Nanoscale Thermoelectrics: A Study of the Absolute Seebeck Coefficient of Thin Films

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Nanoscale Thermoelectrics: A Study of the Absolute Seebeck Coefficient of Thin Films

A Dissertation
Presented to the Faculty
of Natural Sciences and Mathematics
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In Partial Fulfillment
of the Requirements for the Degree
of Doctor of Philosophy

by
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June 2014
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Abstract

The world’s demand for energy is ever increasing. Likewise, the environmental impact of climate change due to generating that energy through combustion of fossil fuels is increasingly alarming. Due to these factors new sources of renewable energies are constantly being sought out. Thermoelectric devices have the ability to generate clean, renewable, energy out of waste heat. However promising that is, their inefficiency severely inhibits applicability and practical use. The usefulness of a thermoelectric material increases with the dimensionless quantity, $ZT$, where, $Z = S^2 \sigma / \kappa$, and $S$, $\sigma$, and $\kappa$ are the Seebeck coefficient and electrical and thermal conductivities respectively. These characteristic material parameters have interdependent energy transport contributions that classically prohibit the optimization of one with the detriment of another. Encouraging advancements of $ZT$ have occurred in the past ten years due to the decoupling of the thermal and electrical conductivity. Further advancements are necessary in order to produce applicable devices. One auspicious way of decoupling or tuning energy transport properties, is through size reduction to the nanoscale. However, with reduced dimensions come complications in measuring material properties. Measurements of properties such as the Seebeck coefficient, $S$, are primarily contingent upon the measurement apparatus. The Seebeck coefficient is defined as the amount of voltage generated by a thermal gradient. Measuring a thermally generated voltage by traditional methods gives, $V = (S_{sample} - S_{lead}) \Delta T$. If accurate values of, $S_{lead}$, are available, simple subtraction provides the answer. This is rarely the case in nanoscale measurement
devices with leads exclusively made from thin film materials that do not have well known bulk-like thermopower values. We have developed a technique to directly measure, $S$, as a function of temperature using a micro-machined thermal isolation platform consisting of a suspended, patterned SiN membrane. By measuring a series of thicknesses of metallic films up to the infinitely thin film limit, in which the electrical resistivity is no longer decreasing with increasing film thickness, but still not at bulk values, along with the effective electron mean free path, we are able to show the contribution of the leads needed to measure this property. Having a comprehensive understanding of the background contribution we are able to determine the absolute Seebeck coefficient of a wide variety of thin films. The nature of the design of the SiN membrane also allows the ability to accurately and directly measure thermal and electrical transport of the thin films yielding a comprehensive measurement of the three quantities that characterize a material’s efficiency. This can serve to further the development of thermoelectric materials through precise measurements of the material properties that dictate efficiency.
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Dedicated to Luke and Noel.
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Chapter 1

Introduction

Thermoelectric materials have the ability to convert heat into energy. With global warming of increasing concern, new sources of renewable energy are essential. Thermoelectric devices could serve to boost power generation anywhere where waste heat is produced, in any of today’s power plants, in conjunction with solar cells, or even in industrial manufacturing process. With thermoelectrics device chargers. Thermoelectrics are currently used to power satellites on long range missions converting minute amounts of heat in space to enough power to run the onboard equipment.

Thermoelectric materials can also be used as solid state heaters or coolers. Refrigerators could be made without harmful halo or hydrocarbons or space heaters that take a fraction of the power to operate. Also, because thermoelectric devices can be made on the nanoscale as well as the macroscale, they can be used in point cooling applications. In some solid state computing devices, it is crucial to have precise temperature control in a microscale region. Thermoelectric devices can provide that control. They are also currently used in some automobile applications to provide fine tuned climate control in luxury vehicles.
There are many possible applications for thermoelectric materials. They need to be more efficient, durable, non-toxic, affordable and easy to produce for thermoelectrics to reach their full potential. Significant advancement in the past ten years in thermoelectric device efficiencies have been due, in part, to the size reduction to the nanoscale. By studying quantum transport at this level it is possible to further probe the mechanisms that drive thermoelectric effects. At this scale, however, measuring material properties becomes more complicated. This thesis will serve to outline these effects and to address the measurement complications in order to further probe the physics governing them. As the scientific understanding of these materials advances, the possibility of increasing the amount of clean renewable energy gets closer to reality.

The main focus of this dissertation is on measuring the absolute thermopower of thin films by applying the effective Fuch-Sondhiemer model to a series of thickness of films to determine the lead contribution present in these measurements. Conventional thermopower measurements are relative measurements of the material being tested and of the lead being used to test them. In bulk material measurements, this contribution can be subtracted. In thin films that do not have well known values, this is not the case.

Thermal and electrical transport in thin film materials are known to deviate from those of bulk. This is due to the geometry dependent scattering mechanisms within the material. The effective Fuch-Sondhiemer model quantifies these effects. By using films of various known geometries, the absolute thermopower of thin films can be extrapolated.

To begin, an overview of thermoelectric device operation and efficiency characterization will be given. A review of current thermoelectric materials will follow. There is an urgent need to improve these materials or to develop new ones. One possible route to device improvement is through optimizing the Seebeck coefficient.
A further understanding of thermoelectric effects is required to accomplish this because the Seebeck coefficient is closely related to other electrical transport properties in thermoelectric materials that are important to efficiency as well.

A detailed explanation of the Seebeck effect and Peltier effects will be given. Efforts into the enhancement of the Seebeck coefficient in thermoelectric materials will be covered. Current measurement techniques will also be discussed. This will lead into the theoretical models that quantify the electrical transport that drives the Seebeck effect. These models quantify the changes in electrical transport that can change the absolute Seebeck coefficient of a thin film from that of a bulk material.

A description on the measurement technique used in this study will be given. It begins with the manufacturing of amorphous suspended SiN membranes that are patterned with heaters and thermometers. These structures have fine 2D temperature control and are capable of measuring thermal conductivity, electrical conductivity and Seebeck coefficients all on the same film. This circumvents errors that can occur when probing geometry dependent material properties. Data will be presented of thin films grown on these devices.

The goal of this study is to characterize the thin film lead contribution to a Seebeck coefficient measurement on such devices. Data will be presented on the measurements conducted to determine the absolute thin film Seebeck coefficients of gold films. With the thin film values calculated, data will be presented absolute Seebeck coefficient of the thin film leads and other metallic thin films. With the leads sufficiently characterized it is possible to make precise 2D measurements of the thermal and electrical conductivity as well as the absolute Seebeck coefficient of candidate thermoelectric materials. With these measurements further advances in the field may be made making it is possible to improve thermoelectric device efficiency, making them more applicable, thereby reducing the amount of fossil fuel burned in the world.
Chapter 2

Thermoelectric Devices

2.1 Introduction

Thermoelectric (TE) devices are promising sources of renewable energy. They generate power out of waste heat. If efficient thermoelectric materials were to available it would change the way we look at converting fuel into energy\[19]\text{,}[65]\text{,}[79]. In the example of a combustion engine, upwards of 50\% of the fuel spent to generate mechanical energy is lost to heat. Capturing and converting heat into electrical energy would significantly reduce the amount of fuel required to power a vehicle. That would be a revolutionary change for the automobile industry\[61]. Thermoelectric power generation can also compliment current sources of energy production, for example solar cells. The sun also produces heat. Solar cell efficiency would improve with the addition of thermoelectric materials. Thermoelectric materials could also be retrofitted into most power generation plants including, coal burning, natural gas burning, and hydroelectric\[79]. All of the these facilities generate heat as a by-product.

Thermoelectric materials revolutionizing the entire world is a lofty idea. There are some current small scale thermoelectric applications that are already in use. For
example, technology has developed a method to charge electric devices when traditional power sources are not available. A backpacker can charge his or her electronic devices with a thermoelectric generator purchased from www.powerpot.com just by lighting a small fire. Radioisotope thermoelectric generator devices are currently being used to power long range satellite missions[61]. These devices are currently impractical or unavailable for widespread use.

TE devices can also be used to precisely heat and cool objects. They are used on the micro-scale to point cool objects in solid state computing devices[11],[55]. TE devices are also used to keep picnic coolers cold when left in the sun and are offered at www.REI.com. They are also used as climate control devices in the seats of some luxury vehicles[62]. If TE devices were more efficient, they could replace costly natural gas burning furnaces or replace conventional refrigerators that contain toxic halo and hydrocarbon gases[61]. An additional benefit of using TE devices in furnaces and refrigerators is that thermoelectric materials operate with no moving parts and their performance is highly stable over time, needing little maintenance or replacement[79].

This chapter will provide an introduction into how thermoelectric materials are employed in devices to convert waste heat into power and transform small amounts of electricity into cooling and heating applications. To describe how well TEs are able to do this, we will characterize their efficiency which is dependent on thermal and electrical transport within the materials. Once that has been established, we can go on to explore current thermoelectric devices and how scientists are still trying to improve them. With the basics of thermoelectric properties outlined, we can then start to understand the dynamic physical properties that govern these effects.
2.2 Thermoelectric Devices

Let us begin with a simple example of two types of thermoelectric devices.

![Thermoelectric Device Cartoon](image)

(a) TE Power Generator  
(b) TE Cooling Device

Figure 2.1: Thermoelectric Device Cartoon

In both configurations, there are two dissimilar types of thermoelectric materials connected in series with conductive contacts. These models use a simple semiconductor model of a TE device with one branch being a p (positive) type and the other an n (negative) type semiconductor\[66\]. In the model of a Power Generating TE device figure (2.1a), one end of the device is connected to a heat source and the other to a heat sink. The heat difference across the material generates opposing potential differences along the two branches which drives a current thereby creating power out of heat. In the TE Cooling device figure (2.1b), a current is applied and allowed to flow through the two branches generating a thermal gradient on either end of the device. The hot side is generally hooked up to a heat sink so that it is constantly pumping out heat, thereby cooling an object[18]. The opposite orientation could be used to pump heat into a system. The direction of the applied current will dictate
the direction of the thermal gradient generated by the device just as the direction of applied thermal gradient will determine the direction of generated current in the other.

These two figures represent the basis of TE devices that will be explored in this thesis. This is the most efficient way of configuring them for their designed applications. TE device efficiency will be explored in the following section.

2.3 Thermoelectric Device Efficiency

A thermoelectric device is an energy conversion system that obeys the laws of thermodynamics. It’s ability to convert heat into energy is characterized in terms of efficiency. In general the efficiency, $\eta$, of a system such as this is defined by the ratio of useful output to a given input. Mathematically, it is expressed as,

$$\eta = \frac{\text{output}}{\text{input}} \quad (2.3.1)$$

To derive the efficiency of a thermoelectric system, we start with the example of a simple thermoelectric cooler as shown in figure (2.1b). We will start by assuming that the electrical contacts have zero resistance and that heat conduction occurs only along the two branches of the thermoelectric device. The expression of the heat conduction then becomes a combination of heat transport due to the Peltier effect and the heat conduction through the material,

$$Q_p = \alpha_p IT - \lambda_p A_p \frac{dT}{dx} \quad (2.3.2a)$$
$$Q_n = -\alpha_n IT - \lambda_n A_n \frac{dT}{dx} \quad (2.3.2b)$$

Where, $Q$, $\alpha$, $I$, $T$, $\lambda$ and $A$ are terms for the heat, thermal conductivity, current, temperature, Seebeck coefficient and area respectively. The $p$ and $n$ indices represent
the positive and negative doped semiconducting branches. It should also be noted that $\alpha$ will have reversed signs in the two branches with the p branch being positive and the n branch being negative. This means that the heat flow due to the Peltier effect will be opposed by the heat conduction through the material in both branches.

We must also include a contribution from Joule heating per unit length in each branch which is equivalent to,

$$\frac{Q}{L} = \frac{I^2 \rho}{A} \tag{2.3.3}$$

where $\rho$ is the resistivity of the material. Joule heating is not uniform across the length of a material. This can be considered by taking a second order derivative of the temperature gradient in heat transport portion of our original equation (2.3.2). For each branch this is expressed as,

$$-\lambda_p A_p \frac{dT^2}{dx^2} = \frac{I^2 \rho_p}{A_p} \tag{2.3.4a}$$

$$-\lambda_n A_n \frac{dT^2}{dx^2} = \frac{I^2 \rho_n}{A_n} \tag{2.3.4b}$$

These equations can be solved further for the rate of heat transported by applying appropriate boundary conditions and then recombined [60]. The cooling that occurs at the hot junction then becomes,

$$Q_c = IT_1 (\alpha_p - \alpha_n) - \frac{I^2 R}{2} - (T_2 - T_1)K \tag{2.3.5}$$

Where $T_1$ and $T_2$ are the temperatures at the hot and cold ends respectively and R and K are electrical resistance and thermal conductance, the geometry independent relations of $\rho$ and $\lambda$.

Where the thermal conductance of the two branches in parallel is,

$$K = \frac{\lambda_p A_p}{L_p} + \frac{\lambda_n A_n}{L_n} = K_p + K_n \tag{2.3.6}$$
The electrical resistance of the two branches in series is,

\[ R = \frac{L_p \rho_p}{A_p} + \frac{L_n \rho_n}{A_n} = R_p + R_n \] (2.3.7)

From looking at equation (2.3.5), we see that the Peltier term varies linearly with electrical current, \( I \), and the Joule term has a square relationship with current. This means that there must be a particular current \( I \) at which the cooling power reaches its maximum value. This is found by setting \( \frac{dQ}{dI} = 0 \). We then find an ideal current of

\[ I_q = \frac{(\alpha_p - \alpha_n)T_1}{R} \] (2.3.8)

Putting this back into our original equation, we then see

\[ Q_c(max) = \frac{(\alpha_p - \alpha_n)^2 T_1^2}{2R} - K(T2 - T1) \] (2.3.9)

From this, if \( T2 - T1 \) is too large, that is if the temperature difference is too great, then the second term of the equation would be reducing the cooling effect and the desired maximum cannot be achieved. By setting \( Q_c(max) = 0 \), we find the maximum temperature difference that can be achieved is,

\[ (T2 - T1)_{max} = \frac{(\alpha_p - \alpha_n)^2 T_1^2}{2KR} \] (2.3.10)

By letting,

\[ Z = \frac{(\alpha_p - \alpha_n)^2}{KR} \] (2.3.11)

Equation (2.3.10) simplifies to,

\[ (T2 - T1)_{max} = \frac{ZT_1^2}{2} \] (2.3.12)

In thermoelectric materials research, \( Z \) is called the figure-of-merit. We will return
to this in moment. At this point, we have an expression for the maximum cooling power of a thermoelectric refrigerator. To finish the efficiency expression, we need to optimize the amount of current supplied to achieve this cooling.

\[
W_p = \alpha_p I(T_2 - T_1) + I^2 R \tag{2.3.13a}
\]

\[
W_n = \alpha_n I(T_2 - T_1) + I^2 R \tag{2.3.13b}
\]

Summing those two equations gives the total power applied

\[
W = (\alpha_p - \alpha_n) I(T_2 - T_1) + I^2 R \tag{2.3.14}
\]

Using the ratio of these two equations, we get a coefficient of performance. By optimizing the coefficient to determine the maximum current with the same method as before, setting \( \frac{dn}{dT} = 0 \)

\[
\eta_{(\text{max})} = \frac{T_1((1 + ZT_m) - \frac{T_2}{T_1})}{(T_2 - T_1)((1 + ZT_m) + 1)} \tag{2.3.15}
\]

This derivation was meant to explain device efficiency from a thermodynamics standpoint and to express the importance of the term Z, or as it more commonly called ZT, the dimensionless figure-of-merit.

\[
ZT = \frac{\alpha^2 \sigma T}{\lambda} \tag{2.3.16}
\]

This is an expression for a single TE material and electrical resistivity \( \rho \) has been replaced by it’s inverse, electrical conductivity \( \sigma \). This expression is widely used in thermoelectric material discussions and will be referred to numerous times throughout this dissertation.
2.4 Dimensionless Figure-of-Merit

Thermoelectric devices seem great in theory they generate energy from waste heat and precisely cool and heat objects. Unfortunately, TE devices have not seen widespread implementation due to their lack of efficiency. To be considered efficient enough for everyday applications, ZT needs to be on the order of about 3-4 at the temperature range of use[64]. Most currently known bulk materials are limited to a $ZT \approx 1$ due to the coupling of the parameters that make up $ZT$.

![Figure 2.2: Electrical conductivity, thermal conductivity and Seebeck coefficient as a function of charge carrier density in a classical model and the limit imposed upon ZT.](image)

Figure 2.2: Electrical conductivity, thermal conductivity and Seebeck coefficient as a function of charge carrier density in a classical model and the limit imposed upon ZT.

Figure(2.2) displays a classical model of how these three parameters depend on carrier concentration in the material and how that dependence limits $ZT$. In materials with a low charge carrier concentration, like insulating materials, the thermal conductivity is low and the Seebeck coefficient is high but the electrical conductivity vanishes. In materials with a high charge carrier concentration, like metals, the electrical conductivity is high and the thermal conductivity is lower than that but the Seebeck coefficient nearly vanishes[77]. This explains why most
thermoelectric material research has focused on semiconducting materials[45]. To further enhance ZT past the classically imposed limit of one, it is essential to tune there properties in such a way that they are essentially decoupled, so that it is possible to optimize one material property with out the detriment of another making efficient thermoelectric materials attainable.

For an example of how this is achieved, the thermal and electrical conductivity can be considered. If the electrical conductivity is increased, the charge carriers are being allowed to flow more freely through the material. By allowing charge carriers to flow more freely in a material, it is possible for heat to flow more freely and in turn increase the thermal conductivity. If this is case, nothing has been done to increase ZT. This is where a more in depth knowledge of these material properties is crucial. For example, the total thermal conductivity is a combination of the heat carried by the electrons through the material and the heat carried by phonons in the lattice,

\[ k = k_e + k_l \]  \hspace{1cm} (2.4.1)

If a material was used with increased phonon scattering sites that do not affect the electron transport significantly, then it is possible to reduce thermal conductivity and increase ZT. This method has been widely employed by TE developers. By bringing \( k_l \) to the amorphous limit without considerably reducing \( \sigma \) has significantly driven recent advancements in TE devices[65]. These advancements have been made due in part, to size reduction to the nanoscale.
Figure 2.3: This is a plot of improvement of ZT over time, increasing in the past 10 years due to nanostructured and nanoscale materials. Materials for thermoelectric cooling are shown as the blue dots and for thermoelectric power generation as red triangles.[19]

Figure(2.3) shows the evolution of ZT over time for some nanoscale and nanostructured materials. The Hicks and Dresselhaus arrow represents when Hicks and Dresselhaus proposed a new way to reduce the thermal conductivity without reducing the electrical conductivity [32]. This will be discussed in greater detail in the next section. The recent materials all have exciting figures-of-merit but due their small size and complex structure. For those same reasons, applying them on a large scale will not be feasible for quite some time[65]. In the mean time, these materials can be studied so that their transport properties can be simulated in bulk materials.

There are still more advancements to be made in increasing ZT. For example, finding ways to increase the Seebeck coefficient with out reducing the electrical conductivity. These two parameters are classically inversely related. There is promising research being conducted into decoupling this relationship through density of states (DOS) tuning[58], charge carrier induced vibrational softening[4] and interface filtering of charge carrier energies[36]. This will be discussed in detail in the chapter.
2.5 Current Thermoelectric Materials

2.5.1 Nanoscale Thermoelectrics

There are many types of nanoscale materials. There thin films[75], nanotubes[54], nanocones[57], nanowires[33][12], and nanodot systems [3] all with higher ZT than their bulk counterparts. This is due the different physical phenomena that are introduced at these length scales. Nanoscale material size gives rise to such things as quantum confinement and interface effects, as well as, drastic changes in the charge carrier density of states. Quantum confinement effects serve to increase ZT by limiting the transport pathways in a material. If the size of the material is smaller than the mean free path of the phonon, for example, it is then confined and no longer contributes to the thermal conductivity, thereby reducing it. Interface effects can serve screen the phonons or the energy of the charge carrier passing through it. If an interface within a nanoscale material requires a defined amount energy to pass through then lower energy electrons can be scattered while higher ones are still able to conduct through the material. This can serve to decrease the total amount of conduction electrons which will increase the Seebeck coefficient while the electrons have significant amounts of energy that the electrical conductivity is not decreased. The density of states with in materials differs with length scale of the material as in figure (2.4). This can allow for precise tuning of the density of states to increase the Seebeck effect, which increases with sharp peaks in the density of states.
Figure 2.4: The change of DOS with size

It hasn’t been fully explained, at this point, how DOS tuning and interface screening can increase ZT. That will be in the next chapter. The point being made here is that, size reduction to the nanoscale gives rise to physical phenomena that can be used as tools to increase ZT. These same tools are not available for bulk materials.

Two examples materials that have enhanced efficiency on the nanoscale are Si and BiTe. Bulk Si is a poor thermoelectric with a low Seebeck coefficient and high electrical conductivity due its high concentration of charge carriers, this relationship was demonstrated in figure(2.2).

Figure 2.5: Cross-sectional SEM of an EE Si nanowire array[33]
When silicon’s size is reduced to one dimension experiences quantum confinement of the phonons, reducing the thermal conductivity and with doping the DOS can be tuned to optimize the electrical conductivity and Seebeck coefficient. The Si nanowires used in the study from figure(2.5) achieved a ZT above 3 when placed in arrays of this nature and above one for a single wire[33]. BiTe is known to be a decent thermoelectric material in bulk form, with ZTs of 1-1.5, as seen in figure(2.3).

![Image of BiTe alloys](image.png)

Figure 2.6: Image of a thin film array of BiTe alloys[71]

When BiTe is reduced to 2D, in a thin film, it also experiences quantum confinement effects and has reduced thermal conductivity and increased ZT of 2-2.5[65] depending on the dopant type and level. These films can also be built into arrays, as in figure(2.6) for large scale applications.

The same small scale that gives rise the high efficiencies of nanoscale thermoelectrics also produces challenges in large scale applications. They can be built into arrays but that is often difficult with current manufacturing technologies. They can also be used to understand thermoelectric processes and improve bulk materials. Quantum confinement techniques have been employed in bulk materials with some success and is the topic of the next section.
2.5.2 Nanostructured Thermoelectric Materials

As seen in figure (2.3), thermoelectric materials suffered a dry spell of about 40 years with a limit reached of $ZT \approx 1$. This was overcome, in part, by a study of nanoscale superlattice structured BiTe[59]. BiTe alloys were a material of interest to the TE community for some time with standard bulk BiSbTe achieving a $ZT$ close to one at room temperature[44]. By placing the BiTe in multilayers, Dressdaus and Hicks were able to confine the transport of the electrons in 2D while phonons were still able to move in 3D. This began a class of quantum well confinement structures in the phylum that would later be termed electron crystal/phonon glass materials by Hicks[32]. With the electrons confined to transport parallel within the layers, their mobility was not significantly inhibited in plane. The phonons, however, were still allowed to travel in 3D and scatter accordingly. Superlattice layers thinner than the mean free path of the phonons significantly reduced their contribution to the thermal conductivity and thereby increased $ZT[7]$.

![Figure 2.7: Image of a BiTe multilayer structure. Phonons can travel in x, y, and z and are scattered accordingly while electrons move freely in x and y.](image-url)
Nanostructured materials have been studied extensively\cite{11,6,32,55,65}. Most materials used in these studies are the heavier elements such as Bi, Pb, Ti and Sn at different mixtures and atomic spacing\cite{26}. These materials have seen increasing success through nanostructuring to achieve ZT’s above 2\cite{32,25,37}. It should also be noted that some of these materials are toxic, Pb for example, and these are not ideal candidates for everyday applications.

### 2.5.3 Rattlers and Cages

![An example of clathrate crystalline structure](image1)

(a) An example of clathrate crystalline structure

![An example of skutterudite crystalline structure](image2)

(b) An example of skutterudite crystalline structure

Figure 2.8: Cages and Rattlers

The concept of the phonon glass/electron crystal (PGEC) transport in materials gave rise to additional classes of thermoelectrics with improved efficiency. Two examples of these are clathrates and skutterudites. These materials achieve comparable TE efficiencies with the same PGEC transport ideal but instead of utilizing nanostructure effects, they rely on inherent crystalline structure. Clathrates are periodic solids in which tetrahedrally coordinated atoms form cages around a dopant atom. Vibrations from the caged atom serve to reduce phonon transport and thereby thermal conductivity\cite{23}. The lattice still allows for the efficient transport of charge carriers\cite{40}. Some Clathrates (SrGaGe) also have sharp peak in the density of states near the fermi level which increases the Seebeck coefficient, it can also increase the
electrical contribution to the thermal conductivity but it is thought that further tuning of the lattice structure with other combinations of clathrate materials will be able to account for that[53]. Skutterudites operate on the same scattering principles. Their cubic crystalline structure comes in many varieties but they are derived from CoAs$_3$ and can be filled by a number of candidate materials. One promising material was a skutterudite filled with Yb, Ca, Al, Ga, and In, producing a n-type thermoelectric with a ZT of 1 above at room temperature[29].

2.6 Summary

Thermoelectric devices can be used to generate electrical power out of heat and can also heat or cool objects with small amounts of power. This is a promising idea that has not yet fully materialized due to the inefficiencies of modern TE materials. Their efficiencies are characterized by the dimensionless figure of merit, ZT and ZTs greater than 3 are desired for significant advancement in the applications of thermoelectric materials. The interconnected parameters that constitute ZT are the source of the detainment in developing practical materials.

Materials with increased ZT have been found due to decreasing the phonon contribution to thermal conductivity with out decreasing electrical conductivity. This was a major advancement for thermoelectric materials. This was made possible by studies of nanoscale and nanosctructered materials. Many current bulk materials have by now reached the amorphous limit of phonon contribution to the thermal conductivity without reducing the electrical conductivity[20], [22]with ZT still less than three. The next step for bulk materials is to increase the Seebeck coefficient without decreasing the electrical conductivity in order to achieve applicable materials[68]. Nanoscale materials have desirable high ZT values but are difficult to manufacture on a scale necessary for widespread implementation. By studying nanoscale materials it is possible to better understand the properties that allow them their high
efficiencies enabling the development of high efficiency bulk materials. For this to occur, precise nanoscale measurements of the thermal and electrical conductivity as well as the Seebeck coefficient are needed. A method for precisely measuring these material properties will be present later in this thesis. Before the measurement is discussed a synopsis of thermoelectric effects and some techniques for enhancing the Seebeck coefficient will be discussed.
Chapter 3

Thermoelectric Effects

3.1 Introduction

As presented in the chapter two, a detailed understanding of thermoelectric effects are essential for the development of TE devices. The application of the phonon glass-electron crystal model for thermal transport has been perfected in a variety of thermoelectric materials with thermal conductivities reaching the amorphous limit. The next step to increase device efficiency is the improvement of the power factor, $S^2\sigma$ of $ZT$. These two electrical transport parameters are closely connected and it takes strategy to increase, $S$, with out decreasing $\sigma$ or increasing the electrical contribution to the thermal conductivity that could bring it above the amorphous limit.

This chapter will serve to outline thermoelectric effects. By deriving the Seebeck coefficient through formal transport theory and statistical thermodynamics, we probe what causes this effect and how to optimize it. Methods of enhancing and measuring the Seebeck coefficient will also be discussed.
3.2 Seebeck Effect

The Seebeck effect was first discovered by Thomas Seebeck in the 1820’s when he observed a magnetic field generated by connecting two materials (Bismuth and Copper) in a closed loop and applying heat to one end.

![Illustration of the first Seebeck Experiment](image)

The magnetic field Seebeck was able to observe was generated by a solid state current produced by opposing thermally generated voltages in the two materials. With the current in the Bi traveling from the hot to cold end while the current in the Cu traveled from the cold to hot end. This is illustrated in figure (3.1).

The Seebeck coefficient of a single material, also known as absolute Seebeck coefficient or thermoelectric power (TEP), is the amount of voltage generated by applied thermal gradient.
This is expressed as,
\[
\alpha = S = -\frac{\Delta V}{\Delta T} \quad (3.2.1)
\]

This effect occurs when hot charge carriers diffuse from the hot side of the material to the lower energy states on the cold side producing potential difference across the material that is a measurable as voltage. In a semiconductor, S is negative for negatively doped materials where electrons are the predominant charge carrier and positive for positively doped materials where holes are the predominant charge carriers[17]. A measurement of the sign of the Seebeck coefficient is often an easy test for determining the dominant charge carrier in simple semiconductor[44]. The is the same concept demonstrated in figure(2.1) of thermoelectric devices. The actual Seebeck coefficient is more intricate than this model would make it seem.

3.2.1 Energy Transport Model of the Seebeck Coefficient

The basic energy transport model for the Seebeck Coefficient of a material is termed, the Mott Equation,
\[
S = -\frac{\pi^2 k^2 T}{3e} \left( \frac{d\ln\sigma(E)}{dE} \right)_{E=E_F} \quad (3.2.2)
\]

Where \( k, e, \) and \( E_F \) are the Boltzman constant, electron charge, and Fermi en-
ergy respectively. The term $d\ln\sigma(E)/dE$ is the energy derivative of the logarithmic electrical conductivity as a function of energy with respect to the Fermi energy. In insulators and semiconductors, the charge carrier density of states is often much less than the density of thermally available states. In this circumstance, the addition of a thermally generated charge carrier above the Fermi surface to the electrical conductivity significantly increases the Seebeck coefficient of the material. This is not the situation that exists for metals with their conduction states, thermal excitable and otherwise, near the Fermi energy. As a result, good electrical conductors have low Seebeck coefficients.

To better understand the Seebeck coefficients in metals, we can use the expression for $\sigma$ from the formal transport kinetic theory \[42\] applicable for Fermi surfaces that are not necessarily round,

$$\sigma = \frac{e^2 \lambda A}{12\pi^3 \hbar}$$

Where $\lambda$ and $A$ are the electron mean-free path and Fermi area respectively. Substituting a simplified version of this in for $\sigma(E)$ we get the expression,

$$S = -\frac{\pi^2 k^2 T}{3eE_F} \left( \frac{d\ln A}{dE} + \frac{d\ln \lambda}{dE} \right)_{E=E_F}$$

The first term depends on the how the interaction between the Fermi surface with respect to the first Brilluion zone (FBZ) changes with energy. As the Fermi surface expands within the FBZ, this term is positive. Once the Fermi surface reaches the zone boundary, it will begin to decrease making the term negative. The change in sign can be made clear by the understanding that when the FBZ is nearly full, the dynamical mass of the electrons becomes negative. This is an indication that there are then holes in the conduction band. In some cases, this negative term can dominate the second making $S$ positive for some metals. A positive $S$ for a metal seems counterintuitive at first glance with the sign of the Seebeck is the predominate
method of measuring the charge carrier concentration type in semiconductors and metals predominately have electrons as charge carries. The location of the FBZ with respect to the Fermi energy is why some metals and all noble metals have positive Seebeck coefficients[10]. This term can large and positive for insulators due to the thermally available conduction bands above the Fermi surface.

The second term should be positive in metals with difficult to scatter high energy electrons with long mean-free paths. The opposite is the case in insulators and it should also be small[81]. Both of these terms can go either way with semiconductors depending on the dopant type and carrier mobility.

### 3.2.2 Thermodynamic Model of the Seebeck Effect

To further understand the Seebeck coefficient, it is helpful approach it from a thermodynamic standpoint. From this aspect, the Seebeck Coefficient is defined, as the amount of electrochemical potential difference or electromotive force, \( emf \), generated by induced thermal gradient divided by its charge, and \( \frac{emf}{q} = \text{Volt} \). This can be described by using a general application of irreversible thermodynamics, or the statistical study of flows of heat, particles and charge[17]. Given that, the electrochemical potential is the potential associated with applied fields plus the materials chemical potential and that charge flow is driven by the electrochemical potential gradients as well as thermal gradients. The electrical current density, or the charge per unit time passing through a unit cross-sectional area, can be expressed as,

\[
qJ_N = -\left( \frac{\sigma}{q} \right) \nabla \mu - \sigma \alpha \nabla T \tag{3.2.5}
\]

Where \( \sigma, \mu \) and \( \alpha \) are the electrical conductivity, electrochemical potential and Seebeck coefficient respectively. In an open circuit configuration where there is no net flow of charge carriers, the current flow driven by the temperature gradient is opposed and canceled by the current flow driven by the electrochemical potential.
This opposition to the temperature gradient induces a gradient of the electrochemical potential. This results in measurable voltage.

$$\nabla \mu = -q \alpha \nabla T$$  \hspace{1cm} (3.2.6)

When the temperature gradient in an electrically open circuit produces the current flow, the emf driving the current flow equals $-\nabla \mu / q$. This is the driving force that produces the Seebeck effect. This creates the general formula for a single material’s Seebeck coefficient to be,

$$\alpha = -\frac{1}{q} \frac{\nabla \mu}{\nabla T}$$  \hspace{1cm} (3.2.7)

When the gradients, both generated and produced, in the measurement of Seebeck coefficients is small, the ratio of the gradients equals the ratio of the differentials. In this case, the definitions of the Seebeck coefficient in equations (3.2.1) and (3.2.7) are seen as equivalent.

We can further show the significance of the Seebeck coefficient by expressing it in terms of heat current density,

$$J_Q = T \alpha q J_N - \kappa_T \nabla T$$  \hspace{1cm} (3.2.8)

where $\kappa_T$ is the thermal conductivity. The entropy current density, $J_S$, can be expressed in terms of heat flow by $J_Q = T J_S$. Substituting this into equation (3.2.8)

$$J_S = \alpha q J_N - \frac{\kappa_T}{T} \nabla T$$  \hspace{1cm} (3.2.9)

In an isothermal situation, this would result in the Seebeck coefficient being the entropy carried per unit charge in a material. It is useful to relate the Seebeck coefficient to the the laws of thermodynamics so that we can see, for example, that by the third law, entropy vanishes at absolute zero and so should the Seebeck
effect[17]. We will not be focusing on low temperature Seebeck coefficients in this thesis, however rather, we are focusing on the range from 77K-325K. Thermoelectric devices are desired to be of use at room temperature and measuring them across a temperature range allows for transport properties of the material to be probed. These material properties vary with temperature and measuring how the thermal electrical transport, measured as the Seebeck coefficient for example, can determine the mechanism behind variation.

It is straightforward to show the relationship between charge carrier concentration and Seebeck coefficient using thermodynamics. Starting from the solution of the linearized Boltzmann equation, which equates the rate of a function to the forces acting upon it, and substituting some known values while setting the charge current density to zero (again Seebeck measurements are conducted with no net current flow across the material), we are left with the result,

\[ \alpha = \frac{k}{q} \frac{\langle (E - \mu) \rangle_{\sigma(E)}}{kT} \]  

(3.2.10)

where \( \langle (E - \mu) \rangle_{\sigma(E)} \) is the average of the energy difference of the charge carriers from the chemical potential with respect to the electrical conductivity per unit energy. Then for simplicity, assume we have a single band in which all \( N \) states of an the band have the same energy. In this limit, the relation between the number of carriers, \( n \), and the chemical potential \( \mu \) is the expression,

\[ n = \frac{N}{e^{(E-\mu)/kT} + 1} \]  

(3.2.11)

We can then rewrite equation (3.2.11) in terms of (3.2.10)

\[ \alpha = -\frac{k}{|q|} \ln \frac{1 - c}{c} \quad \text{with} \quad c = \frac{n}{N} \]  

(3.2.12)
This is an explicit way to show the relationship of the Seebeck coefficient to carrier concentration[17].

If a material scientist was looking for a way to tune the density of states of a material without reducing the electrical conductivity, it is useful to further study these models. One approach to is to have sharp increases of the density of states near the conduction band leaving an overall low density of states, this method is termed, density of states tuning[58]. Low density of states leads to high Seebeck coefficients as equation (3.2.12) illustrates and still having available charge carries in the valence band keeps the electrical conductivity high. The sharpness of the peak is also important and will be detailed in a following section. Other ways to increase the Seebeck coefficient with out significantly effecting the electrical conductivity, that can be understood through this model are, electric conduction through traditional hopping events or even more promising carrier-induced softening of lattice vibrations [22]. This will also be detailed in a following section.

3.3 Peltier Effects

There are other related thermoelectric effects that govern device efficiency. The Seebeck coefficient is often discussed for its role in ZT but Peltier coefficient is also an important to thermoelectric material development. As seen in figure (2.1b), the Peltier effect, another thermoelectric phenomenon, is the basis for cooling devices. It occurs when a current passes through a junction between appropriate dissimilar materials. It can be used to precisely cool objects on the microscale for computing applications or cool large objects using only small amounts of power.

The Seebeck effect is related to the Peltier effect. The Peltier effect occurs when an electrical current is applied and a thermal gradient is produced. In the Seebeck effect, an applied thermal gradient generates a potential difference. The two effects are related by the second Kelvin Relation, named after Lord Kelvin, who observed
the relation between the two. The Peltier coefficient, $\Pi_{AB}$, for a current passing through a junction between two materials A to B, is the difference between the heat flow associated with the carriers leaving the junction, $-J_{Q,A}$, and that associated with carriers entering the junction, $J_{Q,B}$, divided by the electric current passing through the junction, $qJ_N$. This can be related to the Seebeck coefficient of the two materials in an isothermal junction as,

$$\Pi_{AB} = \frac{J_{Q,B} - J_{Q,A}}{qJ_N} = T(\alpha_B - \alpha_A) \quad (3.3.1)$$

This relation was found experimentally by Lord Kelvin. His thermodynamic proof of equation (3.3.1) involved assumptions outside of the first and second laws of thermodynamics. Lars Onsager later proved the existence of reciprocal relations that became the central law of the thermodynamics of irreversible processes, with that the relationship between the Peltier and Seebeck coefficients were fully proven.

The Onsager’s theorem is detailed proof of this relation that may be referenced in various books [28]. The basics of the theory are as follows, suppose there are a set of generalized currents, $J_1, J_2, ..., J_n$, flowing in a system under the influence of generalized forces, $X_1, X_2, ..., X_n$. The currents will be linear functions of the forces such as,

$$J_i = \sum L_{ij}X_i \quad (3.3.2)$$

Where the, $L_{ij}$ term are gradients of electric field and temperature. Suppose that $J_i$ and $X_i$ are defined in such a way that,

$$\tilde{S} = \sum X_iJ_i \quad (3.3.3)$$

is the rate at which entropy is produced in the system, resulting in the symmetrical
matrix of coefficients $L_{ij}$ that is,

$$L_{ij} = L_{ji}$$  \hspace{1cm} (3.3.4)

The electrical and thermal current equations in terms of gradients of electric field and temperature are as follows,

$$\vec{J} = \sigma \begin{pmatrix} 1 & \alpha \\ \Pi & \frac{5}{\sigma} \end{pmatrix} \nabla V$$

$$\vec{Q} = \sigma \begin{pmatrix} 1 & \alpha \\ \Pi & \frac{5}{\sigma} \end{pmatrix} \nabla T$$  \hspace{1cm} (3.3.5)

Given the symmetry of the Onsager relations, it can be seen from equation (3.3.5) that the Peltier and Seebeck coefficients are related to each other. Putting these currents in terms of the entropy of the system and solving it out produces the temperature term that makes up rest of the relationship between the two and equal to (3.3.1).

### 3.4 Some Strategies for Increasing the Seebeck Coefficient

#### 3.4.1 DOS and Fermi Level Tuning

With thermoelectric effects outlined, a further discussion on optimizing the power factor, $S^2\sigma$, of ZT can be made. We will begin with one popular way of increasing this power factor, Density of states (DOS) and Fermi level tuning[21],[58].. This method adjusts the Femi level and/or the DOS of a material by introducing various doping elements in the host semiconducting lattice. The goal of this doping is to create local increases of the DOS over a narrow energy range, $E_R$. These local increases occur when the valence band of a host semiconductor resonates with one energy level of a localized atom in the semiconductor matrix.
This effect can be seen by rewriting the original Mott equation (3.2.2) with electrical conductivity in terms, \( \sigma = n(E)q\mu(E) \) where \( \mu(E) \) is the energy dependent mobility of the charge carriers and \( n(E) \) is the charge carrier concentration given by, \( n(E) = g(E)f(E) \).

\[
S = \frac{\pi^2 k_B^2 T}{3q} \left[ \frac{1}{n} \frac{dn(E)}{dE} + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right]_{E=E_F} 
\]  

(3.4.1)

A side note for clarification of logarithmic rules,

\[
\frac{1}{n} \frac{dn(E)}{dE} = \frac{d \ln n(E)}{dE} 
\]  

(3.4.2)

As can be seen by equation(3.4.2), increasing the energy dependence of the density of states near the Fermi energy can increase, \( S \). This must be accomplished in such a way that does not significantly increase the total charge carrier concentration. If proper dopants are selected this can result in increased Seebeck coefficients with
out decreased electrical conductivity. There are still enough available electrons to conduct energy in the valence band by increasing the energy dependence of those electrons near the Fermi energy and having a low total charge carrier concentration, the Seebeck coefficient is being increased.

This can be a complicated process in which the benefits of the optimization of the power factor leading a rise in the electrical contribution to the thermal conductivity bring it above the amorphous limit [40]. Also, localized increases of the DOS in an energy range where the mobility of the charge carriers is significantly decreased enough to reduce the electrical conductivity[12]. Studies and the selection of dopant elements are conducted with complex band modeling of the materials. These studies have seen some success with a factor of 2 increase in ZT of some nanostructured PbTe alloys. Traditionally, Na was used to dope the PbTe for a p-type thermoelectric material but by using Tl instead and tuning the concentration, the factor of two increase was achieved[9]. Another study on PbTe by doping it with thallium[21]. This study was able to show a high temperature increase in ZT to 1.5 but still not promising at room temperature. It is also interesting to add that this study sources DOS tuning in Bi nanowires[31] that demonstrated high Seebeck coefficients as part of the motivation for this study, since nanoscale material Seebeck coefficients measurements are the main topic of this dissertation.

3.4.2 Electronic Conduction Through Hopping Mechanisms

There are number of ways to utilize charge carrier hopping mechanisms to enhance ZT. In general, a trapped charge carrier has a higher effective mass and a lower mobility[6]. This will lead to the material having a higher Seebeck coefficient. If the charge carrier is trapped in such a way that allows it to hop along the lattice with additionally energy added to the system through thermal or electrical currents the material could have an appreciable electrical conductivity.
One example of an application of electrical condition through hopping mechanisms to improve ZT is variable-range hopping (VRH). This type of hoping mechanism is dominant in disordered semiconductors and depends upon the distance/energy the electron needs to hop in order for conduction to occur. This conduction mechanism leads to an Seebeck coefficient dependence on temperature of $S \equiv T^{1/2}$.[83]. Disordered materials tend to have low thermal conductivities so studies were conducted in semiconductors known to exhibit VRH with little success due to the decrease in the electrical conductivity. There are additional studies and possibilities of enhanced Seebeck coefficients through hopping mechanisms, for example, thermally induced polaron hopping in perzoskites [39]. This method takes advantages of the spin states within the material to enhance the hopping[56].

3.4.3 Carrier-Induced Softening of Atomic Vibrations

Charge carrier induced softening of atomic vibrations occurs through electronic-lattice interactions. Localized charge carriers reduce vibrational stiffness constants in their surroundings. This carrier induced softening augments the Seebeck coefficient of solids whose carriers hop between localized states. The hopping carrier transfers additional vibrational energy with it as it moves. These softening contributions are independent of charge carrier concentrations[17], so the electrical conductivity is not reduced with increasing the Seebeck coefficient. The Seebeck coefficient can be written in terms of of two contributions.

$$S = S_{intrinsic} + S_{transport}$$  \hspace{1cm} (3.4.3)

The additional vibrational energy of the charge carriers increases the second term and increases ZT. It was found in a study of boron carbide that carrier-induced softening doubled the Seebeck coefficient [4]. The effect on the electrical conductivity
is thought to be negligible. The impact on the thermal conductivity of these samples still needs to be determined.

Introducing carrier induced softening of atomic vibrations to a material does produce hopping events of the charge carriers. This is different from traditional hopping enhancements of the Seebeck coefficient. Methods of enhancing the Seebeck coefficient in the last subsection were focused on increasing the effective mass and resistance of thermal currents in charge carriers. This method focuses on transferring more energy with the charge carrier.

3.5 Thermoelectric Effect Measurement Techniques

Seebeck coefficient measurements are traditionally conducted by applying a known thermal gradient to a material and measuring the steady state voltage generated with no current passing through the system. The voltages that are directly measured are that of the material being tested and of the leads being used to test them. The measurement being one of the lead material A from $T_o$ to $T_h$ to material B from $T_h$ to $T_c$ and then back to the lead material A from $T_c$ to $T_o$. This leads to the voltage measured due to applied thermal gradient across a material of interest being a function of the Seebeck coefficient of the two materials. This method has been applied to a wide variety of bulk materials. The contributions of the leads are then subtracted from the relative values and absolute Seebeck coefficients of bulk materials can be attained. This has been made possible by characterization of a variety of bulk lead materials by using superconducting leads that do not contribute to the Seebeck effect [50] over a wide temperature range.

Various techniques have been used to measure the absolute Seebeck coefficients of thin films [47],[76]. Some use bulk leads that are easily subtractable. Some use leads that are known to have small Seebeck coefficients relative to the thin film being tested leading to a negligible measurement errors. This has caused discrepancies in
absolute Seebeck coefficients of TE materials where the lead contribution has not been properly taken into account [46]. With a detailed understanding of the absolute Seebeck coefficients of TE materials necessary for their advancement, this needs to be resolved.

3.6 Summary

The Seebeck coefficient of a film is a measure of the voltage generated across a material when a thermal gradient is applied to it. It can also be defined as the amount of entropy carried per unit charge in a material. It depends on the changes of the Fermi surface and mean free path in the material with respect to energy. This can also be defined in terms of charge carrier concentration in the material.

The Seebeck coefficient is related to Peltier coefficient by the temperature. This relationship was first observed by Lord Kelvin and then proved using the Onsager reciprocal relations of the thermodynamics of irreversible processes. These processes are termed irreversible because they are related through the entropy of the system which is a time irreversible property.

Optimizing the Seebeck coefficient is challenging because it is inversely related to the electrical conductivity. Increasing the Seebeck effect with out significantly decreasing the electrical conductivity is arduous but possible and the next step in increasing the efficiencies of thermoelectric materials. Accurate measurements of thin film Seebeck coefficients could serve to significantly further the understanding of the thermoelectric power by probing the transport properties that govern it.
Chapter 4

Theoretical Models for Electron Transport in Thin Metallic Films

4.1 Introduction

To measure the absolute Seebeck coefficient of thin films and the thin film leads used to test them in this study, it is necessary to employ some mathematical models. This chapter will serve as a brief overview of those models and how they will be utilized.

These models characterize the difference of electronic transport properties in thin films compared to their bulk counterparts. Thin film materials are known to have different characteristic material quantities than their of bulk counterparts[15]. Quantities that are sample size independent in bulk samples, such as the Seebeck coefficient, are size dependent in the thin film regime and do not always agree with bulk values. These disparities emerge from the different thermal and electrical transport occurring within the same materials that are different scales. This is due
to increased scattering events in thin films. Understanding these differences can aid in the development of thermoelectric materials. This understanding can also provide highly accurate measurements of these transport properties, and others, by being used to characterize the thin film lead contribution to a Seebeck coefficient measurement.

To understand how scattering events in thin films can change a material’s thermal and electrical transport properties, it is best to begin with an example of a metal material’s characteristic quantity, electrical conductivity, $\sigma$, or expressed inversely electrical resistivity, $\rho$.

$$\sigma = \frac{1}{\rho} \quad (4.1.1)$$

This property is described through simple kinetic theory through the following equation,

$$\sigma = \frac{nq^2l}{mv} \quad (4.1.2)$$

where $q, l, m,$ and $v$ are the charge, mean free path, mass and velocity of the electron respectively. The number of atoms per unit volume, $n$, is the integral of the Fermi distribution function, $f$, expressed in terms of the $\vec{k}$ space dependent energy over $\vec{k}$ space.

$$n = \int \frac{\epsilon(\vec{k})f(\epsilon(\vec{k}))}{4\pi^3} d\vec{k} \quad (4.1.3)$$

With $\vec{k}$ space being the periodic reciprocal lattice space of the material and the Fermi distribution function being,

$$f(\epsilon) = \frac{1}{e^{(\epsilon - \mu)/k_BT} + 1} \quad (4.1.4)$$

where $\mu$ is the fermi energy. This model yields large mean free paths of electrons that increase rapidly in a metal towards very low temperatures. It assumes that the conduction electrons are free to move through the lattice and the number of those
free electrons is on the same order as the number of atoms [5]. This kinetic theory of electron transport does not directly consider the impact of electron collisions on the electrical conductivity of the material. This is found to be necessary in samples that have reduced geometry that result in electrical conductivity values that deviate from those of bulk materials.

To account for this deviation, Fuchs imposed surface boundary conditions on the mean free path and velocity of the electrons using a ratio of specular and diffuse scattering events at those boundaries to account for the changes in electrical conduction in reduced geometry samples[24]. This was rigorously expanded upon by Sondheimer through the use of the same boundary conditions proposed by Fuchs with a restricted Boltzmann equation on the electron distribution functions[67]. This was taken a step further by solving for multiple scattering events due to impurities, grain boundaries, as well as, film thicknesses by Mayadas and Shatzkes[48]. These two models were related to each other by Tellier and Tosser by the means of an effective electron mean free path model. The main goal of this dissertation is to utilize the Tellier and Tosser version of the Fuchs-Sondheimer (FS) model to calculate the absolute Seebeck coefficient of thin metal films[1]. This chapter will serve to outline these models and describe how it will be put to use.

4.2 Fuchs-Sondheimer Model

In the early 1960’s, a study of thin metal films revealed that as the thickness of the films decreased, the electrical resistivity decreased as well[38]. This prompted Fuchs to impose boundary conditions on a statistical distribution of free paths and velocities of electrons in a sample with a portion of those electrons scattering specularly and diffusely at the surfaces of the films. The degree of scattering defined as $p$ which is the ratio of the electrons scattered specularly to diffusely at the surface of the material. In the event of specular scattering, the velocity vector of the elec-
tron changes sign and in the event of diffuse scattering, it is terminated. To further quantify this effect Sondheimer, applied a strict statistical analysis based on the Boltzmann equation for the distribution function of the conduction electrons. This equation is formed by equating the rate of change in, $f$, due to external fields to the rate of change due to the collision mechanism.

$$\frac{e}{m} (\bar{E} + \frac{1}{c} \bar{v} \times \bar{H}) \cdot \nabla_{\bar{v}} f + \bar{v} \cdot \nabla_{r} f = f(\bar{r}, \bar{v}, t) \quad (4.2.1)$$

By considering a metal film of thickness $a$ with a $z$ axis perpendicular to the plane of the film and the surfaces of the film at $z = 0$ and $z = a$, the problem becomes a 1D one with a distribution function of the form,

$$f(z, \bar{v}_z, t) = f_o + f_1(z, \bar{v}_z, t) \quad (4.2.2)$$

where the function $f_1$ depends on the space variables and $f_o$ is the original distribution function. The 1-D Boltzmann equation, neglecting deviations from Ohms law, reduces to,

$$\frac{\partial f_1}{\partial z} + \frac{f_1}{\tau v_z} = \frac{qE}{mv_z} \frac{\partial f_o}{\partial v_x} \quad (4.2.3)$$

The general solution for $f_1$ then becomes,

$$f_1(\bar{v}, z) = \frac{q\tau E}{m} \frac{\partial f_o}{\partial v_x} \left[1 + F(\bar{v})exp\left(-\frac{z}{\tau v_z}\right)\right] \quad (4.2.4)$$

To determine $F(\bar{v})$, boundary conditions are introduced. The velocity component of this function has two sets of boundary conditions. A solution to both are found and then a reduction factor to the electrical conductivity will be calculated. The first set of boundaries assume totally diffuse scattering of the electrons at the surfaces of the material for $v_z > 0$, electrons moving away from the surface, vanish at $z = 0$ and for $v_z < 0$ they vanish at $z = a$. The second set of boundary condition assumes
completely specular scattering with $v_z > 0$ becoming $v_z < 0$ at $z = 0$ and $v_z < 0$ becoming $v_z < 0$ at $z = a$. With the solution to the two sets of distribution functions, the current density can be calculated by the following equation,

$$\vec{J} = -2q\left(\frac{m}{\hbar}\right)^3 \int \vec{v} f d\vec{v}$$  \hspace{1cm} (4.2.5)$$

and inserting the result into

$$\sigma = \frac{1}{Ea} \int_0^a J(z) dx$$  \hspace{1cm} (4.2.6)$$

and integrating by parts, we are left with the relation for $\sigma$ that is lengthy and cumbersome. It is much more conveniently expressed in terms of a reduction factor of the thin film electrical conductivity to that of the bulk,

$$\frac{\sigma_o}{\sigma} = \frac{F}{\kappa}$$  \hspace{1cm} (4.2.7)$$

Where, $\kappa$, equals the thickness of the film divided by the mean free path of the electrons and, $\sigma$, and, $\sigma_o$, are the thin film and bulk conductivities respectively. The, $F$, term is the reduction factor of the electron mfp. It is expressed as,

$$\frac{1}{F} = 1 - \frac{3}{2} \kappa(1 - p) \int_1^\infty \left(\frac{1}{t^3} - \frac{1}{t^5}\right) \frac{1 - e^{-t\kappa}}{1 - pe^{-t\kappa}} dt$$  \hspace{1cm} (4.2.8)$$

This relationship, in the regime where the thin film thickness is much larger than the mean free path, $\kappa \gg 1$ the reduction ratio becomes,

$$\frac{\sigma_o}{\sigma} = 1 + \frac{3}{8\kappa} (1 - p)$$  \hspace{1cm} (4.2.9)$$
In the regime where the mean free path is much larger than the film thickness, it becomes,

\[
\frac{\sigma_o}{\sigma} = \frac{4}{3} \left( 1 - \frac{1}{1 + \frac{1}{3} \kappa \log(1/\kappa)} \right) \quad (4.2.10)
\]

This model demonstrated excellent agreement with a study of micron thick tin films. It was later shown that in some thin films, surface scattering events were not the only mechanism causing the deviation of the electrical conductivity from bulk values. In this situation the FS model is inadequate. This realization sparked the development of the MS model.

### 4.3 Mayadas-Shatzkes Model

In the late 1960’s, a study of polycrystalline aluminum was conducted over a range of thickness. According to the FS model in the regime \( \kappa \approx a/l \) the ratio of specular and diffuse surface scattering, \( p \) is the only term is responsible for the reduction of the electrical conductivity from that of bulk. The Al study showed changes in thin film electrical conductivity in this regime that were inadequately explained by the surface scattering ratio ratio alone[48]. They found the increasing grain boundary sizes of the films with increasing thickness to be the source of the discrepancy. This prompted Mayadas and Shatzkes (MS) to improve on the model. By using the same derivation method and adding in background and grain boundary scattering boundary restrictions, the model was improved to agree with the data collected.

In the MS model, in addition to the surface scattering ratio \( p \), an additional grain boundary scattering term is defined as,

\[
\alpha = \frac{l_o}{a_g} \frac{r}{1 - r} \quad (4.3.1)
\]
where $a_g$ is the size of the grain and $r$ is the grain boundary reflection coefficient.

![Diagram of boundary scattering conditions](image)

Figure 4.1: Illustration of the boundary scattering conditions imposed in the MS model on the mean free path of the electrons. $l_L$ is the mfp of the electron in the lattice that propagates in the confined spherical solid angle, $l_S$ is the effective mean free path due to scattering events with the surface and $l_{GB}$ is the effective mfp due to scattering events at grain boundaries.

This model has a much more complicated reduction factor with a similar relation to equation (4.2.7), with the addition of the the grain boundary reduction the reduction factor works out to be,

$$\frac{\sigma_o}{\sigma} = \frac{1}{3}(3 - \frac{2}{\alpha} + \frac{1}{\alpha^2} - \frac{1}{\alpha^3 \ln(1 + 1/\alpha)})$$  \hspace{1cm} (4.3.2)

With $\alpha \gg 1$ this reduces to

$$\frac{\sigma_o}{\sigma} \approx 1 + \frac{3}{2}\alpha$$  \hspace{1cm} (4.3.3)

and with $\alpha \ll 1$

$$\frac{\sigma_o}{\sigma} \approx \frac{4}{3}\alpha$$  \hspace{1cm} (4.3.4)

This model was found to be much more effective to predict the reduction of the electrical transport in thin metal films. It matched experimental values of the reduced electrical conductivity within a few percent in thin cobalt films[49]. This model as also been used to predict the reduction of thermal conductivity[41]. and electron mean free path[80] in pure crystalline aluminum and copper films to with in a few percent.
4.4 The effective FS model

These models, while both effective when applied correctly to the proper type of scattering mechanism present in the film, are unwieldy. What Tellier and Tosser proposed is there being a regime in thin films with the same grain size, but not the same grain size present in bulk, where the reduction of the electrical conductivity with increasing thickness is due to the scattering events at the surface of the film. Once thick enough for the electrons not to interact with the surface and any reduction of the electrical conductivity from bulk values will be due to the grain boundary reduction and will not change with thickness\cite{2},\cite{13}. The limit of thickness in this regime is the infinitely thick thin film (ITTF) limit. The purpose of this model is to measure changes in electrical transport of thin films up to the ITTF limit from which these scattering mechanisms can be easily calculated. This is the effective FS model.

This model provides insight into the electrical transport in thin films that can be relatively easily used to probe the Seebeck coefficients of materials. The Seebeck coefficient is related to the electrical conductivity by equation (3.2.2). By measuring the Seebeck coefficients of thin films, it is possible to probe their dependance on the electrical transport occurring within them and possibly determine a mechanism to increase the Seebeck coefficient without significantly reducing the electrical conductivity of the material. While that is a proposed possibility, the way this model will be applied in this dissertation will be to measure the absolute Seebeck coefficients of thin metallic films. By measuring the changes of the relative Seebeck coefficient of thin metallic films up to the ITTF limit, the changes can be quantified using the effective FS model and their absolute values extrapolated. With the absolute Seebeck coefficients of those thin metallic films, the lead contribution to those films is yielded. With the thin film lead contribution measured, simple subtraction will give the absolute Seebeck coefficients of any other film of interest.
By substituting the thin film electrical conductivity in the FS model into equation (3.2.2) Thompson[73, 72] as well as, Leonard[43] calculated the thermoelectric power of a thin film to be,

$$S_{FS} = -\frac{\pi^2 k_B^2 T}{3eE_F} \left( V + u \frac{\beta_f}{\beta_o} \right)$$

(4.4.1)

where $\beta_f$ and $\beta_o$ are the temperature coefficients of the resistance (TCR) of the thin film and bulk material respectively and like before,

$$u = \left( \frac{d\ln l_o}{dE} \right)_{E=E_F}$$

(4.4.2)

is the logarithmic energy derivative of the mean free path with respect to the Fermi energy and

$$V = \left( \frac{d\ln A}{dE} \right)_{E=E_F}$$

(4.4.3)

is the logarithmic energy derivative of the area of the Fermi surface with respect to the Fermi energy. In terms of the effective FS model expression (3.4.1) for an ITTF film becomes,

$$S_F = -\frac{\pi^2 k_B^2 T}{3eE_F} \left( V + u \frac{\sigma_F}{\sigma_o} \right)$$

(4.4.4)

where $\sigma_F$ is the infinitely thick thin film electrical conductivity and the mfp energy derivatives are related to bulk values by,

$$u_g = u \frac{\sigma_g}{\sigma_o}$$

(4.4.5)

We can also derive an expression for a thin film in terms of the effective FS model in the $\kappa \gg 1$ regime [1].

$$S_g = -\frac{\pi^2 k_B^2 T}{3eE_F} \left( V + u \frac{\beta_g}{\beta_o} \left( 1 - \frac{3l_o(1-p)}{8t} \right) \frac{\sigma_g}{\sigma_o} \right)$$

(4.4.6)
The difference between these two expressions,
\[ \Delta S = S_g - S_f \]  
(4.4.7)
gives,
\[ \Delta S = -\frac{\pi^2 k_B^2 T}{3eE_F} \frac{3}{8} (1 - p) \frac{\sigma_g \beta_g u}{\sigma_o \beta_o t} \]  
(4.4.8)
These expressions will be used to find the absolute thin film Seebeck coefficients in this study. A detailed explanation of their implementation will be given in the following chapter.

4.5 Summary

The electrical transport in thin films is reduced from that of bulk materials due to the increased scattering events in thin films. This has been accounted for through solving linearized Boltzmann equations with boundary conditions appropriate to the scattering event. A reduction factor of the electrical transport can be found through the ratio of the electrical conductivity of a bulk material to the reduced thin film electrical conductivity. This method has provided values well in agreement with experimental data. Solving for all of the reductions in the electrical conductivity due to scattering events in thin films is rigorous. A simplified model can be used by relating the changes in electrical conductivity with increasing film thickness to a limit where they are no longer changing but not at bulk values.

The changes in the electrical conductivity are related to the changes of the Seebeck coefficient of thin films. By inspecting the changes in the relative Seebeck coefficients of thin films with increasing thickness, the absolute Seebeck coefficient of a thin film can be determined.
Chapter 5

Device Fabrication and Measurement Technique

5.1 Introduction

In chapter two, it was shown that the thermoelectric figure of merit, $ZT$, depends upon thermal conductivity, electrical conductivity and the Seebeck coefficient. It is important to precisely measure these quantities in order to fully understand the complex thermal and electrical transport of candidate thermoelectric materials. Measuring films on the nano and microscale probes the fundamental physics of these materials through high precision 2D controlled thermal gradients and through demonstrating the geometry dependence of parameters. By understanding these intricate and at times interdependent processes, we can thereby tune thermoelectric materials to be more efficient and applicable.

The typical method for estimating thermal conductivity at high temperatures of bulk metals is by measuring the electrical conductivity and finding the thermal
conductivity through the Wiedemann-Franz law.

\[ L = \frac{k}{\sigma T} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} W/\Omega/K^2 \] (5.1.1)

This law relates the ratio of thermal conductivity and electrical conductivity to a well known constant value. This measurement technique relates the heat carried by the electrons to the electrons ability to propagate through the material. The Lorenz number will equal a constant \(2.44 \times 10^{-8} W/\Omega/K^2\) when electrons are the predominate carrier of heat in the materials and the sample size is within the bulk limit. In materials where the thermal transport is carried by phonons or some combination of phonons and electrons, this measurement technique is invalid. For materials that fall into this category, the thermal conductivity is measured by producing a steady state heat flow along one direction of the material and measuring the temperature difference across it. This technique is highly susceptible to radiative losses to the surroundings of the material.

Thin film materials do not typically have the same value of thermal conductivity as their bulk counterparts. The deviation from bulk values of thermal conductivity emanate from the same mechanisms that cause their electrical conductivities to differ such as scattering events with surfaces, grain boundaries and impurities present in thin films. Transport in thin films is highly sensitive to these scattering mechanisms as outlined in chapter four. This makes it necessary to measure the thermal conductivities directly.

There are several established techniques for measuring thermal properties of thin films, including the 3-\(\omega\)[14] and time-domain thermoreflectance techniques[52]. These methods predominantly measure the thermal conductivity perpendicular to the film’s supporting substrate, terming it cross-plane thermal conductivity. Thin film thermal conductivity is typically anisotropic due to the changing the boundary
conditions of the thermal transport mechanisms leading to differing values for cross and in-plane thermal conductivities.

The $3\omega$ technique uses a single metallic wire in contact with the test sample. An AC current is passed through the wire with frequency $\omega$ to heat the sample. The increase in sample temperature has both AC and DC components with the AC component having a frequency of $2\omega$. The voltage drop across the wire can be measured and solved for the $3\omega$ component which is proportional to the temperature of the heated wire. This technique is precise in thin films down to approximately 20nm where radiative losses to the supporting substrate come into play [74].

The time-domain thermoreflectance technique, also known as picosecond thermoreflectance technique, splits a laser beam into a pump and probe beam. The pump beam hits the sample first pumping heat into it. The probe then arrives and it’s reflectance ascertain the impact of the heating pulse. Changes in reflected energy after a series of pulses indicates the changing temperature of the sample. Thermal conductivity is determined by comparing the measured cooling curve with a theoretical heat flow model. This technique is accurate up to the regime where the diffusion length and the electron mean free path are on the same order [52]. Thermoreflectance measurements have been conducted on same films supported by SiN membranes that this study has utilized. For example, the same film was measured with both a direct in-plane technique and then the exact same film was measured with cross-plane thermoreflectance technique. Details and results on that study will be presented later in this dissertation.

In this study, a direct in-plane measurement of the thermal conductivity facilitated by a micro-machined suspended amorphous SiN membrane is utilized. This allows for the ability to measure thermal conductivity, electrical conductivity and Seebeck coefficient of the same film, not just same material. This reduces error that can arise from the geometry dependent parameters of thin films such as thermal and
electrical transport. The suspended nature of the SiN membrane makes radiative losses negligible and the amorphous insulating structure of the SiN give a low background contribution to our measurement[82]. This chapter will overview the direct in-plane thermal conductivity measurement technique as well as device fabrication and characterization of micro-machined suspended amorphous SiN membranes and their component thermometers and heaters.

5.2 Device Manufacture

Figure 5.1: SEM image of a micromachined suspended SiN membrane used for collection of thermal conductivities, electrical conductivities, and thermopower of thin films

The suspended SiN membranes used in this study were manufactured at the Center for Integrated Nanotechnologies (CINT) in New Mexico. This process is illustrated by a reference cross-section of a device throughout the manufacturing process. This would be similar to the device in figure(5.1) cross section but with different dimensions.

The manufacture process starts with a single-side polished 100mm diameter, 300-525 micron thick Si wafer with thickness variations of less than 5 microns across one wafer. The Si has a resistivity between 1-10 Ohm cm. On to the wafer 500nm
of low stress SiN is grown on both sides.

![Figure 5.2: The first step in device fabrication is to deposit low stress amorphous SiN onto a Si wafer.](image)

A 3-5 micron thick layer of negative photoresist is spin coated onto one side of the wafer. The resist coated side is shadow masked with a pattern that will eventually become the heaters, thermometers, and electrical leads on the finished device.

![Figure 5.3: The next step is to coat the wafer with photoresist.](image)

The masked resist coated wafer is then exposed to UV light. The ultraviolet light serves to solidify the resist in any exposed regions to ensure that the entire wafer can be submerged in developer to remove the unexposed regions.

![Figure 5.4: Once the resist has been sufficiently exposed to UV light, the unexposed regions can we removed.](image)

The developed wafer then has a 10nm Cr layer is deposited immediately followed
by a 40nm Pt layer in an electron beam deposition chamber at pressures of the order 1E-6 torr. The Cr is required as a sticking layer due to the inability of Pt to securely bond with the SiN surface. Cr cannot be used alone because it oxidizes readily when exposed to room temperature atmosphere and this it is capped with with a 40nm layer of Pt.

Figure 5.5: Now we deposit metallic thin films in an e-beam deposition chamber that will become the leads.

After the deposition, the remainder of the resist is developed away leaving only the pattern of heaters, thermometers, and electrical leads.

Figure 5.6: With the remaining of the photoresist removed, only the regions where the Cr made contact to the SiN are left.

A second coat of positive resist is then spin coated, masked and UV exposed again. This time, the portions exposed to the UV light are broken down and sections not covered by the mask are developed away just in the opposite manner as they were in figure(5.4) .
Figure 5.7: A second layer of resist is added over the entire structure.

Next, a fluorine plasma etcher is used to remove the SiN in the desired areas. This type of etching is not effective on the Si below. It uses a plasma system to ionize a variety of source gases forming highly reactive fluorine. This slowly tears away at the highly resistive SiN and leaves the resist coated Cr, Pt and Si unmarred.

Figure 5.8: A fluorine plasma etch is performed to remove the areas of unwanted SiN.

Once the appropriate SiN is removed and the rest of the resist is developed away, the wafer is subjected to a Tetramethylammonium hydroxide etch (TMAH). The TMAH etch eats away the Si in the 1/1/1 plane without effecting the rest of the structure. This etch is conducted until the structure is fully suspended.

Figure 5.9: This is the last step of the manufacturing process. THMA etching in the 1/1/1 plane.
Figure 5.10: THMA etching must continue until the structures are fully suspended and the only thing holding them up are the membrane’s legs.

One wafer prepared this manner yields 52 devices nearly identical devices. With identical devices the leads can be characterized, once characterized many measurements can be made.

5.3 Device Measurement

5.3.1 Thermal Conductivity

Steady state measurements of the thermal conductivity can be complicated by radiative losses. It is essential to measure the thermal transport in the region of interest of the material. The measurement is complicated if undefined heat enters or exits the system. This was a primary motivation for the development of 3-w method[14] which uses an AC technique to eliminate radiative losses and small geometries to reduce black-body radiative influences. One goal of the design of micro-machined SiN membranes is to minimize radiation effects by significantly reducing the geometry of the device.
Figure 5.11: A schematic representation of the thermal model used to describe the micromachined thermal platforms. Before the deposition of a thin film, the only connection between the two islands is the background thermal conductance of the SiN bridge. Adding a thin film adds linearly to the total thermal conductance $K_{total} = K_{SiN} + K_{film}$. The thermovoltage generated by the temperature gradient is measured using the leads on either side of the membrane.

Figure (5.11) illustrates a thermal model of the device where the heat flow due to application of heating power occurs along the bridge and legs of the device. The bridge has a low thermal conductance due to the amorphous nature of the SiN[30]. A film deposited on the bridge will increase the total thermal conductance measured and in most cases dominate it. The conductance through the legs supporting the device can be calculated and accounted for[69]. If radiative losses were to occur in these structures, a non-linear relationship between heating power applied and the measured temperature increase would be observed. A non-linear relationship would be indicative of the heat current flowing significantly in a direction that is not along the bridge. For example, this is the linear relation of heat to temperature difference across the material,

$$Q = K \Delta T = K_{SiN}(T_h - T_c)$$  \hspace{1cm} (5.3.1)

As the heat is increased, the $\Delta T$ responds linearly at a given base temperature if for example, heat was being lost to the surrounding structure. This is most likely to occur in the area where the greatest amount of heat is located leading to a temperature measurement on the hot side of some $T'_h$ where $T_h \neq T'_h$. With $T'_h$ being lower than $T_h$ since heat is being routed away from the measurement system.
This $T'_h$ function of the thermal conductance of the external heat loss source and the temperature difference measured due to applied heat now becomes,

$$(T'_h - T_c) = \left( \frac{Q + K_{ex}T_o + K_{SiN}T_c}{K_{ex} + K_{SiN}} \right) - T_c \quad (5.3.2)$$

This would cause a situation where equation (5.3.1) would no longer be linear. The relationship between applied heating power in these devices to temperature increase is linear in these devices. This is due to the suspended nature and small geometry of the platform and the low thermal conductivity of the amorphous SiN negating radiative losses. This linear relationship will be demonstrated shortly.

![Figure 5.12: An image of a zoom in on one of the islands from figure (5.11) with thermometers, heaters and electrical leads highlighted.](image)

Figure 5.12: An image of a zoom in on one of the islands from figure (5.11) with thermometers, heaters and electrical leads highlighted.

Figure (5.12) is a close up view of an island in figure (5.11). These heaters, thermometers and electrical leads all have wires that run along the legs of the device to bond pads on the outer edges of the device. A sonic bonder tool is used to wire the device into an Au plated Cu sample mount that is then capped to provide an isothermal environment. The loaded sample mount is then connected to the inside of a liquid nitrogen cryostat. The loaded cryostat is then evacuated to less than
1E-5 torr. This is well within the molecular flow of gaseous particles and prevents any radiative losses of heat to the surrounding air.

To test the device, first the thermometry must be characterized. The thermometers consist of 10nm Cr topped with 40nm Pt. These are normal metals with a linear relationship with temperature. By bringing the device to equilibrium, resistance no longer changing at a known temperature and measuring the resistance at that stable value, we are able to calibrate the thermometers. The reference temperature is measured by a Lakeshore thermocouple located above the sample mount. The thermometer resistances are measured using a 4 wire technique that is acquired using a SRS AC resistance bridge. A fit to the 4 wire thermometer resistance versus temperature gives values that will be used to determine the temperature responses when heat is applied to take the actual measurements.

Figure 5.13: The calibration of a thermometer
This thermometer is sensitive for measurements in the temperature range of interest, $S > 0.4$, and do not change from test to test with the addition of subsequent films to the bridge.

![Thermometer Sensitivity over temperature](image)

**Figure 5.14: Thermometer Sensitivity over temperature**

To perform the actual measurement of thermal conductivity and thermopower, the device is first brought to a stable base temperature. This is monitored during testing by a thermometer located on the frame of the device and is stable to within hundreds of mK.
Figure 5.15: An example of stable base temperature in the low temperature range.
Once a stable equilibrium temperature has been reached, a measurement of the voltage across the film is taken to account for thermovoltages generated from the room temperature wiring to the sample. Next, a series of heating currents are applied to the heater on one of the islands with a Keithley 2400 multimeter. At each step in the series of applied heating currents, the resistance of each of the thermometers is measured to determine the thermal conductance and a voltage measurement is taken with a Keithley 2000 across the film to determine the thermopower. A linear fit to the increase of temperature with the increase of heat produces the thermal conductance data.

Figure 5.16: An example of stable base temperature in the high temperature range.
Figure 5.17: An example of the linear increase in temperature with increased heating power.

These slopes are a function of the thermal conductance through the legs and the bridge. The rate of heat flow can in the structure can be written as,

\[
C_h \frac{\partial T_h}{\partial t} = -K_L(T_h - T_o) - K_B(T_h - T_s) + P_h \tag{5.3.3a}
\]

\[
C_s \frac{\partial T_h}{\partial t} = -K_L(T_s - T_o) - K_B(T_s - T_h) + P_s \tag{5.3.3b}
\]

Where \( T_o, T_s \) and \( T_h \) are the base, hot island and cold island temperatures respectively and \( C_h, C_s \) and \( P_h, P_s \) are the specific heats and heating powers of the hot and cold islands respectively. The \( K_L \) term is the thermal conductance through the legs and \( K_B \) is that of the bridge. In a steady state measurement, the time dependent term vanishes and we do not apply power to the cold island so these
equations become,

\[ 0 = -K_L(T_h - T_o) - K_B(T_h - T_s) + P_h \]  \hspace{1cm} (5.3.4a)

\[ 0 = -K_L(T_s - T_o) - K_B(T_s - T_h) \]  \hspace{1cm} (5.3.4b)

Solving these for \( T_h \) and \( T_s \) for \( P_h = P \) gives,

\[ T_h = T_o + \frac{(K_L + K_B)P}{2K_B + K_L}K_L \]  \hspace{1cm} (5.3.5a)

\[ T_s = T_o + \frac{K_B P}{2K_B + K_L}K_L \]  \hspace{1cm} (5.3.5b)

with the slope of \( T_h \) vs \( P \) and \( T_c \) vs \( P \), one can use further algebra to solve for \( K_B \) and \( K_L \).

To find the thermal conductivity the geometry of the device is simple divided.

\[ k = \frac{Kl}{wt} \]  \hspace{1cm} (5.3.6)

where \( l, w \) and \( t \) are the length, width and thickness of the sample.

### 5.3.2 Thermopower

Thermopower is measured as the slope of the increase in magnitude of voltage with the increase of the temperature difference across the two islands, equation(4.2.1). The background voltage due to the temperature difference between the warm side wiring and the device at some base temperature can simply be subtracted away. There is, however, a contribution from the thin film leads are present on the device themselves. Finding their contribution will be the subject of the next chapter.
5.3.3 Electrical Conductivity

The electrical conductivity is measured with a DC 4 wire measurement across the bridge in reference to one or both of the frame thermometers. The polarity of the excitation current is flipped to find any thermovoltages in the lines that could contribute to the measurement. If a thermovoltage is present, then the average of the resistance values of the two current polarities is taken. This is done over the whole temperature range. To find the intrinsic material value of the electrical conductivity of a material from the resistance, the geometry is divided out.

\[
\sigma = \frac{Rl}{wt} \quad \text{(5.3.7)}
\]
5.4 Results and Discussion

5.4.1 Thermal Properties of SiN Membranes

The thermal conductance of a suspended amorphous SiN membrane was measured from 77-325K.

Figure 5.19: The thermal conductance of a suspended amorphous SiN membrane

This has a low thermal conductivity due to the insulating amorphous structure of the SiN. In insulating materials, the thermal current is carried by the phonons without the aid of the electrons. This is gives rise to low values. In amorphous materials, the short wavelength phonons are frozen out due to the lack of short scale periodicity so that only phonon wavelengths large enough to not see the disorder carry the thermal current this gives rise to even lower values[81].

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The thermal conductance can vary slightly from device to device. This is thought to be due to small inhomogeneity in the thickness and amorphous structure of the SiN[69].

Figure 5.20: The thermal conductance of various suspended amorphous SiN membranes of the same geometries.

This is taken into account by conducting a thorough characterization of each device before the addition of a thin film.
Figure 5.21: Two separate thermal conductance measurements of the same SiN membrane.

The thermal conductance of a single membrane is consistent with multiple measurements of the same device yielding the same results. It can be seen that the error of the thermal conductance measurement increases in the high temperature range of the measurement. This is due to the very low thermal conductance of the SiN membrane at these temperatures. The temperature of the hot island is limited to 20K above base temperature to prevent radiative losses. Due to this limitation and the increasingly low thermal conductance, the raise in temperature on the cold island is less than 1K above 200K. There are 100-300 mK random fluctuations in the thermometry due to background noise that cause these higher error values. This can be reduced by taking multiple data points at problematic base temperatures.

The thermal conductance of the supporting legs can be calculated form equations (5.3.5) as well.
Membranes of different geometries and degrees of disorder have been measured. These two membranes have different aspect ratios $n = \frac{w}{t}$ where $w$ and $t$ are the width and thicknesses respectively. The aspect ratio is part of what determines the populations and lengths of the long wavelength phonons carrying the heat in these structures[78]. These two membranes also could have differing degrees of amorphous disorder due to their being fabricated with two different deposition chambers. A further study of their amorphous characteristics and analysis using $n$ to determine the phonon wavelength populations is required to resolve these discrepancies.
5.4.2 Thermal and Electrical Properties of Films on Membranes

A 174 nm Al film was deposited on a SiN membrane. This was done by first shadow-masking the premeasured device so that only a section of the leads required for electrical measurements and membrane itself were exposed. Then it was placed in a thermal deposition chamber that was evacuated to 5E-6 torr. The thermal deposition chamber runs a high amount of current through the sample until it melts and then evaporates. The evaporated Al then sublimates on the surface of the exposed membrane. The thermal conductivity of the structure was then measured again. The difference of the background measurement and combined measurement
produces the conductance of the film.

\[ K_{\text{film}} = K_{\text{bath}} - K_{\text{membrane}} \]  

(5.4.1)

Figure 5.24: The thermal conductance of the SiN membrane (red), the thermal conductance of the membrane and the 174 nm Al film combined (black) and the thermal conductance of the Al film (blue)

A measurement of the Al film’s electrical resistivity was taken as well. This is linear like any metal and is higher than bulk aluminum resistivity which is 2.74 \( \mu \Omega \text{cm} \) [42] at room temperature.
Figure 5.25: The electrical resistivity of an Al thin film plotted over temperature

The thermal and electrical conductivities can then be compared to find the Lorenz number for Al.
The measured Lorenz number value for this thin Al film is smaller than classical $2.4 \times 10^{-8} W\Omega/K^2$ which is not unexpected for non-crystalline or impure films\cite{81}. This is due to the increased scattering mechanisms experienced by thin films. The crystallinity, grain size and impurity concentrations for this film is not known. It is, however, known to have an oxide layer on the surface. This could also cause a lowering of the Lorenz number due to surface effects. A combination of the the reduced size, oxide layer, grain boundary size and impurity concentration of the thin aluminum films causes a decrease in the Lorenz number from that of a pure bulk metal.

Figure 5.26: The Lorenz number of a thin aluminum film.
The relative thermopower of this film was also measured.

Figure 5.27: The relative Seebeck coefficient of 174 nm Al film measured with thin film Pt/Cr leads.

Figure (5.27) is a plot of the thin Al film thermopower and that of the thin Cr and Pt leads used to test it combined. The relative thermopower of the 174 nm Al was measured with two different geometries of Pt/Cr leads. An image of the two leads are in figure (5.12). Both leads are the same width along the legs and same thickness throughout. The outer lead has a larger triangle area on the island while the inner lead other stays thin. The entire area of the island is modeled to be at the same temperature. The thermal gradients only exist along the legs and bridge. Measuring both geometries of leads and yielding the same value serves to confirm the thermal model of the device. The absolute value Seebeck coefficient of Al films will be discussed in a subsequent chapter.
5.5 Summary

Measuring the thermal conductivities of thin films is challenging due to environmental radiative heat loss. It is essential to quantify the amount of heat transported across the material to measure its conductivity. If the heat applied to a thin film is traveling in undocumented or unknown directions through its surroundings, then accurate values for this characteristic material quantity cannot be attained. This problem is circumvented by the use of a micro-machined suspended amorphous SiN membrane with patterned metallic heaters, thermometers and electrical leads. The amorphous insulating SiN provides a low background contribution to the measurement reducing the error associated with subtracting it from measured values of additional films on its surface.

The thermometry on the device yields stable and precise values of the temperature in the range of 77-325K. The heaters on the device serve to measurably apply heating powers to generate 2D thermal gradients. The electrical leads allow for 4 wire film measurements and 2 wire voltage measurements across the film when a thermal gradient is being applied. This yields values for the electrical resistivity and conductivity as well as relative Seebeck coefficients of the films.

A study of thin Al films was presented using the suspended amorphous SiN membranes. The total thermal conductance of the structure with the addition of 174 nm Al film increased and the value for the film thermal conductance can be accurately subtracted. A check of the Lorenz number reveals a reduced value from bulk for a 174 nm Al film. The electrical resistivity of thin Al films is increased from that of bulk Al as predicted by the FS and MS models. The relative thermopower of the Al film was also tested with two different geometries of Pt/Cr thin film leads and yielded the same value for both tests. This device with the 174 nm film is currently being tested in the Seimen’s lab at the University of Denver with a thermoreflectance technique for thermal conductivity data comparison.
The thermal and electrical conductivity as well as relative Seebeck coefficients of thin films can be directly and precisely measured with micro-machined suspended SiN platforms patterned with thin metallic film heaters, thermometers and electrical leads. It is now possible to characterize the lead contribution to this measurement so that accurate absolute Seebeck coefficients measurements can be conducted.
Chapter 6

Absolute Seebeck Coefficient
Measurement of Thin Films

6.1 Introduction

As mentioned previously, the majority of Seebeck coefficient measurements yield values that are a combination of the material under investigation and the leads used to test them. Measuring a thermally induced potential difference by applied thermal gradient on a micro-machined measurement device adds a contribution to the measurement of thin film leads. Thin film leads are required in nanoscale material measurements of this sort. Bulk leads would cause thermal shorts and fine 2D temperature control would be lost. Bulk leads can also have high Seebeck coefficients that would lead to elevated background contribution compromising the accuracy of the measurement. In order to utilize the thin film electrical leads on these devices for absolute Seebeck coefficient measurements of thin films, the lead contribution itself must first be characterized.

To characterize the lead contribution, a series of varying thicknesses of thin metallic films will be deposited on the membrane. By measuring the changes in
thermopower as the thin film thickness is increased as well as the electrical resistivity and effective electron mean free path, we will be able to apply the effective FS model to find the absolute Seebeck coefficients of the thin metallic films.

Once the films have been characterized, the lead contribution can then be subtracted off the total measurement. Leads manufactured with the same methods and of the same thickness will contribute the same way to a measurement. Having accurate values for the lead contribution to measurements of Seebeck coefficients in these devices allows for the measurement of a variety of films.

The micro-machined devices used in this study also allow for accurate measurements of thermal and electrical conductivity of the same film providing a full picture of the parameters used to characterize thermoelectric material efficiency over a wide temperature range. These measurements could be conducted separately, however, due to the strong geometric dependence of these thin film parameters, as outlined by the thermal and electrical transport equations in chapter four, this strategy often leads to increased measurement error. Being able to confidently and precisely measure these three energy transport parameters also provides insight into the film that measuring just one aspect could leave out.

This chapter will serve to detail the measurement of a relative Seebeck coefficient, how the effective FS model is applied to a series of thickness of thin metallic films, and present data on those films. It will also show how the ability to measure thermal conductivity, electrical conductivity, and Seebeck coefficient of the same film sheds light on the scattering mechanisms and transport properties of the films being measured.
6.2 The Measurement

![Figure 6.1: Schematic of the relative thermopower measurement](image)

Figure (6.1) details the voltage measured when heating power is applied to the suspended amorphous SiN structure with a film on the membrane. When the device is held at a steady state base temperature, the thermally generated voltage from the room temperature wiring to the device, at that base temperature, is measured and easily subtracted. Once power is applied to the structure, there is a potential difference generated in the thin film leads. This influences the measurement in the following way,

\[ V_{\text{measured}} = -S_{\text{lead}}(T_h - T_o) + S_{\text{film}}(T_h - T_c) + S_{\text{lead}}(T_c - T_h) \] \hspace{1cm} (6.2.1)

Simple algebra tells us the voltage measured is,

\[ V_{\text{measured}} = (S_{\text{film}} - S_{\text{lead}}) \Delta T \] \hspace{1cm} (6.2.2)
This is from the familiar equation stated in chapter three,

\[ S = -\frac{\Delta V}{\Delta T} \]  \hspace{1cm} (6.2.3)

If the leads had well known bulk like thermopower values, the \( S_{\text{lead}} \) could simply be subtracted. These are thin film leads that do not have well known bulk like values [15]. To deduce the contribution of the leads, the effective FS model for thin films is applied.

### 6.3 Applying the Effective FS Model

By measuring a series of thickness of films deposited on the same membrane, it is possible to determine the absolute Seebeck coefficient of the film and then subtract out the leads. Increasing the thickness of the thin film until the ITTF limit is reached provides a value where the Seebeck coefficient is no longer changing with thickness but not at bulk-like values.

In a thin film that has a thickness smaller or comparable to than the mean free path of the electron, electron-interface scattering events will occur within the material as quantified by the FS model. As the thin film thickness is increased, these scattering events will be reduced. This is demonstrated not only by the change in the Seebeck coefficient but also in the reduction of the electrical resistivity. Once the ITTF limit has been reached, the scattering events will be dominated by the grain boundaries and impurities present within the material. These scattering events are taken into account by the effective FS model by defining the infinitely thick thin film limit. Thin films with thickness that have reached this infinitely thick limit will not have bulk-like Seebeck coefficients or electrical resistivity values. The way thin films are grown, deposited, or sputtered on to a membrane or substrate gives them inherently different structures than that of bulk materials.
If the grain boundaries and impurity concentrations are constant with film thickness, regardless of what they are, this will result in a quantifiable increase of the mean free path of the electron with film thickness. This is what we strive to achieve with a series of thickness of Au films deposited on the SiN membrane of our micromachined measurement devices. The key advantage of the effective FS model is not only its relative simplicity compared to the MS model or the ease in measuring the material properties needed to apply it, electrical resistivity, temperature coefficient of resistivity, and Seebeck coefficient, but the cancellation of the lead contribution when applying it.

By subtracting the relative Seebeck coefficients of the thin film and ITTF the lead contribution falls out,

$$\Delta S_f = S_g - S_f = (S_g - S_{\text{lead}}) - (S_f - S_{\text{lead}}) \quad (6.3.1)$$

From the effective FS model,

$$\Delta S_f = -\frac{\pi^2 k_B^2 T}{2 e E_F} \frac{3}{8} l_g (1 - p) \frac{\sigma_f \beta_g}{\sigma_o \beta_o} u \quad (6.3.2)$$

The ratio of the electrical conductivities, the temperature coefficients of resistivities and the term $\Delta S_f$ are measured directly. To find the mean free path of the electrons in the ITTF film we use this expression from the effective FS model,

$$\rho_f = \rho_g + \frac{3}{8} l_o (1 - p) \frac{\rho_g}{t} \quad (6.3.3)$$

The term $C = \frac{3}{8} l_o (1 - p)$ is given from a linear plot of the thin film resistivities vs inverse film thickness.

$$\rho_f = \rho_g + C \frac{\rho_g}{t} \quad (6.3.4)$$

With the relative Seebeck coefficients of thin and ITT films, the measured resistiv-
ities and $C$ the $u$ term can be calculated. The $u$ term is last key to the puzzle to calculate the absolute infinitely thick thin film Seebeck coefficient.

$$S_g = -\frac{\pi^2 k_B^2 T}{2eE_F} \left( V + \frac{u \beta_g}{\beta_o} \right)$$  \hspace{1cm} (6.3.5)

The $V$ term in this equation is the energy derivative of the natural log of the Fermi surface with respect to the Fermi energy. The Fermi surface and its relationship with energy does not change with film thickness. This is an intrinsic material property that does not depend on the grain boundaries, impurities, or surface scattering events. We will use a previously calculated value of $V = 1.05$ [38] for this term.

Gold was chosen as the thin film material studied for several reasons. Gold is a noble metal with non-interactive properties. It does not oxidize in air so oxide interfaces between the layers is not a concern. It has a relatively uncomplicated Fermi sphere so the first term in equation (6.2.7) can be easily understood. Gold also is known to have smooth grain boundaries so the grain boundary scattering term of the effective FS model can be considered negligible.

With the absolute Seebeck coefficient of a thin Au film calculated from experimental data, we can subtract it from the measured relative Seebeck coefficient to determine the lead contribution. With the lead contribution, it is possible to measure a variety of absolute thin film Seebeck coefficients. The leads on these devices that are manufactured on the same wafer, in the same way, and at the same time as outlined in section 5.2. These leads are made of the same materials, same geometries and same thicknesses.
6.3.1 Electrical Resistivity

With increasing film thickness, we reach a point where the electrical resistivity has ceased decreasing with increasing film thickness. This is the infinitely thick thin film limit and it does not converge to bulk-like values.

Figure 6.2: A plot of the decrease in electrical resistivity with increasing film thickness. The electrical resistance decreases to a point but does not reach bulk values.

The Au films are rather disordered and impure. A measure of the residual resistivity shows an impurity concentration between 400-800 ppm. A measure of the resistivity ratio shows that the lattice contribution to the electrical resistivity is relatively high. Matthiessen’s rule states,

\[ \rho = \rho_L + \rho_i \quad (6.3.6) \]
The residual resistivity gives a value for $\rho_i$ between $4.4 - 6.6 \, \mu\Omega\, \text{cm}$ for the different films resulting in a contribution of the lattice to the electrical resistivity, $\rho_L$, between $2.7 - 5.0 \, \mu\Omega\, \text{cm}$. The lattice contribution is dictated by grain boundaries and their ordering as well as impurities when the concentration is high. With impurities of 400-800 ppm and Au grain boundaries being smooth, the impurities or disordered grains is the cause of the high resistivity ratio. With the high lattice contribution to the electrical resistivity it can be assumed that the Au used in this study is polycrystalline and impure.

This series of Au film thickness has converged to a electrical resistivity value that is no longer decreasing with increasing film thickness and it is confirmed that it is in the ITTF regime. The ratio of the ITTF electrical resistivity to bulk will be an important part of the calculation of thin film absolute Seebeck coefficients.

### 6.3.2 Scattering Coefficients

Following equation (6.2.6) to find the effective mean free path and ratio of surface scattering coefficient $p$, we will use a slope of the linear plot of the thin film resistivity versus inverse thickness times the ITTF resistivity. For the sake of simplification let us define a term $C$ where,

$$C = \frac{3}{8} l_o (1 - p) \quad (6.3.7)$$
Figure 6.3: Electrical resistivity plotted against inverse film thickness at 102K
Figure 6.4: Electrical resistivity plotted against inverse film thickness at 300K

It is clear that this value is decreasing with increasing temperature. To account for this in the effective FS model, a plot of $C$ over temperature is made.
The effective mean free path of the electrons is calculated from these values when the diffuse to specular scattering ratio, $p$, is assumed to be zero. Thus, the electron is no longer scattering diffusely with the surface of the film.
There is a reduction of the mean free path of the electrons with increased temperature. This is typical of metals. As the temperature of a metal is increased, its resistance increases, therefore, its electron mean free path decreases.

Using Sommerfeld electron transport theory as a quick check of the mean free path calculation,

$$l_o = \frac{\hbar k_F}{\rho n e^e}$$

(6.3.8)

and textbook bulk values, the equation reveals a mean free path of pure ideal gold of 380 $\mu$m. The disorder of the Au and the impurities present are the causes for the large reduction in mean free path.
6.3.3 Delta $S$

The relative Seebeck coefficients of a series of thickness of Au films have been measured up to the ITTF limit.

![Graph showing the relative Seebeck coefficient of Au films](image)

**Figure 6.7:** The relative Seebeck coefficient of a series of thicknesses of Au leads up to the ITTF limit

The ITTF relative Seebeck coefficient can be subtracted from the relative thin film Seebeck coefficient to give a lead independent value of $\Delta S$. 
With the information attained in the last three subsections, we can go on to calculate the absolute Seebeck coefficient of the infinitely thick thin film. However, there is one other caveat. It can be seen from equation (6.3.5) with a noble metal like Au, with a negative $V$ term that as the total $u$ term, $u = \frac{\beta_g}{\beta_o} u$, gets more negative $S$ gets more positive. The data in figure (6.7) is decreasing with increasing thickness. That would mean as the thickness is increased, the $u$ term is less negative. A check of figure (6.8) with equation (6.3.2) would lend the opposite result. This is the result of a typo in the paper[1]. It was translated from French in early 1970’s. We will instead use,

$$\Delta S_f = \frac{\pi^2 k_B^2 T^3}{2 e E_F} g (1 - p) \frac{\sigma_f \beta_g}{\sigma_o \beta_o} \frac{u}{t}$$

(6.3.9)

A check of the rest of the model with the FS model and Mott equation still holds. Now all of the information attained can be analyzed and the absolute value of thin Au films can be attained.
6.3.4 Calculating the Absolute Seebeck Coefficients of Thin Films

The differences in relative Seebeck coefficients, electrical resistivity, and temperature coefficients of resistivity used in equation (6.3.9) yield a value for $u$. This value is temperature dependent.

![Figure 6.9: The ITT film $u$ term as a function of temperature](image)

In figure(6.9) $u$ is becoming more negative with increasing temperature which infers that the energy derivative of the electrons is becoming more negative with temperature. This is due to a combination of the electrons responsible for conduction losing energy with increasing temperature near the Fermi surface and increasing electron MFP. This can be seen from equation (3.4.2). The dominating factor causing this reduction is unclear.
With the value of \( u \), the inverse of the mean free path of the charge carrier times the derivative of the charge carrier with respect to energy at the Fermi energy, a value for the infinitely thick thin Au film can be calculated from equation (6.3.5)

Figure 6.10: Absolute Seebeck Coefficient of Au thin films

The value for the absolute Au thermopower is small and positive which agrees with literature on bulk films[16]. Small, positive Seebeck coefficient values are typical for noble metals with their Fermi spheres near the edge of the first Brillouin zone. The values of the thin films measured in this study are larger than bulk due to the addition of the negative, \( u \), to the, \( V \) term. This is deviation from bulk increases at high temperatures.
6.4 Additional Inspection of the Model

6.4.1 Additional Increases in the Relative Thermopower

According to the electrical resistivity data, films 142 nm and above are in the ITTF limit. The thermopower of these films should no longer be changing with thickness. However, we find that they are.

![Figure 6.11: Relative Seebeck Coefficient of Au Thin Films Measured with Pt/Cr Leads](image)

The way in which the Seebeck Coefficient is changing with increasing thickness has altered from that of the thinnest films. Films that are beyond the ITTF limit have a slightly different temperature relationship than those before it, deviating more from previous values at high temperatures.

To confirm that we have indeed reached the ITTF limit, a closer inspection of the electrical resistivity is required.
The changes in electrical resistivity with increasing thickness are in the ITTF limit. Not only are the thickest film values within error bars of each other, using a high or low estimate of any of the three do not account for the decrease in the thermopower with increasing thickness for the thickest films.

To investigate the cause, it is helpful to analyze the thermal conductivity of the films. The thermal conductivity and Seebeck coefficient both depend upon heat currents within the material while the electrical resistivity depends upon the electrical current. How this is helpful and important is detailed in the next subsection.

### 6.4.2 Thermal Conductivity

The thermal conductivity and Seebeck coefficient are steady state measurements with no electrical current flowing through the material. Scattering events that give rise to the resistance of energy transport effect thermal and electrical currents in
different ways. When measuring the electrical conductivity by flowing a known amount of current through the film, that current will encounter differing amounts of resistance than a heat current flowing through the same film to establish a thermal gradient.

Figure 6.13: The Fermi Surface and Distribution Function of (a) in Electrical Conduction; (b) in Thermal Conduction

Figure (6.13) demonstrates the scattering processes that give rise to resistance of electrical and thermal currents. The left figure depicts a situation where electrical current is flowing and this causes a shift in the distribution. The current is essentially pushing more electrons to the right of the Fermi surface. The right figure depicts a scenario where thermal current is applied to the same hypothetical Fermi surface. This causes hot electrons to flow down the thermal gradient which are balanced by colder than average electrons moving up the thermal gradient inside the Fermi surface.

The differing impact these two types of collisions can have on these two scenarios can be now be seen. Large angle scattering, which is approximately elastic, causes
a horizontal scattering effect. This pushes an electron from an excess region to defect region, pushing the distribution function back to equilibrium and giving rise to a resistance. This has relatively the same effect in either scenario. Small angle scattering, which can be elastic or inelastic, causes a vertical scattering effect. Small angle scattering in the case of applied current has little effect since it cannot carry an electron out of the excess region in a single jump. This is not the case in thermal currents. A small angle inelastic scattering event can change a hot electron into a cold one and vice versa giving significant rise to the electronic contribution to the thermal resistance. If this were to occur, we would expect serious deviations from the Wiedeman-Franz law, equation (5.1.1) which defines the Lorenz number. This would mean the electrons are not contributing to the thermal conductivity the same way they are contributing to the electrical conductivity.

To investigate this effect let us first look at the thermal conductivity of the Au films.

![Figure 6.14: The Thermal Conductivity of Au Thin Films](image)

Figure 6.14: The Thermal Conductivity of Au Thin Films
There is a lot of information in this graph. It is easier to analyze what is happening to the thermal transport in these films by separating them into two categories; one with increasing thermal conductivity with increasing thickness and one with decreasing thermal conductivity with increasing thickness.

(a) Thermal conductivity of thin films that increase with increasing film thickness
(b) Thermal conductivity of thin films that decrease with increasing film thickness

Figure 6.15: Thermal Conductivity of Au Thin Films

It is clear from figure(6.15) that there are two types of relationships these films have with thickness. In the thinnest films the thermal conductivity is increasing with increasing film thickness. After the ITTF limit the thermal conductivity begins to decrease with increasing film thickness. Next, it would be useful to see what that means in terms of the Lorenz number of the films. It is also important to point out the deviations from the trend of the two thinnest films in the lowest temperature range are thought to be due to background reduction effects. The long wavelength phonons responsible for the heat transport in the amorphous SiN membrane are scattered when a film is deposited on it. This causes a reduction of the background[70]. For this study, we concern ourselves with the overall trend of the thermal conductivity and neglect the background reduction effects. They are quantifiable, known effects unrelated to this study.
6.4.3 Lorenz Number

The Lorenz number in metallic materials provides insight into how the electrons are contributing to the thermal conductivity. The Lorenz number, equation (5.1.1), is the ratio of thermal and electrical conductivities divided by the temperature. If the electrons are not contributing to the thermal conductivity in the same way they are contributing to the electrical conductivity, deviations of the Lorenz number will be observed [81]. In formal transport theory, the value for the Lorenz number is a constant $2.45 \times 10^{-8} (W \Omega/K^2)$ for a bulk metal. Reduced Lorenz numbers in thin impure metal films have been recorded [51].

![Figure 6.16: The Lorenz number of Au Thin Films](image)

The thinnest film is within error bars of agreement with bulk gold in the high temperature range. Below 200K, the reduction of the SiN background causes the data to deviate. This 19 nm Au film dominated by horizontal scattering processes, due to its thickness being smaller than the mean free path of the electron. This
effects thermal and electrical condition in the same way leading to a Lorenz value that agrees with literature. With increasing thickness, the Lorenz number decreases. This is due to the introduction of more vertical scattering events with thickness. Why the thickest film, (231.4 nm), has an increased value in the low temperature range of this study is unclear at this time.

If we look at the Lorenz number of a single film, the difference between the films with increasing thermal conductivity with thickness and decreasing thermal conductivity with thickness become obvious. This is evident when comparing the thermal conductivity of each film separately as opposed to the total resistivity at that thickness.

Figure 6.17: The Lorenz number of Au Thin Films
It is clear from this graph that the first film is dominated by horizontal scattering and agrees with literature values. The next few films decrease in the Lorenz number until a limit is reached where it drops to nearly zero. The last three films in this regime are dominated by vertical scattering processes.

It is confirmed that vertical scattering processes are occurring in the films. It is important that they be accounted for and their origin be determined.

6.4.4 Vertical Scattering Mechanisms in Thin Metallic Films

There are a few plausible causes of scattering mechanisms in thin metallic films including surface scattering, phonon-electron scattering, impurity scattering and grain boundary scattering. Each possibility is discussed below.

Grain boundary formation is dependent upon the deposition type, rate, and base pressure of the chamber used[8]. These factors were all consistent for each film. This is also confirmed with the residual resistivity measurements of the films having lattice resistivities on the same order. A grain boundary scattering event could give rise to the resistance of thermal currents but not with increasing film thickness or deposition number. Therefore, it is not the scattering event responsible for this behavior.

The series of Au films used in this study do have a relatively high impurity concentration. Impurity scattering is more likely to cause a horizontal scattering event that would be felt by both the thermal and electrical current[81]. In this case, it was causing a vertical scattering event, it is independent of the thickness or deposition number of the film. Therefore, it is not the scattering event responsible for this behavior.

Electron-Phonon scattering at small angles requires a long wavelength phonon. Long wavelength phonons occur at temperatures below the Debye temperature. The Debye temperature of Au is 165K. The increased deviation from the Weideman-
Franz law occurs above these temperatures. Additionally, the electron-phonon coupling in gold has been measured to be small[34]. Therefore, it is not the scattering event responsible for this behavior.

Another possibility is surface scattering. The ratio of diffuse and specular surface scattering is the basis of the effective FS model. In the ITTF regime, this ratio is thought to go to zero. With increasing film thickness, this ratio is reduced as implied by the boundary conditions imposed on the linearized Boltzman equation. There is, however, surface roughness scattering which increases with decreasing electron MFP. Much like long wavelength phonons in amorphous materials, the longer wavelength electrons pass through the material unaffected by surface roughnesses. The mean free path of the electrons are decreasing with increasing temperature. This is shown by the rise in the electrical resistance with increasing temperature. The thermal conductivity and Seebeck coefficient are decreasing with increasing temperature in films beyond the ITTF limit. This indicates that there must be the vertical scattering processes present in these films.

The original ratio of diffuse and specular surface scattering is a thickness dependent quantity. It is still valid to use. It will be shown that the surface roughness scattering is a deposition dependent quantity. Corrections to the model can still be made to account for reductions due to this effect. If one was ambitious enough to go back to the linearized Boltzman equation and solve for surface roughness scattering boundary conditions, a new reduction ratio could be determined. The new boundary conditions would include the height and width of the surface roughness feature and those features are not consistent across the surface. In the textbook for thermal and electrical transport, Electrons and Phonons states, "To describe such surfaces statistically is a serious problem, which has not really been tackled." [81] For purposes of this experiment, it will be sufficient to quantify these effects and correct for them in our analysis. How this is done is outlined in the next subsection.
6.4.5 Accounting for Vertical Scattering Processes in the Effective FS Model

Using literature values for the Lorenz number and the measured thermal conductivity, it is possible to calculate the electrical resistivity of the films. These values of electrical resistivity are effected by the same scattering mechanisms as the thermal conductivity.

![Figure 6.18: The Electrical Resistivity of Thin Au Films Calculated From the Lorenz Number and Thermal Conductivity at 198K as a Function of Film Thickness](image)

The electrical resistivity calculated in this way reduces with thickness to a point and then begins increasing. The turnaround occurs at the infinitely thick thin film limit as established by direct electrical resistivity measurements. The relationship of these changes with thickness are not completely linear. Fitting a line to either behavior, declining or inclining resistivity with temperature, does not provide a direct fit. Plotting these values by deposition number, however, does.
Figure 6.19: The Electrical Resistivity of Thin Au Films Calculated From the Lorenz Number and Thermal Conductivity at 198K as a Function of Deposition Number

It can be concluded from figure (6.19) that each time the sample has a film deposited on it, no matter the thickness of the film, the vertical scattering events are increased. The slope of this line can be used to correct the originally measured electrical resistivities to account for increased vertical scattering events. They are not dominant in the thinnest films but it is intuitive that they are present. This gives a corrected value for the ITTF film and from that, a correct lead contribution.

Using the absolute Seebeck coefficient of the leads calculated from the vertical scattering corrected electrical resistivity values, the absolute Seebeck coefficient of the gold films can be determined.
In figure (6.20) the absolute Seebeck coefficient of the films agrees with that of bulk more so than that of the figure (6.10). The deviations are from the additional scattering mechanisms present in these impure films. These are reduced in magnitude from that of bulk below the Debye of gold, which is 165K\textsuperscript{42}, and increased above it. They deviate more from each other with increasing film thickness at high temperatures. They are positive throughout the majority of the temperature range although there are slightly negative values at the lowest temperatures.
Figure 6.21: Absolute Seebeck coefficient of All the Thin Au Films Tested

Figure (6.21) is a graph of all the thin Au films tested in this study. They continue to decrease in value in the high temperature range with increasing thickness, however, they do not continue to change significantly in the low temperature range. With these values the leads may now be characterized and it is possible to measure the absolute Seebeck coefficient of more films with these devices.
6.5 Results and Discussion

By subtracting the absolute thin film Seebeck coefficient from the relative Seebeck values measured, the lead contribution can be extrapolated as per equation (6.3.1).

The error in this measurement is high compared to the value of the thin Au film. Most thermoelectric materials have Seebeck coefficients above 100µV. The contribution of the error due to the leads in those measurements will only be a few percent.
It is possible to compare the leads to their bulk counterparts.

Figure 6.23: Absolute Seebeck coefficient of thin metallic leads on suspended SiN membranes

The lead contribution is small varying only between 2 to 0.5μV/K. It would seem as though it is the linear addition of the two contributions of bulk material values that constitute the lead. The bulk Pt thermopower value crosses zero near 175K due to change in Fermi energy with repeat to the first Brillouin zone[16]. This is an intrinsic material relationship and is not dependent upon size. It is possible that combination of the 10 nm Cr to the 40 nm of Pt is contributing significantly to the total value. Bulk Cr has small positive absolute thermopower values. It has been measured as negative at room temperature at thicknesses below 10 nm[63]. The effect impurities and grain boundaries have on this combined thermopower is
undetermined. Attaining the value of the absolute Seebeck coefficient of the leads that are required to measure thin film thermoelectric materials Seebeck coefficients is the motivation of this study. This has been acquired and additional measurements can be made.

With the leads characterized, it is then possible to continue to measure more absolute thin film Seebeck coefficients.

Figure 6.24: The Absolute Seebeck coefficients of thin aluminum films
The bulk Seebeck coefficient of aluminum is small and negative with a negative peak at 70K due to phonon drag. This peak spans from about 50-100K.[27] This is not present in the thin aluminum films. They are more positive than bulk values this could be due to a dominating negative $u$ term from equation(6.3.5). The loss of the phonon drag peak could be due to the reduced thickness if the films are thinner than the mean free path of the phonons that cause the drag effects in bulk materials. The relationship of the Seebeck coefficient of these thin aluminum films with temperature could be due to a known oxide layer on the surface of the films, the impurity of the films, the grain boundaries present in the films, and any surface roughness effects that may be present The thicker of the two films shows a slightly exaggerated deviation from bulk values than the thinner film. A comprehensive study into the surface roughness, grain boundary size and impurities of these two films is necessary to quantity this behavior.

6.6 Summary

Measurements of electrical and thermal transport in thin films are geometry dependent. Measuring the thermal and electrical conductivity and Seebeck coefficients of the same thin film circumvents errors that arise from slight difference in geometries. In order to accomplish this with suspended amorphous SiN structures, thin films need to be used to measure the Seebeck effect. In order to characterize the contribution of the thin film leads to a traditional relative Seebeck, measurement the effective FS model was applied. By measuring a series of increasing thicknesses of gold films to the ITTF limit, the absolute Seebeck coefficient of the thin Au films can be calculated.

The conduction of electrons through applied electrical or thermal currents are subject to different scattering mechanisms. The conduction of electrons through applied thermal currents are sensitive to vertical scattering events while conduction
through electrical currents are not. Measuring the electrical resistivity requires applying an electrical current to the film while measuring the thermal conductivity and Seebeck coefficient of the film through applying a thermal current to the film. It is possible to quantify the effects of vertical scattering process on the Seebeck coefficient by using the measured thermal conductivity and known Lorenz number. It is also possible to adjust the effective FS model to account for these effects as well.

Through experimentation, Au was found to have a small Seebeck coefficient that decreased with increasing film thickness. The calculated values were then be subtracted from the relative values to determine the lead contribution. The leads consist of 40 nm of Pt on top of 10 nm of Cr. It was found that the Seebeck coefficient of the combined two is similar to a linear addition of the two bulk values. The exact contribution to the Seebeck effect of each film is unclear. This was done with a set of aluminum films. They were found to have Seebeck coefficients that differed significantly from bulk values. The Al used in this study is a combination of aluminum and aluminum oxide and its impurity concentration is unknown, however, from the room temperature resistivity data indicates that it is much larger than that of pure bulk.

The leads of these micro-machined SiN measurement devices do not change on devices manufactured in the same way. Now that we have determined the contribution of the leads to a measurement of the Seebeck coefficient, a variety of materials can be tested. The thermal and electrical conductivity of those same materials can also be measured. This is beneficial since it will be possible to measure all three factors of the dimensionless figure of merit, $ZT$, on the same device with a high degree of accuracy. It is also provides insight into the scattering mechanisms and differing transport properties of the thin film materials. With this precision and insight, it is possible to make further advancements of thermoelectric material efficiencies.
Chapter 7

Conclusion

Thermoelectric materials are promising sources of renewable energy and technology. They provide the possibility to generate clean, renewable energy out of waste heat which is in abundance in most industrial manufacturing processes, current energy production plants, combustion engines and in the world around us. They also provide the opportunity to heat and cool objects with little power. There could be refrigerators that do not require harmful greenhouse gases to operate and efficient building temperature control systems that do not require natural gas or high amounts of electricity. Thermoelectric systems are also durable since they not require moving parts leading to low maintenance costs.

The restriction of the applicability of thermoelectric materials arises from their lack of efficiency. Material efficiency is characterized by the dimensionless figure of merit $ZT$ with classical limitations of approximately 1. Increasing, $ZT$, past 3 or 4 would have a significant impact on the way we generate power. Breaking past the classical limitations of material efficiencies has become possible due to the decoupling of the parameters that define $ZT$. This was first achieved by adopting the phonon glass-electron crystal approach to thermal conductivity. Expansion of this concept created thermal conductivities that approach or meet the amorphous
limit for materials without reducing the electrical conductivity of the material. This approach has been improved upon with a wide variety of materials achieving $ZT$'s of 2 and above. The next step to further improve material efficiencies is to decouple the parameters that make up the power factor of the dimensionless figure of merit, $S^2\sigma$.

There are many techniques to achieve high Seebeck coefficients without reducing the electrical conductivity or allowing the charge carrier to contribute significantly to the thermal conductivity. These techniques include creating sharp peaks in the density of states of the charge carriers near the Fermi level by doping materials and creating lattices that electrically conduct through hopping mechanisms. To further understand these techniques and develop new methods, precise nanoscale measurements can be made. This serves to probe the geometry dependence of the thermal and electrical transport and scattering mechanisms in 1 and 2D. Nanoscale thermoelectrics themselves have improved efficiencies over many of their bulk counterparts as well. These materials can be built into arrays for widespread applications or used for efficient microscale cooling or heating needs.

Precise measurements of the Seebeck coefficient of nanoscale materials are complicated by the contribution to the measurement of the thin film leads required to test them. To determine to contribution of thin Pt/Cr leads, we have applied the effective FS model. The effective FS model derives from the FS and MS model of electrical conduction in thin metallic films. These models impose boundary conditions on linearized Boltzman equations that are specific to thin metallic films to quantify the reduction of the electrical conductivity in thin films from that of bulk. The effective FS model relates this reduction to the Seebeck coefficient of a thin metallic films.

By using this model, we have been able to determine the contribution of the Pt/Cr leads present on suspended amorphous SiN membranes. These thin film
measurement devices have a low background contribution to the thermal conductivity due to the amorphous nature of the SiN. They also allow for the measurement of all three properties that determine $ZT$. This is advantageous and allows for precise measurements of these geometry dependent parameters with fine 2D temperature control.

It was found that the absolute Seebeck coefficient of the Pt/Cr leads are somewhat similar to the linear addition of bulk Pt and Cr values. The series of Au films used to deduce the absolute Seebeck coefficient of ITTF films are impure, rough, and sensitive to various scattering mechanisms. These scattering mechanisms effect thermal and electrical currents in different ways. As the thickness of the Au films was increased to the ITTF limit and beyond, the significance of these different scattering mechanisms was seen and accounted for in the effective FS model being used. The absolute Seebeck coefficients of the thin Au films measured in this study were similar to bulk Au values. The deviation from bulk is due to the different scattering mechanisms present in the thin films. The dominant scattering mechanisms in the thinnest films were attributed to the mean free path of the electrons being larger or comparable to the thickness of the film. This resulted in small positive Seebeck coefficient values that were reduced from that of bulk in the low temperature range used in this study and increased above it. The thicker the film became, the size restriction of the film on the mean free path of the electron was no longer a factor. Instead, surface roughness became the dominant cause of the deviation from bulk values. As film thickness was increased, the absolute Seebeck coefficient of the film decreased. This decrease was exaggerated at higher temperatures. Above the Debye temperature in these films, a decrease to negative values was observed that continued to decrease with increasing film thickness. This is attributed to the surface being roughened with each subsequent film deposition. The effects of vertical scattering events were seen in both the thermal conductivity and Seebeck coefficient.
and not the electrical resistivity. To take it this into account, the thermal conductivity and known Lorenz number were used to determine the change in resistance of thermal current with increasing surface roughness that was then related back to the traditionally measured electrical resistivity.

The absolute Seebeck coefficients of some thin aluminum films were measured as well as the thermal and electrical conductivity of a 174 nm thick Al film. From the thermal and electrical conductivity, the Lorenz number of the film was calculated. It was found that the absolute Seebeck coefficient of the Al films changes with thickness and deviates from bulk aluminum values. Bulk aluminum experiences a phonon drag effect on the Seebeck coefficient that peaks at 70K. This was not seen in either of the thin films. Instead, in the area of the peak, which causes sharp negative values, the Seebeck coefficient in was more positive than that of bulk. This could be due to the thickness of the films being smaller than the mean free path of the phonons responsible for this drag effect. These films also have an oxide layer on the surface and an unknown amount of impurities and disorder. The effect this has on the films is unclear at this time. The electrical resistivity of the 174 nm Al film was found to be higher than that of bulk. This follows with predicted behavior from the FS and MS models. The Lorenz number of this film had yielded predicted values slightly lower but within error bars of bulk. This lowering can be attributed to the oxide layer and impurities in the film.

The thin film lead contribution to a Seebeck coefficient measurement using a micro-machined suspended amorphous SiN membrane has been deduced. With the contribution now known, it is possible to measure any number of films on a device manufactured in the same way. Measurements of this nature will serve to further contribute to the study of thermoelectric materials and possibly more. The ability to precisely measure all of the parameters that determine a thermoelectric materials's efficiency in the thin film regime stands to advance the development
of thermoelectric devices. Studies of thin film thermoelectrics have contributed significantly to the advancement of bulk materials, that can be used in large scale applications. With the ability to measure these quantities, it is hoped that further significant advancements in thermoelectric research can be made so that applicable materials can be discovered and more sources of renewable energy can be created.
A: AFM Thickness Measurements

The film thicknesses used in this study were measured directly with atomic force microscopy. This measurement was conducted on lithography patterned SiN substrate chips that were deposited on at the same time as the SiN membrane used to measure thermal, electrical conductivity and Seebeck coefficient. This appendix will outline how those thickness measurements were made.

Basic operation of the AFM requires running a cantilever over the surface of a material and measuring the light reflected off of it as it tracts the surface. The atomic force microscope here at the University of Denver uses a super luminescent diode (SLD) to reflect light off a cantilever to measure the cantilevers position on the surface of a material with high precision. It refers to the SLD as a laser but they are not the same thing. An SLD is different from a laser in a number of ways, the important difference is that SLD’s have low temporal coherence lengths while still having the high spatial resolution of a laser. SLD’s produce light by running a current from a p to n type section with an active layer in between. In that active layer spontaneous recombinations of electrons and holes emits photons which are then amplified and reflected of the cantilever. The reflected light’s interference pattern is analyzed by the pre-calibrated software using the temporal coherence length of the light and then able to accurately measure the cantilevers position.

The cantilever is then moved along the surface of the material being studied. Depending on the measurement being conducted different methods of scanning the surface are available. In this study we used a silicon cantilever that drags along the surface of the sample in contact with it. It has a force constant of 0.2 N/m making it flexible so that it may measure height profiles on our samples. A stronger force constant can make precise cans of small features but tends to deflect to a larger degree than lower force constant tips over large features making it hard to resolve height differences (see graph). As the cantilever is scanning the surface of the sample we measure the height and location as detected by the SLD, the deflection amount and amplitude of our signal, and the Z Voltage. The Z voltage is a measure of the piezoelectric voltage on the cantilever. It is not of much use in the actual data collection but serves to show when too much or too little force is being applied to record a sensible
measurement. Being that a high voltage would indicate excessive force that can lead to cantilever damage or a low voltage can indicate a false engagement of the cantilever.

The scans in this study were performed on e-beam lithography patterns that have the same films deposited on them in the same deposition as the films on micro-machined SiN membrane for thermal, electrical and Seebeck measurements. The lithography patterns are made by coating a SiN substrate with a polymeric material, in this case PPMA (polymethyl methacrylate). An exposed area of the PPMA is bombarded with the focused electron beam breaking down the polymer bonds. The broken down areas are washed away with a developer leaving an exposed area of SiN. This patterned can be done with a well focused e-beam with precision on the nanometer scale. The lithography sample is then has the film deposited on it. A simple soak in acetone is enough to break apart the areas of unexposed, still intact polymer, leaving behind only areas of film directly on the SiN substrate.

Once a scan has been completed a few things need to be done before a height measurement of a nanoscale sample can be extracted. First, as the cantilever, or tip as it is most often called, scans an area it does not scan parallel with the surface. This is accounted for my plane fitting to the background. In an x,y scan a fit to the 2D plane is made and then subtracted out to leave a flat background representative of our SiN substrate. The next thing that is done is a flattening function. As the tip scans in the x direction it is deflected by the height step that we are measuring. Large deflections can cause false peaks or valleys the degree of with depend on the force constant of the tip and the height step of the material. This is accounted for by fitting the flat background to a stable value. This procedure is conducted with the material whos thickness in question is masked. With those data points out of the picture we are able to measure the flat, stable background of our SiN.
With the data now having a stable, flat background some averaging happens. A collection of background data points follows a gaussian distribution. A fit to that reveals the value of the background. It is possible at this point to set that to zero but it is not necessary since we are looking at the difference in height from our background to sample to have a measure of the nanoscale thickness. The mean of the gaussian fit is taken as the value of the sample. The width, or the point on the gaussian curve where the sign of the curvature changes, is taken to be the standard deviation of the data.
Simple averaging of many scans gives an accurate value of the thickness. The standard deviation is added in quadrature and the final value for error is taken as $\sigma = 0.67 \text{stdv}$. This is the probabilistic error for a gaussian fit (Taylor).

A check of the values obtained can be done by looking at the cross section of a scan. This will provide an at a glance look at what the thickness of the square is. It will be obvious if a bad fit to the background has been made, the cross section will be tilted. It will also be clear if there is a lot of dust or roughness of the sample. Sharp peaks will be seen in the cross section. These effects can be seen throughout the data analysis, the cross section just serves as one last cross check.

![Figure 3: 2D cross section of an AFM scan](image)

AFM scans and analysis of those scans are relatively straightforward. There are things to beware, like false tip engagements, bad fits to flat backgrounds, damaged tips that give inconsistent values, to name a few. It always best to take a few scans at different speeds, set points, and angles if there is any question to the validity of the recorded scan. If scans taken in different ways result in different thickness measurements then finding out why they are different indicates the issue begun encountered.
B: Devices Measured

The low temperature geometry devices used were termed, LTG. They were some of the first devices I tested and it thought that the geometry of the thermometers does not lead to reliable results when measured with the SRS. The AC measurement taken with the SRS resistance bridge goes out of phase when at high resistances, this is thought to be due their geometry. The data, however, questionable was taken on a few devices. As long as the resistance is linear with temperature, an in phase AC signal can be assumed. Deviations from that should be considered unfruitful data.

<table>
<thead>
<tr>
<th>Device Name</th>
<th>Thermal Data Collected</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6</td>
<td>0.5-100K and 78-300K</td>
<td>Data from 20-100K questionable</td>
</tr>
<tr>
<td>C1</td>
<td>0.5-2K</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>0.5-2K</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: LTG Devices tested

Some of the first devices made for thermoelectric measurements were termed, ZT. These have gel pack stuck to the back of them. Some of them also have a layer of what is thought to be resist on the structures themselves. The resist layer is thought not to contribute as long as it isn’t thermally shorting different parts of the device together. It is difficult to ensure that they make good thermal contact with the sample mount. To ensure this use multiple clips to push it down but these devices are brittle so use caution. The inner leads on these are skinny Au with a thin layer in the center of them, on the bridge. The outer "fat" leads are Mo. There are two platforms on each device. Looking at the DU logo there will be one on the right and one to the left. The right is UR and left is LL, also BG is short for back ground.
The larger ZT devices made at CINT were termed, LZT. These are relatively easy to work with and sturdy compared to the other two. The A,B,C numbered terms are for the device designator. With the other chips we keep a naming scheme like an excel spread sheet. These devices were cleaved and put all over the place so I’ve been just picking a name for these. The W term is the wafer number it came from.

<table>
<thead>
<tr>
<th>Device Name</th>
<th>Thermal Data Collected</th>
<th>Notes</th>
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</thead>
<tbody>
<tr>
<td>A5LL</td>
<td>78-326K BG and 20nm Veeco Au</td>
<td>Film shorted to thermometer</td>
</tr>
<tr>
<td>K9UR</td>
<td>78-326 BG</td>
<td></td>
</tr>
<tr>
<td>A1UR</td>
<td>78-326K BG</td>
<td>I took a couple BG measurements of these</td>
</tr>
<tr>
<td>A1LL</td>
<td>78-326K BG</td>
<td>to see if they changed with time</td>
</tr>
<tr>
<td>B4LL</td>
<td>78-326K BG, 20,40, 80nm 13er Au</td>
<td>these are total thicknesses</td>
</tr>
<tr>
<td>B4UR</td>
<td>78-326K BG, 26, 43nm Au</td>
<td>Annealed</td>
</tr>
<tr>
<td>A2UR</td>
<td>78-326K BG</td>
<td></td>
</tr>
<tr>
<td>A2LL</td>
<td>78-326K BG, 5nm Au</td>
<td>Damaged</td>
</tr>
<tr>
<td>A3LL</td>
<td>78-326K BG, 20,40,80,120nm Veeco Au</td>
<td>Film shorted to lead</td>
</tr>
<tr>
<td>A3UR</td>
<td>78-326K BG</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: ZT Devices tested

<table>
<thead>
<tr>
<th>Device Name</th>
<th>Thermal Data Collected</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1W1</td>
<td>78-326K BG</td>
<td></td>
</tr>
<tr>
<td>B3W3</td>
<td>78-326 BG, 26nm 13er Au</td>
<td>Damaged leads, trans. TEP data</td>
</tr>
<tr>
<td>A2W1</td>
<td>78-326K BG</td>
<td>insulating Veeco Al film</td>
</tr>
<tr>
<td>D7W1</td>
<td>78-326K BG</td>
<td>Veeco Cr/Au film to check contacts</td>
</tr>
<tr>
<td>B1W3</td>
<td>78-326K BG, 174nm Veeco Al</td>
<td>Seimens group</td>
</tr>
<tr>
<td>C2W3</td>
<td>78-326K BG, 26nm Al</td>
<td>Seimens group</td>
</tr>
<tr>
<td>C1W3</td>
<td>78-326K BG, Au thickness series used in this study</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: LZT Devices tested
Bibliography


