiving slits of 0.2 mm were used and an antiscatter slit of 0.3 mm was situated between the receiving slit and the point
detector. All profiles were analyzed using a Motofit software package. The layers’ thickness, density, surface and substrate-film roughness were used as fitting parameters. The software performed the least-squares regression to extract the roughness and the density information from the XRR traces.

In addition to XRR simulations, film microstructural properties, including layer thickness, were also obtained using a JEOL 2010F field emission TEM. The accelerating voltage used was 200keV. Cross-sectional specimens were prepared by focused ion beam liftoff method. In addition, energy filtering TEM was used to identify areas of elemental interdiffusion.

4.2. Transport Measurements

In order to calculate the thermoelectric power factor ($S^2/\rho$) of the samples both the electrical resistivity and Seebeck coefficient measurements are needed. However due to sample geometry and scaling these measurements are not entirely straightforward. This section explains in detail our techniques as well as any assumptions made.

4.2.1. Electrical Resistivity

For the bulk and multilayer QW structures, the electrical resistivity measurements are calculated according to the following equation:

$$\frac{1}{R_{\text{Total}}} = \frac{1}{R_{\text{Substrate}}} + \frac{1}{R_{\text{Film}}} + \frac{1}{R_{CR}} \quad (35)$$
where, the measured resistance $R_{total}$ consists of the resistance of the film, $R_{films}$, the resistance of the substrate, $R_{substrate}$, and the contact resistance between structure-metal-contact-probe, $R_{CR}$. In order to simplify this equation, structures are deposited on high resistivity substrates of 10000:1 electrical resistivity ratio between the substrate and film, allows us to consider the substrate contributions negligible, and allows us to simplify Eq. (35) to:

$$\frac{1}{R_{Total}} = \frac{1}{R_{Film}} + \frac{1}{R_{CR}}$$  \hspace{1cm} (36)

where,

$$R_{Film} = \frac{\rho_{Film}L}{A}. \hspace{1cm} (37)$$

Based on this relationship, we have fabricated structures of different lengths and measured their total resistance in order to back-calculate out the contact resistance. Results indicate that the contact resistance values are $<0.1\text{m}\Omega\text{-cm}$, which accounts for $<5\%$ for the lowest resistivity film. The electrical contact optimization will be discussed in later Sections.

In order to measure the in-plane electronic transport within the quantum wells our plan is to deposit electrical contacts perpendicular to the layers thus contacting each individual layer. Moving forward it was essential to compare our results with the conventional 4-point probe method. In doing so, we used 5 different 200nm thick films consisting of 0, 2, 5, 8, and 10 atomic % indium doping. Both a 4-point probe and 2-probe method were used to measure the electrical conductivity. The results can be seen in Fig. 17.
Fig. 17: Comparison chart of 4-point probe vs. 2-point probe measurements for 0, 2, 5, 8, and 10 atomic % indium samples.

From this chart we note that there is roughly a 10% difference between the measurements with the 2-probe method resulting in the lesser of the two. This can be attributed to additional probe-metal contact resistance, etc. In addition, measurement repeatability was also performed for both the 4-point probe and 2-probe methods which returned in standard deviations of 3, and 5% respectively.
4.2.2. Seebeck Coefficient

The measured thermoelectric voltage of the film, $V_{\text{film}}$, can be expressed in term of the measured voltage, $V_{\text{total}}$, the known voltage of a bare substrate, $V_{\text{substrate}}$, the resistance of the film, $R_{\text{film}}$, and the resistance of the bare substrate, $R_{\text{substrate}}$.

$$V_{\text{film}} = \left(1 + \frac{R_{\text{film}}}{R_{\text{substrate}}}\right)V_{\text{total}} - \left(\frac{R_{\text{film}}}{R_{\text{substrate}}}\right)V_{\text{substrate}}$$  \hspace{1cm} (38)

The Seebeck coefficient is then,

$$S_{\text{film}} = \frac{V_{\text{film}}}{T_H - T_C}$$  \hspace{1cm} (39)

To calculate the thermoelectric power of the sample ($S^2\sigma$), it was necessary to measure the electrical resistivity and Seebeck coefficient. The electrical resistivity was measured using a 4-probe technique. The current was introduced at the ends of the sample and the voltage probes were near the center of the test specimen. The resistance was obtained from the voltage drop, and the resistivity was calculated by knowing the cross-sectional area of the film and the distance between the two voltage probes. The electrical contacts were deposited by a lift off process. For high temperature measurements, a heated stage was used.

In order to measure the Seebeck coefficient two cylindrical heaters were bored into copper blocks, each with different temperature controls. The copper blocks are secured to a Teflon base in order to allow for high temperature operation. Manually one of the copper blocks can be shifted in order to allow increased distance between samples. Using CuNi/NiCr thermocouples at the electrical
contacts and a micro-voltmeter we are able to measure the temperature (ΔT) and voltage (ΔV) differentials across the sample. A schematic of this test system can be seen in Fig. 18. In order to reduce system error a 50°C temperature gradient was also allowed to equilibrate.

![Top-Down Schematic of Setup](image)

Fig. 18: Top-down schematic Seebeck coefficient measurement setup.

In order to calibrate and qualify the test system, samples with known $S$ and $\sigma$ were received from Hi-Z, Inc. They were subsequently tested on our system and the results are shown in Table 2.
Table 2: A comparison for in-House Seebeck measurements vs. 3\textsuperscript{rd} party (Hi-Z)

Numbers in red are measurements with less than 1\% error.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>In-House</th>
<th>External</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg.</td>
<td>St. Dev</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>133.33</td>
<td>3.79</td>
<td>127</td>
</tr>
<tr>
<td>b</td>
<td>436.00</td>
<td>4.38</td>
<td>432</td>
</tr>
<tr>
<td>c</td>
<td>301.33</td>
<td>7.57</td>
<td>303</td>
</tr>
<tr>
<td>d</td>
<td>219.7</td>
<td>8.62</td>
<td>227</td>
</tr>
<tr>
<td>e</td>
<td>198.67</td>
<td>12.42</td>
<td>194</td>
</tr>
</tbody>
</table>

The samples measured in this calibration are each 50 multilayers of Si/Si\textsubscript{0.8}Ge\textsubscript{0.2}, deposited by Hi-Z, Inc. Using our in-house setup, each sample was measured three times and the average was used for comparison purposes. The standard deviation ranges from 3-12.4, which equates to less than 5\% of the total value. Similarly, we note that the in-house measurements are within 5\%, and less than 1\% error as compared to external measurements.
4.2.3. Thermal Conductivity

Thermal conductivity measurements have not been completed for the samples included in this study. The method for taking this measurement at high temperature is complex, especially when dealing with multiple layers of differing materials. However, we did perform a preliminary study of the thermal conductivity for geometrically similar Si/SiC multilayer samples have been performed at Rensselaer Polytechnic Institution, using a \( \omega \)-technique.

This method required two samples, one with 30 periods and the other with 50 periods were deposited and capped with insulating SiN\(_x\). The 30 period sample was our reference, while the 50 period sample is used to extract the effective thermal conductivity across 20 periods of the Si/SiC film. The measurement took place in a cryostat operating from 80K to room temperature. The calculation went as follows; the temperature differential stayed relatively constant and its averaged value over the experimental frequency showed to be linear with input power. Taking the slop of this fitted line then gives an experimental estimate of the thermal resistance over the 20 periods of multilayer film. Next, by fitting this thermal resistance with 2D heat conduction model allows the calculation of the effective thermal conductivity.

The result of this work verified that fabricating quantum well structures of known thermal conductivity may result in a reduced level of \( \kappa \), but will by no means increase \( \kappa \). With this knowledge we have focused our work on improving the electrical transport within the nanostructures.
Chapter 5

Device Fabrication

5.1. Thin Film Deposition

With the growth of the semiconductor and IC industry many methods of thin film deposition have been studied. Some of the more notable are atomic layer deposition (ALD), molecular beam epitaxy (MBE), and physical vapor deposition (PVD). Each deposition technique consists of advantages and disadvantages. Therefore, when choosing a technique, each process must be thoroughly identified in terms of precision, size, throughput demands, as well as scalability and cost.

Atomic layer deposition is a thin film deposition technique that is based on the sequential use of a gas phase chemical process. The majority of ALD reactions use two chemicals, typically called precursors. These precursors react with a surface one-at-a-time in a sequential manner. By exposing the precursors to the growth surface repeatedly, a thin film is deposited. Due to the characteristics of self-limiting and surface reactions, ALD film growth makes atomic scale deposition control possible. By keeping the precursors separate throughout the coating process, atomic layer control of film growth can be obtained as fine as \( \sim 0.1 \text{ Å} \). Using ALD, film thickness depends only on the number of reaction cycles, which makes the thickness control accurate and simple. Other advantages
of ALD are the wide range of film materials available, high density and low impurity level. The major limitation of ALD is its slowness; usually only a fraction of a monolayer is deposited in one cycle. Fortunately, the films needed for future-generation ICs are very thin, but in order to deposit 50+ periods of 10nm layers for our TE device this technique is not feasible.

Molecular beam epitaxy is a technique for epitaxial growth via the interaction of one or several molecular or atomic beams that occurs on a surface of a heated crystalline substrate. It is one of the few methods of depositing single crystal materials. The main issue with MBE is the substrate limitation, meaning one can only epitaxially grow the crystalline material of which the substrate is. The second problem with MBE is that the substrate must be heated to a high enough temperature in order to allow for appropriate diffusion and activation energy in order to achieve the crystalline structure. In our case of depositing quantum wells this may lead to layer and/or dopant diffusion.

Physical vapor deposition refers to a variety of vacuum deposition techniques and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the material onto various surfaces. PVD by sputtering follows the following process, which is also depicted in Fig. 19a. Substrates are placed into a vacuum chamber, and are pumped down to their process pressure. The sputtering starts when a negative charge is applied to the target material (material to be deposited), causing a plasma or glow discharge. In parallel, positively charged gas ions generated in the plasma region are attracted to the negative biased target plate at a very high
speed. This collision creates a momentum transfer and ejects atomic size particles from the target. These particles traverse the chamber and are deposited as a thin film onto the surface of the substrates.

Sputtering has become one of the most widely used techniques for depositing various metallic films on wafers for CDs, optical drives, and such uses materials such as aluminum and aluminum alloys, platinum, gold, and tungsten, but in addition the process also be used for semiconducting films. The advantages of sputtering over the other deposition techniques are: 1) Sputtering can be achieved from large-size targets, therefore warranting excellent uniformity for large substrates; 2) High growth rates can be achieved and are easily controlled by fixing the operating parameters; 3) Control of the film composition can be achieved by independent control of targets. In addition, this is also a relatively clean technique as compared to methods such as mechanical alloying where contamination from milling balls is inevitable.

Sputtering processes are often more difficult to combine with a lot-off process when integrating into IC hardware. Also one of the main issues is that sputtering cannot fully restrict where atoms go, which can lead to contamination problems. In addition, active control for layer-by-layer growth is difficult compared to ALD and MBE.

To fabricate our samples of 50+ periods of ~10nm thick layers on substrates of up to 6\”, we have chosen sputtering as the appropriate technique. For the depositions, a custom designed stainless steel PVD reactor equipped with three confocal magnetron sputtering guns was used (shown in Fig. 19b). The guns
were driven independently by 13.56 MHz RF power supplies. The reactor was evacuated using a mechanical pump and turbomolecular pump combination to achieve a base pressure of $<3 \times 10^{-7}$ torr. The system was also equipped with a load-lock chamber, backside substrate heating component up to 850°C, as well as automated controls.

All films in this study were simultaneously deposited on both 100Ω-cm n-type (100) Si wafer substrates and glass substrates. Before deposition, the substrates were ultrasonically cleaned by acetone, isopropyl alcohol, rinsed with DI water, and subsequently dried in flowing nitrogen gas.

Before the samples can be further used for lithography and contact deposition, they have to be cleaved into pieces. This is done easily by defining a
predetermined breaking line by scratching the wafer with a diamond tip at the edge and subsequently breaking along this line. This is done systematically until pieces with the desired width/length are obtained.

5.2. Optical Lithography

Prior to lithography the films are once again cleaned with acetone, isopropyl alcohol, and DI water. They are then primed with hexamethyldisilazne (HMDS) in order to obtain better photo resist (PR) coverage. Next, a Shipley 1813® series positive photo resist is spun on for 45 sec at 3000rpm resulting in a thickness of 1.5µm. A soft bake was then performed at 115°C for 60sec. on a hot place in atmosphere, thereafter allowing the substrate to cool to room temperature prior to exposure.

The transparency masks used were created in a software program called Synopsys and printed by Curtis Printing, Inc. Two different transparency mask sets were created and printed with negative tone development. The first mask set, shown in Fig. 20a is for the bottom-top electrical contact design. As we can see, four different structures were designed. Structures 1-3 had various bridge widths, and structure 4 has a varied length in between the contacts in order to account for contact resistance as previously described. The sample size is 50, 65, 80, and 80µm for designs 1-4 respectively. In addition a 5µm gap is allowed between all edges bottom-sample, sample-top, etc. in order to avoid shorting. Fig. 20b is the design for side contacts is also printed using negative tone. The individual designs include varying contact thickness and spacing, and are as follows;
50µm/1cm, 75µm/1cm, 100µm/1cm, 75µm/1cm, and 75µm/1cm, for designs 1-5 respectively. Images included in Fig. 20 are representations and are not to scale.

All optical exposures were done with a Karl Suss MJB-3 mask aligner which can handle small samples. The aligner uses vacuum contact, where the sample is pressed against the mask by evacuating the space between the mask and chuck. For our samples of limited size a bordering laminate is provided in order to obtain subsequent vacuum. This way we are able to obtain good contact and thus maintain high resolution. The exposure was done for 12 seconds resulting in a dose of 110mJ/cm².

Thereafter, the resist is developed in Shipley microposit remover 1165® for 180 seconds and rinse with DI water. A second hard bake is then performed on the sample using a 130°C hot plate for an additional 60 seconds, and now the sample is ready for subsequent film deposition.
Fig. 20: a) The transparency mask for bottom-top electrical contact flow, and b) the mask for side-side electrical contacts.
5.3. Electrical Contacts

Electrical contacts are in this study are deposited using RF sputtering in a Denton tool. Contacts were placed both top-bottom and side-side as discussed previously. In order to pattern the top-bottom design, the lift-off method was combined with lithography. During this lift-off, the samples with metal films deposited over the exposed and developed photo resist was submerged in an ultrasonic bath of acetone. This acetone removed the remaining resist and metal top layer leaving a patterned design. This process was then repeated using the sample and top contact photo masks. The side-side contact deposition is a much simpler technique in that we use a custom machined sample holder, as shown in Fig. 21, which allows multiple samples to be placed in the sputter chamber, cleaned, and metal deposited on a sample side. Looking at the image, the sample sits where the penny is located (side contact facing up), and is compressed with the screw directly. The top-side and bottom-sides of the sample are covered by a photo resist layer, which does not allow for subsequent removal of overlap or buildup of metal deposition.
To obtain high performance ZnO-based devices, it is necessary to form reliable, low resistance ohmic contacts. This is necessary both in production and in obtaining accurate and repeatable transport measurements. High-quality ohmic contacts are typically formed as a metal-semiconductor junction, and can be verified by a linear and symmetric current-voltage (I-V) curve. To describe it simply, a metal whose work function is close to the semiconductor's electron affinity should most easily form ohmic contacts. Typically, metals with high work functions form the best contacts to p-type semiconductors while those with low work functions form the best contacts to n-type semiconductors.

To date various types of n-type contacts to ZnO, such as Al-, Ti-, Ta-, and Re-based contacts have been extensively investigated. The results of these studies have produced contact resistances in the range of \( \sim 10^{-4} \) to \( \sim 10^{-6} \, \Omega \text{cm}^{2} \) upon annealing. Current one of the most promising electrical contacts for an n-type III-V film is the Ti/Al/Ni/Au multilayer stack. This design uses a Ni/Au overlayer on
top of the standard Ti/Al metallization, where the Ni acts as an inert diffusion barrier between the top Au and underlying Al layers. However, the problem is that the low Gibbs free energy of Al results in Al$_2$O$_3$ formation which in turn increases contact resistance. The Ti also tends to oxidize at high temperatures. In this work we have replaced Ni with Ti, because according to the phase diagram, shown in Fig. 22, Ti will react with Al during high-temperature annealing to form intermetallic alloys. This will as a result tie up the excess Al in the contacts giving them thermal stability. As a result the Ti and Al layers are expected to undergo enhanced reactions to produce alloys instead of suffering from significant oxygen contamination.

Fig. 22: Ti-Al phase diagram. Red arrow indicates annealing path that our samples undergo.
For this study electrical contact designs with both varying layer type and thicknesses were deposited by RF sputtering and are included in Table 3.

Table 3: Metal layers and corresponding thicknesses of electrical contacts.

Layer 1 is the innermost (contact w/sample) and layer 4 is most external.

<table>
<thead>
<tr>
<th>Contact ID</th>
<th>Layer1 Film</th>
<th>t (nm)</th>
<th>Layer2 Film</th>
<th>t (nm)</th>
<th>Layer3 Film</th>
<th>t (nm)</th>
<th>Layer4 Film</th>
<th>t (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ti</td>
<td>100</td>
<td>Al</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ti</td>
<td>100</td>
<td>Au</td>
<td>100</td>
<td>Ti</td>
<td>50</td>
<td>Au</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>Ti</td>
<td>50</td>
<td>Al</td>
<td>50</td>
<td>Ti</td>
<td>50</td>
<td>Au</td>
<td>50</td>
</tr>
</tbody>
</table>

The titanium layer was pre-determined to be the base layer based on results of published literature and due to the knowledge that gold has poor adhesion to ZnO, and that aluminum is known to rapidly diffuse at high temperatures. The I-V characteristics of the as-deposited contacts on bulk Al-doped ZnO, were determined by the 4-point probe technique and are provided in Fig. 23. As-deposited contacts for all metallizations exhibited non-linear I-V characteristics, but after annealing at 750°C for 45 sec in argon ohmic behavior was exhibited for all, as Fig. 23 indicates.
These results indicate a contact resistivity of $1.0 \times 10^{-3}$, $5.3 \times 10^{-4}$, $1.4 \times 10^{-4}$, and $5.8 \times 10^{-5}$ Ω-cm$^2$ at room temperature for contact IDs 1, 2, 3, and 4 respectively. Based on these results, contact design #4 (Ti/Al/Ti/Au) was chosen and applied to all bulk films with including varying indium concentration in order to identify any behavioral changes with doping level. All films were preliminarily annealed after deposition to obtain ohmic behavior. In Fig. 24, the doping-dependent contact resistivity for each film is plotted as a function of measurement temperature. In order to calculate this specific contact resistance we have fabricated structures of different lengths, which are included in our mask designs and each individual measured for its total resistance. Knowing that the contact resistance is the same
for each type of sample we can then calculate it based on the two resistance points with varying lengths. This will be explained in greater detail in subsequent sections. The results plotted in Fig. 24 show that all contact resistance values are $<0.12\,\text{m\Omega}\cdot\text{cm}^2$, which accounts for $<5\%$ of the total resistance and in theory will not be a limiting mechanism for our device.

![Graph](image)

Fig. 24: Contact resistances of the Ti/Al/Ti/Au contacts to varying levels of indium doped AZO films with varying measurement temperatures.
The AES depth profile of the Ti/Al/Ti/Au electrical contact on Al-doped ZnO sample is shown in Fig. 25. It is evident that significant intermetallic diffusion has occurred, notably Au towards the ZnO interface and outdiffusion of Al and Ti towards the surface. It also seems that both the Ti and Al signals follow each other, which is presumably due to the presence of the (Ti, Al) phases. The Au diffusion could result in a long-term reliability issue, but for this study will have relatively no impact. We are not performing lifetime measurements yet, only an as-deposited and as-annealed at the corresponding operating temperature to obtain data. The Au diffusion happens over an extended period of time and if surface...
oxidation then occurs to the Ti/Al contact resistivity will increase drastically. From both the AES and XRD studies, the present microstructure suggests that the reaction mechanism for the underlying formation of the ohmic contact incorporates the reaction between the Ti and Al as predicted. It can be explained further by the red arrows located on the phase diagram in Fig. 22. The reaction between Ti and Al starts at low temperatures (250-300°C) with the formation of Al₃Ti and α-Ti phases as the primary products. With increasing temperature (>750°C) comes an increase in Al interdiffusion into the Ti layer, and thus results in a more thermodynamically stable phase of Ti₃Al and possibly Ti₂Al, which are both observed in the XRD analysis.
Chapter 6

Results and Discussion

Within this work, sample characterization including texture, composition, and microstructure have all been analyzed using a variety of techniques. In addition, transport measurements have been taken both on-site and off-site by a third party contributor for verification purposes. The results will now be discussed in this Chapter.

6.1. Bulk Films

6.1.1. Al-doped ZnO

The deposited bulk films in this study are targeted to be 200nm thick AZO and In-doped AZO films that were deposited by co-sputtering of two precursor targets. Initially, a study was performed on the deposition of the pure AZO film which will remain the base lattice structure in order to obtain the highest quality films in terms excellent film quality and low film resistivity.

The conduction mechanism can be broken down into two parts: one is the occurrences of intrinsic carriers by oxygen vacancies, and the other is the introduction of extrinsic carriers by impurity doping. The occurrences of the carrier caused by the development of resistivity were greatly affected by impurity
doping rather than oxygen vacancies when the film is deposited by a doped target. For a ZnO target with the same Al dopant concentration, sputtering parameters such as substrate temperature, deposition pressure and power will have a major influence on material properties. Here we have investigated all three and will report their property dependencies.

The growth temperature has been known to play a major role for thin film properties determination including for the focus material of Al-doped ZnO. Here in Fig. 26 is the XRD spectrum of the AZO films deposited at three different substrate temperatures. It is found that the samples all exhibit hexagonal wurtzite structures according to the Joint Committee on Powder Diffraction Standards data base. In addition, the spectrum shows only diffraction peaks of ZnO without any additional diffraction peaks. The (002) peak at 34.18° grows more intense with higher deposition temperature which indicates the enhancement of the crystalline quality of the AZO films. This preferred orientation has been verified to have the lowest surface free energy of all ZnO planes.\(^\text{30}\) The average grain size can be calculated using Scherrers formula:\(^\text{31}\)

\[
G = \frac{0.9 \lambda}{B \cos \theta_B}
\]

where, \(\lambda\) is the X-ray wavelength, \(\theta_B\) is the maximum of the Bragg diffraction peak, and \(B\) is the full-width at half maximum (FWHM) of the XRD peak. As we observe in Fig. 26, the FWHM decreases with increasing the substrate temperature. Since the FWHM is inversely proportional to the grain size of the film, the grain size of the AZO thin films then increases with increasing
temperature. The grain sizes values are 29±1.5 nm, 36±2.1 nm, and 39±1.8 nm for the substrate temperatures of 75°C, 150°C, and 200°C respectively.

Fig. 26: XRD patterns of AZO films deposited at various temperatures.

In addition to XRD analysis, cross-sectional SEM micrographs were prepared to view the morphology of the AZO thin films deposited at 75°C, 150°C, and 200°C and are shown in Fig. 27 (a-c). As observed in the XRD spectra, the grains show a strong preferential orientation along the (002) axis, and result in columnar structure growth. However, higher temperatures appear to have more uniformity
throughout the SEM cross-sectional image. Previous reports on the stages of AZO growth state that initially small grains become distributed at arbitrary sites, which then become larger and then finally large grains with columnar structure are formed. This is due to the fact that higher substrate temperature provides sufficient energy for surface atoms to enhance their mobility and therefore improve the quality of the films crystallite structure.\textsuperscript{32}
Fig 27: Cross-sectional SEM images for various deposition temperature a) 75°C, b) 150°C, and c) 200°C.
In order to correlate the change in deposition temperature to a useful parametric we measured the corresponding electrical resistivity, which is shown in Fig. 28a. As we can see from the plot, increasing deposition temperature results in decreasing resistivity which can be attributed to the increasing crystallinity resulting in improved carrier mobility.

A second important deposition parameter, operating pressure, has also been investigated and correlated to electrical transport. As shown here in Fig. 28b, decreasing operating pressure results in a decrease in film resistivity. This effect is probably due to the bombardment of the film by energetic gas atoms resulting from neutralization and reflection of ions at the target surface. As the pressure increases, the mean free path of ionized atoms decreases, and consequently the Ar ion energy is reduced. This also holds true for increasing RF power. As a result the enhancement of Ar ions energy bombarding the substrate causes the network to relax and the grain size to increase. For example, in plasma at a pressure of 2mT the degree of ionization is very high, and thus the density of neutral atoms is much lower than that of ions. Ultimately this will result in the dissipation of the kinetic energy and thus substrate impact.

In addition to substrate temperature, and operating pressure, the AZO target sputtering power was also optimized in terms of electrical resistivity. It can be seen from Fig. 28c that the resistivity decreases from 50 to 3 mΩ-cm as the sputtering power increases from 100 to 250W. This behavior can be explained by the increased energy available for the Al-Zn substitutional doping mechanism as
the RF power increases. This in turn increases the carrier concentration which results in a decrease in electrical resistivity.

Fig. 28: Variation of electrical resistivity of AZO films for varying 

- \( a \) substrate temperatures, 
- \( b \) operating pressure, and 
- \( c \) target RF power.
6.1.2. (In, Al) co-doped ZnO

To incorporate indium as an additional element in the AZO film, a co-sputtering custom designed tool with the capability automated shutters and independent RF power supplies were used. Based on the results from the AZO film study discussed in the previous section, we have chosen to use the following deposition parameters; Argon (99.999% purity) flow rate of 20sccm, operating pressure of 2mT, temperature of 200°C, and a power of 200W for the AZO target. The sputtering power of the indium target is has been adjusted accordingly to obtain specific concentration within film.

![Fig. 29: Indium Target RF Power Dependence of % In Atomic Concentration in AZO Film and Growth Rate](image)

Fig. 29: Indium Target RF Power Dependence of % In Atomic Concentration in AZO Film and Growth Rate
Fig. 29 shows both the RF power dependence of the film growth rate as well as the atomic composition (at. % In). The growth rate was determined by cross-sectional measurements. For indium target RF powers between 10 to 20W we obtain indium atomic concentration levels from 2 to 10 %, as per the AES scans shown in Fig. 30. These films were all doped at the previously mentioned chamber conditions. Anywhere above this level of doping (>RF power) we determined that indium is no longer soluble in the AZO matrix and results in poor substrate adhesion. This was verified via tape adhesion test, which for this industry/application using Adhesions Standard Test Methods (ASTM D3359). In addition to excellent adhesion, it is also important to note that the concentration levels remain uniform throughout the film. This is in contrary to previously reported literature, which found that the indium doping concentration decreases from surface to substrate, by roughly 2%.33
Fig. 30: AES scans for varying indium concentrations in AZO. All levels of doping are level throughout the film.
The XRD spectra in Fig. 31 confirm that films with 0, and 2 atomic % indium have a sole (002) detectable diffraction peak. These peaks are nearly consistent with that of the (002) standard ZnO crystal plane of 34.18. Using the Debye Scherrer formula the grain sizes for the three highly crystalline films were found to be 39, 45, and 41nm for the 0, 2, and 5 at. % In films, respectively. In addition to a change in grain size we also notice that at 5 at. % indium doping we begin to obtain the (100) ZnO peak, and upon further doping there is a transfer of preferred film orientation from the (002) to (100) ZnO plane. The 8, and 10 at. % In films are poly-crystalline, which is caused by doping levels above the indium solubility limit in the ZnO matrix. This is due to the large indium atoms disrupting the ZnO matrix, resulting in a variety of crystallite orientations, as well as grains of pure indium thru elemental agglomeration, which is verified by the additional In-based peaks.
Measuring the (002) peak position, we notice a slight shift as shown in Table 4. As was predicted, doping with Al shifts the peak to the right due to incorporating the smaller Al atom substitution. For low concentration indium films, (2 - 5at.%), the location of the measured diffraction peak shifts back to the normal ZnO peak. This shift coincides with an increasing in carrier concentration while having no loss in carrier mobility.
Table 4: Peak position for the (002) plane observed in XRD spectrum.

<table>
<thead>
<tr>
<th>Material</th>
<th>ZnO (002) peak position (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO*</td>
<td>34.18</td>
</tr>
<tr>
<td>AZO</td>
<td>34.23</td>
</tr>
<tr>
<td>InAZO2</td>
<td>34.2</td>
</tr>
<tr>
<td>InAZO5</td>
<td>34.18</td>
</tr>
<tr>
<td>InAZO8</td>
<td>34.15</td>
</tr>
<tr>
<td>InAZO10</td>
<td>34.13</td>
</tr>
</tbody>
</table>

Plain-view and cross-sectional morphologies were imaged with a Leo 1550 Schottky source SEM, and shown in Fig. 32. Images were taken at an accelerating voltage of 10 kV. The film surfaces at 0, 2, and 5 at.% indium appear to be smooth and featureless without defects such as crack and protrusions. Further doping results in darker grains and increased granular texture, this is probably due to the indium impurity phase. In agreement to XRD results, the plain-view images reveal that grain size increases with increasing indium doping, and along with that the films become less coherent. Individual film thicknesses were found using similar cross-sectional images to the one shown. It is seen that the 2% In doping sputtered film grows with a crystallographically oriented columnar structure. This columnar growth theory for sputtered films was
proposed by Thornton,\textsuperscript{34} and said to occur when deposited at substrate temperatures less than half of the materials melting point temperature (ZnO \textasciitilde 1975°C).

Also in addition to standard SEM, energy filtered TEM images were taken of the samples in order to investigate any elemental changes/agglomerations, etc. Fig. 33\textit{a} is a zinc map, and thus shows that the zinc is uniform throughout the sample. Fig. 33\textit{b} is an indium map for the 2 at. % indium film and shows a slightly increased surface layer of indium. Fig. 33\textit{c} however is an indium map for 10 at. % indium which shows increased indium diffusion towards the substrate which results in elemental agglomeration.
Fig. 32: SEM images of AZO films with various levels of indium doping. A cross-sectional image is also included to show the columnar growth of the Indoped AZO films.
Fig. 33: Elemental maps produced by TEM for (a) zinc in AZO, (b) indium in 2 at. % indium doped AZO and (c) indium in 10 at. % indium doped AZO.
6.1.3. Bulk Thermoelectric Properties

The electrical resistivity ($\rho$) is determined by $\rho = (N e \mu)^{-1}$, where $N$ is the carrier concentration, $e$ is the electronic charge, and $\mu$ is the Hall mobility. Based on this formula we know that we can lower the electrical resistivity in two ways; by increasing the mobility or the carrier concentration. It was previously shown that in order to increase the mobility we must improve the crystallinity of our films. In our XRD analysis, we show highly crystalline AZO films, which leave little room for improving film crystallinity. The second option is to increase the carrier concentration, which can be done via doping.

As seen in Fig. 34a, all films show a similar negative temperature dependence on film resistivity from 300 to 975K. The electrical resistivity for the samples with 0 and 2 % In doping, exhibit metallic behavior, with resistivity values of 2.2 and 1.5 mΩ-cm, respectively, at room temperature. Consequently, (ZnO)Al$_{0.03}$In$_{0.02}$ gives the lowest resistivity of all measured samples. Further doping increases the film resistivity by an order of magnitude, for the 5 atomic % In film, and 2 order of magnitudes for the 8 and 10% films. This is due to the loss in crystallinity resulting in a decrease in carrier mobility. This theory was similarly identified in a study of oriented Al-doped ZnO thin films with large crystallite sizes and non-oriented polycrystalline bulk with the same composition. The results there showed that the oriented films have an electrical conductivity as high as 2000S/cm, which is about five times large than that of the non-oriented film.

Theoretically, the Seebeck coefficient, $S$, can be solved for by the following equation for an n-type material;
\[ S = -\frac{k_B}{e} \ln \frac{N_c}{N_D}, \text{where } N_c = \frac{2(2\Pi m_e KT)^{3/2}}{h^2} \]  

(41)

This is derived from the aforementioned equation; \( S = \Delta V/\Delta T \). Here, \( k_B \) is the Boltzmann constant, \( e \) is the electron charge, \( N_c \) is the effective density of states (DOS), and \( N_D \) is the doping density. With our method of co-doping we obtain an increase in the effective density of states by strong band restructuring with the ZnO as our majority component and the localized states from Al and In, being the minority components. These low level impurities create subbands near the original band edges. Due to the localized origin of these subbands, a heavy effective carrier mass is achieved, which gives rise to a sharp DOS different from the host material. However, with further doping an increase in DOS will begin to tail-off and therefore it is important to determine an optimum doping concentration in order to maximize \( N_c/N_D \).

The temperature dependence of the Seebeck coefficient is shown in Fig. 34b. The \( S \) values of all the samples are negative, indicating n-type flow. A general trend is seen among the samples with \(|S|\) increasing from 300 to 975K, which is in contrary to bulk ZnO films\(^3\). The \( S \) values for the (ZnO)Al\(_{0.03}\) film is between -100 and -200µV/K, which is comparable to previously reported values\(^6\). It is also important to note that with increased doping we obtain a nearly proportional increase in \(|S|\).

The thermoelectric power factor represents the electrical contribution to the thermoelectric performance. We have calculated it from the measured electrical resistivity and Seebeck coefficient measurements in Fig. 34a-b. For the (ZnO)Al\(_{0.03}\) sample we the power factor increases with increasing temperature,
owing to the increase in $|S|$. The power factor for this sample is from $4.8 \times 10^{-4}$ Wm$^{-1}$K$^{-2}$ over the temperature range of 300 to 975K. These values are roughly 50% lower than the previously reported using a sintering technique. This can be attributed to thickness-dependent resistivity. Here we are investigating thin films of 200nm, while sintering consists of rectangular bars roughly 15 x 5 x 3 mm$^3$ in size. At 2 at.% indium doping, a large increase in power factor is achieved due to its low resistivity and increasing Seebeck coefficient. This film has a large thermoelectric power factor of $22 \times 10^{-4}$ Wm$^{-1}$K$^{-2}$ at 975K. This value is a factor of 275% greater than the sample with no indium doping. As a result, films with greater doping levels have a continually increasing $|S|$, yet the significant degradation in electrical conduction results in low power factors.
Fig. 34: Temperature dependent plots for a) electrical resistivity b) Seebeck coefficient for varying levels of In-doped AZO films.
6.2. Quantum Well Multilayers

6.2.1. AZO/In-AZO Multilayers

The goal of our preliminary depositions of AZO/In-AZO quantum wells multilayer’s (MQW) is to prove an enhancement in thermoelectric properties over that of the bulk materials. The ultimate goal is to provide high-temperature stability of interfaces in comparison to that of the previously reported Si-based material systems. From the results obtained in the bulk thin film study the deposition parameters have been chosen in order to deposit high quality films with low resistivity in 50 periods of alternating layers with thicknesses of 10nm in order to obtain a total layer thickness of 1µm.

In thin films analysis’s the surface morphology majorly impacts the use of spectroscopy techniques, and for this reason we have verified the morphological variation using AFM. A Veeco Dimension 3100 Scanning Probe Microscope at CNSE was used, along with a sharp silicon probe that is ideal for tapping mode at 42N/m and 320kHz. The average surface roughness (Ra) was measured from five, 1µm x 1µm size scans for each sample and the results were 1.1, 1.3, 1.8, and 3.1nm for InAZO2, InAZO5, InAZO8, and InAZO10 respectively. These scans are shown in Fig. 35 where surfaces appear to be contaminant free and without any significant peaks or valleys. We can therefore safely assume that surface variation will have a negligible impact our X-ray spectrographic results. Also noteworthy is the fact that the AZO/InAZO2 appears to have the smallest grains on the surface which is in agreement with the XRD data obtained from the bulk
films. This is attributed to the lowest lattice mismatch between the barrier and well layers for all the samples.

Fig. 35: AFM scans for three multilayer stacks with varying levels of indium doped wells. Results show all films are free of large agglomerations and that grain size increases with increased doping levels.

In order to characterize the microstructure of the QW multilayers in terms of periodicity, layer density, and interface roughness, XRR profiles were recorded by a Rigaku Ultima III X-ray diffractometer equipped with parallel beam optics. Parallel beam optics are capable of delivering high-intensity X-ray beams with
low divergence. The X-ray mirror provided a high-intensity beam with 0.05° divergence; the divergence slit was set at 0.05mm to minimize the sample size illumination effects. The acquired XRR profiles were analyzed by the Motofit software package. The samples are modeled as constant-density multilayer stacks of AZO and In-doped AZO. The layers’ thickness, density, surface and substrate-film roughness were used as fitting parameters. The software performed the least-squares regression to extract the roughness and density information from the XRR traces.

Fig. 36: X-ray reflectivity profiles of 50 periods of AZO/InAZO with various indium doping levels from 2-10%. Plots indicate defined reflections for the 2, 5, and 8 at.% indium films which are indicative of good periodicity of the multilayer structures.
Fig. 36 is a low angle XRR scan where we observe that the MQW samples with 2 – 8 at. % indium doping within the well demonstrate an ordered layer structure with outstanding periodicity. This is inferred from the well-defined first and second-order reflections. However, the sample with 10 at. % indium doping shows evidence of non-periodicity and non-superlattice behavior. This is attributed to elemental agglomeration of the indium resulting in a low layer thickness to interface roughness ratio.

Table 5: XRR analysis summary of quantum well multilayers.

For indium doping of 2-8 atomic %, well-widths are within 2% of the target, and all samples have low IFR.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Periods</th>
<th>Width (nm)</th>
<th>IFR (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO/InAZO2</td>
<td>50</td>
<td>9.8</td>
<td>1.0</td>
</tr>
<tr>
<td>AZO/InAZO5</td>
<td>50</td>
<td>10.2</td>
<td>1.3</td>
</tr>
<tr>
<td>AZO/InAZO8</td>
<td>50</td>
<td>10.1</td>
<td>1.4</td>
</tr>
<tr>
<td>AZO/InAZO10</td>
<td>50</td>
<td>24</td>
<td>23</td>
</tr>
</tbody>
</table>

In order to verify the XRR analysis, cross-sectional TEM microimages were taken with a JOEL 2010-F FEG TEM operated at 200 kV, shows periodic stacking of the constituent layers of the multilayer film as shown in Fig. 37a. A more high resolution image is seen in Fig. 37b, where we can identify the indium doped wells, which appear as dark layers due to their increase in density. These
images are of the AZO/InAZO8 sample and confirm uniform 10nm layer thicknesses.

Fig. 37: Cross-sectional TEM images of a) full sample QW stack and b) high resolution partial stack w/dark layers indicating indium doped quantum wells.

In order to analyze the microstructure of the multilayers, including roughness levels, layer periodicity, etc., XRR analysis was proven to be the most useful technique from the Si/SiC study. Identical scans were used for the analysis of the AZO-based multilayer QWs. Shown here in Fig. 38, are XRR low angle scans for identical samples annealed at various temperatures. From the data fitting, the layer thickness is 10nm ±1.5 with an IFR <2nm. In contrary to the Si-based material system, we observe that after sample annealing, layer periodicity and interfaces still exist. This is observed thru no variation in the 1st and 2nd order reflection peaks.
6.2.2. Thermoelectric Properties

Figures 39 (a-c) exhibit the temperature dependent measurements of the in-plane electrical resistivity, Seebeck coefficient, and thermopower, respectively. Figs. a and b are experimentally measured, and c is a calculation based on the prior. Fig. 6a has been plotted on a log scale in order to show the full range of measured values. We observe that $\rho$ for the QW multilayer structures has been reduced by up to an order of magnitude at specific temperatures (500-750K) and doping levels (1 and 2 at.% indium). The amount of improvement over the parent bulk films varies for each of the QW structures. For example at 575K, the electrical resistivity of the MQW structures as compared to the In-doped AZO
bulk film is improved by 63%, 89%, 91%, and 50% for the 2, 5, 8, and 10 at.% indium doped films, respectively.

Seebeck coefficients were also measured at 50K intervals between 325 and 975K and are shown in Fig. 39b. As expected all samples have negative Seebeck coefficients demonstrating n-type behavior. The bulk and multilayer samples both show a linearly decreasing $\alpha$, with increasing operating temperature. Unlike the $\rho$ measurements we do not see an improvement in $S$ that surpasses the values of the bulk components. The resultant $S$ value is actually an intermediate between that of the two parent films it is composed of. In addition, for all films, we see that with increasing at.% indium concentration there is a trend of decreasing $S$ values. For instance, at 575K the Seebeck coefficients for InAZO2, InAZO8, and InAZO10 are -143, -202, and -210$\mu$V/K, respectively.

Based on the electrical resistivity and Seebeck coefficient measurements, the thermoelectric power factor was then calculated and plotted against temperature in Fig. 39c. We observe that the multilayer structures with 2 and 5 at.% indium doped wells show the most promising power factors. Specifically within the temperature range of 550 to 750K we see an increase in power factor by more than 3x as compared to the parent bulk materials. The AZO/InAZO8 multilayer shows an intermediate level of performance as compared to its bulk counterparts, while AZO/InAZP10 shows no improvement.
Fig. 39 a-c: Plot of electrical resistivity (a), Seebeck coefficient (b), and thermopower (c) vs. temperature for bulk and multilayer films with varying at. % indium. The multilayer films with observed quantum wells show up to a 3x improvement in thermopower.

Our experimental results indicate that the sample structures have significantly reduced electrical resistivity at low levels of In doping within the QW (2 and 5 at.%) as compared to both the parent bulk films, which is attributed to two main factors. First, a portion of the improvement is material dependent. Thru the addition of a more electrically conductive film ($\text{In_xAl_{0.2}ZnO}$) we gain a moderate decrease in the total multilayer structure resistivity. This is proven by the AZO/InAZO10 sample which shows no sign of layer periodicity by XRR, yet
measures a resistivity of 50mΩ-cm at 575K, which is an intermediate values of the parent films, 105 and 1.7mΩ-cm for the In0.1AZO and AZO, respectively. Secondly, when the resistivity is lower than that of either of the bulk films, this is attributed to enhanced quantum confinement effects within the quantum wells. For example, AZO/InAZO5 measures a resistivity 0.93mΩ-cm at 625K, which corresponds to a 55 and 90% improvement over the bulk AZO and InAZO5 films, respectively. From Fig. 39a we also note that similarly to all the bulk films, the resistivity of the multilayer structures also increases with higher operating temperature due to increased scattering. However, at operating temperatures >650K rate of rise (∆ρ/∆T) is much more significant for the MQW structures as compared to bulk films. This in theory can be the result of an increase in multilayer hopping caused by the charge carriers gaining enough thermal energy to cross the band-gap offset of the quantum well.

In order to determine the optimum doping level for the MQW structure it is important to calculate the thermoelectric power factor due to the inter-dependence between electrical resistivity and Seebeck coefficient. The relationship between % doping in the QW and electrical resistivity in not a simple straight-forward relationship as we have just discussed and Fig. 39a exhibits. However, the Seebeck coefficients, from Fig. 39b show an almost linearly trend of improving α for increasing at. % indium. This is attributed to the increase in poly-crystallinity of the ZnO matrix, which results in a reduction in carrier mobility for both phonons and electrons and has been previously been verified by XRD analysis. As a result by taking into account an intermediate level of doping
and obtaining high quality films, the TE power factors achieved signify the advantage of utilizing quantum confinement for AZO and (In, Al) co-doped ZnO multilayers at high operating temperatures.
Chapter 7

Material and Process Optimization

As discussed in Chapter 6, the fabrication of multilayer quantum wells of AZO/InAZO materials has enhanced the thermoelectric performance as compared to the counterpart bulk materials. However, in order to optimize this newly designed structure many additional aspects need to be taken into account. In this chapter, structural parameters including layer thickness, interface roughness, and band-gap offset are investigated in order to optimize the device thermoelectric performance.

7.1. Well-width Thickness

Thermoelectric performance is known to be a function of quantum well width, with a reduction in well-width it is expected that there will be an increase in carrier confinement which results in effectively forming a 2D density of states for the free carriers. In trying to determine the optimum layer thicknesses for quantum wells, there are two important things to note; (1) for typical superlattices, the tunneling transport of carriers across a single indirect barrier depends critically on the barrier thickness, and (2) the majority of the carriers flow within the quantum-well due to quantum confinement. For our study with a focus on the
in-plane transport of MQW systems we want to maximize the quantum-well to barrier-layer thickness ratio.

In order to determine the optimum well and barrier thicknesses a series of samples were deposited with varying layer thicknesses. For this set of samples, two types of electrical contact designs were used as indicated in Fig. 40. The Type I design exploits cross-plane transport via tunneling of the carriers. The Type II design on the other hand utilizes quantum confinement which will result in in-plane carrier transport.

![Sample schematic for well-width thickness optimization experiment.](image)

Using this design methodology and a series of varying well and barrier thicknesses we have measured the sample resistivity in the same way as for the MQW films discussed earlier. Figure 41a-b will therefore help us in determining the optimum layer thicknesses for our structure. Fig. 41a shows the resistivity dependence on varying InAZO5 well-width thicknesses with an AZO barrier thickness fixed at 10nm. With well-widths below 7nm the Type I (cross-plane transport) results in lowest resistivity levels due to increased tunneling, thereafter, with increasing well-widths the Type II design begins to exploit quantum confinement effects and results in low resistivity levels. Fig. 41b is simply the
reverse. It is the resistivity dependence on varying AZO barrier thickness, while the InAZO5 well-width thickness is fixed at 10nm. Here as well Type I electrical transport only supercedes the Type II transport at barrier-widths of <7nm due to limitations on tunneling. As a result the Type I design is dependent on low barrier thickness to allow tunneling, and the Type II design requires increased barrier width, yet small well-widths in the range of 8-11nm in order to exploit quantum confinement. In addition, it is not desirable to fabricate super large barrier layers (>20nm), as we do not want them to account for a large portion of our volume ratio, since our well is where the majority of transport occurs.

Fig. 41a-b: Plots of resistivity dependence on the a) quantum well and b) barrier layer thicknesses.
7.2. Interface Roughness Effect

In order to provide appropriate targets for device fabrication we need to understand the impact of material quality and understand the need for repeatability and fabrication control. From our experimental results we have identified a significant decline in performance for multilayer stacks with high levels of IFR. This agrees with the theory that within a QW any deviation from a perfect interface should impact the electrical conductivity, at that at low temperatures IFR is the limiting mechanism for carrier transport.\textsuperscript{39}

7.2.1. Theory

The following model has been developed based on the fact that roughness at the interface leads to fluctuations in the QW width, which in turn modulates the confinement energies and results in a fluctuating potential for the 2D motion of confined carriers. The fluctuation in band energy is given by the partial derivative of energy $E$, with respect to well width $L$

$$\delta E(r) = \frac{\partial E}{\partial L} \Delta(r)$$

(42)

where, $E$ here is the confinement energy and is given as $h^2 \Pi^2 / 2m_z L^2$, and $m_z$ is the z-direction hole effective mass, $L$ is the well width, $h$ is the reduced Planck constant, and $\Delta(r)$ is the interface roughness at a position $r=(x,y)$. The influence of IFR on the mobility of 2D electrons is never precise since the roughness itself
is not straightforward to model. This roughness is characterized by a z-height $\Delta$ and a correlation length $\Lambda$, and assumes a Gaussian like form because of the always changing interface structure.

$$
\langle \Delta(r)\Delta(r') \rangle = \Delta^2 \exp\left(-\frac{|r-r'|^2}{\Lambda^2}\right)
$$

(43)

Taking into account that the interaction is actually the average over all possible configurations of the IFR, the correlation function is

$$
\langle E(r)E(r') \rangle = \left(\frac{\eta^2 \Pi^2 \Delta}{m_c L^3}\right)^2 \exp\left(-\frac{|r-r'|^2}{\Lambda^2}\right)
$$

(44)

where, the variance of the function, with the energy squared, is

$$
\left(\frac{\eta^2 \Pi^2 \Delta}{m_c L^3}\right)^2.
$$

(45)

Then by using a previous derivation\textsuperscript{40} we can calculate the hole mobility

$$
\mu = \frac{2^{5/2} \epsilon c^2 \frac{L^5 n_p^{1/2}}{\Pi^4 \eta m \Delta^2 \Lambda}}{n_c}
$$

(46)

And put into terms of material resistivity, where $p$ is the hole concentration, and we consider the impact of electrons negligible, due to high $p$ doping.

$$
\rho = \frac{1}{q(\mu_n n + \mu_p p)}
$$

(47)
To model our samples we use roughness data obtained from experimentation. The XRR data gives us both well-width and z-height roughness (the peak height in the Fourier transform). We estimate the correlation length from the assumed Gaussian form of the IFR. Previously, it has been reported that the IFR can be neglected in quantum wells over 4.5nm in width, but this is only true for a low level of roughness (<1nm), which would require a deposition technique other than sputtering. More importantly we believe that it is the ratio of interface roughness to quantum well width that is most important.

Fig. 42: A 3D plot of resistivity in relation to z-height roughness and correlation length for a well-width of 10nm at room temperature. Resistivity increases exponentially with z-height, and linearly with correlation length.
From the 3D plot in Fig. 42, as well as from Eq. (46), we can see that a change in z-height roughness has an exponential affect in determining the sample resistivity, whereas the correlation length impact is linear. It is observed that with $\Lambda$ values below 2nm it is possible to achieve resistivity on the order of $\mu\Omega$-cm for all $\Delta$. Above 2nm, localized areas with varying potentials will begin to develop due to well-width fluctuations. This difference in potentials leads to carrier localization, and thus higher resistivity.

7.2.2. Experimental and Theoretical Correlation

To complement our theoretical findings, AZO/InAZO5 multilayer samples were analyzed with XRR to obtain a set of samples similar in layer thickness, and density, yet with varying IFR. The differences in IFR can be attributed to the location as respect to substrate origin during deposition. From best fit simulations we have chosen four samples with the properties shown in Table 6. Z-height roughness values were taken from XRR analysis and correlation lengths thereafter reduced using Arrhenius plot equations. The roughness values may appear large in comparison to previously reported numbers of 0.1 to 0.4nm for GaN/AlGaN films\textsuperscript{14}, however, this is attributed to the fact that these films were grown by sputtering, not epitaxially. In addition, these values represent the average z-roughness over the full 50 periods, and not just a single quantum well.
Table 6: Summary of IFR values for four samples of AZO/InAZO5 multilayer structures and their respective measured and calculated electrical resistivity at 325K.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>W(nm)</th>
<th>Δ(nm)</th>
<th>Λ (nm)</th>
<th>Δ/w</th>
<th>ρ&lt;sub&gt;meas&lt;/sub&gt; (mΩ·cm)</th>
<th>ρ&lt;sub&gt;calc&lt;/sub&gt; (mΩ·cm)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1009_a</td>
<td>10.0</td>
<td>1.4</td>
<td>9.1</td>
<td>0.14</td>
<td>10.4</td>
<td>9.5</td>
<td>9.47</td>
</tr>
<tr>
<td>1009_b</td>
<td>9.9</td>
<td>2.1</td>
<td>19.5</td>
<td>0.21</td>
<td>14.3</td>
<td>13.2</td>
<td>8.33</td>
</tr>
<tr>
<td>1019_c</td>
<td>10.1</td>
<td>4.1</td>
<td>33.2</td>
<td>0.41</td>
<td>18.7</td>
<td>25.3</td>
<td>26.1</td>
</tr>
<tr>
<td>1025_b</td>
<td>10.2</td>
<td>1.3</td>
<td>8.9</td>
<td>0.13</td>
<td>9.8</td>
<td>9.4</td>
<td>4.26</td>
</tr>
</tbody>
</table>

In order to estimate the correlation length, we use the average z-height roughness (Δ) measured from XRR, and calculate Λ, based on a previously determined Gaussian relationship. The percent error between the measured and calculated values are within 10%, except for sample 1019_c which has a substantially higher level of roughness, which means our QW calculation no longer applies. Therefore we conclude that our theoretical model works for sample level roughness of 2nm or lower, roughly 20% of well-width. At this point that the charge carrier localization is build up to the point that there is a breakdown of the quantum-well effects, which results in an exponential increase in electrical resistivity. Therefore, it is evident that consistent and uniform low levels of roughness within the multilayer quantum well microstructure are of high importance in proceeding with the scaling-up of this technology.
As compared to commercially available n-type PbTe-based materials, which have a thermoelectric power factor between 0.0008-0.0012 W/m²K over the temperature range of 500-700K, our results indicate improved properties ranging from 0.0018 to 0.0023 over the same temperature range. In order to draw further conclusions on material performance however we must obtain thermal conductivity measurements at high operating temperatures. In a separate study on Si/SiC multilayer MQW structures the in-plane thermal conductivity showed no variation from that of the bulk properties for temperatures up to 300K. Using this assumption that our thermal conductivity is a combination of the bulk material properties we can then estimate a $ZT$ of 1.3-1.5 for our highest quality AZO/InAZO5 sample at 600K. Other studies however have shown that both the multilayer interfaces and poly-crystalline grain boundaries will act as scattering mechanisms for phonons, which makes it possible that the QW structure will reduce the thermal conductivity, which would ultimately result in even a larger $ZT$.

7.3. Band-Gap Offset Optimization

Barrier height variation and heating are two important physical processes affecting device properties for MQW thermoelectric materials. Therefore, the determination of losses associated with these processes is essential in designing a device. In theory, the carrier loss related to the temperature and barrier height can be described with the carrier loss mechanism. The multilayer hopping theory states that there is a large probability for a thermally excited carrier to pass over well/barrier interfaces before it emits phonons and settles down into a well.
With temperature increasing, electrons and holes are excited to higher energy states in the conduction and valence bands. The thermal carrier excitation changes the Fermi distribution of carriers in the well and results in carrier leakage from the well to adjacent layers. This process is understood by electron carrier distribution in the conduction band under thermal equilibrium. The number of electrons with energy greater than the barrier height of the conduction band is expressed as

\[
n_b = \sum_i \left[ \int_{E_{\text{int}}} g_{ci} f_{ci}(E_i) dE_i \right], \quad (48)
\]

where, \( E_{\text{int}} \) is the energy of the well barrier, \( g_{ci} \) is the density of electron states in the \( i \)-th sub-band higher than the barrier, and \( f_{ci}(E_i) \) is the Fermi function written as

\[
f_{ci}(E_i) = \frac{1}{1 + \exp\left(\frac{(E_i - E_{\text{fc}})}{k_B T}\right)} \quad (49)
\]

with \( E_{\text{fc}} \) being the quasi-Fermi level in the conduction band. With the Boltzmann approximation, Eq. (48) can then be expressed as

\[
n_b = g_{ci} k_B T^{3/2} \exp\left(-\frac{E_i}{k_B T}\right) \quad (50)
\]
Where $g_{cn}$ is the electron state density in sub-band energy $E_{nt}$, and $E_1 = E_{nt} - E_{fc}$ is energy greater than quasi-Fermi level in conduction band. Thus the overall carries loss involving barrier height variation is given by

$$n_L = G_n T^{3/2} \exp \left( \frac{-E_1 - \Delta E}{k_B T} \right)$$

(51)

where $n_L$ is the overall loss of carriers, $G_n$ is a constant relating the density of states and electron-hole pairs, $E_1$ is the energy greater than the quasi-fermi energy, and $\Delta E$ is the band-gap offset. The overall conductivity is then

$$\sigma = q (\mu_n (n - n_L))$$

(52)

where $\mu_n$ is the electron mobility, $n$ is the total carrier concentration, and $q$ is the charge constant. Now in addition to the carrier loss from multilayer hopping is the change in mobility, which is characterized by itinerant transport in the conduction band, governed by a range of scattering mechanisms. At low temperatures, scattering from ionized and neutral impurities dominate. At higher temperatures, a transition occurs and the dominating scattering mechanism becomes bulk phonon scattering, which in theory should not be impacted by the change in band-gap offset and thus we will assume any variation constant across the samples.
Using Eq. (52) we created a 3D plot of electrical conductivity as a function of operating temperature and band-gap offset, which itself is dependent on the doping concentration, mobility, and temperature. From Fig. 43 we note there is an optimum level of doping that varies with operating temperature. For example as the operating temperature is increased a larger band-gap offset is needed which can be achieved by increasing the indium doping in the well. In addition, Fig. 44 is a plot of the optimum band-gap offset ($E_{\text{opt}}$) for ZnO:Al / ZnO: (Al, In) QW structure over the temperature range of 300 to 1000K.

In comparing this model to our experimental study we see that the data aligns well for all three films. One possible area of miscalculation may come from the need to understand the high temperature impact further, including the bulk scattering mechanisms which was used here. Consequently, the optimal thermoelectric properties of the quantum-confined system take into account many material attributes. Also in addition to the systematic understanding of device performance reliable measurements such as high temperature thermal conductivity measurements must be obtained in order to have verifiable figure of merit data.
Fig 43: The QW electrical conductivity as a function of the indium composition for well and operating temperature.

Fig. 44: Plot of $E_{\text{opt}}$ for band-gap offset between well and barrier and operating temperature. This is a representative plot of the peak max located in Fig. 43.
Chapter 8

8.1. Conclusions

Within this work, a comparative study of the thermoelectric power factor of (Al, In) co-doped ZnO was performed, using a co-sputtering process to obtain 2 atomic % Al, and 0 – 10 atomic % In doped ZnO. The indium concentration level has strongly influenced the material microstructure which ultimately has impacted its thermoelectric power factor. The highest achieved power factor was for 2 at. % indium doping, which is 3 times that of pure AZO. At this indium doping, the large atom substitution into the Zn lattice points counteracts the stress created on the lattice by the smaller aluminum atom substitution. This ultimately allows for an increase in carrier concentration without any impact on mobility. At doping levels >2 at. % we observed an increase in poly-crystallinity, caused by enhanced stress within the lattice. This ultimately resulted in mobility losses and degradation in thermoelectric performance.

By fabricating quantum well multilayer structures of Al-doped ZnO and (In, Al) co-doped ZnO layers were deposited using a multiple target RF sputtering technique. The fabricated multilayer quantum well structures deposited show a reduction in electrical resistivity by an order of magnitude for the 2 and 5 at. % indium doped well structures, as compared to their counterpart bulk films. This result in combination with the material dependent Seebeck coefficient
enhancements results in a 3x improvement in the thermoelectric power factor and an estimated $ZT$ of 1.3 - 1.5 for the AZO/In$_{0.02}$AZO multilayer quantum well sample at 600K. However, process optimization for material parameters including layer thickness, interface roughness, and band-gap offset must be predetermined in order to optimize the device design.

The directionality of the carrier transport is largely dependent on the layer thicknesses. The well-width thickness is dominantly controlled by carrier confinement and thus in-plane transport at widths of 7nm-20nm. Below this thickness carriers have the ability to tunnel in-between wells, and above this thickness quantum confinement no longer is in effect. In addition, the larger the barrier layers the less-leakage thru cross-plane transport. However an ultimate trade off is volume ratio of well to barrier material. The goal is to have the smallest amount of barrier material to prevent leakage.

The local flatness of the multilayer structure has also proven to be critical for achieving optimum thermoelectric performance. Here, multilayer samples deposited resulted in a wide range of interface roughness ranging from 10-40% of the well-width depending on the location point from origin of the deposition chamber. From both experimental and theoretical calculations it is desired to have an interface roughness well-to-width ratio <0.1 in order to eliminate carrier localization and thus have optimized electronic transport within the multilayer structure.

In addition, Al-doped ZnO/(Al, In) co-doped ZnO with varying quantum indium content within the wells have shown degradation in performance for
certain high temperature ranges. A theory has been derived so that the doping of
the well can be altered to change the band-gap offset in order to provide optimum
thermoelectric properties over a specific temperature range. In designing
quantum well based devices this is an important contributing parameter. This
investigation has both experimentally and theoretically proven this concept using
samples of 2, 5, and 8 at. % In doped AZO wells. Our results indicate an
optimum temperature range of; 300-600K, 600-725K, and 725-850K for the 2, 5,
and 8 at. % indium doped wells, respectively.
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