ABSTRACT

ROUNDS, ROBERT BURTON. The Influence of Point Defects on the Thermal Conductivity of AlN and GaN Crystals. (Under the direction of Professors Zlatko Sitar and Ramón Collazo).

The thermal conductivity of bulk single crystal samples of AlN and GaN was measured in the range of 30-325 K using the 3ω method in order to determine the relative influence of crystalline defects in different temperature regimes. Thorough review of prior literature and application of phonon scattering theory were used to assess the principle mechanisms responsible for limiting the thermal conductivity of the III-Nitrides. It was found that point defects exhibited significant influence on thermal conductivity in both GaN and AlN across the entire temperature range.

Secondary ion mass spectrometry (SIMS) and photoluminescence spectroscopy (PL) of AlN grown by both physical vapor transport (PVT) and hydride vapor phase epitaxy (HVPE) were used to determine the type of impurities present and their optical emission spectra. It was found that carbon, oxygen, and silicon were the principal impurities in the crystals and that the formation of a carbon-silicon complex appeared to improve thermal conductivity above 100 K. However, this trend did not hold at temperatures below 100 K in PVT AlN, where significant phonon resonances were present, as indicated by distortions in the thermal conductivity curves. The HVPE-grown AlN showed better agreement of thermal conductivity across the measured temperature range, which was determined to be a result of overall low impurity concentration.

Single crystals of GaN grown by ammonothermal, HVPE, and sodium flux processes were obtained for this work. SIMS was used to measure the impurity concentrations and was correlated with thermal conductivity results. The thermal conductivity of GaN showed a similar inverse relationship with impurity concentration as AlN. While the thermal conductivity curves for GaN did not show significant distortions as in the PVT grown AlN, the ammonothermal samples
showed substantially lower thermal conductivity at low temperature. Fitting using the Debye-Callaway model revealed a significant discrepancy between the thickness of the samples and the unit length necessary to produce adequate curve fits. These conditions suggested the possibility of phonon resonances extending below the measurable temperature range, a behavior observed for other material systems in literature.

Thermal conductivity results in both AlN and GaN were observed to converge between different samples as the temperature increased, indicating that phonon scattering from Umklapp processes was gaining influence with respect to point defect scattering. However, results still showed significant variability as the room temperature values ranged from 268-374 Wm⁻¹K⁻¹ in AlN and 164-224 Wm⁻¹K⁻¹ in GaN. Accordingly, it was concluded that the room temperature thermal conductivity of these materials was not fully dominated by Umklapp scattering, but was still significantly influenced by incorporated point defects. Also concluded was that in order to observe room temperature thermal conductivity values limited only by 3-phonon processes, the point defect concentrations of these materials must be lowered by several orders of magnitude by carefully controlling their incorporation during crystal growth. Nonetheless, the measured thermal conductivity of 374 Wm⁻¹K⁻¹ for AlN at room temperature remains the highest value reported to date, indicating superior crystal quality compared to earlier efforts. The next highest room temperature results in AlN ranged between 339-343 Wm⁻¹K⁻¹ for three different samples, also higher than prior reported values.
The Influence of Point Defects on the Thermal Conductivity of AlN and GaN

by
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DEDICATION

To my wife Hannah, our children present and future, and my Father in heaven, who is the ultimate source of all my blessings and without whom none of my investigations and accomplishments would have been possible.

“It is the glory of God to conceal a matter; to search out a matter is the glory of kings.”

Proverbs 25:2
BIOGRAPHY

Robert Rounds was born on May 18, 1983 and raised in Duluth, Minnesota. He earned a BS in Biochemistry from Bethel University in St. Paul, Minnesota in May of 2006. It would have been beneficial had he somehow developed a sense of ambition during his years as an undergraduate, but unfortunately this did not happen until his subsequent seven years of employment. The desire to achieve and pursue excellence grew out of his trials and frustrations on the job from 2006 to 2010. He met Hannah in late 2010 when he joined the Twin Cities Ultimate League and played for the team “Yetis,” on which Hannah was also rostered. It wasn’t until December when he took the initiative to create circumstances by which they might spend more time together, the first being an invite play pickup broomball with friends. Hannah showed up and demonstrated significant skill and tenacity born from a desire to win, leaving a lasting impression on Rob. He obtained her number and they began a series of dates, the first of which occurred New Year’s Eve of that year. They happily married February 17, 2012. In September of that year, Robert took a position at a startup company called Biogenic Reagents. In January 2013, he received an acceptance letter from the MSE program at NCSU, the only institution to extend and offer from the eight to which applications were submitted. In August of 2013, he moved with wife and child to Raleigh, North Carolina, to begin his graduate studies in the Materials Science and Engineering PhD program at North Carolina State University. In August of 2014 after working as a teaching assistant for two semesters, he was graciously given the magnificent opportunity to study under the direction of Professor Zlatko Sitar in the Wide Bandgaps Lab, which manifested as both a remarkable challenge and a satisfying joy.
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Chapter 1: Introduction to the III-Nitrides

1.1 Dissertation Overview

The III-Nitrides represent technologically important compound semiconductors with current applications in light emitting diodes (LEDs), diode lasers, and transistor devices.\textsuperscript{1–4} Additionally, GaN, AlN, and their alloys have potential for use in both power switching and UVC diode laser applications due to their high breakdown fields and wide bandgaps, respectively.\textsuperscript{5–9} Progress in the production of large, high quality single crystal substrates of the III-Nitrides is ongoing. A significant driving factor is the development effort towards high power density next-generation devices, in which low dislocation density substrates are an essential prerequisite. One important material parameter relevant to these efforts is the thermal conductivity of the substrate. This determines how quickly heat moves through the material during device operation. A review of literature reveals significant discrepancies in reported thermal conductivity values for AlN and GaN.\textsuperscript{10–15} The present work examines the underlying causes for these observations.

Chapter 1 introduces the III-Nitrides, discusses their historical context, reviews their potential for next-generation applications, and highlights the current challenges present in growth of single crystal substrates. Chapter 2 describes the background theory pertinent to thermal conductivity and presents the traditional formalism used in modeling thermal conductivity through phonon relaxation times. Chapter 3 reviews literature results in order to illustrate the effect of specific phonon scattering mechanisms on the thermal conductivity of non-metallic solids. Chapter 4 describes common approaches used in measuring thermal conductivity.
Chapter 5 provides a detailed explanation of the technique used in obtaining the results in the body of this work. This includes the physical model behind the technique, a derivation of the equation used for calculating thermal conductivity, and the pertinent details regarding technique implementation. Chapters 6 and 7 take the theory presented in chapter 2 and apply it to the temperature-dependent thermal conductivity of AlN and GaN, respectively. Chapter 8 illustrates the methodology used to account for the propagated error of $3\omega$ method thermal conductivity measurements. Chapter 9 describes details regarding the high temperature vacuum probe system that was built as part of the present work for characterizing semiconductor devices in the Wide Bandgaps Laboratory. The final chapter summarizes the work performed, highlights the most significant findings, and provides an outlook regarding unanswered questions that may be useful in directing subsequent research efforts in the thermal conductivity of the III-Nitrides.

1.2 History

III-Nitride semiconductors are generally recognized as materials containing binary compounds of nitrogen with aluminum, gallium, or indium and respective alloys thereof. The wurtzite crystal structure of the III-nitrides was first demonstrated by Heinrich Ott for AlN\textsuperscript{16} in 1924 and by Robert Juza and Harry Hahn in 1934 for GaN and InN,\textsuperscript{17} but the realization that nitrides held promise for semiconductor devices certainly could not occur until after the invention of the transistor in 1947 at Bell Labs. Nonetheless, the first report of the III-nitrides as semiconductors did not come out until 1959, when Renner described synthesis of nitrides of boron, aluminum, gallium, and indium and reported preliminary electrical conductivities.\textsuperscript{18} The first investigations into the electrical properties of the III-nitrides with specific emphasis
towards devices did not take place until nearly a decade later. In 1967, Cox et al. were the first to describe synthesis of AlN thin films on sapphire and their electrical characteristics.\textsuperscript{19} That same year, a publication originating from Westinghouse Research Labs by Chu et al. and funded by the Air Force Aero Propulsion Laboratory described epitaxial growth of AlN on silicon carbide (SiC) substrates with the specific goal of devices capable of operation at high temperature.\textsuperscript{20} In 1969, Maruska and Tietjen at RCA Labs were the first to report the electrical properties of single crystal GaN epitaxially grown on sapphire.\textsuperscript{21} One year later, a publication emerged from Bell Labs by MacChesney et al. regarding the thermal stability of InN at elevated temperatures.\textsuperscript{22} While no electrical characterization was reported in the article, the authors specifically motivated their work with the potential for use of III-nitrides in semiconductor injection lasers. In 1971, Pankove et al. at RCA labs were the first to report on operation of a light emitting diode (LED) fabricated from GaN. A recurring theme across many of these different works was the substantial difficulty involved with the III-nitride thin film synthesis and the latent strain in the epitaxial layers due to the difference between the lattice constants and coefficients of thermal expansion of the substrate and the thin film. As a result of these and other challenges, progress in nitride devices was slow, and it wasn’t until 1993 that the first transistor fabricated from GaN was reported by Khan et al.\textsuperscript{23} One year later, the first commercially available nitride-based light emitting diodes (LEDs) were reported by Nakamura et al. from Nichia Chemical Industries.\textsuperscript{24} Characterization of these early devices revealed that radiative recombination was insensitive to the high dislocation densities of around $10^{10}$ cm$^{-2}$ in the device layers.\textsuperscript{25} In 1996, the first nitride diode lasers were reported by different research groups in Japan.\textsuperscript{26–28} Even though nitride technology had been thoroughly proven by these
works, the performance and longevity of these early devices was mediocre at best. Further work carried out between 1997 and 1999 demonstrated device current leakage and service lifetime could be improved by orders of magnitude by using material grown by the epitaxial lateral overgrowth (ELO) technique,\textsuperscript{29–31} a method shown to reduce dislocation density by at least two orders of magnitude. These reports clearly demonstrated the limitation presented by epitaxy of III-nitrides on foreign substrates in terms of resulting thin film material quality. The only way to eliminate the adverse effects of threading dislocations would be to remove them, meaning that instead of using SiC or sapphire substrates for growth, high quality III-nitride single crystals would be necessary. Accordingly, efforts directed towards growth of bulk GaN and AlN single crystals of adequate size for seeded substrate production began in earnest between 1995 and 1999.\textsuperscript{32–37} During this time, researchers in Poland were successful in demonstrating spontaneously nucleated GaN crystals using a high pressure method in liquid gallium\textsuperscript{32} and a solvothermal method in supercritical ammonia, now known as the ammonothermal method.\textsuperscript{34} While the results of these experiments showed promise for later optimization of self-seeded crystal growth, the techniques lacked immediate scalability. The first freestanding GaN substrate sufficient for epitaxy was announced in 2000 by Motoki et al. at Sumitomo Electric Industries.\textsuperscript{38} The substrate was not produced by self-seeded growth, but had been grown by hydride vapor phase epitaxy (HVPE) on a two inch GaAs seed crystal using an adapted ELO technique that yielded a total dislocation density around $10^5 \text{cm}^{-2}$ in the crystal. The first report of wafer-scale crystals of AlN grown by physical vapor transport (PVT) on spontaneously nucleated seeds appeared in 2001 from Crystal IS, Inc.\textsuperscript{39} Subsequent reports demonstrating similarly sized spontaneously nucleated AlN single crystals appropriate for
seeded AlN boule growth came out in 2006 from groups at North Carolina State University and the University of Erlangen-Nürnberg. To date, there are relatively few groups that perform bulk III-nitride crystal growth using substrates originating from spontaneously nucleated seed crystals. Among these are Ammono S.A., Mitsubishi Chemical Corporation, and Soraa for GaN and Crystal IS, Hexatech, and the Leibniz Institute for Crystal Growth (IKZ) for PVT AlN. Other producers of III-nitride single crystals use quasi-bulk approaches involving HVPE growth of either GaN or AlN on sapphire or SiC. There are currently no groups that produce bulk InN of any kind due to physical limitations arising from its low decomposition temperature, but recent work has demonstrated that an adapted HVPE process may offer a route to quasi-bulk synthesis of InN in the near future.

1.3 III-Nitride Properties and Applications

GaN and AlN attract significant interest for use in deep UV light emitting diodes (LEDs), laser diodes (LDs), and power semiconductor devices. The III-Nitrides of InN, GaN, and AlN can assume either wurtzite (α-phase; space group P6\textsubscript{3}mc) or zinc-blend (β-phase; F\textsuperscript{4} 3m) crystal structure. The wurtzite phase is the most thermodynamically stable, but some work has demonstrated growth of the metastable zinc-blend phase on substrates having cubic symmetry. The layers of III and N atoms in the Wurtzite structure represent two alternating hexagonal close packed (HCP) sub-lattices ordered as A\textsubscript{III}A\textsubscript{N}B\textsubscript{III}B\textsubscript{N} along the c axis. III-Nitride binary compounds show ionic-covalent bonding character. This causes the formation of dipoles in the III-N bonds with a net dipole moment parallel to the c-axis, which is the origin of the spontaneous polarization observed in the III-Nitrides. A 1/3 schematic rendering of the III-Nitride wurtzite unit cell and polarization vector are shown in Figure 1-1.
The bandgaps of 0.7 for InN, 3.47 eV for GaN, and 6.1 eV for AlN correspond to emission wavelengths of 1772 nm, 357 nm, and 203 nm, respectively. As AlN and GaN demonstrate complete miscibility, alloys with composition of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ can be grown with any variation of $x$ between 0 and 1 for tuning the peak emission wavelength between these limits. This also applies to alloys of InGaN, which allow the fabrication of LEDs capable of emission at any wavelength within the visible spectrum, but InGaN alloys remain challenging due to the miscibility gap present in this system. Ternary alloys of the III-Nitrides exhibit linear dependence of the lattice constant upon composition given by Vegard’s law, where

$$a_x = x a_{\text{AlN or GaN}} + (1-x) a_{\text{GaN or InN}}.$$  \hspace{1cm} (1.3.1)

While the dependence is linear for the lattice constant, the bandgap of ternary III-Nitrides displays quadratic behavior. This requires an additional term that includes an empirically derived bowing parameter “b” with significant dependence on residual strain, where
\[ E_g = xE_g^{\text{AlN or GaN}} + (1-x)E_g^{\text{GaN or InN}} - bx(1-x). \]  

(1.3.2)

Figure 1-2 shows the dependence of bandgap and emission wavelength on the lattice constant in the III-Nitride alloys. The plot takes into account contributions from the respective bowing parameters relevant to each of the ternary alloy systems.

Figure 1-2: Bandgap and wavelength as a function of lattice constant in the ternary III-Nitrides. Bowing parameters were taken from Pelá et al and Orsal et al.\textsuperscript{55,56}

The high breakdown fields of 3.75 MV/cm in GaN\textsuperscript{57} and 15 MV/cm in AlN\textsuperscript{58} present the opportunity for power semiconductor devices operating in the kilovolt range.\textsuperscript{48} Table 1-1 presents a comparison of the III-Nitrides and semiconductor materials either in use or under investigation regarding power device applications.
Table 1-1: Comparison of properties for the III-Nitrides and some other semiconductor materials.\textsuperscript{13,49--52,57--79}

<table>
<thead>
<tr>
<th>Property</th>
<th>Si</th>
<th>4H-SiC</th>
<th>β-Ga\textsubscript{2}O\textsubscript{3}</th>
<th>InN</th>
<th>GaN</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap [eV]</td>
<td>1.11</td>
<td>3.26</td>
<td>4.8</td>
<td>0.7</td>
<td>3.47</td>
<td>6.1</td>
</tr>
<tr>
<td>Breakdown field $E_C$ [MV/cm]</td>
<td>0.3</td>
<td>3</td>
<td>5.5\textsuperscript{a}</td>
<td>0.71\textsuperscript{a}</td>
<td>3.75</td>
<td>15</td>
</tr>
<tr>
<td>Mobility $\mu_e$ [cm\textsuperscript{2}/V s]</td>
<td>1760</td>
<td>715</td>
<td>153</td>
<td>3570</td>
<td>1265</td>
<td>426</td>
</tr>
<tr>
<td>Dielectric constant $\varepsilon$</td>
<td>11.7</td>
<td>9.7</td>
<td>9.9</td>
<td>15.3</td>
<td>8.9</td>
<td>8.5</td>
</tr>
<tr>
<td>Saturation Velocity $v_{e, sat}$ [cm/s]</td>
<td>$1\times10^7$</td>
<td>$4.77\times10^7$</td>
<td>$2\times10^7$</td>
<td>$2.5\times10^7$</td>
<td>$2.7\times10^7$</td>
<td>$1.4\times10^7$</td>
</tr>
<tr>
<td>Thermal conductivity $\kappa$ [W/m\textsuperscript{1}K\textsuperscript{-1}]</td>
<td>150</td>
<td>370</td>
<td>27</td>
<td>176</td>
<td>269</td>
<td>340</td>
</tr>
<tr>
<td>Baliga’s power device figure of merit $\left(\varepsilon_r\mu_e E_C^3\right)$</td>
<td>1</td>
<td>337</td>
<td>453</td>
<td>35</td>
<td>1068</td>
<td>21981</td>
</tr>
<tr>
<td>Baliga’s high frequency figure of merit $\left(\mu_e E_C^3\right)$</td>
<td>1</td>
<td>41</td>
<td>29</td>
<td>11</td>
<td>112</td>
<td>605</td>
</tr>
<tr>
<td>Combined figure of merit $\left(\kappa\mu_e v_{e, sat} E_C^2\right)$</td>
<td>1</td>
<td>478</td>
<td>11</td>
<td>33</td>
<td>544</td>
<td>1920</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculated using Hudgins scheme.$^80$

The table clearly demonstrates the superiority of GaN and AlN in terms of their high power and high frequency handling characteristics compared to traditional silicon devices. Additionally, the above estimates predict that devices made from these materials should also outperform devices fabricated from 4H-SiC and β-Ga\textsubscript{2}O\textsubscript{3}, which are regarded as promising materials for power device applications. It should be noted that the experimentally measured breakdown field of 3.8 MV/cm by Green et al.$^81$ in β-Ga\textsubscript{2}O\textsubscript{3} is much lower than the prediction in Table 1-1. If further efforts yield higher $E_C$ results than the above theoretical estimate, β-Ga\textsubscript{2}O\textsubscript{3} may prove to be a better power device material than GaN, however, the thermal conductivity is lower by an order of magnitude. This means that power devices fabricated from β-Ga\textsubscript{2}O\textsubscript{3} will suffer more significantly from self-heating effects than will power devices fabricated from the III-Nitrides. When comparing semiconductor material systems for power device applications, a plot of the specific on-resistance ($R_{on,sp}$) vs. breakdown voltage provides additional perspective. This relationship is shown below in Figure 1-3.
Figure 1-3: Comparison of $R_{on,sp}$ vs. design breakdown voltage of semiconductors featured in Table 1-1.

The figure plainly shows that GaN and AlN are ideal materials for power devices, as they have $R_{on,sp}$ values that are orders of magnitude lower than those found in devices made from silicon. This means that working devices fabricated from either AlN or GaN will waste less power in the on state than will devices made from any of the other featured material systems.

While the ideal qualities of the III-Nitrides represented above make them desirable materials for optoelectronics and power devices, numerous obstacles prevent wide scale implementation. Power devices that operate on the kilovolt scale must be fabricated from material with very low dislocation density to avoid current leakage paths that degrade performance and cause premature breakdown. This means that bulk single crystal material must be used, but native substrates of GaN and AlN come with significant cost due to challenges inherent to their
production. The majority of III-Nitride thin film growth is carried out on less expensive foreign substrates as a consequence, resulting in layers full of dislocations that preclude the possibility of III-Nitride power devices. Furthermore, the difficulty of controlling point defect incorporation during III-Nitride crystal growth complicates efforts to achieve desired electrical or optical properties. Examples of this include the UV absorption in PVT AlN caused by carbon impurities, the formation of the silicon DX center that pins the Fermi level below the conduction band in AlN, the high impurity concentrations in GaN grown by the ammonothermal method, and the numerous challenges in producing p-type conductivity in GaN and AlGaN.
Chapter 2: Thermal Conductivity

2.1 Introduction

As shown in Table 1-1, the III-Nitride compounds GaN and AlN exhibit high thermal conductivity compared to silicon or other traditional III-V compound semiconductors. While the thermal conductivity parameter communicates how well a material conducts heat, it does not convey information regarding the physical mechanisms that determine the thermal conductivity of a particular material. This chapter explains the fundamental principles behind thermal conductivity and the physical processes that limit it.

The thermal conductivity parameter describes a material’s ability to transport heat. Thermal energy is transmitted through materials by many different processes. In metals, the dominant mechanism of thermal transport is through energy exchange between free electrons. In semiconductors with low numbers of free carriers, thermal transport is achieved predominantly by lattice vibrations known as phonons. Consequently, thermal conductivity significantly depends on temperature, as the number of lattice vibrations within a given system is a function of the total thermal energy. Acoustic phonons, rather than optical phonons, account for the majority of thermal energy transport in semiconductor materials. Since phonons exist entirely within the context of the crystal lattice, they are extremely sensitive to crystalline defects that interrupt lattice periodicity, such as dislocations, stacking faults, grain boundaries, voids, secondary phases, and point defects arising from impurities or native vacancies. Temperature dependent measurement of thermal conductivity is therefore a powerful tool for revealing the relative contributions of different phonon scattering phenomena within a given sample. In the
technologically important III-Nitride materials, the thermal conductivity is a crucial parameter that must be taken into account during initial design for devices that will be subject to heavy thermal loads, such as power devices and laser diodes.

2.2 Phonons

In condensed matter, atoms vibrate around equilibrium positions as determined by the periodicity of the crystal lattice and the interatomic forces of crystal bonds. The quanta of these lattice vibrations are traditionally treated as particles for purposes of simplified modeling and given the term “phonons.” Phonons exist in two kinds. Acoustic phonons are characterized by lattice waves in which the vibration frequency approaches zero in the limit of long wavelength while optical phonons have a finite vibration frequency at the same limit. In addition, the atomic displacement for a given atom and its nearest neighbors is in the same direction for acoustic phonons, but in opposite directions for optical phonons. Phonons can be further classified in terms of the atomic displacement with respect to the direction of wave propagation. For longitudinal phonons, the direction of atomic displacement is in the direction of wave propagation. For transverse phonons the atomic displacement is orthogonal to the direction of wave propagation. Phonon dispersion curves show the difference in frequency as a function of momentum between the acoustic and optical phonons in Figure 2-1.
The solid lines in Figure 2-1 a) and b) represent the acoustic and optical phonon branches. The acoustic branches originate at the Γ point starting at zero frequency and reach their maximum frequencies at the boundaries of the first Brillouin zone. Since the atomic displacement of a given atom and its nearest neighbors is in the same direction for acoustic phonons, the acoustic phonon branches allow for rapid transfer of thermal energy in crystalline solids. The total number of phonon branches that can be accommodated for a specific material depends on the unit cell of the crystal lattice according to the relation $3Z$, where $Z$ is the number of atoms per unit cell and 3 represents the degrees of freedom in which the atoms can vibrate. For any crystalline material, there are always three acoustic branches: one longitudinal phonon mode and two transverse modes. Consequently, the remaining $3Z-3$ branches represent the optical phonons. For the III-Nitrides in which there are four atoms per primitive unit cell, there are a total of nine optical phonon modes. The lack of twelve distinct phonon dispersion curves in Figure 2-1 a) & b) is simply a result of crystal symmetry, which makes some phonon modes degenerate.
2.3 The Debye Model of Thermal Conductivity

An exact calculation of thermal conductivity due to the contributions of all acoustic phonon branches is neither necessary nor feasible. In practice, the Debye model of the phonon density of states is used to provide an acceptable approximation of thermal energy for a given system. Within the Debye model, the material is assumed to be an isotropic medium in which all phonon modes have a constant speed and the anharmonicity of atomic bonds is ignored. The phonon dispersion relation is represented as

$$\omega = v|\vec{q}|, \quad (2.3.1)$$

where $v$ is the speed of sound in the material and $\vec{q}$ is the phonon wave vector. The phonon density of states representing the number of modes $\vec{q}$ per unit frequency having angular frequency $\omega(\vec{q})$ equal to $\omega$ is then

$$D(\omega) = \frac{V \omega^2}{2\pi^2 v^3}, \quad (2.3.2)$$

where $V$ is the volume for a given sample. For a sample containing $N$ total atoms, there are a total of $N$ acoustic modes. Since phonons are confined to the crystal lattice, the allowed momentum that a phonon can have will never exceed the dimensions of the first Brillouin zone. This momentum limit is understood as the cutoff wavevector. The Debye frequency associated with the cutoff wavevector is given by

$$\omega_d = \left( \frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} v. \quad (2.3.3)$$
The quantity $N/V$ is equivalent to the atomic density and is typically calculated using the number of atoms per unit cell volume of the material. The thermal energy present between all three acoustic phonon modes is

$$U = 3 \int_0^{\omega_0} D(\omega)n(\omega)\hbar\omega d\omega = 3 \int_0^{\omega_0} \frac{V\omega^2}{2\pi^2v^3} \frac{1}{\frac{\hbar\omega}{\hbar^2}-1} \hbar\omega d\omega,$$

where $n(\omega)$ represents the phonon distribution function. Substituting and rearranging yields

$$U = \frac{3Wk_B^4T^4}{2\pi^2v^3\hbar^4} \int_0^{\omega_0} \frac{x^3}{e^x-1} dx,$$

where the substitution $x = \hbar\omega/k_BT$. When the phonon mode $\vec{q}$ reaches the cutoff wavevector, this becomes $x_D = \hbar\omega_D/k_BT \equiv \theta_D/T$. The quantity $\theta_D$ is referred to as the Debye temperature, which is represented as

$$\theta_D = \frac{\hbar v}{k_B} \left( \frac{6\pi^2N}{V} \right)^{1/3}. $$

This quantity represents the temperature at which point the excited phonon modes reach the momentum limit imposed by the first Brillouin zone boundary. This implies that materials having a shorter lattice constant should therefore have a higher Debye temperature, which is exactly what is observed. Differentiation of the thermal energy with respect to temperature yields the Debye expression for heat capacity at constant pressure:

$$C(x) = \frac{3Wk_B^4T^3}{2\pi^2v^3\hbar^3} \int_0^{\omega_0} \frac{x^4e^x}{(e^x-1)^2} dx.$$
Normalizing the above expression to volume yields the Debye expression for specific heat.

Within the Debye model, the contribution of a specific phonon mode to the total specific heat is termed the spectral specific heat, which is represented by the expression

\[ C_q(x) = \frac{3k_B^4 T^3}{2\pi^2 v^3 h^3} \frac{x^4 e^x}{(e^x - 1)^2}. \]  

This relationship is shown below for AlN and GaN in Figure 2-2 as a function of \( \omega \) assimilated into the dimensionless parameter \( x \) and plotted against phonon wavelength.

Figure 2-2: The spectral specific heat for a) AlN and b) GaN. The lower limit of wavelength in the above representations is the unit length derived from the average volume of an atom within each compound. The above models illustrate the presence of a dominant phonon wavelength for any given temperature.

From simple kinetic theory we know that thermal conductivity is represented as

\[ \kappa = \frac{1}{3} C v l, \]  

where \( l = v \tau \) is the mean free path a phonon travels before scattering and \( C \) is the volumetric specific heat. Substitution of \( v \tau \) for the mean free path, \( \theta_D / T \) for \( x_D \) in the integration limit,
and replacing specific heat $C$ with the volume-normalized expression for Debye heat capacity yields

\[
\kappa = \frac{k_B}{2\pi^2v\hbar^3} \int_0^\infty \frac{\tau_R(x)}{x} \frac{x^4e^x}{(e^x-1)^2} dx.
\]  

(2.3.10)

The above expression is known as the Debye approximation for lattice thermal conductivity. The objective then becomes to estimate the quantity $\tau_R(x)$, which is the effective relaxation time for phonons in the material. If the various relaxation times for different scattering mechanisms can be adequately assessed, then the effective relaxation time can be found by using Matthiessen’s rule for adding the scattering rates according to

\[
\tau_R^{-1}(x) = \sum_i \tau_i^{-1}(x).
\]  

(2.3.11)

The relaxation times taken into account by this expression are resistive. Accordingly, the thermal conductivity of crystalline materials will decrease in proportion to each successive phonon scattering mechanism that comes into play due to the associated phonon relaxation time. Phonon relaxation mechanisms can be categorized as being either intrinsic or extrinsic in nature. Intrinsic phonon scattering depends on the crystal system while extrinsic phonon scattering results from phonon collisions with crystalline defects. Intrinsic phonon scattering includes Normal and Umklapp scattering, both of which are termed 3-phonon scattering processes. The difference between these mechanisms is shown below in Figure 2-3.
In Normal scattering, two colliding phonon wavevectors produce a third having a momentum value remaining within the boundaries of the first Brillouin zone. Since the magnitude of the momentum still stays within the limits afforded by the crystal lattice, Normal scattering does not result in a loss of direction with respect to the original colliding phonons and phonon momentum is conserved. In contrast, Umklapp scattering results when two colliding phonon wavevectors produce a third one for which the momentum exceeds the first Brillouin zone boundary. The wavevector cannot propagate as a result, and the scattered wavevector ends up being the sum of the two original colliding wavevectors and a reciprocal space lattice vector, denoted “G” in the above schematic. The key effect is that the scattered wavevector has a directional component opposite of the two original colliding wavevectors with a portion of phonon momentum being lost to the crystal lattice. This is the origin of thermal resistance resulting from Umklapp scattering. Since Normal scattering conserves phonon momentum and is thereby not a resistive phonon scattering process, it cannot be summed into the expression.
for $\tau_R^{-1}(x)$, but must be accounted for by an adjustment to the expression for the equilibrium phonon distribution. This was first discussed by Callaway,\textsuperscript{89} and his model provides a good approximation for the effect of Normal processes on thermal conductivity. A full derivation of Callaway’s model for thermal conductivity will not be presented here, but is available in the literature.\textsuperscript{88,89} Callaway’s main result for thermal conductivity is summarized by two components:

$$\kappa = \kappa_1 + \kappa_2 = \frac{k_B^4 T^3}{2\pi^2 \nu h^3} \int_0^\theta_T \tau_C x^4 e^x \, dx + \frac{k_B^4 T^3}{2\pi^2 \nu h^3} \left( \int_0^{\theta_R} \frac{\tau_C x^4 e^x}{\tau_N (e^x - 1)} \, dx \right)^2.$$

(2.3.12)

The first component is the same as the Debye expression for lattice thermal conductivity, but the quantity $\tau_R$ has been replaced with $\tau_C$, which is a combined phonon relaxation time that takes into account Normal scattering according to

$$\tau_C^{-1} = \tau_R^{-1} + \tau_N^{-1}.$$

(2.3.13)

The second component in the Callaway model arises from the contribution of Normal scattering to thermal conductivity. While Normal processes are not resistive in nature, they significantly influence the thermal conductivity by exchanging thermal energy between different phonon modes, as can be seen in Figure 2-3. Due to its similarity to Debye’s model, Callaway’s expression is commonly referred to as the Debye-Callaway approximation for thermal conductivity. When impurity concentration is high within a material, resistive scattering mechanisms dominate such that $\frac{1}{R} \approx \frac{1}{N}$. This causes $\tau_C^{-1} \approx \tau_R^{-1}$ with the effect
that $\kappa_2 \approx 0$. Thermal conductivity can be approximated by the Debye expression in such instances. Conversely, for crystals with substantially low impurity concentrations and isotopically enriched compositions, the contribution of Normal scattering from $\kappa_2$ is necessary in order to produce model thermal conductivity curves that agree with measured results.\textsuperscript{90}

Although the Debye-Callaway model of thermal conductivity is more rigorous in its approach, the main objective of calculating the different phonon scattering rates remains unchanged. Consequently, a discussion on the various expressions for phonon scattering rates arising from different sources is necessary.

\section*{2.4 Phonon Scattering Mechanisms and Rates}

Intrinsic Normal and Umklapp scattering processes exhibit strong temperature dependence. Prior work has shown the scattering rate for Normal processes is well described by the relation\textsuperscript{90}

$$
\tau_N^{-1} = \frac{k_B^3 \gamma^2 V}{M \hbar^5 v^5} \left( \frac{k_B}{\hbar} \right)^2 x^5 T^5, \quad (2.4.1)
$$

where $\gamma$ is the Grüneisen parameter and $M$ the average atomic mass of an atom in the host crystal. Likewise, the scattering rate for Umklapp processes is given by\textsuperscript{90}

$$
\tau_U^{-1} = \frac{\hbar \gamma^2}{Mv^2 \Theta_D} \left( \frac{k_B}{\hbar} \right)^2 x^2 T^3 \exp \left[ -\frac{\Theta_D}{3T} \right]. \quad (2.4.2)
$$

It is clear that from the exponential term in the expression for Umklapp scattering that these processes do not begin to have significant influence until higher temperatures. Additionally, the rate of Umklapp scattering is inversely proportional to the Debye temperature. This means
that the point at which Umklapp processes gain significance occurs at higher temperatures for materials with higher values of $\theta_D$.

Extrinsic scattering represents phonon scattering mechanisms caused by crystalline defects, which incorporate either in the crystal growth process or during post growth handling. These occur due to anything that interrupts the periodicity of the crystal lattice, such as differences in the atomic mass due to a different isotope or an impurity atom, differences in bond strength in the instance of an impurity atom, a vacant lattice site, charge carriers either free or bound, crystal boundaries, strain fields arising from dislocations, crystalline inclusions such as secondary phases or voids, stacking faults, or any combination thereof. The scattering rate due to crystal boundary is given by

$$\tau^{-1}_b = \frac{v}{d},$$

where $d$ is the characteristic length of the crystal. In a rod-shaped perfect single crystal with a thermal gradient established along the rod axis, this value is equivalent to the diameter orthogonal to the thermal gradient. For perfect crystals with square cross sections, the characteristic length is equivalent to $1.1d$.\textsuperscript{91} In practice, the apparent characteristic length can be shorter than the physical cross section based on other phonon scattering effects.\textsuperscript{91} The scattering rate due to mass differences arising from impurities or isotopes is represented by\textsuperscript{92}

$$\tau^{-1}_I = \frac{V}{4\pi v} \left(\frac{k_B}{\hbar}\right)^4 x^4 T^4 \Gamma,$$

where $\Gamma$ is the scattering factor taking into account the mass difference according to\textsuperscript{90,93}
\[ \Gamma = \sum_j f_j \left[ \frac{m_j - \bar{m}}{\bar{m}} \right]^2, \]  

(2.4.5)

where \( f_j \) is the fractional abundance of isotope or impurity atom \( j \) in the host crystal, \( m_j \) is the mass of the isotope or impurity atom, and \( \bar{m} \) is the average mass of the host atom replaced by the isotope or impurity atom. In binary compounds such as the III-Nitrides, each atomic species of the host crystal will have a dedicated scattering factor that accounts for their isotopes and relevant substitutional impurities. Consequently, the overall phonon scattering factor \( \Gamma_{III-N} \) must be calculated according to\(^{90,93} \)

\[ \Gamma_{III-N} = 2 \left[ \left( \frac{m_{III}}{m_{III} + m_N} \right)^2 \Gamma_{III} + \left( \frac{m_N}{m_{III} + m_N} \right)^2 \Gamma_N \right]^2. \]  

(2.4.6)

Ratsifaritana and Klemens derived a scattering rate for vacancies according to\(^{94} \)

\[ \tau_v^{-1} = f_v \frac{9V}{4\pi \nu^3} \left( \frac{k_B}{\hbar} \right)^4 x^4 T^4, \]  

(2.4.7)

in which \( f_v \) is the abundance of vacancies per unit volume relative to the number of lattice sites per unit volume. This resembles the scattering rate for isotopes and impurities, but takes into account the enhanced phonon scattering effect due to the loss of atomic linkages, which is the origin of the factor of nine.

The use of the different relaxation times presented above is sufficient to describe the thermal conductivity behavior observed in Ge, Si, diamond, and many of the III-V compounds. However, problems arise when the simplifying assumptions that allowed for the derivation of the various phonon scattering rates do not apply to the specific sample in question. Example
cases include incorporated impurities that interact in ways that lower their phonon scattering
cross sections or specific impurity species that act as inelastic phonon scattering centers.
Chapter 3: The Effect of Phonon Scattering Mechanisms on Thermal Conductivity

3.1 Introduction

Having now introduced the theory of traditional phonon scattering mechanisms and their rates, the question remains as to how these processes actually affect the thermal conductivity in real systems. A summary of results on crystalline materials from the literature is therefore necessary in order to understand the trends in thermal conductivity that can be expected for specific temperature regimes based on the influence of specific phonon scattering processes. This also provides an indispensable context for the interpretation of the forthcoming temperature dependent thermal conductivity results of the III-Nitrides. Before examining the effect of different phonon scattering mechanisms, it is first necessary to become familiar with how thermal conductivity behaves as a function of temperature for crystalline materials. Accordingly, Figure 3-1 shows compiled results of thermal conductivity vs. temperature for single crystals of sapphire and quartz.

Figure 3-1: Thermal conductivity as a function of temperature for a) single crystal sapphire\textsuperscript{95–97} and b) single crystal quartz\textsuperscript{98–101} The data between room temperature and 1300 K for quartz were calculated using the thermal diffusivity of Branlund et al.\textsuperscript{98} and the heat capacity data from Hemingway,\textsuperscript{102} Anderson,\textsuperscript{103} and Lord et al.\textsuperscript{104}
The curves in both a) and b) resemble Planck’s distribution. The maximum thermal conductivity appears at cryogenic temperatures. At temperatures below the maximum, thermal conductivity shows linear dependence on the log of temperature. This trend is known as the $T^3$ regime, where thermal conductivity scales with the cube of temperature. To the right of the maximum, thermal conductivity exhibits exponential decay. This regime is marked by the dominance of Umklapp phonon scattering processes. The vertical distribution of results in Figure 3-1 b) at temperatures above the maximum represent measurements taken both perpendicular and parallel to the c-axis. The difference is caused by crystal anisotropy, making thermal conductivity a tensor property. Another feature visible in Figure 3-1 b) is the phase transformation of $\alpha$-quartz to $\beta$-quartz at approximately 846 K. This anomalous behavior occurs as a result from the changes in heat capacity for the material. With the behavior of thermal conductivity as a function of temperature now adequately introduced, the effects of different scattering mechanisms can be more closely examined.

3.2 Crystal Surfaces and Dislocations

The boundaries of a crystal impose a limit on thermal conductivity, as no crystal can be truly infinite. The effect of crystal boundaries on thermal conductivity comes into effect at temperatures below the thermal conductivity maximum, which is often not observed until temperatures in the single digits and below on the Kelvin scale are reached. Figure 3-2 shows the effect of the crystal’s cross sectional dimension on thermal conductivity in the boundary scattering regime as reported by Thacher.\textsuperscript{105}
Figure 3-2: Effect of crystal size on the thermal conductivity in isotopically enriched LiF.\textsuperscript{165}

The plot demonstrates that thermal conductivity in the boundary scattering regime scales proportionally with the crystalline cross section. Additionally, the location of the thermal conductivity maximum also depends on the crystal diameter. As the relative size of the crystal increases, the maximum shifts to lower temperatures. The boundary scattering regime is understood as the range of temperatures for which the dominant phonon wavelength is on the order of the crystalline cross section. Therefore, larger crystals can accommodate longer phonon wavelengths, and the thermal conductivity is increased relative to crystals of smaller size. As the cross section and phonon velocity are constant for a given crystal, the temperature dependence within the boundary scattering regime scales with heat capacity, which is proportional to $T^3$ in the Debye model. For crystals that contain dislocations, the apparent crystal cross section is reduced compared to a crystal with none. As a result, the length parameter used for modeling thermal conductivity is termed the characteristic length, which is equivalent to the effective dimension of the crystal due to the action of both crystal boundaries.
and dislocations. The effect of dislocations is shown in Figure 3-3 according to Sproull et al.\textsuperscript{106} and Suzuki et al.\textsuperscript{107}

![Graph](image)

Figure 3-3: The thermal conductivity of natural LiF according to a) Sproull et al.\textsuperscript{106} and b) Suzuki et al.\textsuperscript{107} for samples containing dislocations. The reported numbers are values for etch pit density (EPD).

Sproull et al. argues that the dependence of thermal conductivity scales to $T^2$ while Suzuki et al. claims the dependence is $T^3-T^{3.5}$. Either way, the presence of dislocations effectively decreases the characteristic length of the crystal in the boundary scattering regime. It must be noted that the scattering of phonons by dislocations is strongly dependent on the angle of incidence, as the strain field surrounding a dislocation is anisotropic. As a result, the strain fields surrounding dislocations exhibit the least influence on propagating phonons so long as the direction of phonon propagation remains orthogonal to the strain field components of the dislocation lines.

### 3.3 Point Defects

Within the Debye-Callaway approximation, point defects influence thermal conductivity through a simple mass difference relationship according to the previously defined scattering
rate in 2.2.2. Using this formalism, there is no distinction between an isotope atom and an impurity atom in the crystal lattice except for their difference in mass with respect to the host atom they replace. This scheme neglects any difference in force constants for atomic linkages connecting impurity atoms to the host lattice or strain due to larger atomic radii which would otherwise influence phonon propagation. Some efforts have been made to account for these differences, but their success is limited.\textsuperscript{91,108}

3.3.1 Isotope Scattering

The effect of isotopes on thermal conductivity in LiF according to Thacher\textsuperscript{105} and on Ge according to Asen-Palmer et al.\textsuperscript{109} is shown below in Figure 3-4.

![Figure 3-4: Thermal conductivity of a) natural and enriched LiF according to Thacher\textsuperscript{105} and b) natural and enriched Ge single crystals from the results of Asen-Palmer et al.\textsuperscript{109}](image)

Both plots show that the regime most affected by differences in atomic mass is the region at and near the thermal conductivity maximum. The curves also demonstrate that the greatest phonon scattering occurs in the crystals having the largest difference in atomic mass of the constituent isotopes. The reduction in thermal conductivity is relatively uniform as isotopic
mass disorder increases, preserving the curvature of the maximum. As expected, the effect of isotopes on thermal conductivity at temperatures below and above the thermal conductivity maximum decreases as boundary scattering and Umklapp scattering rates increase in these regimes, respectively.

3.3.2 Impurity Scattering

The question now remains as to how substitutional atomic species affect the thermal conductivity in crystalline materials. Multiple attempts have been made to address this issue. The general result is that substitutional impurities often do not influence phonon wave propagation in the same manner as isotopes of the host lattice atoms as presented in (2.4.4). Instead, the introduction of impurities distorts the curvature of the thermal conductivity curve. The curvature distortions can be present at temperatures above or below where the thermal conductivity maximum would otherwise appear in a pure crystal and depends on the vibrational behavior of the impurity within the host lattice. The characteristic curvature distortions result from inelastic phonon scattering due to the interference of localized point defect modes with host lattice waves. This effect is termed phonon resonance scattering. Prior work demonstrates that certain impurities can have either translational or rotational degrees of freedom within the occupied host lattice site. For single atomic impurities in solid solution with identical charge state to the replaced host atom, the most characteristic distortions frequently appear at temperatures higher than the maximum. This effect was demonstrated extensively by Caldwell et al. in the NaCl system and their results for NaCl:Br and NaCl:K are shown below in Figure 3-5.
Figure 3-5: Thermal conductivity of a) NaCl:Br and b) NaCl:K according to Caldwell et al. The reduction in thermal conductivity is not uniformly distributed about the maximum as in isotope scattering, but produces indentations at temperatures above the maximum. The concentrations are calculated from the mole fractions given in their work.

The behavior of thermal conductivity curves for NaCl containing bromine and potassium dopants appears similar. The closeness in appearance demonstrates the degenerate effect of impurities on thermal conductivity, but a dependence of this trend upon ionic radius and or electronegativity is unmistakable due to slight differences in the location of inflection points and the curvature of indentations in the thermal conductivity results for these doped crystals. However, identically charged impurity species can show drastically different resonance behavior within two different material systems. This is demonstrated below in Figure 3-6.
Figure 3-6: The thermal conductivity of a) NaCl:Li according to Caldwell et al.\textsuperscript{115} and b) KCl:Li according to Baumann et al.\textsuperscript{112} The effect of Li\textsuperscript{+} differs significantly between the two systems as demonstrated by the location of curvature features and their active temperature ranges.

The plots show that the influence of a single impurity species within a crystal on the thermal conductivity can change significantly between materials. Unlike the examples in Figure 3-5, Li\textsuperscript{+} introduces a resonance state above the thermal conductivity maximum in NaCl and below the thermal conductivity maximum in KCl. The difference in ionic radii between the cation species helps explain this trend, as Li\textsuperscript{+} has an ionic radius of 90 pm, while those of Na\textsuperscript{+} and K\textsuperscript{+} are 116 pm and 152 pm, respectively. This leads to the expectation that the much smaller lithium has more vibrational freedom within the KCl lattice, resulting in different temperature dependent behavior on the thermal conductivity compared to the NaCl system. The translational freedom of the Li\textsuperscript{+} ion in KCl was demonstrated by Baumann et al.\textsuperscript{112}

3.3.3 Vacancy Scattering

While native vacancies exist in any crystalline material in thermodynamic equilibrium, most vacancies result from substitutional impurities that have a different charge state than the host
atom they replace. Substitutional impurities meeting this criteria are typically far more abundant in concentration than native vacancies in the III-nitrides. Consequently, it is more relevant to examine the changes in thermal conductivity caused by dopants with dissimilar valence. Nevertheless, vacancies do not only result from the introduction of differently charged atomic species, but can be produced by radiation exposure to yield F centers, also called color centers, which in the alkali halide crystals are anion vacancies containing a trapped electron. The effect of vacancy introduction on thermal conductivity in KCl doped with calcium and in NaF containing F centers caused by irradiation was studied by Walker et al.\textsuperscript{111} and Walker,\textsuperscript{116} respectively.

![Graph](image1.png)

**Figure 3-7**: Thermal conductivity of a) KCl:Ca according to Walker et al.\textsuperscript{111} and b) NaF containing F centers introduced by irradiation according to Walker.\textsuperscript{116}

The thermal conductivity response in Figure 3-7 a) is close to that observed in Figure 3-5 a) and b) and in Figure 3-6 a). However, it’s unclear how much of the curvature distortion is due to the vacancies introduced by divalent calcium. In Figure 3-7 b), the response appears similar to the isotope effect observed in Figure 3-4, but with an indentation analogous to those
observed for doped crystals. Since no dopants are added to the NaF crystals reported in Figure 3-7 b), the observed effect of F centers on thermal conductivity represents the most plausible behavior for phonon scattering by vacancies.

3.3.4 Secondary Phases

The agglomeration of impurities or point defects within the bulk of the crystal results in the formation of secondary phases that act as effective phonon scattering centers within the host lattice. Their influence on thermal conductivity occurs within the boundary scattering regime as they scatter phonons in proportion to their geometric cross section.\textsuperscript{117} The influence of secondary phases on thermal conductivity is demonstrated below by reviewing the work of Caldwell et al.,\textsuperscript{115} Worlock,\textsuperscript{117} and Walton\textsuperscript{118} in crystals of NaCl:Ag. Their work highlights the difference between dissolved silver and colloidal silver as shown in Figure 3-8.

![Figures 3-8](image-url)

Figure 3-8: The influence of a) dissolved silver having the same valence as host lattice cation according to Caldwell et al.\textsuperscript{115} and b) secondary phase of elemental silver in the form of dispersed colloids in the composite data from Worlock\textsuperscript{117} and Walton\textsuperscript{118} on the thermal conductivity of NaCl.

The thermal conductivity of NaCl with monovalent silver as seen in Figure 3-8 a) has a similar phonon resonance depression as observed in Figure 3-5 a) and b) and in Figure 3-6 a). The
thermal conductivity of the different curves is clearly converging to the same value at approximately 1 K. However, once ionic silver is reduced at the surface of the crystal in the presence of potassium vapor, the thermal conductivity curve behavior changes significantly, as seen in Figure 3-8 b). The indentation around 30 K is no longer observed, and the location of the curve maximum depends on the total density of colloids in the crystal, which is proportional to the concentration of silver. The slope at temperatures below the maximum follows a $T^3$ trend to about 1 K, at which point the curves begin converging. This reduction in thermal conductivity within the boundary scattering regime results from both the concentration and geometric cross section of elemental silver particles within the crystal bulk. This trend has also been observed for slowly annealed KCl:Ca, in which case the divalent calcium aggregates and forms secondary phases of CaCl$_2$ precipitates. Additionally, neutron irradiation of diamond produces a similar effect.
Chapter 4: Measurement Techniques for Thermal Conductivity

4.1 Introduction

In the previous chapter, the effect of different phonon scattering mechanisms on thermal conductivity were described and demonstrated through results from the literature. However, no discussion on how these results were obtained was given. Therefore, this chapter seeks to outline standard techniques used in measuring the thermal conductivity of condensed matter. Numerous methods have been developed and are broadly classified as being either steady state or transient with respect to the temperature gradient that becomes established in the sample under test. Steady state methods require a thermal gradient within a sample of interest to reach a steady state prior to testing, whereas transient methods do not. Sample geometry typically determines which techniques can be used for measurement. Bulk samples with dimensions on the order of millimeters can be tested using most techniques, whereas thin films on substrates are usually tested using transient techniques due to limitations imposed by thermal transport boundary conditions resulting from the heterogeneous nature of the sample. This section seeks to identify and describe the most commonly used measurement methods for determining thermal conductivity.

4.2 Steady-State Methods

Steady state techniques that utilize equilibrium temperature gradients confine thermal transport to one dimension. These techniques include the traditional absolute method, the comparative technique, the radial flow method, and the parallel thermal conductance method. These approaches examine the temperature difference established between two points on a sample in response to a known amount of heat flow. Samples are typically rod or rectangular shaped with
the temperature gradient established along their length. However, in the radial flow method, the temperature gradient becomes established along the radius of a rod-shaped sample with a heater positioned in the sample core along its entire length.\textsuperscript{120} This geometry has the advantage of lowering errors due to radiation that would otherwise result from an exposed heat source. Due to the one dimensional nature of thermal transport, the thermal conductivity of anisotropic materials can be determined with respect to specific crystallographic directions so long as the crystallographic orientation of the sample along the thermal gradient is known. The thermal conductivity of a material is determined by a simple rearrangement of the heat conduction equation:

\[ \kappa = \frac{Q}{A \Delta T}, \]

(4.2.1)

where \( Q \) is the heat flowing through the sample, \( L \) is the separation distance between the points of temperature measurement, \( A \) is the cross sectional area of the sample, and \( \Delta T \) is the difference in temperature between the points of measurement. During a test, a linear power increase results in a linear increase in the temperature difference. Figure 4-1 shows a typical experimental configuration used for the traditional absolute thermal conductivity measurement.
Figure 4-1: Schematic of the absolute thermal conductivity technique experimental setup adapted from Pope et al.\textsuperscript{111} Power flows out of heater and into the sample during a test. The temperature gradient is established between the two copper studs that are anchored to the sample. The jumper wire between the copper studs completes the circuit of a differential thermocouple. In Pope et al., the differential thermocouple circuit was comprised of constantan lead wires and a chromel jumper.

Although the thermal conductivity equation appears simple, the successful implementation of the method depends on a proper determination of $Q$. This becomes challenging in the presence of thermal losses through other media besides the sample, such as heat lost to radiation, convection of surrounding gasses, or conduction through lead wires. While heat losses from convection and conduction are proportional to the exposed or cross sectional area and temperature difference, heat losses from radiation can be considerable at higher temperatures if the difference between the sample and its surroundings is significant, as radiation heat transfer is proportional to the fourth power of temperature:

$$Q_{\text{rad}} = \epsilon A \sigma \left( T_O^4 - T_S^4 \right)$$  \hspace{1cm} (4.2.2)
Where $\epsilon$ is the emissivity of the object, $A$ is the exposed object area, $\sigma$ is the Stefan-Boltzmann constant ($\sigma = 5.6703 \times 10^{-8} \, \text{W} / \text{m}^2 \text{K}^4$), $T_O$ is the temperature of the object, and $T_S$ is the temperature of the surroundings. Considering these different loss mechanisms, the $Q$ term in the thermal conductivity equation must therefore be broken down into two separate components:

$$Q = Q_I - Q_L,$$  \hspace{1cm} (4.2.3)

where $Q_I$ is the initial heating power produced in the heater and $Q_L$ is the heat lost to all other mechanisms besides conduction through the sample. Both minimization and careful accounting of heat losses improves the accuracy of thermal conductivity values obtained using steady state techniques. Consequently, good practice of steady state methods implements the fewest possible lead wires having small cross sections from metal alloys with good electrical conductivity but lower thermal conductivity. Additionally, the sample is surrounded with a highly reflective radiation shield that is thermally sunk to the same base as the sample heat sink.\textsuperscript{121} This lowers the effect of black body radiation, which would otherwise result in significant errors.

### 4.3 Transient Methods

Unlike steady state methods, transient thermal conductivity characterization techniques do not significantly depend on a condition of thermal steady state for accurate measurements. For measurement of semiconductors, the most utilized methods include the pulse-power method, laser flash, thermo-reflectance (which includes both the time and frequency domain
configurations), and the 3-omega method. Many other techniques fit into this category, but will not be discussed here for the sake of brevity.

### 4.3.1 Pulse-Power Technique (Maldonado Method)

The pulse-power method uses a similar sample configuration as the traditional steady-state method, but the application of the heating power differs significantly. Instead of using fixed DC currents as in the steady state technique, a DC square wave is applied to the heater. Additionally, the temperature of the thermal substrate in contact with the sample is not held constant. A controlled rate of change allows the sample base temperature to drift slowly with respect to the heater driving current. A plot of the temperature difference observed across the sample with respect to time reveals saw-tooth behavior as shown below in Figure 4-2.

![Figure 4-2: Temperature difference vs. time for a sample as measured using the Maldonado method.](image)

The slope of the dashed curves drawn through the maxima and minima indicate the temperature drift. The typical experimental setup and equivalent thermal circuit for the pulse-power technique are shown below in Figure 4-3.
The square wave excitation current establishes a heat balance that depends on the heater resistance, heat capacity, and thermal conductance of the sample as labeled in the schematic above in Figure 4-3. This relationship is given by

\[ Q(t) = C(T_1) \frac{dT_1}{dt} = R(T_1) I^2(t) - K(T_1 - T_0), \]  

where \( Q(t) \) is the heat accumulated at the heat source as a function of time, \( C, T_1, \) and \( R \) are the heater heat capacity, temperature, and resistance, respectively, and \( K \) is the sample thermal conductance in units of \( \text{W/K} \). In order to solve the heat balance equation analytically, simplifications are made. Since the functions \( C, R, \) and \( K \) are all smooth with respect to temperature, \( T_0 \) is substituted for \( T_1 \). Additionally, \( T_0 \) is assumed constant. Using the peak to peak amplitude of the saw-tooth temperature response as shown in Figure 4-2 allows calculation of the thermal conductance according to

\[ K = \frac{R_0^{T^2}}{\Delta T_{pp}} \tanh \left( \frac{K \tau}{2C} \right), \]  

where \( K \) is the sample thermal conductance in units of \( \text{W/K} \), \( R_0 \) is the resistance at the temperature of interest, \( T \) is the temperature difference, \( \Delta T_{pp} \) is the peak to peak temperature difference, \( C \) is the heat capacity, \( \tau \) is the time constant, and \( \tanh \) is the hyperbolic tangent function.
where $K$ is the thermal conductance, $I_0$ is the excitation current, $\Delta T_{pp}$ is the peak to peak amplitude temperature response, and $\tau$ is the half period of the square wave excitation current. The appearance of $K$ on both sides of the equation makes numerical iteration necessary. Calculation of thermal conductivity is simply carried out by multiplying thermal conductance into $l/A$, where $l$ is the sample length and $A$ is the cross sectional area. The accuracy of thermal conductivity as measured by this technique significantly depends on the terms most sensitive to error, which are $\Delta T$ and the sample dimensions.

4.3.2 Laser Flash Technique

The laser flash method does not directly measure thermal conductivity, but instead determines thermal diffusivity. This technique uses a short laser pulse to heat the front face of a test sample. An IR detector observes the temperature rise on the back surface of the sample in response to the laser pulse. A schematic of the experimental setup is shown below in Figure 4-4.

![Figure 4-4: Typical configuration of laser flash method. A computer controls the laser pulse power and measures the temperature response observed by the IR detector on the back surface of the sample.](image)

Due to the instantaneous delivery and absorption of the laser pulse, the temperature rise on the back side of the sample depends only on the thermal properties of the sample. The theoretical time dependent temperature rise on the back surface is represented as...
\[ T(d,t) = \frac{Q}{\rho C_P d} \left[ 1 + 2 \sum_{n}^{\infty} (-1)^n \exp \left( -n^2 \pi^2 \alpha t / d^2 \right) \right], \]  

where \( d \) is the thickness of the sample, \( Q \) is the energy of the laser pulse absorbed by the front face of the sample, \( \rho \) is the density, \( C_P \) is the heat capacity, and \( \alpha \) is the thermal diffusivity. In order to extract \( \alpha \), two dimensionless parameters are defined

\[ V(d,t) = \frac{T(d,t)}{T_M}, \quad \omega = \pi^2 \alpha t / d^2, \]  

where \( T_M \) is the maximum temperature reached at the back surface of the sample. Based on the behavior of temperature vs. time, which resembles a simple population growth curve, when \( V \) is equivalent to 0.5, \( \omega \) will equal 1.38. A simple rearrangement then yields

\[ \alpha = 1.38 d^2 / \pi^2 t_{1/2}, \]  

where \( t_{1/2} \) is the time elapsed at which point the temperature is half the maximum value. The thermal conductivity measured using this method is then simply the product of \( \alpha, \rho, \) and \( C_P \). In practice, the quantities of \( \rho \) and \( C_P \) are often determined using other characterization techniques. Samples are typically coated with graphite on both surfaces to ensure ideal emissivity, which allows instantaneous absorption of the laser pulse and optimal black body radiation at the back surface. If adequate adhesion does not exist between the sample and coating, significant errors will be introduced during measurement.

### 4.3.3 Thermo-reflectance Methods (Time and Frequency Domain)

The thermo-reflectance techniques use either continuous or pulsed lasers to heat a small spot on the surface of a sample. The advantage of the thermo-reflectance techniques lies in their ultrafast sampling times, which correspond to thermal penetration depths on the order of
nanometers. This enables thermal conductivity measurement of similarly sized features, such as thin films, superlattices, and other multilayered structures. A schematic showing an example of a system configuration using a pulsed laser capable of both FDTR and TDTR is shown below in Figure 4-5.

In the TDTR technique, a transducer layer, typically a thin metal film of aluminum, is deposited onto a sample. The sample is placed in the instrument and the beam from a pump laser is focused onto the surface of the transducer. The pulse from the frequency-fixed pump beam causes a rapid temperature rise, which changes the reflectivity of the metal film proportionally. The change in reflectivity of the transducer as it cools is observed by a time-delayed probe beam that overlaps with the target area of the pump beam. Thermal conductivity is calculated by comparing the change in reflectivity as a function of delay time to a simulation based on conduction heat flow from the transducer to the sample layer. Delay time is changed by repositioning the delay stage. In the FDTR configuration, the delay stage is fixed and the pump

Figure 4-5: Schematic layout of a FDTR/TDTR setup adapted from Zhu et al.\textsuperscript{124}
beam modulation frequency is changed. Unlike the TDTR technique, the FDTR configuration
has the advantage of fixed optical configuration, which eliminates problem of probe beam drift
encountered with the moving delay stage in the TDTR technique. In these methods, modulation
of the pump and probe beams along with their target areas enables determination of in-plane
vs. cross plane thermal conductivity for anisotropic materials.

4.3.4 The 3ω Method

This technique represents one of the most widely used thermal conductivity characterization
methods due to its simplicity. It minimizes errors in black body radiation due to a significant
reduction in effective sample size, unlike typical samples used in the various steady state
techniques. As the 3ω method produced all the thermal conductivity results in the body of this
work, a simple review of the basic technique framework will not be sufficient. Therefore, the
next section provides a judicious description of this technique and its implementation in
achieving all the subsequently discussed results. In addition, a theoretical derivation of the 3ω
thermal conductivity equation is provided as well as a discussion of the relevant boundary
conditions and limits of this technique.
Chapter 5: The 3ω Method

5.1 Introduction

The core instrumentation of the 3ω technique consists of a thin film Kelvin style resistor with four contact pads deposited onto the surface of a sample. Two contact pads supply an AC signal that provides the excitation current for the resistor while the other two contact pads are used to measure the voltage response. A schematic of a typical thin film resistor used in the 3ω technique is shown below in Figure 5-1.

In the 3ω technique, the thin film wire acts as both a heater and thermometer. Excitation of the wire with a driving voltage at frequency ω results in resistance oscillation at 2ω. This is simply because joule heating is independent of the sign of voltage across the wire, hence the swing of the AC driving voltage below zero produces the same effect as the driving voltage above zero. The resistance oscillation at 2ω creates a voltage oscillation also at 2ω in response to Ohm’s Law. The interference of the voltage waveforms at ω and 2ω produce a voltage oscillation at 3ω, also called the 3rd harmonic. Measurement of the 3ω voltage response requires a lock-in amplifier, as the amplitude of the signal at 3ω is typically three orders of magnitude smaller.
than the original driving voltage at $\omega$, which is also known as the fundamental frequency. A schematic of the cross section of the thin film wire on a sample is shown below in Figure 5-2.

![Diagram of the wire cross section and semi-infinite solid. The wire half-width is the quantity $b$ as shown. The red lines denote isothermal surfaces caused by the AC excitation of the wire that proceed radially into the sample.](image)

**5.2 Theoretical Framework of the 3$\omega$ Technique**

Understanding the basis of the 3$\omega$ method requires insight regarding how thermal excitations from the thin film metal wire propagate into a sample under test. In order to build a model describing the relevant physics, we begin with the three dimensional differential equation that represents conductive heat transfer in an isotropic solid (without volumetric heat generation) within the Cartesian coordinate system:

$$
\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} - \frac{1}{D} \frac{\partial T}{\partial t} = 0, \quad (5.2.1)
$$

where thermal diffusivity $D = \kappa / \rho C$, $\rho$ is the density, and $C$ is specific heat. Approximation of the metal wire as an infinitely long and narrow line source of heat simplifies the analysis by turning the isotherms into perfect half-cylinder surfaces. Consequently, the equation for
conductive heat transfer is best represented in the cylindrical coordinates of $r$, $\theta$, and $z$. After transformation, the differential equation becomes

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} - \frac{1}{D} \frac{\partial T}{\partial t} = 0.$$  (5.2.2)

Under the assumption of an infinitely long and narrow metal wire coincident with the $z$ axis of the cylindrical coordinate system, the thermal distribution represented by isothermal surfaces is independent of $\theta$ and $z$, allowing these terms to be dropped and reducing the above expression to

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} - \frac{1}{D} \frac{\partial T}{\partial t} = 0.$$  (5.2.3)

Since the temperature distribution is an oscillatory function of both time and radius due to the periodic nature of the heat source, it can be represented using

$$T(r,t) = u(r)e^{i\omega t},$$  (5.2.4)

where $u(r)$ is some function of the radius in cylindrical coordinates and the exponential term designates the dependence on time and frequency. Upon substitution using $u(r)$ and multiplication of all terms by $r^2$, the heat conduction equation converts to

$$r^2 \frac{\partial^2 u}{\partial r^2} + r \frac{\partial u}{\partial r} - r^2 \frac{i\omega}{D} u = 0.$$  (5.2.5)

The above relationship resembles the differential equation form of the modified Bessel Function of the Second Kind:

$$z^2 \frac{\partial^2 u}{\partial r^2} + z \frac{\partial u}{\partial r} - (z^2 + v^2) u = 0,$$  (5.2.6)
where \( \nu \) represents the order of the function. With \( \nu = 0 \), the expression becomes the modified Bessel Function of the Second Kind of order 0

\[
\frac{z^2 \partial^2 u}{\partial r^2} + z \frac{\partial u}{\partial r} - z^2 u = 0,
\]

which matches the form of the heat conduction equation. The solution to the heat conduction equation is a complex exponential function of the form

\[
u(r) = AI_0 \left( \sqrt{\frac{\imath \omega}{D}} r \right) + BK_0 \left( \sqrt{\frac{\imath \omega}{D}} r \right),
\]

where \( A \) and \( B \) are constants and \( I_0 \) and \( K_0 \) are the modified Bessel functions of the first and second kind of order zero, respectively, which are represented in infinite summation notation according to

\[
I_0(z) = \sum_{m=0}^{\infty} \frac{(z)^{2m}}{2^{2m} (m!)}
\]

\[
K_0(z) = -\left( \frac{\ln{\left| \frac{z}{2} + \gamma \right|}}{2} \right) I_0(z) + \sum_{m=1}^{\infty} \frac{(z)^{2m}}{2^{2m} (m!)^2} \sum_{m=1}^{\infty} \frac{1}{m},
\]

where \( \gamma \) is Euler’s constant approximately equal to 0.5772. Accordingly, the solution to the time and radius dependent temperature profile in an infinite cylinder in which the periodic heat source and \( z \) axis coincide is represented by the relation

\[
T(r,t) = \left[ AI_0 \left( \sqrt{\frac{\imath \omega}{D}} r \right) + BK_0 \left( \sqrt{\frac{\imath \omega}{D}} r \right) \right] e^{\imath \omega t}.
\]
The function $I_0$ diverges with increasing values of $z$, whereas the function $K_0$ converges with increasing $z$. The constant $A$ must therefore be zero, as temperature can only decrease with increasing radius with respect to the cylinder axis. The solution then reduces to

$$T(r,t) = BK_0\left(\frac{i\omega r}{D}\right)e^{i\omega t}.$$  \hfill (5.2.12)

Constant $B$ remains as the last unaccounted term. Fortunately, a review of the boundary conditions pertinent to the $3\omega$ method provide the correct representation of $B$. An excitation current $J$ at frequency $\omega$ applied across the thin film wire is given by

$$J = J_0e^{i\omega t},$$  \hfill (5.2.13)

in which $J_0$ represents the RMS current. In accordance with Ohm’s Law, the excitation current produces a heat flux $Q$ due to power dissipation at twice the fundamental frequency:

$$Q = P_0 = J_0^2 R_0 e^{i2\omega t}.$$  \hfill (5.2.14)

The heat flux proceeding into a radial volume element of a half cylinder will depend on the unit length of the thin film metal wire and unit angle of the volume element. Assuming the heat flux evenly distributes along the total wire length and all unit angles between 0 and $\pi$, the amplitude of the temperature oscillations should be proportional to the dissipated power $P_0$ and inversely proportional to the wire length, unit angle, and the thermal conductivity of the medium:

$$T(r,t) \propto \frac{P_0}{\pi l \kappa}.$$  \hfill (5.2.15)
This represents the constant of proportionality $B$ in the solution to the temperature distribution. Now that the boundary conditions have been adequately described, the exact solution is given by

$$T(r,t) = \left[ \frac{P_0}{\pi l_\kappa} K_0 \left( \sqrt{\frac{i2\omega}{D}} - r \right) \right] e^{i2\omega t}. \quad (5.2.16)$$

The magnitude of the quantity $(D/i2\omega)^{1/2}$, also known as $1/q$, represents the depth to which heat penetrates after one full thermal excitation cycle at $2\omega$. In practice, as long as $|qr| \ll 1$, the truncated and time-independent form of the infinite summation of $K_0(qr)$ provides an acceptable approximation to the temperature oscillations:

$$\Delta T(r) = \frac{P_0}{\pi l_\kappa} \left[ \frac{1}{2} \ln \frac{D}{r^2} + \ln 2 - \gamma - \frac{1}{2} \ln (2\omega) - i\pi \right]. \quad (5.2.17)$$

The above expression separates the real and imaginary parts of the temperature oscillations. While this allows a good approximation for determining the amplitude of the temperature oscillations in the material, this expression is not ideal for the purpose of determining a closed form solution for the thermal conductivity $\kappa$ using the $3\omega$ technique. Fortunately, this goal is achieved with the help of waveform representations and further derivation. At an excitation frequency $\omega$, the time-dependent current in the thin film wire is given by

$$J = J_0 \cos(\omega t). \quad (5.2.18)$$

The resistance of the thin film wire will vary as a function of the sinusoidal temperature oscillations in accordance with

$$R = R_0 (1 + \alpha T_0), \quad (5.2.19)$$
in which $R_0$ is the no-load resistance of the thin film metal wire and $\alpha$ designates the temperature coefficient of resistance equivalent as defined by

$$\alpha = \frac{1}{R_0} \frac{dR}{dT}.$$  \hspace{1cm} (5.2.20)

Using Ohm’s Law, the voltage across the wire is defined as

$$V = JR = J_0 \cos(\omega t) R_0 \left(1 + \alpha T_0\right).$$ \hspace{1cm} (5.2.21)

This is split into separate frequency dependent components to isolate the $3\omega$ term as shown by\textsuperscript{127}

$$V = J_0 R_0 \cos(\omega t) + \frac{J_0 R_0}{2} \alpha T_0 \cos \left(\omega t - \frac{\pi}{4}\right) + \frac{J_0 R_0}{2} \alpha T_0 \cos \left(3\omega t - \frac{\pi}{4}\right).$$ \hspace{1cm} (5.2.22)

The last term in the equation above represents voltage element accounting for the $3^{rd}$ harmonic response of the thin film metal wire. Therefore, the voltage at $3\omega$ is given by

$$V_{3\omega} = \frac{J_0 R_0}{2} \alpha T_0 \cos \left(3\omega t - \frac{\pi}{4}\right).$$ \hspace{1cm} (5.2.23)

Rearranging the above expression and setting the output of the cosine function to unity provides a means to solve for the magnitude of the temperature oscillations in the thin film wire:

$$\Delta T = \frac{2V_{3\omega}}{J_0 R_0 \alpha}.$$ \hspace{1cm} (5.2.24)

Setting this expression equivalent to the previously formulated solution for sinusoidal temperature and substituting $\omega$ in place of $2\omega$ provides a means to derive an expression for thermal conductivity.
\[
\frac{2V_{3\omega}}{J_0 R_0 \alpha} = \frac{P_0}{\pi l \kappa} \left[ \frac{1}{2} \ln \frac{D}{r^2} + \ln 2 - \frac{1}{2} \ln(\omega) - \frac{i\pi}{4} \right]. \tag{5.25}
\]

Differentiating both sides with respect to \(\ln(\omega)\) yields

\[
\frac{2}{J_0 R_0 \alpha} \frac{\partial V_{3\omega}}{\partial \ln(\omega)} = -\frac{1}{2} \frac{P_0}{\pi l \kappa}. \tag{5.26}
\]

Finally, rearranging the above expression with respect to \(\kappa\) presents a solution for the thermal conductivity of the material

\[
\kappa = -\frac{J_0 R_0 \alpha P_0}{4\pi l} \frac{\partial \ln(\omega)}{\partial V_{3\omega}}. \tag{5.27}
\]

Using Ohm’s Law grants further simplification, producing an expression similar to that displayed in the works of Cahill.\textsuperscript{126,128}

\[
\kappa = -\frac{V_{3\omega}^3}{4\pi l R_0^2} \frac{dR}{dT} \frac{\partial \ln(\omega)}{\partial V_{3\omega}}. \tag{5.28}
\]

The negative sign may initially cause concern, but the slope of the 3\textsuperscript{rd} harmonic response as a function of \(\ln(\omega)\) is negative, ultimately producing a positive result for \(\kappa\). This forms the basis for determining the thermal conductivity of a material using the 3\(\omega\) technique.

### 5.3 Experimental Implementation of the 3\(\omega\) Technique

Achieving good results using the 3\(\omega\) method requires careful sample preparation. The sample surface is first cleaned using acetone, isopropanol, and methanol in combination with a piece of melamine foam (also known as a magic eraser) brushed across the surface with tweezers. This process removes organic contamination and particulates. The sample is then prepared using photolithography in preparation for deposition of the metal layers. An oxygen plasma treatment after exposure and development greatly improves adhesion of the metallization.
Metal stacks of 10 nm V, 200 nm Ni, and 20 nm Au are typically deposited. The use of vanadium ensures adhesion of the metal layers to the sample surface while the top coating of gold ensures good adhesion of indium, which acts as the interface between the sample contact pads and the printed circuit board (PCB). The process of sample assembly is shown below in Figure 5-3.

![Figure 5-3](image1.png)

**Figure 5-3:** The 3ω sample assembly process. The redundancy of wire patterns on the mask decreases the risk that rework will be necessary due to wires having adhesion problems or breaks in continuity.

Once the sample assembly is ready for testing, a small drop of silver paste is placed on the back surface of the sample immediately prior to mounting to the cold finger attachment. The silver paste provides thermal continuity during a test. The cold finger and sample assembly are then fixed to the cold head of the Janis SHI-4-15 cryostat as shown below in Figure 5-4.

![Figure 5-4](image2.png)

**Figure 5-4:** Sample and cold finger attachment mounted on the cold head of the cryostat.
Basic application of the $3\omega$ method requires the use of a few key components. These include an excitation source for the fundamental frequency $\omega$, a variable resistor (most frequently a potentiometer), a sample containing the thin film wire, two differential amplifiers, a lock in analyzer (SR830), and a multimeter for measuring the voltage and current across the wire. A schematic showing these with the exception of the multimeter is shown below in Figure 5-5.

![Schematic of $3\omega$ technique](image)

**Figure 5-5: Diagram showing the core instrumentation of the $3\omega$ technique.**

Adjustment of the potentiometer during an experiment allows for close matching of the sample wire resistance. Since the potentiometer has no 3rd harmonic response, the subtraction of the common mode voltage present at the signal outputs of both differential amplifiers by the lock-in analyzer leaves behind a small signal containing the $3\omega$ voltage, which is then isolated by the SR830. Analysis of the temperature dependent thermal conductivity requires mounting the sample in a temperature controlled environment. Additionally, the measurement of current, voltage, and resistance requires switching between modes on the multimeter as well as doing
a full frequency sweep of $V_{3\omega}$ vs. $\ln(\omega)$. This necessitates a more complicated system design as shown below in Figure 5-6.

![Figure 5-6: Schematic of the $3\omega$ measurement system (at left) and an image of the required instrumentation (at right).](image)

Data is collected for an arbitrary number of temperature set points, typically comprising an array of 42 rows by 12 columns for the voltage and frequency measurements. Resistance as a function of temperature is also collected in a separate 22×4 array. MATLAB is used for batch data analysis in order to determine the temperature dependent thermal conductivity, which is calculated according to the relation$^{128}$

$$\kappa = \frac{V_{\omega}^3}{4\pi l R^2} \frac{dR}{dT} \frac{\ln(f_z/f_i)}{V_{3\omega,f_i} - V_{3\omega,f_2}},$$  \hspace{1cm} (5.3.1)

where $V_{\omega}$ is the voltage drop over the metal wire at excitation frequency $\omega$, $l$ is the wire length as defined by the distance of thin metal trace between the orthogonal intersection points of the $V^{HI}$ and $V^{LO}$ lead traces as in Figure 5-1, $R$ the resistance across the metal wire at a given
temperature without applied excitation voltage, \( \frac{dR}{dT} \) is the slope of the resistance vs. temperature curve of the metal wire at a given temperature, \( f_2(f_1) \) is the ending (starting) excitation frequency, and \( V_{3\omega,f1}(V_{3\omega,f2}) \) is the third harmonic voltage response at the starting (ending) excitation frequency. The color coding of the last two terms indicates the slope of fitting curves used for the thermal conductivity calculation as shown below in Figure 5-7.

Figure 5-7: Numerical fits for a) resistance as a function of temperature (\( \frac{dR}{dT} \)) and b) the 3rd harmonic voltage response as a function of frequency (the inverse slope of this curve is used in the calculation of thermal conductivity).

The wire resistance as a function of temperature is adequately described by the Bloch-Grüneisen relation of order \( 3 < x < 5 \). As this function is non-linear, the derivative of the fitting curve is used at the set point temperature for which thermal conductivity is calculated. The ideal behavior of the 3\( \omega \) voltage is a linear decrease as a function of \( \ln(\omega) \).

One important limiting factor of the 3\( \omega \) method is the range of cryogenic temperatures in which the technique can be used. Results in literature typically do not report data for temperatures below \( \sim 30 \) K. There are a few reasons for this. First, as temperature approaches zero, so does
specific heat. This means that the self-heating of the thin film wire causes larger relative temperature responses in the material at colder temperatures. Second, the resistance of the metal wire decreases and approaches a residual value with cooling. The value of \( \frac{dR}{dT} \) goes to zero once the wire reaches the residual resistance limit. Third, for samples with thermal conductivity >1000 Wm\(^{-1}\)K\(^{-1}\) at cryogenic temperatures, the response of \( V_{3\omega} \) with frequency is nearly flat. The combination of these complicating factors sets the lower limit for measurement at approximately 30 K for the 3\( \omega \) method.

5.4 Limitations within the 3\( \omega \) Method

The main assumptions used in the 3\( \omega \) method are that the wire acts as a line source of heat and the substrate is semi-infinite. Since all thin film wires have finite width and all samples are finite in their dimensions, it is necessary to assess the validity of these assumptions. This is accomplished with the help of the thermal penetration depth. Cahill’s original works describe this metric, which is given by the expression

\[
\left| \frac{1}{q} \right| = \frac{D}{\sqrt{i2\omega}}
\]  

(5.4.1)

As discussed previously, this number represents the length that heat penetrates within one period of a 2\( \omega \) excitation cycle and depends on both thermal diffusivity and excitation frequency. In order for the line source approximation to remain valid, the thermal penetration depth must satisfy the expression\(^{129}\)

\[
\left| q^{-1} \right| > 5 \frac{b}{\sqrt{k_{xy}}}
\]  

(5.4.2)
Where d is the substrate thickness and \( k_{xy} \) is the ratio of the in-plane thermal conductivity to the cross-plane thermal conductivity. In the case of an isotropic substrate, the denominator reduces to unity. The semi-infinite substrate approximation remains valid so long as the inverse thermal penetration depth and substrate thickness meet the requirement \(^{(5.4.3)}\)

\[
qd > 5
\]

Since q depends on thermal diffusivity and therefore the thermal conductivity of the sample, it can only be calculated once the results from a 3\( \omega \) test have been collected. As an example, the thermal conductivity results for a sample of gallium phosphide and the corresponding thermal penetration depth using the Debye model for specific heat is shown below in Figure 5-8.

![Thermal Conductivity of GaP](image1)

![Thermal Penetration Depth in GaP](image2)

Figure 5-8: Temperature dependent thermal conductivity results a) of a GaP sample and b) the corresponding frequency-dependent thermal penetration depth at each temperature set point. The flat lines indicate the thickness d of the sample and the quantity 5b.

The results in Figure 5-8 b) clearly indicate two things: 1) the thin film wire can be treated as a line source of heat and 2) the thermal penetration depth remains within the thickness of the sample for only a few of the measurement temperatures, as the thermal penetration depth starts exceeding sample thickness somewhere around 167 K for low frequencies. The question
becomes whether or not the product $qd$ satisfies the requirement for the semi-infinite approximation in this particular sample. This is answered below in Figure 5-9.

Figure 5-9: The product $qd$ at each temperature set point for the GaP sample. The flat line indicates the required condition for $qd$ above which the substrate can be approximated as semi-infinite.

The results clearly show that there is no point at which the sample can be assumed to be semi-infinite. Since the sample is finite within the bounds of the experiment, the question now turns to how the thermal conductivity results are influenced when the thermal penetration depth exceeds sample thickness. This can be assessed by comparing results from the $3\omega$ method against values in literature for reference materials. Figure 5-10 shows this for standard III-V compounds below.
The comparison above clearly demonstrates that the 3ω technique produces results in agreement with reported literature values. Since the thermal conductivity at each set point temperature remains within an order of magnitude for these compounds, the thermal penetration depth can be assumed to exceed sample thickness somewhere between 100 & 200 K in all the above samples. Nevertheless, the results obtained appear unaffected by large thermal penetration depths. Heuristically speaking, the thermal penetration depth should not influence measurements so long as the thermal waves exit the sample into the cryostat cold
finger once they reach the back side. However, if some portion of the thermal waves are reflected at the back surface, the temperature of the sample rises until a condition of steady state heat flow becomes established. Since samples are always mounted with silver paste, conditions of bad thermal continuity between the sample back surface and the cold finger are rare. In the event of a significant temperature rise, the resistance of the wire noticeably increases, and tests are discontinued to allow for corrections.

5.5 The Thermal Attenuation Length in the 3ω Method

One important consideration in the application of the 3ω technique is how quickly the temperature oscillations induced by the wire decrease in amplitude with respect to increasing distance the thin film wire. The simplest way to describe this quantity is by defining a new parameter that represents the thermal attenuation length in the material, termed $\delta$. One expects this quantity is the distance from the wire that satisfies the relationship:

$$\frac{\partial T_\delta}{\partial T_{wire}} = \left[ \frac{P_0}{\pi \kappa} K_0 \left( \sqrt{\frac{2\omega}{D \delta}} \right) \left( \frac{V_0 \alpha}{2V_{3\omega}} \right) \right] = \frac{1}{e}$$  \hspace{1cm} (5.5.1)

In practice, using equation (5.2.25) in the above expression does not produce physically meaningful results. Additionally, using the built-in function for $K_0$ in MATLAB reveals that the temperature oscillations at the interface between the wire and sample disagree with numerical calculations based on the previously derived relation (5.2.24):

$$\Delta T = \frac{2V_{3\omega}}{J_0 R_0 \alpha}$$  \hspace{1cm} (5.5.2)
Therefore, the value of the thermal attenuation length in the case of a cylindrical steady-state temperature distribution produced by on-axis heating geometry provides an upper limit for the value of \( \delta \) in the \( 3\omega \) method. This quantity is described by the expression:\(^{125}\)

\[
\left( \frac{\partial T_{\text{wire}}}{\partial T_{\text{wire}}} \right)_{\delta_{\text{ss}}} = \frac{\ln(d/\delta_{\text{ss}})}{\ln(d/a)} = \frac{1}{e}
\]

Where \( d \) is the sample thickness, \( \delta_{\text{ss}} \) is the steady-state thermal attenuation length, and the quantity \( a = \frac{2b}{\pi} \), which represents the radius length when the width of the thin film wire is transformed into a half-circle. In this configuration, the temperature on the back surface of the wafer is assumed constant, which would be the case if mounted to the cold finger of the cryostat. From the above relationship, the steady-state thermal attenuation length is easily solved for known quantities of \( d \) and \( a \). Table 5-1 shows the input parameters and the steady-state thermal attenuation lengths for the samples used in the benchmarking analysis of Figure 5-10.

Table 5-1: Parameters and steady-state thermal attenuation lengths for tested III-V materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( 2b ) [( \mu \text{m} )]</th>
<th>( d ) [( \mu \text{m} )]</th>
<th>( \delta_{\text{ss}} ) [( \mu \text{m} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>10</td>
<td>520</td>
<td>80</td>
</tr>
<tr>
<td>GaAs</td>
<td>10</td>
<td>370</td>
<td>63</td>
</tr>
<tr>
<td>InP</td>
<td>10</td>
<td>560</td>
<td>83</td>
</tr>
<tr>
<td>InAs</td>
<td>10</td>
<td>915</td>
<td>114</td>
</tr>
</tbody>
</table>

The results in the above table show that the value of \( \delta_{\text{ss}} \) is typically somewhere between 10-20\% of total sample thickness. In the event of periodic heating as in the \( 3\omega \) method, the value of \( \delta \) is expected to be lower due to the transient nature of the input heating.
Chapter 6: Thermal Conductivity and Point Defects in AlN

6.1 The influence of point defects on the thermal conductivity of AlN crystals

6.1.1 Introduction

Since chapter 5 demonstrated that the 3ω method could be used to obtain accurate results at temperatures as low as 30 K, the next chapters describe the application of this technique in measuring the thermal conductivity of the III-Nitrides. This chapter correlates thermal conductivity measurements collected using the 3ω method with data from secondary ion mass spectrometry (SIMS) and photoluminescence spectroscopy (PL) to connect the temperature-dependent thermal conductivity of AlN to the effect of point defects.

The ultra-wide bandgap semiconductor AlN attracts interest due to its potential use in UV-C LEDs, diode lasers, and high power semiconductor devices. Next-generation power devices based on AlN are expected to operate at high power densities due to its bandgap of 6.1 eV and its 15 MV cm⁻¹ breakdown field. The anticipated higher power-switching capabilities of AlN devices will create additional challenges to thermal management, as heat generated during use diminishes both device service lifetime and efficiency. Consequently, the thermal conductivity of AlN is a crucial parameter to consider during its implementation for power devices. Detailed investigations regarding thermal conductivity have been reported for both crystalline thin films and polycrystalline samples of AlN, but such specimens suffer from pervasive crystalline defects such as misfit and threading dislocations, grain boundaries, and high concentrations of impurities, all of which decrease thermal conductivity.

By comparison, bulk single crystal AlN has a minimal amount of crystalline defects and is therefore the ideal material for estimating the thermal conductivity most relevant to device
work. Prior efforts have shown that the thermal conductivity of AlN is significantly affected by incorporated oxygen\textsuperscript{10,11} but a discussion on other impurities or point defect types and their corresponding effect on thermal conductivity is not provided in these earlier works. The purpose of the present work is to examine the influence of point defects on the thermal conductivity of low dislocation density, single crystal AlN.

6.1.2 Theory

Thermal conductivity in non-metallic solids depends on heat transport by collective vibrations of atoms in the crystal lattice called phonons, which can be treated as a gas of particles having an average time between collisions termed the relaxation time. In the relaxation time approximation, thermal conductivity depends on both intrinsic and extrinsic phonon relaxation times, the inverse of which are phonon scattering rates. Normal and Umklapp scattering processes are intrinsic to any crystal system, while extrinsic scattering is due to crystalline defects like grain boundaries, dislocations, and point defects. Point defects can be substitutional impurities, interstitials, vacancies, and their corresponding complexes. Extrinsic scattering sources can be controlled to some extent by growing low dislocation density single crystals that have also low concentrations of extrinsic impurities. Any reduction in the number of phonon scattering sources is therefore advantageous for improving the thermal conductivity of crystals. Specifically, a reduction of extended crystalline defects in AlN can be achieved by growing bulk single crystals from high quality crystal seeds\textsuperscript{5,40,143} The resulting AlN bulk crystals have dislocation densities of 10\textsuperscript{3}-10\textsuperscript{4} cm\textsuperscript{-2}\textsuperscript{143} Accordingly, the expected dominant extrinsic phonon scattering mechanism in these crystals is associated with point defects, as the effect of dislocation density is negligible\textsuperscript{144} and grain boundaries in the bulk are absent. Such
AlN bulk samples are expected to be ideally suited for highlighting the effect of point defects on thermal conductivity.

Thermal conductivity can be modeled using the Debye-Callaway approximation:

\[
\kappa = \frac{k_B T^3}{2\pi^2 v^3} \left[ \int_0^{\theta_D/T} \frac{\tau_C x^4 e^x}{(e^x - 1)^2} \, dx + \frac{\int_0^{\theta_D/T} \tau_C x^4 e^x}{\tau_N \left(e^x - 1\right)^2} \, dx \right],
\]

where \( \nu \) is the speed of sound in the material, the Debye temperature is expressed as \( \theta_D = \frac{\hbar \omega_D}{k_B} \) in which \( \omega_D \) is the Debye frequency, \( x = \frac{\hbar \omega}{k_B T} \), \( \tau_C \) is the collective phonon relaxation time, \( \tau_N \) is the relaxation time for normal scattering and \( \tau_R \) is the phonon relaxation time accounting for all scattering mechanisms that reduce thermal conductivity. In the limit of high impurity concentrations, the second term is omitted and \( \tau_C \approx \tau_R \), as extrinsic phonon scattering by point defects is the predominant phonon scattering mechanism. All relaxation times are discussed at length elsewhere.

In general, the expected shape for thermal conductivity curves resembles that of a Planck distribution, with a characteristic maximum at cryogenic temperatures. For temperatures lower than the maximum, thermal conductivity is dominated by extrinsic scattering at geometric boundaries,\(^\text{145}\) dislocations,\(^\text{105,106}\) and inclusions.\(^\text{111,117}\) These interact to produce a characteristic length smaller than the physical dimensions of the crystal, whereas an ideal crystal characteristic length is dimensionally equivalent. Thermal conductivity in this regime is proportional to \( T^3 \) and scales with specific heat.\(^\text{88}\) At the maximum, thermal conductivity
depends on scattering from both characteristic length and point defects. If the point defects are isotopes of the host atoms, the associated scattering rate has a Rayleigh-like dependence on the fourth power of phonon frequency ($\omega^4$).

If the point defects are not isotopes, the shape of the maximum can suffer from distortions caused by the disruption of normal host lattice phonon modes. This effect is known as phonon resonance scattering and occurs when the point defect introduces a localized impurity mode that disrupts thermal transport by acting as an inelastic phonon scattering center. The mechanism of phonon resonance can involve either translational motion or rotational motion of the point defect within the lattice site in response to excitation by a host lattice phonon. The interference of these localized modes with host lattice vibrations effectively reduces thermal transport. Curvature at and near the maximum of the $\kappa(T)$ curve is significantly deformed as a result. Moreover, the distribution of a given point defect type within the crystal can affect the shape of the curve, such as a uniform decrease of the maximum for isolated point defects in solid solution or a decrease at temperatures below the maximum due to a reduction of characteristic length if the point defects cluster or precipitate into a secondary phase. At a transition temperature above the maximum, thermal conductivity becomes dominated by intrinsic Umklapp scattering, which scales directly with temperature.

Naturally, it can be expected that for different samples of a specific material, the thermal conductivity begins to converge with increasing temperature as Umklapp scattering becomes the limiting scattering mechanism. For different materials, the Debye temperature ($\theta_D$) offers a simple way to understand the relative influence of Umklapp scattering on thermal conductivity. Figure 6-1
illustrates this relationship using InAs ($\theta_D = 280$ K), Si ($\theta_D = 643$ K), and Diamond ($\theta_D = 1870$ K) as examples.

Figure 6-1: Thermal conductivity as a function of temperature for InAs, Si, and diamond with $\theta_D$ of 280, 643, and 1870 K, respectively.

Figure 6-1 shows that for materials with higher $\theta_D$, the transition of thermal conductivity to limitation by intrinsic Umklapp scattering occurs at higher temperatures, as evidenced by the thermal conductivity decay tail to the right of the curve maxima. An important consequence of this effect is that extrinsic phonon scattering by point defects persists at higher temperatures in high $\theta_D$ materials. Since AlN has a $\theta_D$ of 988 K, phonon-point defect scattering is expected to have a significant influence on thermal conductivity even at room temperature.

The goal of this study is to establish the role of point defects in the thermal conductivity of AlN. The approach taken here compares results from a collection of single crystal AlN samples containing varying amounts of point defects that were grown by two techniques: physical vapor transport (PVT) and hydride vapor phase epitaxy (HVPE) using PVT crystals as seeds. The development of commercial AlN wafers makes use of both growth methods,
thereby making the present work pertinent to the progress of AlN technology. The thermal conductivity of AlN shows strong temperature dependence between cryogenic and room temperatures. This dependence allows the effect of different point defect types and their concentrations on the thermal conductivity of AlN to be qualitatively assessed.

**6.1.3 Experimental**

The AlN crystals were selected to have a broad range of point defect concentrations to observe the effect of point defects on thermal conductivity and to allow comparison of thermal conductivity results from both growth methods, as HVPE growth of AlN typically yields crystals with impurity concentrations at least an order of magnitude below those observed in PVT AlN.\textsuperscript{155} The HVPE crystals were grown on top of PVT seeds, which were subsequently removed to yield free-standing, low dislocation density HVPE wafers that were of similar crystalline quality as the PVT wafers. Table 6-1 lists the SIMS data for the samples in the present work.

**Table 6-1: Impurity concentrations measured by SIMS (atoms cm\(^{-3}\)).** Values listed for PVT AlN B are averages based on typical values found in PVT AlN substrates.\textsuperscript{82,155,157,158} Dashes mean there is no record for the specific impurity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H</th>
<th>B</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Cl</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVT AlN A</td>
<td>---</td>
<td>---</td>
<td>1.1\times10^{19}</td>
<td>2.8\times10^{17}</td>
<td>1.1\times10^{19}</td>
<td>---</td>
<td>2.2\times10^{19}</td>
</tr>
<tr>
<td>PVT AlN B</td>
<td>---</td>
<td>---</td>
<td>\approx2.5\times10^{19}</td>
<td>\approx8.6\times10^{18}</td>
<td>\approx9.4\times10^{18}</td>
<td>---</td>
<td>\approx4.3\times10^{19}</td>
</tr>
<tr>
<td>PVT AlN C</td>
<td>---</td>
<td>---</td>
<td>9.9\times10^{18}</td>
<td>2.0\times10^{18}</td>
<td>1.3\times10^{19}</td>
<td>---</td>
<td>2.5\times10^{19}</td>
</tr>
<tr>
<td>HVPE AlN A</td>
<td>&lt;1\times10^{17}</td>
<td>1.5\times10^{16}</td>
<td>&lt;5\times10^{16}</td>
<td>4.2\times10^{17}</td>
<td>1.6\times10^{18}</td>
<td>9\times10^{14}</td>
<td>2.0\times10^{18}</td>
</tr>
<tr>
<td>HVPE AlN B</td>
<td>1.8\times10^{17}</td>
<td>2.6\times10^{15}</td>
<td>5.1\times10^{16}</td>
<td>9.6\times10^{17}</td>
<td>1.3\times10^{17}</td>
<td>6.5\times10^{14}</td>
<td>1.3\times10^{18}</td>
</tr>
<tr>
<td>HVPE AlN C</td>
<td>---</td>
<td>---</td>
<td>4.6\times10^{16}</td>
<td>3.1\times10^{17}</td>
<td>2.8\times10^{17}</td>
<td>---</td>
<td>6.3\times10^{17}</td>
</tr>
</tbody>
</table>

All samples were measured by the 3\(\omega\) method and were prepared by patterning with photolithography followed by electron beam deposition of a metal stack consisting of 10 nm
Ti, 200 nm Ni, and 10 nm Au. The metallized samples were then subjected to lift-off in either acetone or NMP and flip-chip soldered onto a printed circuit board (PCB) to ensure that the integrity of the metallization pattern remained intact during handling and testing. A completed sample assembly is shown below in Figure 6-2.

Figure 6-2: Image showing finished sample assembly. The transparency of this particular sample makes the metallization pattern visible through the back of the test specimen.

The dimensions of the completed thin film wires were stripes of 1 mm in length and a width of 10 μm. The assemblies were then mounted to the cold finger of a Janis SHI-4-15 closed cycle cryostat. The average bulk thermal conductivity was calculated using the equation derived and described by Cahill\textsuperscript{126,128}:

\[
\kappa = \frac{V_0^3}{4\pi lR^2} \frac{dR}{dT} \frac{\ln(f_2/f_1)}{V_{3\omega,f_1} - V_{3\omega,f_2}},
\]

(6.1.2)

where \(V_0\) is the voltage drop over the stripe at excitation frequency \(\omega\), \(l\) is the stripe length, \(R\) the resistance across the stripe at the setpoint temperature without applied excitation voltage, \(dR/dT\) is the slope of the resistance curve at the setpoint temperature, \(f_2\) \((f_1)\) is the ending (starting) excitation frequency, and \(V_{3\omega,f_1}\) \((V_{3\omega,f_2})\) is the third harmonic voltage response at the starting (ending) excitation frequency. The resistance without excitation was measured at
multiple temperature set points and fitted with a Bloch-Grüneisen relation with typical order $3 < x < 5$ to provide accurate derivation of the $dR/dT$ term at any given temperature. Propagated uncertainty for thermal conductivity was calculated at each measurement set point based on the limits of accuracy for the instrumentation used in measuring each term. Thorough benchmarking of the system using several other III-V semiconductors demonstrated reproducibility of literature data well within the margins of propagated error down to 30 K, indicating negligible contributions from systematic error. Repeat measurements of specimens indicated that random errors were also within the margins of propagated error. The majority of thermal conductivity data in the literature contains no quantitative error estimates, making the approach used here unique in this respect. PL measurements of AlN were performed using an argon fluoride excimer laser as an excitation light source (5 ns pulse width at an emission wavelength of 193 nm). The luminescence was directed onto a 0.75 m focal length Acton Series SP-2750 monochromator where a 150 grooves/mm diffraction grating was used and the intensity was recorded using a PIXIS-XO: 2KB CCD detector. The large midgap region below the band edge of AlN affords less degeneracy in emission energies for specific point defects compared to lower bandgap materials. Accordingly, PL spectroscopy, in conjunction with SIMS and DFT, provides valuable information regarding the types of point defects present in the AlN samples based on their optical emission energies.\textsuperscript{159,160}

6.1.4 Results and Discussion

Photoluminescence spectra recorded over the defect related spectral region for AlN crystals reveal contributions of various point defects indicated by multiple distinct emission peaks. Emission varied significantly between the samples due to the different concentrations of
incorporated point defects. Figure 6-3 shows room temperature photoluminescence spectra for each of the six selected crystals.

Previous work has assigned the emission bands at 3.2 eV and 3.6 eV to related transitions involving aluminum vacancy complexes with oxygen or silicon\textsuperscript{161–164}. As discussed in Gaddy et al., emission at 2.7 eV, 3.9 eV, and 4.3 eV are related to substitutional carbon and carbon-silicon complexes.\textsuperscript{158,165} SIMS data demonstrates that the dominant impurities present in PVT AlN crystals are carbon, silicon and oxygen. Samples PVT A and B show the characteristic carbon-related emission peaks at 2.7 and 3.9 eV. In contrast, pronounced emission from aluminum vacancy-related complexes at 3.2 eV and 3.6 eV and carbon-silicon complexes at 4.3 eV are found for PVT C. The samples HVPE B and C show the carbon related emission lines while HVPE A shows emission from aluminum vacancy-related complex transitions. The relative intensities at 3.2 and 3.6 eV for the HVPE samples are expected to depend on the concentration of aluminum vacancy-related defects.\textsuperscript{162,166} Although similar types of point defects are expected for PVT AlN and HVPE AlN, their absolute and relative quantities are
significantly different. Only the emission of the carbon-silicon complex is different between the two types of samples, as this seems to depend on the absolute quantities of these impurities in the crystals.

Figure 6-4 (a) and (b) shows the measured thermal conductivity for AlN samples grown by PVT, and HVPE in the temperature range between 30 and 325 K. In addition, results from Kyocera ceramic AlN are included as reference. For comparison, reported literature values of Slack et al.\textsuperscript{10,11} are included as dashed curves. Table 6-2 lists the wafer thickness as well as the thermal conductivity results at room temperature.

![Figure 6-4](image-url)

Figure 6-4: Temperature dependent thermal conductivity results for (a) PVT and (b) HVPE AlN single crystals. The dotted curve for PVT AlN B is a guide for the eye. The dashed lines represent literature values for single crystal AlN as reported by Slack et al.\textsuperscript{10,11}. 

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>PVT AlN A</th>
<th>PVT AlN B</th>
<th>PVT AlN C</th>
<th>Ceramic</th>
<th>Ref. 15</th>
<th>Ref. 16</th>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>HVPE AlN A</th>
<th>HVPE AlN B</th>
<th>HVPE AlN C</th>
<th>HPVE B Fit</th>
<th>HVPE C Fit</th>
<th>Ref. 15</th>
<th>Ref. 16</th>
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</table>
Table 6-2: Room temperature values of the thermal conductivity of single crystal AlN samples depicted in Figure 6-4.

<table>
<thead>
<tr>
<th>AlN Sample</th>
<th>Thickness [mm]</th>
<th>( \kappa ) at 295K [Wm(^{-1})K(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVT A</td>
<td>0.47</td>
<td>301 ± 5</td>
</tr>
<tr>
<td>PVT B</td>
<td>2</td>
<td>268 ± 5</td>
</tr>
<tr>
<td>PVT C</td>
<td>0.55</td>
<td>339 ± 7</td>
</tr>
<tr>
<td>HVPE A</td>
<td>0.208</td>
<td>297 ± 7</td>
</tr>
<tr>
<td>HVPE B</td>
<td>0.205</td>
<td>325 ± 9</td>
</tr>
<tr>
<td>HVPE C</td>
<td>0.204</td>
<td>341 ± 6</td>
</tr>
<tr>
<td>Kyocera Ceramic</td>
<td>2.8</td>
<td>72 ± 1</td>
</tr>
</tbody>
</table>

The results between different samples of PVT grown AlN show significant variability over the investigated range of temperatures as evident in Figure 6-4 (a). The spread is lowest at the highest temperatures, as expected, but Table 6-2 shows a substantial difference of 71 Wm\(^{-1}\)K\(^{-1}\) between the lowest and highest results for PVT AlN samples. The total impurity concentrations between PVT A and C are on the order of \(10^{19}\) cm\(^{-3}\), but oxygen concentration is greater in PVT C by nearly an order of magnitude. Silicon and carbon in both samples show concentration differences on the order of \(10^{18}\) cm\(^{-3}\). Total impurity concentration in PVT C is greater than the amount in PVT A by \(\sim2.6 \times 10^{18}\) cm\(^{-3}\), yet PVT C shows higher thermal conductivity across the measured range. This behavior deviates from the expected simple inverse relationship between the impurity concentration and thermal conductivity as predicted by the Debye-Callaway model. This suggests the possibility that impurity interactions such as the formation of complexes reduce the phonon scattering cross sections of the associated impurities and thus their corresponding relaxation rates. This behavior has been reported in bulk GaN.\textsuperscript{167} Furthermore, this is consistent with the emission energies in Figure 6-3 a), which show that an increased intensity at 4.3 eV from C-Si complexes corresponds with higher
thermal conductivity between room temperature and about 100 K in PVT A and C than in PVT B, which has strong emission at 2.7 eV and 3.9 eV from substitutional carbon. The higher thermal conductivity in this range is likely caused by the increase in distance between point defect centers that results from complex formation, which decreases the phonon-point defect scattering rate of higher frequency phonons. Conversely, low frequency phonons are more strongly scattered at lower temperatures due to the increased size of point defect centers. Similar behavior has been observed previously by Walker et al.\textsuperscript{111} PVT B has the fewest C-Si complexes as shown by the PL results and carbon being the most abundant impurity in this sample. The lack of complexes and relatively larger thickness explain the higher thermal conductivity at low temperatures while its high impurity concentration explains the low thermal conductivity at higher temperatures. The transition to boundary scattering dominance is not evident for any of the curves, but this trend typically dominates thermal conductivity between 2-10 K (not measured).\textsuperscript{105} The behavior of the PVT sample curves does not match the expectation for thermal conductivity of a typical crystalline material, but all show curvature distortions due to phonon resonances related to point defects. While examples of phonon resonance behavior abound in the literature, general awareness of this effect appears to be absent in more recent publications. Accordingly, Figure 6-5 a) shows results from Baumann et al.\textsuperscript{112} exhibiting significant phonon resonances caused by the presence of point defects. Figure 6-5 b) compares experimental results against the behavior expected for single crystal AlN and GaP as given by Eq. (6.1.1) (solid curves) using the limit of high impurity concentration as described previously.
The set of curves in Figure 6-5 a) demonstrates that the addition of lithium into KBr introduces distortions that deviate from the expected behavior of thermal conductivity represented by the curve for pure KBr. The same trends have been observed in the KCl, NaCl, and RbCl systems with many different dopant species. This phonon resonance behavior is not considered within the traditional Debye-Callaway model. Nevertheless, Figure 6-5 b) shows good agreement between the experimental results for a GaP single crystal and an ideal curve as predicted by (6.1.1) for a sample with $1 \times 10^{18}$ Si cm$^{-3}$, suggesting that not all point defects in other crystalline systems produce this behavior. For the case of AlN, the model breaks in the presence of a phonon resonance as indicated by the lack of agreement between the ideal curve and the experimental results for PVT AlN C. The same resonance dip observed in this sample is also seen in the ceramic AlN sample in Figure 6-4 a), which has high impurity concentrations from sintering aids. In contrast to the observations of phonon resonances in AlN, a review of
the literature reveals that no prominent curvature distortions in thermal conductivity from point defects appear in the lower Debye temperature III-V arsenides and antimonides.\textsuperscript{132,134,169,170} Not enough published literature exists to make the same assessment on either GaP or InP, but if the trend with the Debye temperature holds, no phonon resonances would be expected for these materials, either. The appearance of phonon resonances in the thermal conductivity of PVT AlN is a predictable tendency considering that both the Debye temperature and concentrations of impurities that incorporate during bulk growth are high. Results for HVPE AlN show closer agreement in both measured values and curve behavior. Fitting curves for HVPE B and C in Figure 6-4 b) were calculated using Eq. (6.1.1) as shown, taking into account intrinsic normal scattering. This was done under the assumption that extrinsic phonon scattering processes occur less frequently in these samples due to their lower impurity concentrations. While the indentations that appear in the results for the HVPE samples may arise from a point defect not characterized by SIMS, the inclusion of intrinsic normal scattering into the Debye-Callaway approximation reproduces the observed indentations in the experimental results for the HVPE samples. The coincidence of curves for HVPE A and B over much of the temperature range indicates similar influence from point defect scattering. The curve for HVPE C shows the highest thermal conductivity of all three, consistent with the lowest impurity concentration according to SIMS. The most significant difference in the fitting curves is the concentration of point defects. The fit for HVPE C uses the impurity data from Table 6-1, a vacancy concentration of $1.5\times10^{18}$ cm$^{-3}$, and a characteristic length of 200 microns. In contrast, the fit for HVPE B uses the impurity data from Table 6-1, a vacancy concentration of $2.5\times10^{18}$ cm$^{-3}$, and a characteristic length of 250 microns. The discrepancy in
characteristic length comes from the fact that the width of the HVPE B wafer is larger than that of HVPE C. Both fits use the same Grüneisen parameter of 1.29. The vacancy concentrations used in the modeling show good agreement with the PL data from Figure 6-3, which shows greater V$_{\text{Al}}$-related emission intensity at 3.2 and 3.6 eV for HVPE C than in HVPE B. This is assumed to result from vacancies introduced by Si impurities, which in HVPE C are more than twice the concentration observed in HVPE B, according to Table 6-1. The satisfactory agreement demonstrated between the results and the fits made using the Debye-Callaway expression suggest that point defects in the HVPE AlN samples are sufficiently described as isolated phonon scattering centers within the current measurement temperature range. This implies that the point defect concentration rather than the nature of the point defect influences the thermal conductivity at these lower concentrations.

Regardless of the differences in impurity concentrations between the samples, the trend common to both sample sets presented in Figure 6-4 is the convergence behavior of the thermal conductivity curves at higher temperatures. This trend indicates that the transition between the extrinsic point defect dominated phonon scattering and intrinsic Umklapp dominated scattering has not yet been reached. The spread of measured thermal conductivity values in Table 6-2 corroborates this observation. Since 295 K remains within the point defect dominated scattering regime for AlN, thermal conductivity depends strongly on point defect concentration even at room temperature. Additionally, the non-ideal curve behavior seen in Figure 6-4 is observed in other crystal systems and only appears in the presence of point defects, sometimes even in concentrations as low as $10^{16}$ cm$^{-3}$. The observation that different impurity types can have a degenerate influence on thermal conductivity curve
behavior\textsuperscript{115} complicates interpretation within the current analysis, as the presence of multiple impurities in the AlN samples precludes any attempt to attribute the observed phonon resonances to a single point defect species. The difference between thermal conductivity curve behaviors is consistent within the following framework: a) the distribution of the incorporated impurities (i.e., isolated or complexed) is unknown, b) impurity concentrations in the PVT AlN crystals are 1-2 orders of magnitude greater than amounts necessary to produce phonon resonance distortions as seen in prior thermal conductivity doping studies in other crystal systems,\textsuperscript{112,114,168} c) interaction between point defects may affect thermal conductivity by changing point defect phonon scattering cross sections, and d) the concentration of phonon-scattering vacancies either in connection with impurities or as isolated point defects within the present samples remains unknown.

\textbf{6.1.5 Conclusions}

The average bulk thermal conductivity in free-standing PVT and HVPE AlN is found to be limited by extrinsic point defect scattering over the entire investigated temperature range from 30 K to above room temperature. Significant thermal conductivity curve distortions appear in all of the studied samples and are attributed to phonon resonances due to the presence of multiple point defects. Samples having C-Si complexes according to PL show higher thermal conductivity above 100 K. Point defect scattering declines with increasing temperature while intrinsic Umklapp processes intensify. The results from modeling show qualitative agreement with the measurements. PL and SIMS indicate that carbon, oxygen, and silicon are the most abundant impurities in PVT and HVPE AlN. It is expected that the measured thermal conductivity of AlN would be substantially increased in the 30-325 K range, should point
defect concentration be lowered further. More work is necessary to determine the point defects responsible for the observed phonon resonances and to observe if their separate effects result in degenerate thermal conductivity curve behavior in AlN, nevertheless, possible complex formation significantly influences the role of point defects on the scattering processes. Room temperature thermal conductivities of ~340 Wm⁻¹K⁻¹ were measured for both the best PVT and HVPE samples.

6.2 The thermal conductivity of single crystalline AlN: relation to UV transparency

6.2.1 Introduction

While the previous chapter describes the effect of point defects on the thermal conductivity of AlN, it does not connect the observed thermal conductivity results with transparency below 300 nm, an important metric for AlN substrates intended for homoepitaxy of LEDs and laser structures emitting in the UVC region. The following chapter links the thermal conductivity of AlN to both impurity concentration and UV transparency at 265 nm.

Aluminum nitride (AlN) is a wide bandgap material with use in next generation UV light emitting diodes, laser diodes, and power semiconductor devices.5,7,8,172 Future devices based on AlN are expected to operate at high power densities due to the 15 MVcm⁻¹ breakdown field.58,136,173 High power densities will directly affect thermal management approaches, making the thermal conductivity of AlN a crucial device design parameter. Prior work has shown that the concentration of point defects incorporated during AlN crystal growth significantly affects the thermal conductivity of AlN.10,93,174 Carbon impurities create an additional problem by introducing an absorption band at 265 nm,82 precluding the intended use in some UV-C optoelectronic devices. The introduction of additional oxygen and silicon
restores UV transparency by compensation of carbon\textsuperscript{158,175} but this is expected to decrease thermal conductivity in proportion by increasing the rate of phonon-point defect scattering. The present work studies AlN crystals containing different point defects and examines the effects of defects on thermal conductivity and the connection to UV transparency.

### 6.2.2 Experimental

In order to observe the relationship between UV transparency and thermal conductivity, AlN single crystals with absorption coefficients at 265 nm in the range of 7 to \( \sim \)1000 cm\(^{-1} \) were selected. Expected dislocation densities were \( <10^4 \) cm\(^{-2} \) for all crystals based on typical results from PVT and HVPE AlN growth processes.\textsuperscript{9,143,155,175} The PVT AlN samples were prepared in schematically alike reactors at IKZ and HexaTech, the details of which are described elsewhere.\textsuperscript{176,177} Sample thickness ranged from 200 \( \mu \)m in the HVPE AlN and lowest absorbing PVT AlN sample to 2 mm in the highly absorbing PVT AlN. Table 6-3 lists the results of secondary ion mass spectrometry (SIMS) for the studied samples. Table 6-4 lists the absorption coefficients at 265 nm, the thermal conductivity results at room temperature, and the thickness of the samples.

Table 6-3: Impurity concentrations according to SIMS (atoms cm\(^{-3} \)). Values for PVT AlN 5 are estimates based on average impurity concentrations found in UV absorbing PVT AlN substrates.\textsuperscript{82,155,157,158}

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Total</th>
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</thead>
<tbody>
<tr>
<td>HVPE AlN</td>
<td>4.59\times10^{16}</td>
<td>3.08\times10^{17}</td>
<td>2.80\times10^{17}</td>
<td>6.34\times10^{17}</td>
</tr>
<tr>
<td>PVT AlN 1</td>
<td>1.68\times10^{18}</td>
<td>6.94\times10^{18}</td>
<td>6.92\times10^{17}</td>
<td>9.31\times10^{18}</td>
</tr>
<tr>
<td>PVT AlN 2</td>
<td>2.09\times10^{18}</td>
<td>8.13\times10^{18}</td>
<td>2.28\times10^{18}</td>
<td>1.25\times10^{19}</td>
</tr>
<tr>
<td>PVT AlN 3</td>
<td>9.90\times10^{18}</td>
<td>2.00\times10^{18}</td>
<td>1.30\times10^{19}</td>
<td>2.49\times10^{19}</td>
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<tr>
<td>PVT AlN 4</td>
<td>1.10\times10^{19}</td>
<td>2.80\times10^{17}</td>
<td>1.10\times10^{19}</td>
<td>2.23\times10^{19}</td>
</tr>
<tr>
<td>PVT AlN 5</td>
<td>\sim2.5\times10^{19}</td>
<td>\sim8.6\times10^{18}</td>
<td>\sim9.4\times10^{18}</td>
<td>\sim4.3\times10^{19}</td>
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Table 6-4: Absorption coefficients of AlN at 265 nm, room temperature thermal conductivity, and sample thickness.

<table>
<thead>
<tr>
<th>AlN Sample</th>
<th>$\alpha$ at 265 nm [cm$^{-1}$]</th>
<th>$\kappa$ at 295K [Wm$^{-1}$K$^{-1}$]</th>
<th>Thickness [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HVPE AlN</td>
<td>7</td>
<td>341 ±6</td>
<td>204</td>
</tr>
<tr>
<td>PVT AlN 1</td>
<td>21</td>
<td>374 ±9</td>
<td>200</td>
</tr>
<tr>
<td>PVT AlN 2</td>
<td>53</td>
<td>343 ±7</td>
<td>340</td>
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<tr>
<td>PVT AlN 3</td>
<td>70</td>
<td>339 ±7</td>
<td>550</td>
</tr>
<tr>
<td>PVT AlN 4</td>
<td>277</td>
<td>301 ±5</td>
<td>470</td>
</tr>
<tr>
<td>PVT AlN 5</td>
<td>&gt;1000</td>
<td>268 ±5</td>
<td>2000</td>
</tr>
</tbody>
</table>

The wafers were patterned for $3\omega$ measurements using photolithography and metallized using a UHV electron beam metal evaporation system. The metallization layers were rendered with liftoff in NMP, after which samples were placed into a vacuum cryostat for testing. Details on the $3\omega$ setup are described elsewhere. Measuring the dependence of the thermal conductivity on temperature reveals the relative contributions of different phonon scattering mechanisms. For the studied temperature range, the dominant phonon scattering mechanisms are primarily three phonon/Umklapp processes and scattering by point defects, such as vacancies and impurities. The incorporation of point defects significantly affects thermal conductivity at lower temperatures as seen in Figure 6-6.
6.2.3 Results and Discussion

The technologically important room temperature thermal conductivity of the PVT AlN samples ranges from 268 to 374 Wm\(^{-1}\)K\(^{-1}\), significantly higher than results in prior literature.\(^{10,11}\) The convergence of the curves at higher temperatures indicates a dominating 3 phonon/Umklapp scattering rate relative to the rate of point defect scattering, a trait clearly illustrated in other crystalline materials.\(^{105,132,150,151}\) In order to put the measured results in context to the expected behavior of a pure crystal of AlN containing no point defects, a simulated curve using the Debye approximation of thermal conductivity is provided below in Figure 6-7.

Figure 6-6: The thermal conductivity of AlN as a function of temperature.
Figure 6-7: Experimental results and simulated curve for pure AlN as given by the Debye approximation. The calculated curve neglects phonon scattering contributions from normal processes, uses a sound velocity of 7094 m/s, a Debye temperature ($\theta_D$) of 967 K, a characteristic length of 2 mm, and a Grüneisen parameter ($\gamma$) of 2. Sound velocity and $\theta_D$ were determined using the elastic constants for AlN, leaving $\gamma$ as the only adjustable parameter.

The model curve generally matches the data at temperatures above 200 K and compares well with prior modelling for pure AlN, but the results at low temperature significantly diverge from the simulation. Prior literature from studies of other crystal systems demonstrates a similar lack of low temperature behavioral resemblance between model curves and measured results. The presence of this same discrepancy between the ideal curve and the experimental data for all the AlN samples studied indicates substantial phonon resonance scattering, an effect described in previous work. The absence of alignment between the measured results at low temperature and the $\sim T^3$ dependence shown between 20-30 K in
the model curve also indicates that thermal conductivity is not yet within the boundary scattering regime and therefore is still under the influence of point defects for all the crystals. The measured thermal conductivity for PVT AlN 2 and 3 coincides to around 100 K, indicating similar influence from Umklapp scattering. PVT AlN 1 shows a maximum of 736 Wm\(^{-1}\)K\(^{-1}\) at 114 K and has the highest thermal conductivity at temperatures above 240 K, but this sample exhibits the lowest thermal conductivity for all temperatures below 140 K. The thermal conductivity for PVT AlN 2 exhibits a clear maximum between 60 and 70 K of 1641 Wm\(^{-1}\)K\(^{-1}\) and demonstrates the smoothest temperature dependent behavior. However, the apparent shift towards the boundary scattering regime occurs at a higher temperature than expected, as the boundary scattering length should be approximately equal between samples PVT AlN 2, 3, and 4. Accordingly, the thermal conductivity results of PVT AlN 2 are most likely still dominated by point defect scattering below 60 K. PVT AlN 4 shows lower transparency and thermal conductivity reaches a maximum of \(~840\) Wm\(^{-1}\)K\(^{-1}\) near 100 K, below which the thermal conductivity decrease is nearly linear with the log of temperature. Due to the lower thermal conductivity in PVT AlN 4 as compared to PVT AlN 3, one would expect to find a relatively higher point defect density in the former, but this is not observed in Table 6-3. The curve for PVT AlN 5 shows significant influence of point defects, as indicated by its lower thermal conductivity between room temperature and 100 K. Nonetheless, this sample shows less sensitivity to low temperature phonon resonances compared to the other samples, as it has the highest thermal conductivity below 50 K. The HVPE AlN curve shows some overlap with the curve for PVT AlN 4, but reaches a maximum thermal conductivity of 1723 Wm\(^{-1}\)K\(^{-1}\) near 50 K. While the HVPE AlN sample has the fewest impurities, it lags behind PVT AlN 2 and 3 in
thermal conductivity between room temperature and 80 K. PVT AlN 4 has $3 \times 10^{18}$ fewer impurities than PVT AlN 3, but has poorer thermal conductivity over the entire temperature range. PVT AlN 1 has the lowest impurity concentration of the PVT AlN samples, yet it shows the lowest thermal conductivity below 140 K. Finally, PVT AlN 2 has half the impurities of PVT AlN 3, but thermal conductivity results from both samples coincide between room temperature and 100 K.

While these results partially contradict the expectation of a simple inverse relationship between thermal conductivity and impurity concentration, prior thermal conductivity studies of other single crystal materials have shown that a) the dimensional arrangement of incorporated impurities within the lattice significantly affects location of the curve maximum with respect to temperature,\textsuperscript{111} b) curve distortion from phonon resonances occurs at impurity concentrations as low as $10^{16}$ cm$^{-3}$ and is positively correlated,\textsuperscript{112,114,168} c) interplay between impurity types may also affect curve behavior if their interaction changes the associated phonon scattering cross section within the crystal lattice,\textsuperscript{167} and d) the concentration of vacancies as well as heavy elements from the PVT crucible materials was not quantified.

The distribution of point defects within the crystals of the present work as well as the degree to which they interact is unknown, but the findings of prior work indicate that reduction or compensation of carbon is necessary for reducing absorption at 265 nm.\textsuperscript{82,158,165,179} Thermal conductivity above 200 K appears to scale directly with the concentration of carbon in the PVT samples as well as relate inversely to the absorption coefficient at 265 nm. Compensation of carbon in the PVT AlN samples may partially explain their high UV transparency, but the influence of carbon complex formation on thermal conductivity by modification of the
impurity-phonon scattering cross sections cannot be determined within the present work. Finally, the distortion seen in the curve for HVPE AlN indicates that phonon resonances are still significantly active, even with impurity concentrations two orders of magnitude lower than in the PVT AlN samples.

### 6.2.4 Conclusions

Thermal conductivity was measured for AlN single crystals with varying point defect concentrations in the range of 30 K to 325 K using the 3ω method. UV-transparent PVT-grown AlN showed comparable thermal conductivity to HVPE AlN at room temperature. Curve distortion was evident in all samples but PVT AlN 1 and was attributed to the phonon resonances caused by point defects. Comparison of measured results against an ideal model curve for pure AlN showed significant behavioral departures in the temperature dependence of the experimental data with respect to anticipated behavior, once again suggesting active phonon resonances. Room temperature thermal conductivity values ranged from 268 to 374 Wm$^{-1}$K$^{-1}$, the latter being the highest reported room temperature thermal conductivity of AlN. Thermal conductivity curves converged at higher temperatures and nearly coincided at room temperature with values around 340 Wm$^{-1}$K$^{-1}$. Results from SIMS showed total impurity concentration was on the order of 10$^{19}$ cm$^{-3}$ in the PVT crystals and 10$^{17}$ cm$^{-3}$ in the HVPE crystal, but contrary to expectation, thermal conductivity did not always follow an inverse relationship to impurity concentration. Thermal conductivity between room temperature and 200 K scaled directly with carbon concentration and UV transparency in the PVT AlN crystals. The discrepancy between the experimental results, the model curve, and the traditional understanding of point defect influence on thermal conductivity indicates either a more
complicated relationship than the simple case of dispersed and non-interacting point defects or the presence of other point defects that were not measured, such as vacancies or heavy elements from the surrounding crucible used in PVT AlN growth.\textsuperscript{180}
Chapter 7: Thermal Conductivity and Point Defects in GaN

7.1 The thermal conductivity of GaN: influence of crystal growth technique and impurities

7.1.1 Introduction and Theory

GaN attracts significant attention due to its status as a wide bandgap semiconductor with potential for use in UV LEDs, diode lasers, and high power devices.\textsuperscript{1-3,7} Next generation devices are expected to operate at higher power densities than traditional silicon devices due to the high breakdown field of 3.75 MVcm\textsuperscript{-1} in GaN.\textsuperscript{57} This creates a significant thermal engineering challenge, as heat produced during operation decreases both device efficiency and service lifetime. Thermal conductivity is therefore a crucial parameter that must be taken into consideration during device design and development. Unfortunately, agreement on the room temperature thermal conductivity of GaN remains elusive, as results range from 130 Wm\textsuperscript{-1}K\textsuperscript{-1} to 269 Wm\textsuperscript{-1}K\textsuperscript{-1} in literature.\textsuperscript{12-15} The present work uses experimental results, theory, and relevant prior findings in order to explain the underlying causes responsible for affecting the thermal conductivity of GaN.

Transport of thermal energy through semiconductors is achieved through collective oscillations of atoms within the crystal lattice, which are termed phonons. Phonons are typically modelled as a gas of particles with a mean time interval between collisions referred to as the relaxation time. Phonon collisions involving only other phonons are referred to as intrinsic scattering processes, while collisions of phonons with crystalline defects are referred to as extrinsic scattering processes. Examination of the response of thermal conductivity as a function of temperature reveals the relative strength of intrinsic and extrinsic scattering...
processes that dominate thermal conductivity within specific temperature regimes. Thermal conductivity curves typically resemble a Planck distribution in which the maximum appears at cryogenic temperatures. At temperatures less than the maximum, phonon scattering at the surface of the crystal, dislocations, and inclusions dominates thermal conductivity.\textsuperscript{105,106,111,117,145} The combined effect of these extrinsic scattering mechanisms reduces the characteristic length of the crystal, which in the ideal case is dimensionally equivalent. For crystals with natural isotopic compositions and incorporated impurities, phonon scattering at isotopes and point defects dominates thermal conductivity at and near the maximum.\textsuperscript{92,105,181} These point defects can be substitutional impurities, vacancies, and their corresponding complexes. The presence of point defects can additionally impact thermal conductivity by distorting the curvature at and near the maximum if they introduce a localized phonon mode that acts as an inelastic phonon scattering center, disrupting thermal transport.\textsuperscript{110–112} At temperatures greater than the maximum, phonon scattering off of other phonons is the predominant limiting process for thermal conductivity. In this temperature regime, measured results from different crystals of the same material begin to overlap with increasing temperature.\textsuperscript{105,132,150,151}

Numerous models have been proposed in order to describe the behavior of thermal conductivity as a function of temperature. Within the present analysis, the Debye-Callaway model provides an acceptable approximation of thermal conductivity and is given by the expression
\[
\kappa = \frac{k_B T^3}{2\pi^2 v \hbar^3} \left\{ \int_0^{\theta_D/T} \frac{\tau_C x^4 e^x}{(e^x - 1)^2} \, dx + \int_0^{\theta_D/T} \frac{\tau_C x^4 e^x}{\tau_N (e^x - 1)^2} \, dx \right\}, \tag{7.1.1}
\]

where \( v \) is the average speed of sound in the material, \( \theta_D \) is the Debye temperature, \( \tau_C \) is the collective phonon relaxation time, \( \tau_N \) is the relaxation time for normal scattering, and \( \tau_R \) is the phonon relaxation time accounting for all scattering mechanisms that reduce thermal conductivity. All relaxation times are discussed at length elsewhere.\(^{88,90}\)

This study seeks to establish the role of point defects in the thermal conductivity of GaN. The approach taken here compares results from a collection of single crystal GaN samples containing varying amounts of point defects that were grown by ammonothermal, HVPE, and sodium flux processes. The development of commercial GaN wafers makes use of both ammonothermal and HVPE methods, thereby making the present work pertinent to the progress of GaN technology. The thermal conductivity of GaN fluctuates significantly between cryogenic and room temperatures. This temperature dependence allows qualitative assessment of the effect that different point defects and their concentrations have on the thermal conductivity of GaN.

7.1.2 Experimental Background

GaN single crystals produced by different growth methods were selected for the present analysis. These techniques included the ammonothermal, hydride vapor phase epitaxy (HVPE), and sodium flux methods. Since impurities in GaN originate from the immediate surroundings at the surface of the growing crystal, the distinct environments within each
growth technique can be expected to yield bulk crystals with varying point defect profiles. In the case of some of the ammonothermal samples, impurities were deliberately added to yield insulating crystals. The varying point defect concentrations caused by both the growth environments and intentional doping afford the opportunity to examine their effect on the thermal conductivity of GaN. Impurity concentrations for samples used in the current analysis are presented below in Table 7-1. The thermal conductivity results at room temperature as well as the sample thicknesses are listed below in Table 7-2.

Table 7-1: Impurity concentration according to SIMS (atoms cm⁻³). Dashes indicate no record for the impurity while BDL stands for “below detection limit.”

<table>
<thead>
<tr>
<th>Sample</th>
<th>H</th>
<th>C</th>
<th>O</th>
<th>Mg</th>
<th>Si</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
<th>Zn</th>
<th>Σ_{tot}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Flux</td>
<td>---</td>
<td>BDL</td>
<td>3×10¹⁶</td>
<td>---</td>
<td>BDL</td>
<td>1×10¹⁶</td>
<td>---</td>
<td>BDL</td>
<td>---</td>
<td>4×10¹⁶</td>
</tr>
<tr>
<td>HVPE</td>
<td>---</td>
<td>1×10¹⁶</td>
<td>1×10¹⁶</td>
<td>---</td>
<td>2×10¹⁷</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>2.2×10¹⁷</td>
</tr>
<tr>
<td>Ammono 1</td>
<td>1.5×10¹⁹</td>
<td>6.2×10¹⁶</td>
<td>1.4×10¹⁸</td>
<td>1.2×10¹⁷</td>
<td>1.6×10¹⁷</td>
<td>---</td>
<td>9.8×10¹⁴</td>
<td>2.9×10¹⁵</td>
<td>5.2×10¹⁶</td>
<td>2.5×10¹⁹</td>
</tr>
<tr>
<td>Ammono 2</td>
<td>3.5×10¹⁸</td>
<td>2.6×10¹⁷</td>
<td>1.4×10¹⁸</td>
<td>9.3×10¹⁷</td>
<td>3.1×10¹⁷</td>
<td>---</td>
<td>4.7×10¹³</td>
<td>6.8×10¹³</td>
<td>7.6×10¹⁷</td>
<td>5.7×10¹⁸</td>
</tr>
</tbody>
</table>

Table 7-2: The thermal conductivity results at room temperature and thicknesses of the samples in this study.

<table>
<thead>
<tr>
<th>GaN Sample</th>
<th>( \kappa ) at 295K [Wm⁻¹K⁻¹]</th>
<th>Thickness [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Flux</td>
<td>211 ± 5</td>
<td>550</td>
</tr>
<tr>
<td>HVPE</td>
<td>224 ± 5</td>
<td>315</td>
</tr>
<tr>
<td>Ammono 1</td>
<td>164 ± 3</td>
<td>350</td>
</tr>
<tr>
<td>Ammono 2</td>
<td>196 ± 4</td>
<td>440</td>
</tr>
<tr>
<td>Ammono 3</td>
<td>184 ± 4</td>
<td>410</td>
</tr>
</tbody>
</table>

As displayed above in Table 7-2, all crystals within the present work are between 300-600 µm thick. The sodium flux sample is a cross section removed from thick GaN grown on the surface of a sapphire wafer with the sodium flux method according to Mori et. al. The HVPE crystal is a wafer that was grown on an ammonothermal GaN substrate, which was subsequently
removed in the manner described by Bockowski et. al.\textsuperscript{183} The ammothermal GaN samples were produced using the eponymously titled method.\textsuperscript{34} Dislocation density is \(\leq 10^4\) in the Ammono and HVPE samples\textsuperscript{184} and estimated at \(\sim 10^5\) in the sodium flux sample.\textsuperscript{185} At these concentrations, the effect of dislocations on the thermal conductivity of GaN is negligible.\textsuperscript{186} 

Table 7-3 shows typical growth conditions for each process and resulting crystal qualities.

<table>
<thead>
<tr>
<th>Growth Method</th>
<th>Precursor Source</th>
<th>Temperature [°C]</th>
<th>Pressure [Pa]</th>
<th>Growth Rate [μm hr(^{-1})]</th>
<th>Typical Seed Impurities [cm(^{-3})]</th>
<th>Dislocation Density [cm(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-Flux</td>
<td>Solution</td>
<td>870</td>
<td>3.2\times10^6</td>
<td>(\leq 50)</td>
<td>Foreign</td>
<td>~10^{17}</td>
</tr>
<tr>
<td>HVPE</td>
<td>Gas</td>
<td>~1000-1100</td>
<td>(\leq 1.0\times10^5)</td>
<td>&gt;100</td>
<td>Foreign</td>
<td>~10^{17}-10^{19}</td>
</tr>
<tr>
<td>Ammonothermal</td>
<td>Solution</td>
<td>~200-750</td>
<td>1.6\times10^4</td>
<td>&lt;50</td>
<td>Native</td>
<td>~10^{18}-10^{20}</td>
</tr>
</tbody>
</table>

The thermal conductivity of the samples was measured using the 3\(\omega\) method.\textsuperscript{126} Metallization layers for 3\(\omega\) thermal conductivity testing were produced using photolithography followed by electron beam evaporation of metal stacks consisting of 10 nm of either Ti or V, 200 nm Ni, and 10-20 nm Au. Lift-off in either acetone or NMP was used to render the metallization patterns. Flip-chip soldering of samples to a printed circuit board (PCB) was used to ensure the integrity of the metallization pattern during handling and testing remained intact. The completed thin film wires had dimensions of 1 mm in length and 10 μm in width. Figure 7-1 shows an example of the 3\(\omega\) metallization pattern used for testing the samples.
Figure 7-1: Metallization pattern for a single 3ω metal wire. Contact pads are labeled with their corresponding connections.

The assemblies were then mounted to the cold finger of a Janis SHI-4-15 closed cycle cryostat and tested. The thermal conductivity was calculated using the equation derived and described by Cahill.\textsuperscript{126,128}

\[ \kappa = \frac{V_\omega^3}{4\pi l R^2} \frac{dR}{dT} \frac{\ln(f_2/f_1)}{V_{3\omega,f_1} - V_{3\omega,f_2}}, \]  

(7.1.2)

where $V_\omega$ is the voltage drop ($V_{HI} - V_{LO}$) over the metal wire at excitation frequency $\omega$, $l$ is the wire length as defined by the distance of thin metal trace between the orthogonal intersection points of the $V_{HI}$ and $V_{LO}$ leads, $R$ the resistance across the metal wire at a given temperature without applied excitation voltage, $dR/dT$ is the slope of the resistance vs. temperature curve of the metal wire at a given temperature, $f_2$ ($f_1$) is the ending (starting) excitation frequency, and $V_{3\omega,f_1}$ ($V_{3\omega,f_2}$) is the third harmonic voltage response at the starting (ending) excitation frequency. The resistance without excitation was measured at multiple temperature setpoints and fitted with a Bloch-Grüneisen relation of arbitrary order\textsuperscript{187} to provide accurate derivation of the $dR/dT$ term at any given temperature.
7.1.3 Results and Discussion

The smallest difference between the maximum and minimum measured thermal conductivity results occurs at room temperature and significant divergence of the results becomes apparent as the temperature decreases. Figure 7-2 shows the measured thermal conductivity results for the GaN single crystals tested within this work.

![Thermal Conductivity Curve](image)

Figure 7-2: Thermal conductivity curves for the samples tested. Solid lines represent the calculated thermal conductivity fits according to (7.1.1).

The vertical distribution of experimental results in Figure 7-2 follows the total impurity concentrations in Table 7-1. This trend behavior matches the expectation that thermal conductivity improves as impurity concentration decreases. The Ammono 1 and 2 samples show lower thermal conductivity resulting from the impurities added to produce electrically
insulating substrates. The results for these samples also drop off sooner at lower temperature than the others. The shallow nature of the decline for these samples matches phonon resonance behavior as observed in the work of Pohl,\textsuperscript{171} where the presence of impurities causes thermal conductivity to drop by orders of magnitude at lower temperatures compared to measurements on undoped crystals. Some of the result curves cross between 110 and 140 K. These crossovers result from intra-crystal variation of the phonon relaxation times. For the conductive Na-Flux and Ammono 3 samples, the larger error bars result from a 40 nm PECVD deposited SiO\textsubscript{2} electrical isolation layer used to prevent parasitic current flow through the sample. This layer increases the amplitude of the $V_{3\omega,f1}$ and $V_{3\omega,f2}$ terms because of its poor thermal conductivity, but does not affect the difference of these terms. This causes a larger propagated error. Since the present measurements use the slope method of the 3\omega technique, the thermal boundary resistance of this layer has negligible influence on the final results.\textsuperscript{188} Though the Ammono 3 sample has no associated SIMS data, the location of its result curve with respect to those of HVPE and Ammono 2 indicate that point defect concentration is somewhere between the levels present in these two samples. Although the results between samples span three orders of magnitude at low temperature, they begin converging as temperature increases. This results from an increase in Umklapp scattering. While the convergence behavior is clear, the separation between the result curves of different samples indicates a non-trivial phonon-point defect relaxation time at room temperature. At some point beyond room temperature, the thermal conductivity curves are expected to coincide as thermal conductivity becomes limited by phonon-phonon scattering rather than phonon-point defect scattering. Cross referencing
Table 7-1 with Figure 7-2 clearly illustrates that the thermal conductivity of GaN is dominated by point defect scattering across the entire temperature range within the present work.

Model fits using (7.1.1) agree qualitatively with the experimental results. The fitting curves take into account a number of parameters necessary for calculation of thermal conductivity. As the parameters used for thermal conductivity curve fitting vary significantly in literature, values from the present work are listed below in Table 7-4.

**Table 7-4: Fitting parameters used in creating the model curves of Figure 7-2.** Parameter \( v \) represents average phonon velocity, \( \theta_D \) is the Debye temperature, \( d \) is the crystal’s characteristic length, \( \Gamma \) represents the phonon scattering factor used in the impurity scattering rate as discussed elsewhere,\(^90,93 \) \( \gamma \) is the Grüneisen constant, \( b \) is the coefficient inside the exponential for the intrinsic Umklapp scattering rate as discussed by Morelli et al.,\(^90 \) and \( \beta \) is a coefficient from the present work.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Na-Flux</th>
<th>HVPE</th>
<th>Ammono 1</th>
<th>Ammono 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancies [cm(^{-3})] *</td>
<td>0</td>
<td>2.0\times10^{17}</td>
<td>3.24\times10^{18}</td>
<td>4.0\times10^{17}</td>
</tr>
<tr>
<td>( v ) [m s(^{-1})] a</td>
<td>4759</td>
<td>4759</td>
<td>4759</td>
<td>4759</td>
</tr>
<tr>
<td>( \theta_D ) [K] a</td>
<td>650</td>
<td>650</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>( d ) [x 10(^{-6}) m] a</td>
<td>330</td>
<td>40</td>
<td>2.25</td>
<td>6.2</td>
</tr>
<tr>
<td>( \Gamma ) [x 10(^{-4})] a</td>
<td>2.74448</td>
<td>2.75547</td>
<td>2.83149</td>
<td>2.82827</td>
</tr>
<tr>
<td>( \gamma ) b</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td>( b ) c</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>( \beta ) d</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* From present work.

a Calculated from B4 in Dames et al.\(^{189}\) using method of Deguchi et al.\(^{190}\) with Polian et al.\(^{191}\) elastic constants.

b From Ježowski et al.\(^{13}\)

c Factor from present work multiplied into intrinsic normal scattering rate from Morelli et al.\(^{90}\)

The vacancy parameter represents the number of vacancies added to the fitting model to yield the best fit for each sample curve. Impurities having dissimilar valence to the Ga and N host atoms introduce vacancies in accordance with charge neutrality, so vacancy concentration approximately follows the total concentration of point defects. The expression for vacancy
scattering within the present work is the same as discussed by Ratsifaritana et al.\textsuperscript{94} The parameter $\Gamma$ is the phonon scattering factor arising from a) impurity mass differences relative to the host atoms and b) the natural isotopic abundance in GaN, both of which are calculated in the manner of Slack et al. and Morelli et. al.\textsuperscript{90,93} Accordingly, the values for $\Gamma$ shown in Table 7-4 are calculated based on the fractions of impurities as reported in Table 7-1, in contrast to previously reported estimates of less rigorous origin.\textsuperscript{13} It must be noted that the calculation of $\Gamma$ neglects hydrogen, as it’s not a substitutional impurity within the host lattice. The average acoustic wave velocity, Debye temperature, Grüneisen constant $\gamma$, and factors $b$ and $\beta$ for intrinsic phonon scattering rates are identical between the fitting curves. This means that within the model, the only parameters adjusted to accommodate the experimental results are the vacancy concentration and characteristic length. The characteristic lengths required for adequate fitting of the experimental results compare poorly to the wafer thicknesses shown in Table 7-2, as they are much smaller. In addition, the model fits for the HVPE and Ammono 1 samples show a pronounced deviation from the experimental results. When impurity concentrations are on the order of $\sim 10^{17}$ cm$^{-3}$ and higher, discrepancies of this nature typically result from phonon resonance scattering, that is, when point defects introduce a localized impurity mode that causes inelastic phonon scattering.\textsuperscript{110–112} The mechanism of phonon resonance scattering can involve either translational motion\textsuperscript{112} or rotational motion\textsuperscript{113,114} of the point defect within the lattice site in response to excitation by a host lattice phonon. Phonon resonances suppress thermal conductivity in the cryogenic regime and in the present work are believed to be at fault for the apparent lowering of characteristic length with respect to actual crystal dimensions. Some success has been reported with curve fitting that accounts for phonon
resonances within the Debye-Callaway model,\textsuperscript{113,114} but for the sake of simplicity, no attempt is made in the present analysis. Since the HVPE sample has a total impurity concentration two orders of magnitude below that in Ammono 1, the expectation is that it should show less influence from phonon resonances. Nonetheless, the curve for this sample shows indentation between 50 and 140 K, characteristic behavior of phonon resonances.

If the characteristic length is not adjusted within (7.1.1) to produce satisfactory fits to the experimental data, but is instead set to the actual sample thickness, the behavior of thermal conductivity curves given by the Debye-Callaway approximation changes insignificantly. This is demonstrated below in Figure 7-3, which also shows the results for the Na-flux GaN for comparison.
Figure 7-3: Model curves for the studied GaN samples using the Debye-Callaway approximation with characteristic length set to actual sample thickness. Results from the Na-flux sample are shown for purposes of comparison. The trend in thermal conductivity is similar between the simulated curves.

Within the present model according to (7.1.1), impurities are assigned phonon scattering cross sections proportional only to their difference in mass, which is taken into account by the term $\Gamma$ in Table 7-4. Comparing the simulated curves in Figure 7-3 against the experimental data in Figure 7-2 highlights the fact that mass-difference scattering by impurities in GaN is not sufficient to explain the observed measurements. This tendency has been discussed previously for other crystal systems in prior literature.\textsuperscript{111} While lowering the characteristic length in the Debye-Callaway model is able to produce acceptable fits for the present analysis as displayed in Figure 7-2, this treatment is not expected to remain valid at colder temperatures. Were the
3ω method able to achieve reliable measurements on the current samples down into mK temperatures, behavior similar to the results reported by Jezowski et al.\textsuperscript{13,14} is expected until a characteristic inflection point similar in appearance to the trends in Baumann et al.\textsuperscript{112} and Narayanamurti et al.\textsuperscript{114}, which indicates the transition of thermal conductivity to limitation primarily by boundary scattering. Their results show that phonon resonances can be active even to temperatures far below 10 K, which is usually where boundary scattering in pure crystals becomes dominant. The observation that impurity concentrations as low as \( \sim 10^{17} \text{ cm}^{-3} \) produce curvature distortions in the thermal conductivity of GaN is consistent with prior work in other crystal systems, which has demonstrated significant phonon resonances with similar impurity concentrations.\textsuperscript{110–112,114,115,168,171} While prior efforts have produced numerous reports of phonon resonance scattering in the literature, general awareness of this phenomenon appears to be absent in more recent publications. Consequently, a more detailed discussion of this effect benefits the current analysis by placing the observed results in proper context. Figure 7-4 provides an example of phonon resonance scattering from Pohl\textsuperscript{171} and illustrates the effect as seen in the insulating ammonothermal samples.
Figure 7-4: a) Phonon resonance scattering in KCl single crystals doped with nitrite. b) Selected results from Figure 7-2 showing the phonon resonances in the GaN samples with high impurity concentrations. The red arrows highlight the change in curve behavior with increasing impurity concentration.

The resemblance between the trends in Figure 7-4 a) and b) clearly indicates the presence of a similar phonon scattering mechanism at work in GaN. The Na-Flux results in Figure 7-4 b) represent the GaN reference curve as it matches the trend of thermal conductivity vs. temperature for a crystal with low impurity concentrations. While the curvature distortion in the doped KCl crystals is clearly due to the presence of nitrite ions, the principal defects responsible for the behavior observed in the ammonothermal GaN samples is less clear due to the presence of multiple different impurity species. Nonetheless, prior work has shown that different impurity species often have degenerate influence on thermal conductivity, where the substitution of single cation or anion species produces the same temperature dependent trend.\textsuperscript{115}

7.1.4 Conclusions

Thermal conductivity analysis of GaN grown by different techniques using the 3\textomega\, method shows the dominance of extrinsic point defect scattering between 30 K and 295 K and an
inverse relationship with the concentration of impurities. This produces a large variation of results from 164 to 224 Wm\(^{-1}\)K\(^{-1}\) at room temperature within the present work and is believed to be a significant contributing factor behind the disparity of measurements reported in literature. The thermal conductivity results from different crystals begin converging at higher temperature due to increasing Umklapp scattering. Curve fitting using the Debye-Callaway approximation shows qualitative agreement with the experimental results within the measured range of temperatures. The deviation of model curves from experimental data for the HVPE and Ammono 1 samples and the discrepancy between the modeled characteristic lengths and the actual sample thicknesses indicate that phonon resonances are active in GaN.
Chapter 8: Uncertainty analysis on thermal conductivity of bulk GaN

8.1 Introduction
The chapter describes an uncertainty analysis for thermal conductivity results determined by the 3ω method that pertain to measurements from GaN single crystals. Example calculations summarize the technique used in determining absolute uncertainties. Examination of the uncertainties in connection to temperature dependent thermal conductivity reveals an inverse relationship between propagated uncertainty and temperature. Comparison of measured input parameter magnitudes and the final propagated uncertainties explains the observed trend. This work establishes a context by which the significance of results obtained with the 3ω technique can be assessed and discusses approaches toward reduction of overall measurement uncertainty.

8.2 Background
Temperature dependent thermal conductivity measurements expose the temperature regimes where different phonon scattering mechanisms dominate. In technologically important high thermal conductivity materials like GaN, characterization indicates the relative strength of point defect phonon scattering centers in the crystal lattice, which primarily result from impurities incorporated during bulk crystal growth. The 3ω method is particularly useful due to fast equilibration times and insensitivity to the introduction of systematic error from blackbody radiation. However, reported 3ω results frequently neglect to include uncertainty limits. Results obtained using other thermal conductivity measurement techniques prove equally deficient. Consequently, questions regarding reproducibility or measurement
reliability for samples or materials under investigation remain overlooked. However, such concerns justify the need for rigorous uncertainty analysis.

Establishment of statistical uncertainty bounds for temperature dependent $3\omega$ thermal conductivity tests requires repeat testing of the same sample. Following the required thermal stabilization time, this becomes an unpractical approach. A more practical approach to estimate the uncertainty of $3\omega$ thermal conductivity measurements is to account for the individual propagated uncertainties connected to each term within the thermal conductivity equation. This approach assumes that the uncertainty in the collected data follows the limits of measurement accuracy reported for each instrument used during data collection. The instruments and their associated accuracy limits are stated below in Table 8-1.

Table 8-1: Instruments and accuracy limits used in data collection.

<table>
<thead>
<tr>
<th>Term</th>
<th>Instrument</th>
<th>Accuracy Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_\omega$</td>
<td>Keithley 2000</td>
<td>±50 μV ±30 ppm</td>
</tr>
<tr>
<td>$l$</td>
<td>µScope Camera</td>
<td>N/A</td>
</tr>
<tr>
<td>$R$</td>
<td>Keithley 2000</td>
<td>±4 mΩ ±100 ppm</td>
</tr>
<tr>
<td>$dR/dT$</td>
<td>MATLAB</td>
<td>N/A</td>
</tr>
<tr>
<td>$f_2$</td>
<td>SR830 Lock-In</td>
<td>±30 μHz ±25 ppm</td>
</tr>
<tr>
<td>$f_1$</td>
<td>SR830 Lock-In</td>
<td>±30 μHz ±25 ppm</td>
</tr>
<tr>
<td>$V_{3\omega,f_1}$</td>
<td>SR830 Lock-In</td>
<td>±2000 ppm</td>
</tr>
<tr>
<td>$V_{3\omega,f_2}$</td>
<td>SR830 Lock-In</td>
<td>±2000 ppm</td>
</tr>
<tr>
<td>$V_{\text{Diode}*}$</td>
<td>LakeShore 336</td>
<td>±80μV ±50 ppm</td>
</tr>
</tbody>
</table>

*used internally within MATLAB script

The last term in the above table corresponds to the voltage drop across a silicon diode, which acts as a temperature sensor and is embedded in the Janis SHI-4-15 cryostat that controls the sample temperature during each test. Values for this term go unseen by the user during a test,
but the uncertainty calculation of $dR/dT$ requires this accuracy limit and will be discussed later. Silver paste thermally interfaces the sample to the cold finger of the cryostat to minimize the thermal gradient between the sample and the temperature sensor. In the cases of wire length and $dR/dT$, no published accuracy limit exists for the method used in acquisition. For wire length, the uncertainty is taken to be ±1 pixel when measured using the imaging software connected to the microscope. This corresponds to an amount of ±0.96 μm on an absolute scale.

The $dR/dT$ term is the numerically derived slope of a Bloch-Grüneisen function of arbitrary order$^{187}$ fitted to the resistance and temperature measurements from the thin film wire used in the test. Application of the accuracy limits to measured parameters yields absolute uncertainties in relation to calculated $3\omega$ thermal conductivity results. Table 8-2 shows the room temperature $3\omega$ thermal conductivity results and their associated absolute uncertainties for the GaN samples tested in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\kappa$ [Wm$^{-1}$K$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammono 1, Compensated</td>
<td>164 ± 3</td>
</tr>
<tr>
<td>Ammono 2, Compensated</td>
<td>196 ± 4</td>
</tr>
<tr>
<td>Ammono 3</td>
<td>184 ± 4</td>
</tr>
<tr>
<td>HVPE</td>
<td>224 ± 5</td>
</tr>
<tr>
<td>Na-Flux</td>
<td>201 ± 7</td>
</tr>
</tbody>
</table>

8.3 Uncertainty Analysis

The following discussion describes the methodology used in obtaining the uncertainties stated in Table 8-2. Fractional uncertainties of each measured datum are added in quadrature
according to the quadratic sum method described by Taylor.\textsuperscript{192} The multiplication and division of measured values in the \(3\omega\) thermal conductivity expression necessitates the use of fractional uncertainties in order to avoid the problem of adding dissimilar quantities for the express purpose of uncertainty propagation. Summation in quadrature assumes that the uncertainties of the collected data are independent, random, and follow a normal distribution. The assumption of independence holds for all unique variables in the \(3\omega\) thermal conductivity expression. As a result, the uncertainties for the starting and ending excitation frequencies must first be totaled prior to summation in quadrature. The uncertainties of the \(3\omega\) voltage responses receive this same treatment. Since thermal conductivity is a function of several variables, obtaining expressions for the relevant fractional uncertainties involves division of the magnitude of each term-specific partial derivative of the \(3\omega\) thermal conductivity equation by the original thermal conductivity expression. The terms and their resulting associated fractional uncertainty expressions are shown below in Table 8-3.
Table 8-3: Terms in the 3ω thermal conductivity expression and their fractional uncertainties.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Fractional Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_\omega$</td>
<td>$3 \frac{\Delta V_\omega}{V_\omega}$</td>
</tr>
<tr>
<td>$l$</td>
<td>$\frac{\Delta l}{l}$</td>
</tr>
<tr>
<td>$R$</td>
<td>$2 \frac{\Delta R}{R}$</td>
</tr>
<tr>
<td>$\frac{dR}{dT}$</td>
<td>$\Delta \frac{dR}{dT} / \frac{dR}{dT}$</td>
</tr>
<tr>
<td>$f_2$</td>
<td>$\frac{\Delta f_2}{f_2} (\ln (f_2 / f_1))^{-1}$</td>
</tr>
<tr>
<td>$f_1$</td>
<td>$\frac{\Delta f_1}{f_1} (\ln (f_2 / f_1))^{-1}$</td>
</tr>
<tr>
<td>$V_{\alpha, f_1}$</td>
<td>$\frac{\Delta V_{\alpha, f_1}}{V_{\alpha, f_1}}$</td>
</tr>
<tr>
<td>$V_{\alpha, f_1}$</td>
<td>$\frac{\Delta V_{\alpha, f_1}}{V_{\alpha, f_1}}$</td>
</tr>
</tbody>
</table>

In keeping with the summation of fractional uncertainties in quadrature, the total relative uncertainty for thermal conductivity as determined by the 3ω method is therefore:

$$\frac{\Delta \kappa}{\kappa} = \sqrt{\left(3 \frac{\Delta V_\omega}{V_\omega}\right)^2 + \left(\frac{\Delta l}{l}\right)^2 + \left(2 \frac{\Delta R}{R}\right)^2 + \left(\frac{\Delta \frac{dR}{dT}}{\frac{dR}{dT}}\right)^2 + \left(\ln (f_2 / f_1)\right)^2 \left(\frac{\Delta f_2}{f_2} + \frac{\Delta f_1}{f_1}\right)^2 + \left(\frac{\Delta V_{\alpha, f_1}}{V_{\alpha, f_1}} + \frac{\Delta V_{\alpha, f_1}}{V_{\alpha, f_1}}\right)^2}$$

The final result from the above expression is multiplied by the value from the 3ω thermal conductivity equation in order to obtain the absolute uncertainty. MATLAB numerical analysis software is used to handle the computation of the above expression and the thermal conductivity equation at each temperature. Values measured at 295 K for the sample Ammono 3 from Table 8-2 are shown below in Table 8-4 as an example of uncertainty propagation.
Table 8-4: Propagation of numerical uncertainties for Ammono 3 at 295 K.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Instrument Readout</th>
<th>Uncertainty</th>
<th>Fractional Uncertainty</th>
<th>Numerical Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_\omega$</td>
<td>1.0308 V</td>
<td>$8 \times 10^{-3}$ V</td>
<td>$\frac{8 \times 10^{-3} V}{1.0308 V}$</td>
<td>$2 \times 10^{-4}$</td>
</tr>
<tr>
<td>$l$</td>
<td>9.8705 $\times 10^{-4}$ m</td>
<td>$9.6 \times 10^{-7}$ m</td>
<td>$\frac{9.6 \times 10^{-7} m}{9.8705 \times 10^{-4} m}$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$R$</td>
<td>51.4859 $\Omega$</td>
<td>$9.2 \times 10^{-3}$ $\Omega$</td>
<td>$\frac{9.2 \times 10^{-3} \Omega}{51.4859 \Omega}$</td>
<td>$4 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\frac{dR}{dT}$</td>
<td>0.190561 $\frac{\Omega^*}{K}$</td>
<td>$6 \times 10^{-6} \frac{\Omega^*}{K}$</td>
<td>$\frac{6 \times 10^{-6} \frac{\Omega}{K}}{0.190561 \frac{\Omega}{K}}$</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>$f_2$</td>
<td>4500 Hz</td>
<td>0.1 Hz</td>
<td>$\frac{0.1 Hz}{4500 Hz} \left( \log \frac{4500 Hz}{3000.0 Hz} \right)^{-1}$</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>$f_1$</td>
<td>300.0 Hz</td>
<td>$8 \times 10^{-3}$ Hz</td>
<td>$\frac{8 \times 10^{-3} Hz}{300.0 Hz} \left( \log \frac{4500 Hz}{3000.0 Hz} \right)^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$V_{300,f_i}$</td>
<td>5.060 $\times 10^{-4}$ V</td>
<td>$1 \times 10^{-6}$ V</td>
<td>$\frac{1 \times 10^{-6} V}{0.0909 \times 10^{-3} V}$</td>
<td>$2 \times 10^{-2}$</td>
</tr>
<tr>
<td>$V_{300,f_2}$</td>
<td>4.151 $\times 10^{-3}$ V</td>
<td>$8 \times 10^{-7}$ V</td>
<td>$\frac{8 \times 10^{-7} V}{0.0909 \times 10^{-3} V}$</td>
<td></td>
</tr>
</tbody>
</table>

*Value derived from Bloch-Grüneisen fitting curve within MATLAB script.

All digits of the values reported in the instrument readout column are significant figures. The values from the third and final column of Table 8-4 represent intermediate values obtained during execution of the MATLAB script, but are rounded in the table for the sake of simplicity. The numerical results are handled according to the summation in quadrature equation (squaring, summing, and taking square root of the sum). In the above instance, the result returned from this expression is 0.02003. In order to get the absolute uncertainty, this result is multiplied by the calculated thermal conductivity of 183.9 Wm$^{-1}$K$^{-1}$ to yield ±3.7 Wm$^{-1}$K$^{-1}$. Reporting up to four significant figures in thermal conductivity is consistent with the least
number of significant figures in the measured quantities, but in practice, results are rounded to the nearest one to reduce the number of digits in the absolute uncertainty, producing $184 \pm 4$ Wm$^{-1}$K$^{-1}$ at 295 K for sample Ammono 3. The plot in Figure 8-1 shows the entire temperature dependent data set for this sample.

![Graph showing temperature dependent thermal conductivity for Ammono 3.](image)

**Figure 8-1:** Temperature dependent thermal conductivity curve for GaN single crystal Ammono 3.

The inverse relationship between absolute uncertainty and temperature is clearly represented in the data and requires further investigation. Accordingly, Table 8-5 presents the propagation of uncertainties for Ammono 3 at 30 K in order to reveal which terms contribute the most towards this trend.
Table 8-5: Propagation of numerical uncertainties for Ammono 3 at 30 K.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Instrument Readout</th>
<th>Uncertainty</th>
<th>Fractional Uncertainty</th>
<th>Numerical Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_\omega$</td>
<td>0.36669V</td>
<td>6.1×10^-5 V</td>
<td>$\frac{6.1\times10^{-5}V}{0.36669V}$</td>
<td>5×10^-4</td>
</tr>
<tr>
<td>$l$</td>
<td>9.8705×10^-3 m</td>
<td>9.6×10^-7 m</td>
<td>$\frac{9.6\times10^{-7} m}{9.8705\times10^{-3} m}$</td>
<td>1×10^-3</td>
</tr>
<tr>
<td>$R$</td>
<td>9.4167Ω</td>
<td>4.9×10^-3 Ω</td>
<td>$\frac{2\times4.9\times10^{-3} \Omega}{9.4167\Omega}$</td>
<td>10×10^-4</td>
</tr>
<tr>
<td>$\frac{dR}{dT}$</td>
<td>4.8559×10^-2 Ω* / K</td>
<td>225×10^-6 Ω* / K</td>
<td>$\frac{225\times10^{-6} \Omega}{4.8559\times10^{-2} \Omega \ / \ K}$</td>
<td>463.3×10^-4</td>
</tr>
<tr>
<td>$f_2$</td>
<td>4500Hz</td>
<td>0.1Hz</td>
<td>$0.1Hz \left(\frac{\ln(4500Hz)}{\ln(300.0Hz)}\right)^{-1}$</td>
<td>1.8×10^-5</td>
</tr>
<tr>
<td>$f_1$</td>
<td>300.0Hz</td>
<td>8×10^-3 Hz</td>
<td>$8\times10^{-3} Hz \left(\frac{\ln(4500Hz)}{\ln(300.0Hz)}\right)^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$V_{3\omega,f_1}$</td>
<td>4.311×10^-4 V</td>
<td>9×10^-7 V</td>
<td>$\frac{9\times10^{-7} V}{0.0086\times10^{-7} V}$</td>
<td>20×10^-2</td>
</tr>
<tr>
<td>$V_{3\sigma,f_1}$</td>
<td>4.225×10^-4 V</td>
<td>8×10^-7 V</td>
<td>$\frac{8\times10^{-7} V}{0.0086\times10^{-7} V}$</td>
<td></td>
</tr>
</tbody>
</table>

*Value derived from Bloch-Grüneisen fitting curve within MATLAB script.

Treatment of the numerical results from the final column in the same manner as before yields 0.20006. Multiplication of this by the calculated thermal conductivity of 633 Wm\(^{-1}\)K\(^{-1}\) produces an absolute uncertainty of 127 Wm\(^{-1}\)K\(^{-1}\) to yield a result of 633 ±127 Wm\(^{-1}\)K\(^{-1}\).

Justification for three significant figures in the absolute uncertainty comes from three facts: (1) a minimum of four significant figures is maintained in the measured quantities used in calculating propagated uncertainty, (2) the last significant figure of both the thermal conductivity and absolute uncertainty must be of the same order of magnitude, and (3) rounding the uncertainty to fewer significant figures in the present example equally constrains
the thermal conductivity and produces the untenable outcome of results with a quantized appearance. Notable increases of uncertainty contribution come from $dR/dT$ and the $3\omega$ voltage response, with gains of two and one order of magnitude, respectively. The $3\omega$ voltage response has the single largest contribution to propagated uncertainty in both examples. Efforts directed toward reducing the size of this error would be of benefit based on the uncertainty analysis. Nonetheless, the hundred-fold gain in uncertainty for $dR/dT$ demands further consideration. In fact, the $dR/dT$ term introduces a physical limitation to the $3\omega$ technique in that as temperature decreases, electron-phonon interactions decrease, lowering measured resistance. At temperatures below 30 K, phonon-electron scattering rates decrease, thus the resistance in the $3\omega$ metallization becomes limited more by crystalline defects like impurities and grain boundaries. This finite limit is the residual resistance. As resistance measurements approach the residual resistance, the value of $dR/dT$ reduces until it reaches zero at the limit. Based on this, thermal conductivity measurements with the $3\omega$ method at temperatures significantly below 30 K are challenging. Using dilute magnetoresistive alloys as the metallization layer provides a solution to achieve lower propagated uncertainty as they demonstrate Curie temperatures in the region of typical $dR/dT$ collapse.193–195

8.4 Uncertainty Analysis of $dR/dT$

Calculation of the uncertainty relevant to $dR/dT$ differs from the terms previously discussed due to the fact that it is not a measured quantity. This presents a difficult impediment to uncertainty quantification. A MATLAB based solution was developed to overcome this limitation. The approach used in the present analysis works by converting the known
uncertainty in $V_{\text{Diode}}$ from Table 8-1 to the uncertainty in $dR/dT$. The LakeShore 336 instrument calculates temperature by matching $V_{\text{Diode}}$ measurements reported from inside the cryostat with temperature from a reference calibration curve. The diode temperature sensor relevant to the present work is a DT-670, which has a corresponding calibration curve provided in the instrument reference literature. During execution, the MATLAB script references a spreadsheet containing the transcribed calibration data. The script generates matrices of the input data and creates a piecewise cubic Hermitian interpolating polynomial (PCHIP) fitting curve for $V_{\text{Diode}}$ and temperature data. This is necessary for two reasons: (1) not all the temperatures in the calibration curve match with setpoint temperatures used in a thermal conductivity test, (2) there is a singularity in the calibration curve caused by the onset of carrier freeze-out in the diode. The PCHIP fit creates a smooth interpolation from one datum to the next despite the singularity as demonstrated below in Figure 8-2.
While the PCHIP fit to the calibration data doesn’t change between thermal conductivity measurements on different samples, this procedure is necessary because of the sample-specific input data that the script references to the fit. Upon completion of the PCHIP curve synthesis, MATLAB matches the setpoint temperatures from the thermal conductivity test with interpolated diode voltages. The script calculates absolute uncertainties for the interpolated voltages in accordance with the $V_{\text{diode}}$ specification in Table 8-1. The script then adds absolute voltage uncertainties to the interpolated voltages previously matched to the temperature setpoints to make voltage overestimates. The script takes these voltage overestimates and references them back to the PCHIP curve to obtain temperature underestimates. The script feeds the temperature underestimates to the Bloch-Grüneisen function used for fitting the
resistance and temperature data. Figure 8-2 displays typical resistance vs. temperature data and the associated Bloch-Grüneisen fitting curve.

Figure 8-3: Typical resistance vs. temperature and Bloch-Grüneisen fit for a thin film 3ω wire.

Finally, the script derives the slope of the Bloch-Grüneisen function at the temperature underestimates to produce $dR/dT$ values. The difference between $dR/dT$ results at the temperature setpoints and the temperature underestimates corresponds to the absolute uncertainty in $dR/dT$ for every setpoint temperature in a 3ω thermal conductivity test.

**8.5 Systematic Error**

Quantification of systematic error presents a significant challenge within the present analysis. Testing samples in an alternate 3ω instrument offers the option of determining if systematic error is present, but this method is unable to tell the user which system is affected.
Benchmarking provides an acceptable solution, whereby 3ω results obtained in the present work are compared to thermal conductivity results from literature. Unfortunately, literature results most often contain no uncertainty estimates to compare during benchmarking. However, such an exercise helps determine if the instrumentation reports accurate results. Consequently, 3ω system performance was checked through thermal conductivity testing of different reference materials. Figure 8-4 shows 3ω measurement results for the III-V compound semiconductors GaP, GaAs, InP, and InAs and compares them to values reported in literature.
Figure 8-4: Results from thermal conductivity tests of a) GaP,\textsuperscript{130,131} b) GaAs,\textsuperscript{132} c) InP,\textsuperscript{133} and d) InAs,\textsuperscript{134}. Red curves represent data collected using the 3ω method within the present work. Other curves are from prior literature.

Plots a) through d) clearly demonstrate agreement between 3ω method results and literature. If large systematic errors are present, one expects disagreement between the red curves and values reported in literature, but no such discrepancy appears within the present work. Systematic error likely affects measurements within the present analysis, but upon review of Figure 8-4, any such effects produce negligible deviations in the results.
8.6 Conclusion

This chapter demonstrated a rigorous account detailing the propagated uncertainties involved in the calculation of thermal conductivity using the $3\omega$ method. The propagated uncertainty exhibited an inverse relationship with temperature that depended heavily on the contribution from the $3\omega$ voltage response. The individual uncertainty arising from the $dR/dT$ term increased the most with decreasing temperature and became significant as the residual resistance limit was approached. Contributions from systematic error sources did not appear to adversely affect the measurements.
Chapter 9: High temperature vacuum probe system for semiconductor characterization

9.1 Introduction

This chapter describes a custom designed instrument for measuring III-Nitride devices at temperatures up to and exceeding 1000°C. The high operating temperatures require special considerations to ensure dependable system performance and longevity. The following account provides details of construction regarding components and subsystems of the final instrument and the reasoning used in their design and material composition.

Development of electronic devices for use in high temperature applications has received considerable interest. Recent initiatives have focused on creation of sensors for high temperature environments, aircraft and rocket propulsion systems, aircraft distributed control systems, engine mounted automotive electronics, and NASA missions to Venus. Due to the wide bandgap of GaN and AlN, these materials are ideally suited for semiconductor devices operating at higher temperatures. In order to conduct research on the high temperature physics of devices composed of these materials and their alloys, it is necessary to use a tool that allows for testing of semiconductor material and devices at high temperature in a controlled environment. While off-the-shelf probe systems are available from Janis (at the time of this writing), the quoted maximum achievable temperature for their products is just 675 K. Considering that AlN single crystals have proven to be stable at temperatures up to 1373 K, an off-the-shelf system will not suffice to meet the need for high temperature characterization. It is therefore necessary to design a system capable of stable operation up to and exceeding 1273 K. A detailed description of the system and components
necessary for accomplishing the goal of high temperature characterization of AlN, GaN, and their alloys is the subject of this chapter.

9.2 Description

The proposed high temperature probe system is shown below in Figure 9-1. It has a total of eight horizontal feedthroughs. Six of these are 2.75” CF flanges that can connect directly to triple axis manipulators for positioning of electrical probes. The other two are 6” CF flanges, one of which has an attached turbomolecular pump for direct pumping of the chamber.

![High temperature UHV probe system with top viewport door open.](image)

The central chamber has a 10 inch CF flange on both the top and the bottom as well as a 6 inch CF flange on both the front and back. A water cooled jacket surrounds the central cylinder of the chamber and provides even cooling during high temperature operation of the system. The central chamber is shown below in Figure 9-2.
The custom built flange that attaches to the bottom of the chamber can be seen below in Figure 9-3. It has a total of six feedthrough ports. Four are 1.33 inch and the other two are 2.75 inch. Two of the 1.33” ports have electrical feedthroughs for high current and the other two have thermocouple feedthroughs. One of the 2.75” ports has a Pfeiffer vacuum gauge attached while the other is vacant. There is a stud attached to the center of the vacuum side of the flange in order to accommodate a rigid shaft coupler, which is supplied by McMaster-Carr and has part # 61005K422. The shaft coupler joins the binding post for the heater module to the flange. The binding post is a shortened version of a hardened steel precision shaft supplied by McMaster-Carr and has part # 8350T650. The shaft and coupler allow for solid attachment of the heater module to the flange and ensure stability during thermal cycling.
The core of the instrument is the heater module, which is a modified version of Heatwave Labs part # 101868. It can be seen below in Figure 9-4. It is capable of stable operation up to 1473 K in vacuum. It relies on a resistive heating element coiled inside a 2” diameter molybdenum disc. The side and bottom of the heating disc are surrounded by several layers of inconel foil to reduce radiative heat transfer to the surroundings. For an analysis of radiation heat transfer both with and without thermal shielding, see Appendix A.
Figure 9-4: Top view (left) and isometric view (right) of the heater module. Three sample clips are available to secure a sample in place during thermal cycling. The heater cathode and anode interconnects are visible at the bottom of the image at right.

Three mesas are visible on the outer radiation shield of the heater module. These are used for attachment of a horizontal radiation shield that is used in the instance that the sample under test has relevant test features much smaller than the 2” diameter of the heating disc. The horizontal radiation shield is shown below in Figure 9-5.
Figure 9-5: Horizontal radiation shield (left) and shield/heater module assembly (right). The shield decreases radiation losses towards the top of the chamber and allows the heater to more quickly reach test temperature.

A custom built quick entry door having a 2.75” CF flange in the middle is attached to the top flange of the chamber. The quick entry door can be seen below in Figure 9-6. The door features a high temperature Kalrez seal with a maximum operation temperature of 600 K. The lid of the viewport door has a water cooling trace to allow for cooling during operation, as the viewport door is subjected to the most intense exposure of thermal radiation from the heater module.
Figure 9-6: Quick entry door showing 2.75” viewport window on top (left) and the internal water cooling trace (right). The hinge of the viewport door was inverted from the normal configuration in order to allow for a design that maximized the length of water cooling trace. Had the hinge been left in the standard configuration, it would require placement of the water inlet and outlet outside of the radial angle occupied by the hinge, thereby decreasing the active cooling area.

The probes that make contact with the devices must be composed of a material that allows for repeated operation at extreme temperatures. Standard beryllium-copper probes melt between 1138 and 1228 K, much too low for use in the present system. Two material options available for high temperature application are tungsten carbide (WC) and tungsten-rhenium (WRe). Both systems resist formation of surface oxides during repeated use at high temperature. At the time of this writing, tungsten carbide probes were available as an off-the-shelf purchase from Semprex Corporation while tungsten rhenium needles were available as a special order from Accuprobe Corporation. A batch of 20 WC needles and one of 25 WRe needles were purchased from these respective firms for initial testing purposes. In addition to the temperature stability of the probes, the probe mounting arm must also be of similar temperature stability. Standard probe arms are typically fabricated from brass, which melts between 1173 and 1213 K, also
too low to meet the needs of the present system. Therefore, the material of the probe mounting arm designed for the system is molybdenum, which has a melting point of 2896 K. The probe and mounting arm assembly are shown below in Figure 9-7. The probe rests in a slot machined into the head of the mounting arm and is secured in place by a molybdenum washer with titanium screw and nut.

Figure 9-7: Probe needle and mounting arm assembly.

The probe and mounting arm assembly are attached to the vacuum side of an electrical feedthrough with a rigid shaft coupler. The electrical feedthrough central conductor is composed of nickel metal and provides electrical continuity between the outside of the chamber and the end of the probe needle on the inside. The electrical feedthrough is shown below in Figure 9-8. It is a customized version of Kurt J. Lesker part # EFT0511253. It is longer than the stock version and has a flatted end.
In addition, the electrical feedthrough mechanically couples the probe needle to a triple axis positioner on the outside of the chamber. The triple axis positioner is supplied by Thermionics Vacuum Products and has part number EC-1.39-2. It can be seen below in Figure 9-9. The triple axis positioner allows for repositioning of the electrical probe during device testing. This allows the user to move between multiple devices on a single wafer at any temperature.
The atmosphere side of the electrical feedthrough is covered by a custom guard machined from clear PVC pipe. The guard prevents accidental contact of the energized feedthrough conductor during testing. In addition, an aluminum extrusion surrounds the atmosphere side of the electrical feedthrough conductor and has a miniature cooling fan attached to assist in dissipation of heat conducted along the length of the electrical feedthrough during high temperature testing. The full assembly from the tip of the probe needle to the atmosphere side of the electrical feedthrough is shown in Figure 9-10 below. The rigid shaft coupler is supplied by McMaster-Carr and has part # 6099K210. It allows for easy maintenance of probe needles as just one screw on the coupler can be loosened to remove the probe mounting arm.
The screws of the rigid shaft coupler contact flatted areas that are machined into the back of the probe mounting arm and the end of the electrical feedthrough. The clear plastic guard is visible at the far left, while the cooling fan and aluminum extrusion are visible inside. The object attached to the middle of the guard is an electrical interconnect for the 12 VDC cooling fan power feed.

The length between the tip of the probe needle and the vacuum side of the feedthrough flange is 13.75 inches, which poses some potential problems. First, any vibration incident on the chamber will cause vibration of the entire probing arm as it acts like a cantilever beam. If the amplitude of vibration is large enough, this could cause breakage of the tungsten carbide probes at the interface of the tip and contact pad during a test, as tungsten carbide is a ceramic material and exhibits brittle fracture. Second, significant deflection resulting from loading at the probe end of the cantilever beam can cause plastic deformation along the length of the electrical feedthrough rod. The risk of plastic deformation can be mitigated by selecting a material having high yield strength. At the time of this writing, the standard options for feedthrough conductor material included copper, stainless steel, and nickel metal, which have yield strengths of 70, 207, and 345 MPa, respectively. As nickel has the highest yield strength it is the obvious choice as the feedthrough conductor material.

The high temperature probe system is mounted on a cart that houses all the peripheral equipment necessary for operation. A schematic showing the chamber and cart is shown below in Figure 9-11.
Figure 9-11: High temperature probe system with cart. Peripheral equipment is visible below the table top.

The peripheral equipment necessary for the chamber includes a DC power supply for the heater module, temperature controller for interfacing with the power supply, vacuum pumping system, source/measure unit for device analysis, 12 VDC power supply for the cooling fans, a long working distance microscope with attached camera (not shown in Figure 9-11), and water cooling lines for the chamber jacket and viewport door. A computer interfaces with the microscope camera and the source/measure unit for image capture and parameter control during tests. A table containing the more important peripheral equipment items can be seen below in Table 9-1.
Table 9-1: List showing peripheral equipment needed for operation of the high temperature probe system.

<table>
<thead>
<tr>
<th>Item</th>
<th>Model Number</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC Power Supply</td>
<td>ESS 40-375-2-D-RSTL</td>
<td>TDK-Lambda</td>
</tr>
<tr>
<td>Temperature Controller</td>
<td>CN8PT-144-006</td>
<td>Omega</td>
</tr>
<tr>
<td>Vacuum Pumping System</td>
<td>PM 163 936 AT</td>
<td>Pfeiffer Vacuum Inc.</td>
</tr>
<tr>
<td>Source/Measure Unit</td>
<td>B2901A</td>
<td>Keysight Technologies</td>
</tr>
<tr>
<td>Microscope</td>
<td>Omano OM99-V7</td>
<td>Microscope LLC</td>
</tr>
<tr>
<td>Scope Camera</td>
<td>Summit D3K2-14</td>
<td>Microscope LLC</td>
</tr>
</tbody>
</table>

9.3 Summary

Characterization of devices operating at temperatures near 1000°C and higher requires specialized analysis equipment. The instrumentation needs to withstand repeated cycling to temperature extremes while demonstrating minimal performance degradation. The high temperature vacuum probe system described in this chapter allows for testing devices up to 1473 K and is robust enough to operate continuously. It is expected that the instrument will be able to meet the needs of both short term and long term high temperature research goals as sufficient effort has been devoted to ensure its utility and durability over extended time scales.
Chapter 10: Conclusions and potential for future work

10.1 Conclusions

The prior literature results summarized in Chapter 3 demonstrate that crystalline defects significantly affect the temperature-dependent thermal conductivity in non-metallic solids at temperatures below 100 K. The influence of crystal boundaries, dislocations, and nanoscale secondary phases typically appears at temperatures below 10 K where thermal conductivity shows a dependence proportional to $T^3$. The influence of point defects on thermal conductivity shows the greatest influence at the maximum and closely adjacent temperatures. Phonon resonance effects appear when point defects introduce localized vibrational modes that scatter host lattice phonons within this regime, causing significant reductions in thermal conductivity. At temperatures significantly higher than the maximum, phonons scatter more off of each other than crystalline defects in 3-phonon/Umklapp processes.

State-of-the-art bulk crystals of the III-Nitrides having low dislocation density and structural defects were selected for this work in order to determine which phonon scattering mechanisms are most dominant in these materials. Since the lowest measurement temperature in this work was 30 K, contributions from scattering sources in the $T^3$ regime were not observed. However, the measurements performed on AlN and GaN in this work reveal that point defects significantly influence the thermal conductivity of these materials, even up to room temperature. Also active in these materials are low temperature phonon resonances due to incorporated impurities. Their appearance in these materials reveals that the incorporated impurities frequently have significant motile degrees of freedom within the host lattice sites they occupy, although it remains unclear whether their motions are translational or rotational.
in character. The principle impurity responsible for the observed resonances is equally unclear due to the presence of multiple species. The influence of Umklapp processes is clear in both materials, as curves from different crystals show convergence behavior as temperature increases. The Debye-Callaway model for thermal conductivity is able to produce adequate fits for the experimental data in the case of the GaN and HVPE grown AlN samples, but it fails for PVT grown AlN due to the presence of significant phonon resonances around 60 K. While modeling shows decent fits for the GaN curves, the possibility of phonon resonances below 30 K or influence from nanoscale secondary phases cannot be eliminated. This is indicated by the boundary scattering parameters in Table 7-4, which are significantly lower than the actual thicknesses of the samples.

10.2 Future work

The findings of this work raise new questions that present numerous opportunities for future investigations. Included among these are:

- Isolation of the impurities responsible for phonon resonances in GaN and AlN. The possibility exists that more than one species causes phonon resonances in the III-Nitrides.
- Determination of the effect of point defect interactions on thermal conductivity. Preliminary results suggest that compensation of carbon with silicon in AlN forms a complex that reduces their overall phonon scattering cross section, improving thermal conductivity. Other point defect interactions may also exist in the III-Nitrides.
- Using a different measurement method to extend deep into the boundary scattering regime in order to determine the point at which phonon resonances disappear. This
would present the option to distinguish between curvature distortions caused by true point defect resonances and those caused by nanoscale secondary phases.

- Measurement of thermal conductivity at high temperature. This would show when the dominance of Umklapp processes finally results in the same measured thermal conductivity value between different samples.

- Determination of the thermal attenuation length $\delta$ for the $3\omega$ method using the modified Bessel equations at radius values $0 \leq r \leq \infty$. The original approximation derived by Cahill only assumes a solution at $r = \infty$, which works for calculating thermal conductivity but not for determining the amplitude of the temperature oscillations at any arbitrary distance from the metal wire.
REFERENCES


170 V.V. Kosarev, P.V. Tamarin, and S.S. Shalyt, Physica Status Solidi (b) 44, 525 (1971).


187 D. Cvijovic, Theoretical and Mathematical Physics 166, 37 (2011).


W.J. Pulliam, P.M. Russler, and R.S. Fielder, in Environmental and Industrial Sensing (International Society for Optics and Photonics, 2002), pp. 229–238.


Cryogenic Micromanipulated Probe Stations from Janis Research (2018).

APPENDICES
Appendix A

The net power of radiative heat transfer in vacuum from a gray body to cooler surroundings is understood in terms of the Stefan-Boltzmann Law:

\[ Q = \epsilon A \sigma \left( T_{\text{object}}^4 - T_{\text{surroundings}}^4 \right), \]

where \( \epsilon \) is the emissivity of the gray body, \( A \) is the surface area, \( \sigma \) is the Stefan-Boltzmann constant \( \left( 5.6703 \times 10^{-8} \text{W} / \text{m}^2 \text{K}^4 \right) \), and \( T \) is temperature. If the surroundings reflect thermal radiation, the relationship is represented as radiative heat transfer between two gray bodies.

Assuming both surfaces are infinite and parallel, net thermal power transfer from surface 1 to surface 2 is represented as

\[ Q_{1\rightarrow2} = \Sigma \text{absorbed energy} - \Sigma \text{reflected energy}. \]

Suppose that during an infinitesimal amount of time, the amount of thermal radiation emitted from surface 1 is represented by

\[ Q_1 = \epsilon_1 A \sigma T_1^4. \]

The fraction of this radiation absorbed by surface 2 is equivalent to

\[ \epsilon_2 \left( \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \right). \]

The amount that is reflected from surface 2 back to surface 1 is represented by

\[ (1-\epsilon_2) \left( \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \right). \]

The amount reflected back to surface 2 from this incident radiation is equivalent to

\[ (1-\epsilon_1)(1-\epsilon_2) \left( \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \right). \]

From this amount of incident radiation, surface 2 absorbs an amount given by
\[ \epsilon_2 (1 - \epsilon_1) (1 - \epsilon_2) \left( \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \right). \]

With one more round trip of reflection cycles the radiation absorbed by surface 2 becomes

\[ \epsilon_2 (1 - \epsilon_1)^2 (1 - \epsilon_2)^2 \left( \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \right). \]

Continued reflections increase the exponents assigned to the terms in parenthesis, and the total amount of thermal radiation transferred from surface 1 to surface 2 is represented by an infinite summation:

\[
Q_{(1-2)} = \epsilon_2 \left( \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \right) + \epsilon_2 (1 - \epsilon_1) (1 - \epsilon_2) \left( \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \right) \\
+ \epsilon_2 (1 - \epsilon_1)^2 (1 - \epsilon_2)^2 \left( \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \right) + \ldots \\
+ \epsilon_2 (1 - \epsilon_1)^N (1 - \epsilon_2)^N \left( \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \right)
\]

This can be simplified to

\[
Q_{1-2} = \epsilon_2 \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \sum_{N=0}^{\infty} (1 - \epsilon_1)^N (1 - \epsilon_2)^N.
\]

The infinite summation term on the right is a geometric series of the form

\[
\sum_{N=0}^{\infty} x^N,
\]

where \( x = (1 - \epsilon_1) (1 - \epsilon_2) \). For the range of values \(-1 < x < 1\), the summation converges as \( N \to \infty \) such that

\[
\sum_{N=0}^{\infty} x^N = \frac{1}{1-x},
\]

Since emissivity for gray bodies is always such that \( 0 < \epsilon < 1 \), the resulting expression becomes
\[ Q_{1-2} = \epsilon_2 \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \left( \frac{1}{\epsilon_1 (1 - \epsilon_1)(1 - \epsilon_2)} \right). \]

Rearrangement of this equation produces
\[ Q_{1-2} = \epsilon_2 \epsilon_1 A \sigma \left( T_1^4 - T_2^4 \right) \left( \frac{1}{\epsilon_1 + \epsilon_2 - \epsilon_1 \epsilon_2} \right). \]

This can finally be reduced to
\[ Q_{1-2} = \frac{A \sigma \left( T_1^4 - T_2^4 \right)}{\left( \frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1 \right)}. \]

In the case where a radiation shield treated as a gray body having equivalent geometry to surfaces 1 and 2 is placed between the surfaces, the net power of radiation transferred from surface 1 to surface 2 becomes
\[ Q_{1-2} = \frac{A \sigma \left( T_1^4 - T_2^4 \right)}{\left( \frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1 \right) + \left( \frac{1}{\epsilon_{3,1}} + \frac{1}{\epsilon_{3,2}} - 1 \right) + \ldots + \left( \frac{1}{\epsilon_{n,1}} + \frac{1}{\epsilon_{n,2}} - 1 \right)}, \]

where \( \epsilon_{3,1} \) and \( \epsilon_{3,2} \) are the emissivities of the intervening shield surface that faces surface 1 and 2, respectively. With an amount \( n \) of gray bodies between surfaces 1 and 2, the net radiation transfer between surfaces 1 and 2 becomes
\[ Q_{1-2} = \frac{A \sigma \left( T_1^4 - T_2^4 \right)}{\left( \frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1 \right) + \left( \frac{1}{\epsilon_{3,1}} + \frac{1}{\epsilon_{3,2}} - 1 \right) + \ldots + \left( \frac{1}{\epsilon_{n,1}} + \frac{1}{\epsilon_{n,2}} - 1 \right)}. \]

In the case where all emissivity values are equal, the expression reduces to
The effectiveness of additional shields at reducing the radiative heat transfer between surfaces 1 and 2 can be analyzed by inserting the above expression into a ratio that accounts for thermal transfer in the case of no shields and n shields.

\[
\frac{\frac{A\sigma(T_1^4 - T_2^4)}{\left(\frac{2}{\epsilon} - 1\right)}}{\frac{A\sigma(T_1^4 - T_2^4)}{(n+1)\left(\frac{2}{\epsilon} - 1\right)}} = \frac{A\sigma(T_1^4 - T_2^4)}{\left(\frac{2}{\epsilon} - 1\right)}
\]

This expression reduces to

\[
\frac{n}{1+n}.
\]

In the case of four radiation shields where all emissivities are equivalent, the reduction of thermal transfer is thereby equivalent to 80%.
This appendix contains the necessary code to perform 3ω thermal conductivity calculations and simulation using the Debye-Callaway approximation.

MATLAB code: 3ω Thermal Conductivity Calculation

```matlab
% 3rd Harmonic Response Analysis
clc;
clear all;
close all;

% Get the Excel Data Files
[infile1n, infile1p] = uigetfile('*.xls')
infile1 = [infile1p, infile1n]

% Telling MATLAB where the data is in the Excel file
fresponse = xlsread(infile1, 1);
resistance = xlsread(infile1, 2);

% 3-omega wire lengths
L = [1e-3, 1e-3, 1e-3];

% Definition of variable matrices.
T_1 = resistance(:, 1);
MeasuredR_L1 = resistance(:, 2);
MeasuredR_L2 = resistance(:, 3);
MeasuredR_L3 = resistance(:, 4);
CorrectedR_L1 = MeasuredR_L1;
CorrectedR_L2 = MeasuredR_L2;
CorrectedR_L3 = MeasuredR_L3;
ExcHz = fresponse(1, 3:end-1);
T_2 = fresponse(2:3:end, 1);
Vomega_L1 = fresponse(2:3:end, 2);
Vomega_L2 = fresponse(3:3:end, 2);
Vomega_L3 = fresponse(4:3:end, 2);
Iomega_L1 = fresponse(2:3:end, end);
Iomega_L2 = fresponse(3:3:end, end);
Iomega_L3 = fresponse(4:3:end, end);
R_L1 = Vomega_L1./Iomega_L1;
R_L2 = Vomega_L2./Iomega_L2;
R_L3 = Vomega_L3./Iomega_L3;

% Defining size of 3rd harmonic response data array.
V3omegaMatrixmV = zeros(size(fresponse, 1) - 1, length(ExcHz));

% Builds the 3rd harmonic response data array based on size of input array.
for i = 1:length(ExcHz)
    V3omegaMatrixmV(:, i) = fresponse(2:end, 2+i);
end
```
end
V3omegaMatrixmV;
V3omegaMatrix=V3omegaMatrixmV/1;
V3omega_L1=V3omegaMatrix(1:3:end,:);
V3omega_L2=V3omegaMatrix(2:3:end,:);
V3omega_L3=V3omegaMatrix(3:3:end,:);

% Defines parameters for wire resistance and the Bloch-Gruneisen
% regression function used for fitting of the resistance vs. T curves.
Lt=9e-5;
h=220e-9;
wi=10e-6;
wf=100e-6;
funcL1L3 = @(p,x) (Bloch_GruneisenFunction2(p,x)).*(2*(415e-6/(wf*h)+integral(@(l)(1./(h*wi+h*l*(wf-wi)/Lt)),0,Lt)+100e-6/(wi*h))+1e-3/(wi*h));
funcL2 = @(p,x) (Bloch_GruneisenFunction2(p,x)).*(2*(1030e-6/(wf*h)+integral(@(l)(1./(h*wi+h*l*(wf-wi)/Lt)),0,Lt)+100e-6/(wi*h))+1e-3/(wi*h));

guessesL1=[430.2491e-009 195.3375e+000 13.0528e+000 12.6968e+000 27.3669e-009];
% guessesL1=[396.6532e-009 194.9838e+000 13.1628e+000 12.8065e+000 25.2106e-009];
% guessesL2=[421.6087e-009 195.9770e+000 12.7617e+000 12.4051e+000 27.4714e-009];
% guessesL3=[451.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL2=[495.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 42.3669e-009];
% guessesL3=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL3=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL1=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL3=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL1=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL3=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL1=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL3=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL1=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];
% guessesL3=[515.2491e-009 135.3375e+000 12.7528e+000 12.6968e+000 44.3669e-009];

if isequal(zeros(size(CorrectedR_L1,2),length(CorrectedR_L1))',CorrectedR_L1)
    coeffsL1=[0 0 0 0 0];
else
    coeffsL1=nlinfit(T_1,CorrectedR_L1,funcL1L3,guessesL1,opts);
end
if isequal(zeros(size(CorrectedR_L2,2),length(CorrectedR_L2))',CorrectedR_L2)
    coeffsL2=[0 0 0 0 0];
else
    coeffsL2=nlinfit(T_1,CorrectedR_L2,funcL2,guessesL2,opts);
end
if isequal(zeros(size(CorrectedR_L3,2),length(CorrectedR_L3))',CorrectedR_L3)
    coeffsL3=[0 0 0 0 0];
else

coeffsL3 = nlinfit(T_1, CorrectedR_L3, funcL1L3, guessesL3, opts);
end
% coeffs=guesses;

% Defining resistance values for all wires based on regression fit.
Ts = linspace(10, 330, 3300);

if coeffsL1 == [0 0 0 0 0];
    Rvals_L1 = 0;
    T_L1 = zeros(size(T_2, 2), length(T_2))';
else
    Rvals_L1 = funcL1L3(coeffsL1, Ts);
    T_L1 = interp1(Rvals_L1, Ts, R_L1);
end

if coeffsL2 == [0 0 0 0 0];
    Rvals_L2 = 0;
    T_L2 = zeros(size(T_2, 2), length(T_2))';
else
    Rvals_L2 = funcL2(coeffsL2, Ts);
    T_L2 = interp1(Rvals_L2, Ts, R_L2);
end

if coeffsL3 == [0 0 0 0 0];
    Rvals_L3 = 0;
    T_L3 = zeros(size(T_2, 2), length(T_2))';
else
    Rvals_L3 = funcL1L3(coeffsL3, Ts);
    T_L3 = interp1(Rvals_L3, Ts, R_L3);
end

% Plot Resistance and Fit according the Bloch-Gruneisen Relation and display
% R^2 values
format long
figure(1);
fig = figure(1);
newT_1 = linspace(min(T_1), max(T_1), 100);
set (fig, 'Units', 'normalized', 'Position', [0.1, 0.1,.8,.8]);

subplot(1,3,1);
plot(T_1, CorrectedR_L1, 'o');
fit1_L1 = Rvals_L1;
hold on
plot(Ts, Rvals_L1, 'r--')
Rcorrelation = corrcoef(CorrectedR_L1, funcL1L3(coeffsL1, T_1))
Rsq_RvsT(1) = Rcorrelation(1, 2)^2;
xlabel('Temperature (K)');
ylabel('Resistance (Ohms)');
title(sprintf('L1'))
hold off

subplot(1,3,2);
plot(T_1, CorrectedR_L2, 'o');
fit2_L2 = Rvals_L2;
hold on

subplot(1,3,3);
plot(T_1, CorrectedR_L3, 'o');
fit3_L3 = Rvals_L3;
hold off

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plot(Ts,Rvals_L2,'r--')
Rcorrelation=corrcoef(CorrectedR_L2,funcL2(coeffsL2,T_1))
Rsq_RvsT(2)=Rcorrelation(1,2)^2;
xlabel('Temperature (K)');
ylabel('Resistance (Ohms)');
title(sprintf('L2'))
hold off

subplot(1,3,3);
plot(T_1,CorrectedR_L3,'o');
fit3_L3=Rvals_L3;
hold on
plot(Ts,Rvals_L3,'r--')
Rcorrelation=corrcoef(CorrectedR_L3,funcL1L3(coeffsL3,T_1))
Rsq_RvsT(3)=Rcorrelation(1,2)^2;
xlabel('Temperature (K)');
ylabel('Resistance (Ohms)');
title(sprintf('L3'))
hold off

Rsq_RvsT

%Calibration data for LakeShore 336 Diode Temperature Sensor
infile2='LakeShore 336 Curve Tables.xlsx';
DT670=xlsread(infile2,1);
DT470=xlsread(infile2,2);
DT670T=DT670(1:end,1)';
DT670V=DT670(1:end,2)';
DT470T=DT470(1:end,1)';
DT470V=DT470(1:end,2)';
% T=(0:1:500);
% plot(DT670T,DT670V,'o',T,pchip(DT670T,DT670V,T));
% legend('DT-670 diode','pchip fit',4);
% Uncertainty in LakeShore 336 Si Diode voltage reading:
dDT670V=pchip(DT670T,DT670V,T_2).*5e-5+80e-6;
% Voltage reading plus maximum uncertainty:
HighV=pchip(DT670T,DT670V,T_2)+dDT670V;
% Underestimate of Temperature based on result from HighV:
LowT=pchip(DT670V,DT670T,HighV);
% Relative Uncertainty in Temperature reading:
dT=T_2-LowT;

% The next lines preallocate the size of output data arrays.
dRdT_L1=zeros(size(T_2,2),length(T_2));
dRdT_L2=zeros(size(T_2,2),length(T_2));
dRdT_L3=zeros(size(T_2,2),length(T_2));
dRdT_L1err=zeros(size(T_2,2),length(T_2));
dRdT_L2err=zeros(size(T_2,2),length(T_2));
dRdT_L3err=zeros(size(T_2,2),length(T_2));
k1=zeros(size(Vomega_L1,2),length(T_2));
k2=zeros(size(Vomega_L2,2),length(T_2));
k3=zeros(size(Vomega_L3,2),length(T_2));
Rsq_EvsV=zeros(size(L,2),length(T_2));

%For-loop that plots best fit line for 3rd harmonic response vs. log frequency for every wire at every temperature.
for j=1:size(V3omega_L1,1)
    figure(j+1);
    fig=figure(j+1);
    set(fig, 'Units', 'normalized', 'Position', [0.1,0.1,.8,.8]);
    subplot(1,3,1);
    if lt(20,T_2(j));
        ExcHz=fresponse(1,3:end-1);
    else ExcHz=[2000 2339 2736 3199 3742 4376 5118 5985 7000];
    % else ExcHz=[3000 3487 4054 4712 5477 6367 7401 8603 10000];
    % else ExcHz=[40 47 55 64 75 88 102 120 140];
    % n2=input('Enter order for polynomial fit:');
    n2=1;
    newExcHz=linspace(min(ExcHz),max(ExcHz),100);
    plot(log10(ExcHz),V3omega_L1(j,:),',o');
    p1=polyfit(log10(ExcHz),V3omega_L1(j,:),n2);
    fL1=@(x)funcL1L3(coeffsL1,x);
    dRdT_L1(j)=nDerive(T_L1(j),fL1);
    dRdT_L1err(j)=nDerive((T_L1(j)-dT(j)),fL1);
    if isnan(Vomega_L1(j));
        k1(j)=0;
    else
        k1(j)=(Vomega_L1(j).*Vomega_L1(j).*Vomega_L1(j).*dRdT_L1(j).*log(max(ExcHz)/min(ExcHz)))/(4.*pi.*T_L1(j).*funcL1L3(coeffsL1,T_L1(j)).*funcL1L3(coeffsL1,T_L1(j)).*fL1);
    end
    hold on
    plot(log10(newExcHz),fL1,'r--');
    Rsq_EvsV(1,j)=1-sum((V3omega_L1(j,:)-polyval(p1,log10(ExcHz))).^2)/(length(V3omega_L1(j,:))-1).*var(V3omega_L1(j,:));
    xlabel('log10(ExcHz) (Hz)');
    ylabel('V3omega (V)');
    title(sprintf('L1 T=%i',T_L1(j)))
    hold off
    subplot(1,3,2);
    plot(log10(ExcHz),V3omega_L2(j,:),',o');
end
p2=polyfit(log10(ExcHz),V3omega_L2(j,:),n2);
fit2_L2=polyval(p2,log10(newExcHz));
fl2=@(x)funcL2(coeffsL2,x);
dRdT_L2(j)=nDerive(T_L2(j),fl2);
dRdT_L2err(j)=nDerive((T_L2(j)-dT(j)),fl2);
if isnan(Vomega_L2(j));
k2(j)=0;
else
    k2(j)=(Vomega_L2(j).*Vomega_L2(j).*Vomega_L2(j).*dRdT_L2(j).*log(max(ExcHz)/min(ExcHz)))/
    ...((4.*pi.*L(1,2).*funcL2(coeffsL2,T_L2(j))).*funcL2(coeffsL2,T_L2(j)).*...
    (polyval(p2,log10(min(ExcHz)))-polyval(p2,log10(max(ExcHz))))./1000));
end

hold on
plot(log10(newExcHz),fit2_L2,'r--')
Rsq_EvsV(2,j)=1-sum((V3omega_L2(j,:)-polyval(p2,log10(ExcHz))).^2)/...
    (length(V3omega_L2(j,:))-1).*var(V3omega_L2(j,:)));
xlabel('log10(ExcHz) (Hz)');
ylabel('V3omega (V)');
title(sprintf('L2 T=%i',T_L2(j)))
hold off

subplot(1,3,3);
plot(log10(ExcHz),V3omega_L3(j,:),'o');
p3=polyfit(log10(ExcHz),V3omega_L3(j,:),n2);
fit3_L3=polyval(p3,log10(newExcHz));
fl3=@(x)funcL1L3(coeffsL3,x);
dRdT_L3(j)=nDerive(T_L3(j),fl3);
dRdT_L3err(j)=nDerive((T_L3(j)-dT(j)),fl3);
if isnan(Vomega_L3(j));
k3(j)=0;
else
    k3(j)=(Vomega_L3(j).*Vomega_L3(j).*Vomega_L3(j).*dRdT_L3(j).*log(max(ExcHz)/min(ExcHz)))/
    ...((4.*pi.*L(1,3).*funcL1L3(coeffsL3,T_L3(j))).*funcL1L3(coeffsL3,T_L3(j)).*...
    (polyval(p3,log10(min(ExcHz)))-polyval(p3,log10(max(ExcHz))))./1000));
end

hold on
plot(log10(newExcHz),fit3_L3,'r--')
Rsq_EvsV(3,j)=1-sum((V3omega_L3(j,:)-polyval(p3,log10(ExcHz))).^2)/...
    (length(V3omega_L3(j,:))-1).*var(V3omega_L3(j,:)));
xlabel('log10(ExcHz) (Hz)');
ylabel('V3omega (V)');
title(sprintf('L3 T=%i',T_L3(j)))
hold off
%Temperature oscillation amplitude of wire resulting from excitation
deltaT_L1=zeros(size(T_2,1),length(ExcHz));
deltaT_L2=zeros(size(T_2,1),length(ExcHz));
deltaT_L3=zeros(size(T_2,1),length(ExcHz));
for k=1:length(ExcHz)
    deltaT_L1(:,k)=2.*(1./dRdT_L1').*R_L1./Vomega_L1.*V3omega_L1(:,k)./1e3;
    deltaT_L2(:,k)=2.*(1./dRdT_L2').*R_L2./Vomega_L2.*V3omega_L2(:,k)./1e3;
    deltaT_L3(:,k)=2.*(1./dRdT_L3').*R_L3./Vomega_L3.*V3omega_L3(:,k)./1e3;
end

%Temperature oscillation amplitude at depth r in the material resulting
from wire excitation
%Volumetric heat capacity is calculated below using either a fit or input
%data from file
infile3='AlN Lattice Constants vs. T.xlsx';
func2 = @(p,x) (SpecificHeat(p,x));
guessesCp=[1.2132e+000  980.5792e+000];
dataInCp=xlsread(infile3,7); %AlN:3; GaP:4; GaAs:5; InP:6; InAs:7
TCpIn=dataInCp(:,1);
CpIn=dataInCp(:,2);
coeffsCp=nlinfit(TCpIn,CpIn,func2,guessesCp);
Cvol=zeros(size(T_2,2),size(T_2,2));
for m=1:size(T_2,1)
    Cvol(m)=func2(coeffsCp,T_2(m))./12.5659e-006; %AlN
    Cvol(m)=pchip(TCpIn,CpIn,T_2(m))./24.3229e-006; %GaP
    Cvol(m)=pchip(TCpIn,CpIn,T_2(m))./27.18899e-006; %GaAs
    Cvol(m)=pchip(TCpIn,CpIn,T_2(m))./30.3102e-006; %InP
    Cvol(m)=pchip(TCpIn,CpIn,T_2(m))./33.4638e-006; %InAs
end

% t=520e-6; %GaP wafer thickness
% t=360e-6; %GaAs wafer thickness
% t=490e-6; %InP wafer thickness
t=805e-6; %InAs wafer thickness
a1=1e-5/pi; %Radius when wire area is transformed to cylindrical area
DelT_L1=Iomega_L1.^2.*R_L1./(pi.*L(1,1).*k1').*besselk(0,(abs((1i.*2.*Exc Hz./(k1'./Cvol')).^(1/2)).*t)));
DelT_L2=Iomega_L2.^2.*R_L2./(pi.*L(1,2).*k2').*besselk(0,(abs((1i.*2.*Exc Hz./(k2'./Cvol')).^(1/2)).*t)));
DelT_L3=Iomega_L3.^2.*R_L3./(pi.*L(1,3).*k3').*besselk(0,(abs((1i.*2.*Exc Hz./(k3'./Cvol')).^(1/2)).*t)));

% DelT_L1=abs(Iomega_L1.^2.*R_L1./(pi.*L(1,1).*k1').*(.5.*log((k1'./Cvol')./ r^2)+log(2)-0.5.*log(2.*ExcHz)-0.5772-li*pi/4))
% DelT_L1=Iomega_L3.^2.*R_L3./(pi.*L(1,3).*k3').*(.5.*log((k3'./Cvol')./r^2)+log(2)-0.5.*log(2.*ExcHz)-0.5772-abs(li*pi/4))
del_L1=zeros(size(T_2,1),length(ExcHz));
del_L2=zeros(size(T_2,1),length(ExcHz));
del_L3=zeros(size(T_2,1),length(ExcHz));
for n=1:size(T_2,1)
    for o=1:length(ExcHz)
        syms r;
        assume(2e-3>r & r>0);
        if isnan(deltaT_L1(n,o))
            del_L1(n,o)=0;
        else
            del_L1(n,o)=vpasolve(log(t./r)./(log(t/a1))==1/exp(1),r);
%steady state thermal attenuation length
%        end
        if isnan(deltaT_L2(n,o))
            del_L2(n,o)=0;
%steady state thermal attenuation length
        else
            del_L2(n,o)=solve(((Iomega_L1(n).^2.*R_L1(n)./(pi*L(1,1).*k1(n)').*besselk(0,(abs((li.*2.*ExcHz(o)./k1(n)')../Cvol(n')).^((1/2)).*t))))./deltaT_L1(n,o)==1/exp(1),t,'Real',true);
%        end
        if isnan(deltaT_L3(n,o))
            del_L3(n,o)=0;
%steady state thermal attenuation length
        else
            del_L3(n,o)=solve(((Iomega_L2(n).^2.*R_L2(n)./(pi*L(1,2).*k2(n)').*besselk(0,(abs((li.*2.*ExcHz(o)./k2(n)')../Cvol(n')).^((1/2)).*t))))./deltaT_L2(n,o)==1/exp(1),t,'Real',true);
%        end
    end
end

ratio_L1=zeros(size(T_2,1),length(ExcHz));
ratio_L2=zeros(size(T_2,1),length(ExcHz));
ratio_L3=zeros(size(T_2,1),length(ExcHz));
for n=1:length(ExcHz)
    for o=1:size(T_2,1)
        ratio_L1(o,n)=(((Iomega_L1(o).^2.*R_L1(o)./(pi*L(1,1).*k1(o)').*besselk(0,(abs((li.*2.*ExcHz(n)./k1(o)')../Cvol(o')).^((1/2)).*del_L1(o,n)))')./deltaT_L1(o,n)));
%the temp oscillation in wire
        ratio_L2(o,n)=(((Iomega_L2(o).^2.*R_L2(o)./(pi*L(1,2).*k2(o)').*besselk(0,(abs((li.*2.*ExcHz(n)./k2(o)')../Cvol(o')).^((1/2)).*del_L2(o,n)))')./deltaT_L3(o,n)));
%the ratio of temp oscillation at thermal attenuation length to
ratio_L3(o,n)=(((Iomega_L3(o).^2.*R_L3(o)./(pi*L(1,3).*k3(o)').*besselk(0, ((abs((1i.*2.*ExcHz(n)./(k3(o)./Cvol(o)').^1/2).*del_L3(o,n)))).^1/2).*del_L3(o,n)))... /deltaT_L3(o,n));
end
end

% plotting thermal conductivity for each wire
figure(j+2);
fig=figure(j+2);
set (fig, 'Units', 'normalized', 'Position', [0.1,0.1,.8,.8]);
subplot(1,3,1);
plot(T_2,k1,'o');
xlabel('Temperature (K)');
ylabel('k (W/m K)');
title(sprintf('L1'))
% xlim([0 300]);
% ylim([0 250]);
subplot(1,3,2);
plot(T_2,k2,'o');
xlabel('Temperature (K)');
ylabel('k (W/m K)');
title(sprintf('L2'))
% xlim([0 300]);
% ylim([0 250]);
subplot(1,3,3);
plot(T_2,k3,'o');
xlabel('Temperature (K)');
ylabel('k (W/m K)');
title(sprintf('L3'))
% xlim([0 300]);
% ylim([0 250]);

format shortEng

% Uncertainty Analysis

% Voltage resolution limit from Keithley 2000 datasheet:
dVomega_L1=(Vomega_L1.*30e-6+0.00005)./Vomega_L1;
dVomega_L2=(Vomega_L2.*30e-6+0.00005)./Vomega_L2;
dVomega_L3=(Vomega_L3.*30e-6+0.00005)./Vomega_L3;

% Microscope pixel length resolution limit:
dl=0.9615/987.05.*ones(length(dVomega_L1),1);

% Resistance resolution limit from Keithley 2000 datasheet:
dR_L1=(funcL1L3(coeffsL1,T_2).*100e-6+0.004)./
funcL1L3(coeffsL1,T_2);
dR_L2=(funcL2(coeffsL2,T_2).*100e-6+0.004)./
funcL2(coeffsL2,T_2);
dR_L3=(funcL1L3(coeffsL3,T_2).*100e-6+0.004)./
funcL1L3(coeffsL3,T_2);

% Limit from calculation:
ddRdT_L1=abs((dRdT_L1err'-dRdT_L1')./dRdT_L1');
ddRdT_L2=abs((dRdT_L2err'-dRdT_L2')./dRdT_L2');
ddRdT_L3=abs((dRdT_L3err'-dRdT_L3')./dRdT_L3');

% Frequency resolution limit from SR830 datasheet:
\[
df_1 = \frac{((\min(\text{ExcHz}).\times (25e-6)+0.00003)/\min(\text{ExcHz})) \times (\log(\max(\text{ExcHz})/\min(\text{ExcHz}))) - 1) \times \text{ones(length(dVomega_L1)),1)}}{
\min(\text{ExcHz}).\times (25e-6)+0.00003)/\max(\text{ExcHz}))) \times (\log(\max(\text{ExcHz})/\min(\text{ExcHz}))) - 1) \times \text{ones(length(dVomega_L1),1))};
\]
\[
df_2 = \frac{((\max(\text{ExcHz}).\times (25e-6)+0.00003)/\max(\text{ExcHz}))) \times (\log(\max(\text{ExcHz})/\min(\text{ExcHz}))) - 1) \times \text{ones(length(dVomega_L1),1))};
\]

% Voltage resolution limit from SR830 datasheet:
\[
dV3omega_L1 = (0.002 \times (V3omega_L1(:,1)+V3omega_L1(:,\text{size(V3omega_L1,2)))))/\{V3omega_L1(:,1)-V3omega_L1(:,\text{size(V3omega_L1,2)})};
\]
\[
dV3omega_L2 = (0.002 \times (V3omega_L2(:,1)+V3omega_L2(:,\text{size(V3omega_L2,2)))))/\{V3omega_L2(:,1)-V3omega_L2(:,\text{size(V3omega_L2,2)})};
\]
\[
dV3omega_L3 = (0.002 \times (V3omega_L3(:,1)+V3omega_L3(:,\text{size(V3omega_L3,2)))))/\{V3omega_L3(:,1)-V3omega_L3(:,\text{size(V3omega_L3,2)})};
\]

% Propagated Fractional Uncertainties for each wire (maximum possible):
\[
dk_1 = 3 \times dVomega_L1 + dL + 2 \times \text{dR}_L + \text{ddRdT}_L + \log(\max(\text{ExcHz})/\min(\text{ExcHz})).\times (df_1 + df_2) + 2 \times dV3omega_L1;
\]
\[
dk_2 = 3 \times dVomega_L2 + dL + 2 \times \text{dR}_L + \text{ddRdT}_L + \log(\max(\text{ExcHz})/\min(\text{ExcHz})).\times (df_1 + df_2) + 2 \times dV3omega_L2;
\]
\[
dk_3 = 3 \times dVomega_L3 + dL + 2 \times \text{dR}_L + \text{ddRdT}_L + \log(\max(\text{ExcHz})/\min(\text{ExcHz})).\times (df_1 + df_2) + 2 \times dV3omega_L3;
\]

% Propagated Fractional Uncertainties for each wire (in quadrature)
\[
\text{quaddk1} = \sqrt{(3 \times dVomega_L1)^2 + (dL)^2 + (2 \times \text{dR}_L)^2 + (\text{ddRdT}_L)^2 + (df_1 + df_2)^2 + 2 \times (dV3omega_L1)^2)};
\]
\[
\text{quaddk2} = \sqrt{(3 \times dVomega_L2)^2 + (dL)^2 + (2 \times \text{dR}_L)^2 + (\text{ddRdT}_L)^2 + (df_1 + df_2)^2 + 2 \times (dV3omega_L2)^2)};
\]
\[
\text{quaddk3} = \sqrt{(3 \times dVomega_L3)^2 + (dL)^2 + (2 \times \text{dR}_L)^2 + (\text{ddRdT}_L)^2 + (df_1 + df_2)^2 + 2 \times (dV3omega_L3)^2)};
\]

% Uncertainty Contribution Matrices:
\[
\text{UCM}_L1 = \frac{\{\sqrt{(3 \times dVomega_L1)^2)} / \text{quaddk1}, \sqrt{(dL)^2)} / \text{quaddk1}, \sqrt{(2 \times \text{dR}_L)^2)} / \text{quaddk1}, \sqrt{(\text{ddRdT}_L)^2)} / \text{quaddk1},... \}}{\{\sqrt{(df_1 + df_2)^2)} / \text{quaddk1}, \sqrt{(dV3omega_L1)^2)} / \text{quaddk1}};
\]
\[
\text{UCM}_L2 = \frac{\{\sqrt{(3 \times dVomega_L2)^2)} / \text{quaddk2}, \sqrt{(dL)^2)} / \text{quaddk2}, \sqrt{(2 \times \text{dR}_L)^2)} / \text{quaddk2}, \sqrt{(\text{ddRdT}_L)^2)} / \text{quaddk2},... \}}{\{\sqrt{(df_1 + df_2)^2)} / \text{quaddk2}, \sqrt{(dV3omega_L2)^2)} / \text{quaddk2}};
\]
\[
\text{UCM}_L3 = \frac{\{\sqrt{(3 \times dVomega_L3)^2)} / \text{quaddk3}, \sqrt{(dL)^2)} / \text{quaddk3}, \sqrt{(2 \times \text{dR}_L)^2)} / \text{quaddk3}, \sqrt{(\text{ddRdT}_L)^2)} / \text{quaddk3},... \}}{\{\sqrt{(df_1 + df_2)^2)} / \text{quaddk3}, \sqrt{(dV3omega_L3)^2)} / \text{quaddk3}};
\]

% absolute error
if isnan(dk1)
    absdk1=0;
else
    absdk1=quaddk1'*k1;
end
if isnan(dk2)
    absdk2=0;
else
    absdk2=quaddk2'*k2;
end
if isnan(dk3)
    absdk3=0;
else
    absdk3=quaddk3'*k3;
end
% plotting average thermal conductivity
hold on
if (isnan(Vomega_L1) & isnan(Vomega_L2)) | (isnan(Vomega_L3) & isnan(Vomega_L3))
    numLs=1;
elseif isnan(Vomega_L1) | isnan(Vomega_L2) | isnan(Vomega_L3);
    numLs=2;
elseif ~isnan(Vomega_L1) & ~isnan(Vomega_L2) & ~isnan(Vomega_L3);
    numLs=3;
end
figure(j+3);
fig=figure(j+3);
set (fig, 'Units', 'normalized', 'Position', [0.1,0.1,.8,.8]);
errorbar((T_L1+T_L2+T_L3)/numLs, (k1+k2+k3)/numLs, (absdk1+absdk2+absdk3)/numLs, 'o');
errorbar((T_L1+T_L2+T_L3)/numLs, (k1+k2+k3)/numLs, (absdk1+absdk2+absdk3)/numLs, 'o');
herrorbar(T_2, (k1+k2+k3)/numLs, dT)
% xlim([0 300]);
% ylim([0 250]);
hold off

% output file
outfile=[T_2';k1;k2;k3; (k1+k2+k3)/numLs; (absdk1+absdk2+absdk3)/numLs]';
% outfile=[((T_L1+T_L2+T_L3)/numLs)';k1;k2;k3; (k1+k2+k3)/numLs; (absdk1+absdk2+absdk3)/numLs]';
% creating new excel sheet
write=input(sprintf('Write output data to file? n1: Write output file \n2: Close program \n(default=2, close without saving) \n'));
if isempty(write)
    write=2;
end

% output file location
if write==1
    [outName outPath]=uiputfile({'*.xls'}, 'Save Output File', 'Thermal Conductivity Curve');
    xlswrite([outPath '\ outName], outfile);
end

MATLAB code: Bloch_GruneisenFunction2

function [rho]=Bloch_GruneisenFunction2(coeffs,T)
A=coeffs(1);
thetaR=coeffs(2);
n=coeffs(3);
s=coeffs(4);
z=coeffs(5);
% rhovalsout=[];
rhovalsout=zeros(size(T,2),size(T,1));
for
    i=1:length(T)
        rhovalsout(i)=A*(T(i)/thetaR).^n.*integral(@(x)((x.^s.*exp(x))./((exp(x)-1).^2)),0,thetaR./T(i))+z;
end
rho=rhovalsout';

MATLAB code: Thermal Penetration Depth for 3ω Method

% Thermal Penetration Depth Calculation

clear;
close all;
cic;

HBar = 1.05457e-34;
kB = 1.38066e-23;

% GaP Wafer Parameters:
rho=4.14/1000*(100)^3;
thetaD=445;
v=((1/3).*(1/5830^2+2/4120^2)^-1)^(1/2);
d=400e-6;
b=12.11e-6./2;
kxy=1;

% Fused Quartz Wafer Parameters:
% rho=2.65/1000*(100)^3;
% thetaD=470;
% v=5968;
% d=1100e-6;
% b=12.11e-6./2;

% %Sapphire Wafer Parameters:
% rho=3.98/1000*(100)^3;
% thetaD=1620;
% v=11100;
% d=430e-6;
% b=10.5e-6./2;

% 3C SiC Wafer Parameters:
% rho=3.21/1000*(100)^3;
% thetaD=1200;
% v=9500;
% d=465e-6;
% b=14.15e-6./2;

% 4H SiC Wafer Parameters:
% rho=3.21/1000*(100)^3;
% thetaD=1300;
% v=1306;
% d=465e-6;
% b=14.15e-6./2;

% 6H SiC Wafer Parameters:
% rho=3.21/1000*(100)^3;
% thetaD=1200;
% v=13300;
% d=230e-6;
% b=10.5e-6./2;

% GaN Parameters:
% rho=6.15/1000*(100)^3;
% thetaD=600;
% v=7960

% % AlN Parameters:
% rho=3.26/1000*(100)^3;
% thetaD=989;
% v = (((1/3).*(1/10127^2+2/6333^2))^(-1))^(1/2);
% d=200e-6;
% b=10.5e-6./2;
% kxy=(4.15e-6/5.27e-6)^(-1/2);
% kxy is square root of the ratio of in plane to cross plane thermal
% conductivity
% the linear expansion coefficients in the a & c directions were used

% omega=[303 446 656 965 1419 2087 3069 4513 6637];
omega=[300 421 590 828 1162 1630 2287 3208 4500];
% omega=[2000 2339 2736 3199 3742 4376 5118 5985 7000];

% Get the Excel Data File
[infile1n, infile1p] = uigetfile('*.*')
infile1=[infile1p, infile1n]
infile1='041816 HVPE AlN Thermal Conductivity Curve, last 4 Hz.xls'
dataIn=xlsread(infile1,1);
TIn=dataIn(:,1)';
% TIn=linspace(54.801,766.547,950);
kappaIn=dataIn(:,5)';
lambda=zeros(size(omega,2),length(kappaIn));
z=zeros(size(omega,2),length(kappaIn));
slope=zeros(size(omega,2),length(kappaIn));
qd=zeros(size(omega,2),length(kappaIn));
lowHzlim=zeros(size(omega,2),length(TIn));
highHzlim=zeros(size(omega,2),length(TIn));
C=zeros(size(TIn,1),length(TIn));
for i=1:length(omega)
    for j=1:length(TIn)
        T=TIn(j);
        kxy=(4.15e-6/5.27e-6)^(-1/2);
       =lambda(i,j)=kappaIn(j)/kxy;
        z(i,j)=(1/(1/omega(i))+(1/omega(i))^2)^(-1/2);
        slope(i,j)=TIn(j)/z(i,j);
        qd(i,j)=((1/(1/omega(i))+(1/omega(i))^2)^(-1/2))^2;
        lowHzlim(i)=TIn(j)/z(i,j);
        highHzlim(i)=TIn(j)/z(i,j);
        C(i,j)=zeros(size(TIn,1),length(TIn));
    end
end

for i=1:length(omega)
    for j=1:length(TIn)
        T=TIn(j);
        ...
\[ \lambda(i,j) = \left| \frac{\kappa_{\text{In}}(j)}{2 \omega(i) \epsilon_0 \sqrt{3/2} \kB^4 T^3 / (\pi^2 v^3 \Hbar^3)} \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} \right|^{1/2} \]

\[
\text{lowHzlim}(i,j) = \left| \frac{\kappa_{\text{In}}(j)}{2 \epsilon_0 \sqrt{3/2} \kB^4 T^3 / (\pi^2 v^3 \Hbar^3)} \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} \right| \cdot d^2
\]

\[
\text{highHzlim}(i,j) = \left| \frac{\kappa_{\text{In}}(j)}{2 \epsilon_0 \sqrt{3/2} \kB^4 T^3 / (\pi^2 v^3 \Hbar^3)} \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} \right| \cdot b^2
\]

\[ C(j) = \frac{3}{2} \kB^4 T^3 / (\pi^2 v^3 \Hbar^3) \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} \]
semilogx(qd,slope);
    xlabel('qd');
    ylabel('slope');

% figure(3);
% set(figure(3),'position',[353 126 660 520]);
% semilogx(z,slope);
%     xlabel('z');
%     ylabel('slope');

% axis 'auto y'
hold off;
format shortEng

% output file
outfile=[TIn',lambda'.*1e6,lowHzlim(1,:),highHzlim(1,:)'
];
% creating new excel sheet
write=input(sprintf('Write output data to file?\n1: Write
output file
2: Close program\n(default=2, close without saving)\n'));
if isempty(write)
    write=2;
end
% output file location
if write==1
    [outName outPath]=uiputfile({'.xls'},'Save Output File','Thermal
Penetration Depth');
    xlswrite([outPath '\' outName],[T (K)],1,'A1');
    xlswrite([outPath '\' outName],omega,1,'B1');
    xlswrite([outPath '\' outName],outfile,1,'A2');
    xlswrite([outPath '\' outName],lowHzlim,1,'K1');
    xlswrite([outPath '\' outName],highHzlim,1,'L1');
end

MATLAB code: Debye-Callaway Approximation of Thermal Conductivity (AlN & GaP)

function [k,tN,tU,tI,tB,tR,tC,alpha] = kappafunction5(coeffs,T)
% KAPPA: The Debye-Callaway approximation for thermal conductivity
% This code contains the necessary constants and expressions for phonon
% relaxation times used in creating fits for temperature-dependent
% thermal conductivity results. This version has been used for fitting
% AlN and GaP data.

HBar = 1.05457e-34;
kB = 1.38066e-23;
u=1.66054e-27;

% % AlN Parameters
% N=9.581e22;
% v = ((1/3).*(1/10127^2+2/6333^2))^-1)^1/2;
\% \% \( v = \left( \frac{1}{3} \cdot \left( \frac{1}{10970^2 + 2/6220^2} \right)^{-1} \right)^{1/2} \);
\% \( V = \left( \frac{3.11e-10^2 \cdot 4.98e-10 \cdot \sin(\pi/3)}{4} \right)^{1/2} \);
\% \( \theta_D = 2\pi \cdot HBar \cdot \left( 3^1 / (4 \cdot \pi \cdot V) \right) ^{1/3} \cdot v / k_B \);
\% \( M = u \cdot \left( 26.9815386 + 14.0067 \right) / 2 \);

% GaP Parameters
N=4.94e22;
\( v = \left( \frac{1}{3} \cdot \left( \frac{1}{5830^2 + 2/4120^2} \right)^{-1} \right)^{1/2} \);
\( V = \left( \frac{5.4505e-10^3}{2} \right) / 2 \);
\% \( \theta_D = 445 \);
\% \( \theta_D = 314 \);
\( M = u \cdot \left( 69.723069 + 30.973762 \right) / 2 \);
C=kB^4 /(2*(pi^2)*HBar^3*v);

\% GammaN = 0*kB^3*gamma^2*V/(M*HBar^2*v^5);
\% GammaGa = 0*gamma^2*V/(M*HBar^3*v^5);
\% GammaB_AlN = fB/(1*N)*(((mBav)-(mAlav))/(mAlav))^2;
\% GammaC_AlN = fC/(1*N)*(((mCav)-(mNav))/(mNav))^2;
\% GammaO\_AlN = fO.\/(1\*N).\*(((mOav)-(mNav)).\/(mNav)).^2;
\% GammaSi\_AlN = fSi.\/(1\*N).\*(((mSiav)-(mAlav)).\/(mAlav)).^2;
\% GammaCl\_AlN = fCl.\/(1\*N).\*(((mClav)-(mNav)).\/(mNav)).^2;
\% GammaVac\_AlN=(1/N).\*(*(fc/3+fO/3+fSi/3+2*fCl/3+fVac);
\% GammaVac\_AlN=(1/N).\*(*(fVac);
\% GammaN = 0.99632.\*(*(mNav-14.0030740052).\/(mNav)).^2+0.00368.\*(*(mNav-15.00108984).\/(mNav)).^2;
\% GammaGa = 0.60108.\*(*(mGaav-68.92558).\/(mGaav)).^2+0.39892.\*(*(mGaav-70.9247005).\/(mGaav)).^2;
\% GammaB\_GaP = fB.\/(1\*N).\*(((mBav)-(mGaav)).\/(mGaav)).^2;
\% GammaC\_GaP = fC.\/(1\*N).\*(((mCav)-(mPav)).\/(mPav)).^2;
\% GammaO\_GaP = fO.\/(1\*N).\*(((mOav)-(mPav)).\/(mPav)).^2;
\% GammaSi\_GaP = fSi.\/(1\*N).\*(((mSiav)-(mGaav)).\/(mGaav)).^2;
\% GammaCl\_GaP = fCl.\/(1\*N).\*(((mClav)-(mPav)).\/(mPav)).^2;
\% GammaVac\_GaP=(1/N).\*(*(fc/3+fO/3+fSi/3+2*fCl/3+fVac);
\% Gamma\_Cation=GammaSi\_AlN+GammaB\_AlN;\%GammaMg\_AlN+GammaMn\_AlN;
\% Gamma\_Anion=GammaN+GammaC\_AlN+GammaO\_AlN+GammaCl\_AlN;
\% GammaAlN = 2.\*(*(mAlav.\/(mAlav+mNav)).^2+2.\*Gamma\_Anion+(mNav.\/(mAlav+mNav)).^2).\*Gamma\_Anion);
\% Gamma\_Cation=GammaSi\_GaP+GammaB\_GaP;
\% Gamma\_Anion=GammaC\_GaP+GammaO\_GaP+GammaCl\_GaP;
\% GammaGaP = 2.\*(*(mGaav.\/(mGaav+mPav)).^2+2.\*Gamma\_Cation+(mPav.\/(mGaav+mPav)).^2).\*Gamma\_Cation;
\% tauN = @(x)(BN.\*(*(kB.\/HBar)).^2.*x.^2.*T.^5).\^\((-1);\n\% tauU = @(x)(BU.\*(*(kB.\/HBar)).^2.*x.^2.*T.^3.*exp((-thetaD./3.0*T)))).\^\((-1);\n\% tauI = @(x)(V.\/(4*pi.*v.^3).*(*(kB.\*T./HBar)).^4.*x.^4).\*(*(GammaAlN+9.*GammaVac\_AlN ))).\^\((-1);\n\% tauI = @(x)(V.\/(4*pi.*v.^3).*(*(kB.\*T./HBar)).^4.*x.^4).\*(*(GammaGaP+9.*GammaVac\_GaP ))).\^\((-1);\n\% tauI = @(x)(3.*V.\/(pi.*v.^3).*(*(kB.\*T./HBar)).^4.*x.^4).\*(*(GammaAlN+9.*GammaVac\_AlN ))).\^\((-1);\n\% tauB = (v./d).\^\((-1);\n\% tauR = @(x)(tauU(x).\^\((-1)+tauI(x).\^\((-1)+tauB.\^\((-1)).\^\((-1);\n\% tauC = @(x)(tauU(x).\^\((-1)+tauR(x).\^\((-1)).\^\((-1);\n\% tauC = tauR;
\% kappa=(@x)(C.*T.^3.*{\%integral(@(x)((tauC(x).*x.^4.*exp(x))./\%(exp(x)-1).^2)},0,thetaD./T)+...\% C.*T.^3.*{\%integral(@(x)((tauC(x).*x.^4.*exp(x))./\%(tauN(x).*x.*exp(x))./\%(exp(x)-1).^2)},0,thetaD./T).\^\(2/...\% integral(@(x)((tauC(x).*x.^4.*exp(x))./\%(tauN(x).*tauR(x).*x.*exp(x))./\%(exp(x)-1).^2)},0,thetaD./T));
kappa=@(x)C.*T.^3.*(integral(@(x)((tauC(x).*x.^4.*exp(x))./(exp(x)-1).^2),0,thetaD./T));
k=kappa(T);
tN=tauN(T);
tU=tauU(T);
tI=tauI(T);
tB=tauB;
tR=tauR(T);
tC=tauC(T);
alphaT=@(x)tauC(x).*(1+(integral(@(x)((tauC(x).*x.^4.*exp(x))./(tauN(x).*tauR(x).*(exp(x)-1).^2)),0,thetaD./T).^1./... integral(@(x)((tauC(x).*x.^4.*exp(x))./(tauN(x).*tauR(x).*(exp(x)-1).^2)),0,thetaD./T)))./tauN(x));
alpha=alphaT(T);
end

MATLAB code: Debye-Callaway Approximation of Thermal Conductivity (GaN)

function [k,tN,tU,tI,tB,tR,tC,alpha] = kappafunction6(coeffs,T)
%KAPPA: The Debye-Callaway approximation for thermal conductivity
% This code contains the necessary constants and expressions for phonon relaxation times used in creating fits for temperature-dependent thermal conductivity results. This version has been used for fitting GaN data.

HBar = 1.05457e-34;
kB = 1.38066e-23;
u=1.66054e-27;
% % AlN Parameters
% N=9.581e22;
% v = (((1/3).*((1/3).*(1/7960^2+2/4140^2))^(-1/2)));
% V=((3.189e-10^2*5.178e-10)*sin(pi/3))/4;
% thetaD=2*pi*HBar*(3*1/(4*pi*V))^(1/3)*v/kB;
% thetaD=989;
% M=u.*(26.9815386+14.0067)/2;
% GaN Parameters
N=8.77119e22;
 v = (((1/3).*((1/7960^2+2/4140^2))^(-1/2)));
 V=((3.189e-10^2*5.178e-10)*sin(pi/3))/4;
% thetaD=2*pi*HBar*(3*1/(4*pi*V))^(1/3)*v/kB;
thetaD=989;
M=u.*(69.723069+14.0067)/2;
C=kB.^4./(2.*(pi^2).*HBar.^3.*v);
d=coeffs(1);
gamma=coeffs(2);
fB=coeffs(3);
\[ fC = \text{coeffs}(4); \]
\[ fO = \text{coeffs}(5); \]
\[ fMg = \text{coeffs}(6); \]
\[ fSi = \text{coeffs}(7); \]
\[ fCl = \text{coeffs}(8); \]
\[ fCa = \text{coeffs}(9); \]
\[ fMn = \text{coeffs}(10); \]
\[ fFe = \text{coeffs}(11); \]
\[ fZn = \text{coeffs}(12); \]
\[ fVac = \text{coeffs}(13); \]

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

\[ BN = 0.2 \times (k_B \times 3 \times \gamma^2 \times V) / (M \times HBar \times 2 \times v \times 5); \]
\[ BN = 1.0 \times (k_B \times 3 \times \gamma^2 \times V) / (M \times HBar \times 2 \times v \times 5); \]
\[ BN = (k_B \times 4 \times \gamma^2 \times V) / (M \times HBar \times 3 \times v \times 5); \]
\[ BU = 1.0 \times (HBar \times \gamma^2) / (M \times v \times 2 \times \theta D); \]

\[ mBav = (10.012937 \times 0.199 + 11.009305 \times 0.801); \]
\[ mCav = (12.0 \times 0.9893 + 13.0033548378 \times 0.0107); \]
\[ mNav = (14.0030740052 \times 0.99632 + 15.000108984 \times 0.00368); \]
\[ mOav = (15.99491463 \times 0.99575 + 16.9991603 \times 0.00205); \]
\[ mMgav = (23.9850423 \times 0.7899 + 24.9858374 \times 0.1 + 25.9825937 \times 0.1101); \]
\[ mAlav = 26.9815386; \]
\[ mSiav = (27.9769271 \times 0.922297 + 28.9764949 \times 0.046832 + 29.9737707 \times 0.030872); \]
\[ mClav = (34.968852721 \times 0.7578 + 36.96590262 \times 0.2422); \]
\[ mCaav = (39.9625906 \times 0.96941 + 41.9586176 \times 0.00647 + 42.9587662 \times 0.00135); \]
\[ mMnav = (54.9380471); \]
\[ mFeav = (53.9396127 \times 0.05845 + 55.9349393 \times 0.91754 + 56.9353958 \times 0.02119); \]
\[ mZnav = (63.9291448 \times 0.4863 + 65.9260347 \times 0.0279 + 66.9271291 \times 0.041); \]
\[ mGaav = (68.92558 \times 0.60108 + 70.9247005 \times 0.39892); \]
\[ mAlNav = 2 \times (mAlav + mNav); \]

\[ \Gamma_{B-\text{GaN}} = fB / (1 \times N) \times (((mBav) - (mGaav)) / (mGaav)).^2; \]
\[ \Gamma_{C-\text{GaN}} = fC / (1 \times N) \times (((mCav) - (mNav)) / (mNav)).^2; \]
\[ \Gamma_{O-\text{GaN}} = fO / (1 \times N) \times (((mOav) - (mNav)) / (mNav)).^2; \]
\[ \Gamma_{\text{Cl-GaN}} = fCl / (1 \times N) \times (((mClav) - (mNav)) / (mNav)).^2; \]
\[ \Gamma_{\text{Mg-GaN}} = fMg / (1 \times N) \times (((mMgav) - (mGaav)) / (mGaav)).^2; \]
\[ \Gamma_{\text{Si-GaN}} = fSi / (1 \times N) \times (((mSiav) - (mGaav)) / (mGaav)).^2; \]
\[ \Gamma_{\text{Mn-GaN}} = fMn / (1 \times N) \times (((mMnav) - (mGaav)) / (mGaav)).^2; \]
\[ \Gamma_{\text{Fe-GaN}} = fFe / (1 \times N) \times (((mFeav) - (mGaav)) / (mGaav)).^2; \]
\[ \Gamma_{\text{Zn-GaN}} = fZn / (1 \times N) \times (((mZnav) - (mGaav)) / (mGaav)).^2; \]
\[ \Gamma_{\text{Vac-GaN}} = fVac / (1 \times N) \times (((mZnav) - (mGaav)) / (mGaav)).^2; \]
Gamma_Anion = GammaN + GammaC_GaN + GammaO_GaN + GammaCl_GaN;
GammaGaN = 2.0*(mGaav./(mGaav+mNav)).^2.*Gamma_Cation + (mNav./(mGaav+mNav)).^2.*Gamma_Anion);

tauN = @(x)(BN.*(kB./HBar).^2.*x.^2.*T.^5).^(-1);
tauU = @(x)(BU.*((kB./HBar).^2.*x.^2.*T.^3.*exp(-thetaD./(2.0*T)))).^(-1);
tauI = @(x)(V./(4.*pi.*v.^3).*((kB.*T./HBar).^4.*x.^4).*GammaGaN+9.*GammaVac_GaN)).^(-1);
tauB = (v./d).^(-1);
tauR = @(x)(tauU(x).^(-1)+tauI(x).^(-1)+tauB.^(-1)).^(-1);
tauC = @(x)(tauN(x).^(-1)+tauR(x).^(-1)).^(-1);
% tauC = tauR;

kappa=@(x)C.*T.^3.*(integral(@(x)((tauC(x).*x.^4.*exp(x))./(exp(x)-1).^2),0,thetaD./T)+...)
C.*T.^3.*(integral(@(x)((tauC(x).*x.^4.*exp(x))./(tauN(x).*exp(x)-1).^2),0,thetaD./T).^2./...
integral(@(x)((tauC(x).*x.^4.*exp(x))./(tauN(x).*tauR(x).*exp(x)-1).^2),0,thetaD./T));
% kappa=@(x)C.*T.^3.*(integral(@(x)((tauC(x).*x.^4.*exp(x))./(exp(x)-1).^2),0,thetaD./T));
kappaOut=ones(length(x),1);
tN=tauN(T);
tU=tauU(T);
tI=tauI(T);
tB=tauB;
tR=tauR(T);
tC=tauC(T);
alphaT=@(x)tauC(x).*((integral(@(x)((tauC(x).*x.^4.*exp(x))./(tauN(x).*exp(x)-1).^2),0,thetaD./T).^1./...
integral(@(x)((tauC(x).*x.^4.*exp(x))./(tauN(x).*tauR(x).*exp(x)-1).^2),0,thetaD./T))/tauN(x));
alpha=alphaT(T);

MATLAB code: Function to pass thermal conductivity simulation data to plotting script

function [ kappaOut,tN,tU,tI,tB,tR,tC,alpha ] = kappafuctionfeedthrough( p,x )
%kappafuctionfeedthrough: Performs calculations using the referenced
%kappafuction and passes them to the kappafitter function
% Detailed explanation goes here
kappaOut=ones(length(x),1);
tN=ones(length(x),1);
tU=ones(length(x),1);
tI=ones(length(x),1);
tB=ones(length(x),1);
% tPR=ones(length(x),1);
tR=ones(length(x),1);
tC=ones(length(x),1);
alpha=ones(length(x),1);
for i=1:length(x)
    kappaOut(i)=kappafunction5(p,x(i),gamma(i));
    [kappaOut(i),tN(i),tU(i),tI(i),tB(i),tR(i),tC(i),alpha(i)]=kappafunction5(p,x(i));
end
kappaOut=kappaOut';
tN=tN';
tU=tU';
tI=tI';
tB=tB';
% tPR=tPR';
tR=tR';
tC=tC';
alpha=alpha';
end

MATLAB code: Plotting script for “guess and check” thermal conductivity fitting

% This script takes input data from a 3 omega thermal conductivity output
% file and overlays a fitting curve based on a selected set of coefficients
% denoted by "coeffs."

clear;
close all;
clc;

% The output data file is selected below by uncommenting the desired file
% fitkappa
% Get the Excel Data File
% [infile1n,infile1p]=uigetfile('*.*')
% infile1='020216 HT 8-503.6 PVT AlN Thermal Conductivity Curve 3.xls'[::-1]
% infile1='103015 HT3209 Thermal Conductivity Curve.xls'[::-1]
% infile1='021216 HT 2921-3 PVT AlN Thermal Conductivity Curve 2.xls'[::-1]
% infile1='090816 HVPE AlN 6346 Thermal Conductivity Curve last 7 omitted.xls'[::-1]
% infile1='110717 Slack W201 Thermal Conductivity Curve'
% infile1='110717 Slack Pure AlN Thermal Conductivity Curve'
% infile1='082516 HVPE AlN 021 Thermal Conductivity Curve, appended'
% infile1='092115 HVPE GaN Thermal Conductivity Curve'
% infile1='040417 Na Flux GaN Thermal Conductivity Curve'
(infile1='100515 X2192 GaN Thermal Conductivity Curve'
% infile1='092815 X7192 GaN Thermal Conductivity Curve'
% infile1='082916 HVPE AlN 3279 Thermal Conductivity Curve, last 3
omitted, appended'
infile1='052417 GaP 1 Thermal Conductivity Curve'
infile2='AlN Gruneisen Parameter vs. T.xlsx';

dataIn1=xlsread(infile1,1);
dataIn2=xlsread(infile2,1);
TIn1=dataIn1(:,1)';
kappaIn=dataIn1(:,5)';
% gamma=dataIn2(:,2)';
% run('AlN_Lattice_Parameters.m');
% kfunction=@(p,x,gamma)kappafunctionfeedthrough(p,x,gamma);
% guesses=[1e19, 1e19, 5e17, 5e15, 5000e-6, .8];
% coeffs=nlinfit(TIn,kappaIn,kfunction,guesses);
% coeffs=[500e-6, 1.29, 0e16, 0e16, 0e17, 0e16, 0e15, 0e18,
0e15, 0e16, 0e17];
% coeffs=[40e-6, 1.35, 1e16, 1e16, 0e18, 2e17, 0e16, 0e17, 0e15, 0e18,
0e15, 0e16, 2e17];
% coeffs=[330e-6, 1.35, 0e19, 3e16, 0e18, 0e17, 1e16, 0e17, 0e15, 0e18,
0e15, 0e16, 0e16];
% coeffs=[500e-6, 1.35, 0e19, 0e16, 0e18, 0e17, 0e16, 0e15, 0e18,
0e15, 0e16, 0e16];
% coeffs=[500e-6, 1.35, 0e18, 2.58e17, 1.35e18, 9.34e17, 3.08e17, 0e17,
0e15, 4.7e17, 6.79e15, 7.59e17, 0.4e18];
% coeffs=[2.25e-6, 1.35, 0e19, 6.16e16, 1.35e18, 1.21e17, 1.62e17, 0e17,
0e15, 9.82e18, 2.93e15, 5.24e16, 3.24e18];
% coeffs=[300e-6, 1.29, 0e14, 4.59e16, 3.08e17, 0e16, 2.80e17, 0e15, 0e16,
0e16, 0e16, 1.5e18];
% coeffs=[200e-6, 1.29, 0e14, 4.59e16, 3.08e17, 2.80e17, 0e15, 1.5e18];
% coeffs=[500e-6, 1.29, 0e15, 0e16, 0e17, 0e16, 0e14, 0e18];
% coeffs=[7500e-6, 1.99, 0e14, 0e16, 0e17, 0e14, 0e15, 0e18];
% coeffs=[550e-6, 1.79, 0e14, 9.9e18, 2e18, 1.3e19, 0e15, 1e18];
% coeffs=[4000e-6, 2.25, 0e14, 0e18, 1.3e20, 0e19, 0e15, 0e18];
% coeffs=[250e-6, 1.29, 0e14, 0e18, 0e18, 0e19, 0e15, 0e18];
% coeffs=[250e-6, 1.29, 2.6e15, 5.1e16, 9.6e17, 1.3e17, 6.5e14, 2.5e18];
% coeffs=[250e-6, 1.29, 0e15, 0e16, 0e17, 0e14, 0e18];
% coeffs=[20000e-6, 1.09, 0e14, 2e19, 1e19, 0e15, 0e19];
coeffs=[200e-6, 1.79, 0e14, 0e16, 0e17, 0e18, 0e15, 0e18];
% coeffs=[0e18, 0e17, 3e18, 0e17, 50e-6, 0.56, 0e14, 0e16];
% Ceramic AlN grain sizes: CoorsTek=1.5625e-6, Kyocera AN216A=2.6316e-6,
Kyocera
% AN2000=10e-6;
% options=fitoptions('nlinfit','lower',[0,0,0,0,0]);
%
% coeffs for HVPE 3279 = [7.9e18, 0e17, 0e17, 0e17, 300e-6, 1.29, 0e14,
0e15] (11/22/16);
% coeffs for HVPE 3279 = [250e-6, 1.29, 2.6e15, 5.1e16, 9.6e17, 1.3e17, 6.5e14, 2.5e18];
% coeffs for HVPE 021 = [5.2e18, 0e17, 0e17, 0e17, 200e-6, 1.29, 0e14, 0e15] (11/22/16);
% coeffs for HVPE 021 = [200e-6, 1.29, 0e14, 4.6e16, 3.1e17, 2.8e17, 0e15, 1.5e18]; (11/02/17);
% coeffs for lg 8-503.6 = [5e19, 5e19, 5e18, 1e15, 5000000e-6, .25];
% coeffs for sm 8-503.6 = [5e19, 5e19, 5e18, 1e15, 5000e-6, .13];
% coeffs for 8-503.6 = [5e19, 9e17, 4e17, 4e16, 2000e-6, 1.51];
% coeffs for 8-503.6 = [5e19, 9e17, 4e17, 4e16, 2000e-6, 1.51];
% coeffs for 8-503.6 = [5e19, 1e19, 1e18, 0e16, 20000e-6, 0.56];
% coeffs for HT3209 = [2.7e19, 5e18, 5e18, 2e18, 470e-6, 0.165];
% coeffs for HT3209 = [1e20, 2e19, 2e19, 8e18, 470e-6, 0.33];
% coeffs for HT3209 = [3e19, 1e19, 1e18, 0e16, 470e-6, 0.56];
% coeffs for HT3209 = [3e19, 2e19, 5e18, 0e16, 470e-6, 0.56];
% coeffs for HT2921-3 = [2e18, 1e19, 4e18, 2e18, 550e-6, 0.59];
% coeffs for HT2921-3 = [2e19, 1e19, 5e17, 0e15, 5000e-6, 0.56];
% coeffs for HVPE 6346 = [4e16, 4.2e17, 1.6e18, 2e19, 208e-6, 0.89];
% default values: coeffs=[1e18, 1e18, 1e18, 1e18, 7e-25, 1e-24, 450e-6];

fitTs=logspace(-1,3.3,500);
% kappaFit=kappafuctionfeedthrough(coeffs,fitTs,gamma);
% [kappaFit, tN, tU, tI, tB, tR, tC, tPR, alpha]=kappafuctionfeedthrough(coeffs,fitTs);
% [kappaFit, tN, tU, tI, tB, tR, tC, alpha]=kappafuctionfeedthrough(coeffs,fitTs);
% tU=kappafuctionfeedthrough(coeffs,fitTs);
% tI=kappafuctionfeedthrough(coeffs,fitTs);
figure(1);
set(figure(1), 'position', [13 126 660 520]);
% set(figure(1), 'units', 'normalized')
% figure('units', 'normalized', 'position', [.1 .1 .4 .4])
hold on;
scatter(TIn1,kappaIn);
% ylim([10,1000000]);
xlim([0,1,4000]);
xlabel('Temperature (K)')
ylabel('Thermal Conductivity (W/mK)')
title('Thermal Conductivity vs. Temperature')
ax=gca;
set(gca, 'XTick', [25, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200, 250, 300, 350, 400, 1800])

% ax.XMajorTick = 'on'
% set(gca, 'XTick', [.1, 35, 300])
grd on
box on
loglog(fitTs,kappaFit);
% hold off;
figure(2);
set(figure(2), 'position', [693 126 660 520]);
hold on;
% ylim([10e-25,10e10]);
% xlim([.7,4300]);
% loglog(fitTs, tN);
% loglog(fitTs, tI);
% loglog(fitTs, tU);
% loglog(fitTs, tB);
% loglog(fitTs, tR);
% loglog(fitTs, tC);
loglog(fitTs, alpha);
set(gca, 'XScale', 'log', 'YScale', 'log')
% set(gca, 'XTick', [25,30,40,50,60,70,80,90,100,150,200,250,300,350,400])

% figure(3);
% set(figure(3), 'position', [403 126 660 520]);
% hold on;
% loglog(fitTs, tI);
% loglog(fitTs, tU);
% set(gca, 'XScale', 'log', 'YScale', 'log')

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Appendix C

This appendix contains the standard operating procedure (SOP) for assembly of $3\omega$ samples in preparation for testing.

| Title: 3\omega method Sample Assembly | Author: Robert Rounds | Implementation Date: 7/7/2014 |

Purpose
To provide a robust assembly process that when followed properly will produce repeatable results independent of user technique.

Definitions
- Reflow – the process by which electrical contact metal visibly melts and wets electrical contacts.
- Contact pad – an exposed metal pad on a printed circuit board that is for the purpose of providing an electrical connection with an interfacing part
- Indium sphere – a ball of indium that has been shaped to specific dimensions prior to being placed in an assembly in preparation for reflow.
- PCB – acronym for Printed Circuit Board
- Flux pen—a tool containing liquid flux that wets a workpiece surface when the soft pen tip touches it
- Tip-tinner – a hard matrix containing cleaning agents that melts upon contact with a hot soldering iron tip and cleans the oxide buildup on the tip of the iron.

Associated Documents
- N/A

Equipment and/or Materials Required
- 0.5mm 99.99% Indium spheres (5g, supplier number 47245-06, VWR catalog # AA47245-06)
- Flux pen (SRA No. 80 – Neutral, Water Soluble Flux by SRA soldering Products)
- Fine-Point Probe
- Hot Plate
- Omega HH502 Thermometer with K-type thermocouple
- Optical Glass Slide
- Tweezers
- Metallized Sample Wafers
- Sample PCBs (marked with P67513 on one side)
- Header Pins (Part # TSW-224-08-G-S made by Samtec)
- Fine Point Sharpie
• Fluke Multimeter
• Alligator Clip
• Soldering Iron
• Sn 63/Pb 37 Rosin core solder
• Tip tinner
• Brass wool

Safety Notes
• The hot place becomes very hot; please do not touch it while it’s on.
• Never touch the metallized side of the sample wafers with anything.

Responsibilities
• Take extreme care to ensure that the vial of indium spheres does not spill. They are very small and you will regret it if they become spilled and lost.
• Turn off hotplate once PCB/wafer assembly is finished.
• Clean up and put away all materials after assembly is completed.

Procedure
1. Gather together all necessary materials for assembly.
2. Take the SRA #80 flux pen.
3. Take a sample PCB and paint all 12 contact pads with #80 flux.
   a. Each contact pad measures 1.27mm (0.05”) square. Fluxed contact pads should resemble the following image:

   ![Fluxed Contact Pads]

4. Repeat step 3 for any remaining PCBs that need to be assembled.
5. Take the fine point probe and touch the tip to the end of the flux pen.
6. Carefully dip only the end of the probe point into the indium spheres in the jar.
   a. The flux on the tip will pick up a small cluster of indium spheres as shown below.
7. Transfer the indium spheres from the probe tip to the contact pads, one sphere per pad.
8. Working in a clock-wise fashion, ensure that the spheres are in the middle of the contact pads.
   a. PCB/indium sphere assemblies should resemble the following image:

9. Repeat steps 6-8 for the remaining PCBs that must be assembled.
10. Take the Omega HH502 and a K-type thermocouple and proceed with PCB/flux/solder ball assemblies to the hotplate.
11. Take the tip of the thermocouple and an optical glass slide and arrange them such that
    the glass slide sits atop the thermocouple and the thermocouple sits 3-5 cm from the back edge of the hot plate.
    a. The glass slide weighs down the probe tip and allows the operator to verify that the probe tip rests on the surface of the hotplate.
12. Turn on the HH502 Thermometer and verify the temperature is displayed in °C.
13. Turn on the hotplate and allow it to warm up. Ensure that the temperature will not exceed 275 °C.
14. Once the HH502 reads 200 °C, use tweezers to place a PCB/flux/indium sphere assembly at the center of the hotplate surface.
   a. The indium spheres will melt once their temperature reaches 157 °C, but not all at once. The following images show progression of reflow:

![Progression of reflow images]

15. Once all the indium spheres have achieved reflow, use the tweezers to remove the PCB assembly and place it aside to cool.
16. Repeat steps 14 & 15 with all remaining PCB assemblies.
17. Using the tweezers, transfer a metallized sample wafer to the reflowed PCB. Arrange the sample so that the metallized wires on the sample wafer run parallel with the metal traces that join the PCB edge contacts to the center contact pads and so that the metallized contact pads of the sample wafer are resting on the indium-covered contact pads of the PCB.
18. Using the tweezers, carefully transfer the PCB/wafer stack to the center of the hotplate, taking care that the wafer does not fall out of alignment.
19. Wait for reflow of all 12 contact pads.
a. Full reflow can be verified by gently touching the edge of the sample wafer and observing if it self-centers from the surface tension of the molten indium.

20. At the moment that all solder contacts have reflowed, immediately and carefully remove the sample from the hotplate using tweezers and allow the PCB/wafer duplex to cool.
   a. If the PCB/wafer stack is left on the surface of the hotplate for too long after reflow, the integrity of the sample metallization layer wire will be destroyed by alloying with indium.

21. Repeat steps 17-20 for all remaining sample wafers.

22. Turn off the hotplate once all PCB/wafer duplexes have been assembled.

23. Turn on the Fluke and set it to provide audible feedback on the resistance setting.

24. Verify electrical continuity of all four contact pads per metallized wire on the wafer by using the Fluke multimeter. The resistance should be below 100 ohms.

25. Use the fine point sharpie to mark any wire samples that have breaks in continuity.
   a. Broken wires are of no use and therefore will not require further work. Usable wires will require header pins for electrical interconnection with the sample.

26. Take some Samtec header pin connectors and note that the black plastic carriage has a bumpy side facing one end of the pins and a flat side facing the opposite end.
   a. The following image shows the difference:

27. Use the flux pen to paint the through holes of the metal traces on the PCB for the side opposite the wafer.

28. Flux the ends of the header pins that extend from the bumpy side of the black plastic carriage.

29. Turn on the soldering iron.

30. Once the soldering iron has reached operating temperature, gently dip the tip into the tip-tinner. This will produce a small amount of smoke.

31. Clean the soldering iron tip by poking it into the brass wool a few times.
32. Take a fluxed Samtec header pin connector and use an alligator clip to clamp it such that the bumpy side of the black plastic carriage rests against the edge of the PCB and the legs of the header pins rest flat on the surface of the PCB and are slightly offset from the contact pads on two of the metal traces. Make sure that the connection you’re about to make is for a good wire on the wafer sample and not a broken one.

33. Take the soldering iron and melt a small amount of rosin core solder onto the tip.
34. Carefully apply the molten solder at the intersection of the header pin legs the PCB edge contacts. There are a total of four through holes per connector that must be soldered.
35. Repeat steps 32 – 34 for all remaining edge contacts that match with the good non-broken wires on the PCB/wafer duplexes.
   a. Finished PCBs that have a wafer with three good samples should resemble the following image when all header pins are soldered in place:

36. Use the fine point sharpie to label the PCB with the sample name and specify any other relevant information.
Attachments

- N/A

Revision History

<table>
<thead>
<tr>
<th>Revision #</th>
<th>Revision Date</th>
<th>Author</th>
<th>Summary of Changes</th>
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<td>1</td>
<td>7/7/2014</td>
<td>Robert Rounds</td>
<td>Wrote the document</td>
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<tr>
<td>2</td>
<td>4/30/2018</td>
<td>Robert Rounds</td>
<td>Updated with indium contact metal procedure</td>
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Appendix D

This appendix contains operating instructions for the High Temperature Vacuum Probe System.

- Removing/Loading a sample
  - Check that the turbo pump rotations are at 0 Hz on the user interface of the Pfeiffer HiCube pumping station.
  - If the chamber is under vacuum, vent it to atmospheric pressure using the air bleed knob on the chassis of the turbo pump. Close the bleed knob once finished with venting.
  - Check the positions of the electrical probes. If removing or loading the sample risks collision with the probes, use the triple axis manipulators to move the electrical probes out of the way.
  - Unscrew the top viewport door knob and lift the viewport door against the hinge springs until the door stays open.
  - Using a pair of tweezers, carefully remove or load the sample of interest.
  - Close the viewport door and tighten the door knob.
  - Start the Pfeiffer HiCube vacuum pump to evacuate the chamber of air.

- Using the hot stage
  - First verify that the HiCube pressure displays ~10^{-6} HPa or below. Do not turn on the heater above this pressure or the heater components will oxidize.
  - Next, ensure that there is process chill water flowing through the lines. This may be verified by checking that the ball valve handles are parallel to the cooling water hoses and by holding the hoses in your hands to see if they are cold to the touch. Do not use the chamber if cooling water is not flowing.
  - Verify that the black and red cables are connected to both the power supply and the feedthroughs on the bottom flange of the chamber.
  - Ensure that all the electrical probes are not in contact with the sample. Raise any probes that are touching the sample. Due to the large unit length drifts associated with large temperature changes, it is best to avoid probe and sample damage caused by overdrive that results from thermal expansion.
  - Use the Stefan-Boltzmann law (highly non-linear) and the data below to determine the necessary power settings associated with the desired steady-state temperature.
    - Tests using a Raytek Marathon series optical pyrometer yielded:
      - 656° C at 7 V and 10 A (70 W radiated power)
      - 767° C at 10 V and 12 A (120 W radiated power).
o Turn on the 60 A main breaker on the front panel of the TDK Lambda DC power supply. The on-board cooling fan will begin moving air and the indicator lights will come on. Adjust the knobs to the desired power settings.
  ▪ Never drive the heater above 22 V at 21 A. This is the maximum sustainable power, and should correspond to 1200° C. Anything above this risks self-destruction of the heating filament. The heater module costs ~$6000, so don’t ruin it.
  ▪ Since there is no feedback control loop connected to the output temperature of the heater, response is slow unless the user adjusts the control knobs to achieve the desired temperature ramp rate.

o The output thermocouple reading of the temperature PID controller is only accurate near room temperature. There is not yet a calibration curve that correlates a temperature value measured by the Raytek pyrometer and the reading given by the PID device on the front panel display. It is advised that this be done at the earliest convenience of the next regular user.
  ▪ The thermocouple is a bare type R/S and measures the heater temperature from the back side of the substrate heater module.

o If operation is expected for extended periods of time, turn on the probe fans using the front panel switch to cool the probe feedthroughs on the atmosphere side. These may be turned off during measurements if they introduce unacceptable noise.

- Positioning electrical probes
  o Turn on the station computer if it’s not already on.
  o Turn on the ring light of the long-working-distance microscope.
  o Move the microscope boom such that the microscope field of view is over the device to be tested on the sample.
  o Looking through the eyepieces of the microscope, adjust focus if necessary.
  o If not already open, start the image software on the station computer. Verify that the output image appears on the monitor.
  o Adjust the positions of the electrical probes as necessary. Do not overdrive the probes below the first point of contact, or else they will bend.

- Maintenance
  o If maintenance on the heater is necessary, the entire bottom flange must be removed. The ~9 kg weight of the bottom flange assembly on the chamber makes this a two-person job.
  o Prior to removal of the flange, find an appropriately shaped object on which to set the flange such that it remains horizontal. The power and vacuum gauge feedthroughs must not bear the weight of the flange, so be sure that the
supporting object holds the flange assembly at the edges of the flange away from connected feedthroughs.

- Loosen the set screws on the feedthrough side of the in-line cylindrical power connectors that couple the DC power supply output to the heater and disconnect the cables.
- Disconnect the green thermocouple wire at the in-line plug.
- Remove all flange bolts except for two bolts on opposite sides of the flange.
- With one person supporting the weight of the flange, remove the last two bolts and place the flange on the supporting object.
- Perform any necessary maintenance.

- Moving the instrument to another room
  - If the instrument must be moved outside its current lab, the monitor, microscope, and pyrometer (if any) must first be carefully dismounted.
  - Detach the monitor by supporting the mounting arm while unscrewing the clamp that attaches the arm to the table top.
  - Gently set the monitor down such that nothing damages the screen.
  - Remove the microscope head from its mounting arm by loosening the set screw that secures the head to the arm.
  - Gently set the microscope down such that it doesn’t become damaged.
  - Remove the red plastic cap from the microscope mounting arm clamping bolt.
  - Use an adjustable wrench to loosen the clamping bolt, then remove the mounting arm from the table top.
  - If there is a mounting arm supporting a pyrometer that is clamped to the table top, carefully remove it so that the pyrometer doesn’t sustain damage.
  - Move the instrument to the new location.
  - Reassemble the table top equipment.
Appendix E

This appendix contains a list of parts for the High Temperature Vacuum Probe System. Custom parts are detailed in the relevant SolidWorks model files available among the group files stored on the cloud.

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