UNIVERSITY OF CALIFORNIA, SAN DIEGO

Determination of the Thermal Conductivity of Dielectric Thin Films through Experimental Measurement and Crystallographic Analysis

A dissertation submitted in partial satisfaction of the requirements for the degree
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in

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by

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The dissertation of Max S. Aubain is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

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2013
DEDICATION

For my parents, who tirelessly fostered my passion for learning, and my brother, who supported me throughout each step of the process.
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ABSTRACT OF THE DISSERTATION

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The prediction and measurement of the thermal conductivity, $\kappa$, of crystalline materials, particularly in those with nano-scaled structural features, continues to pose a challenge to the heat transfer community. One difficulty arises in the correlation of experimental data with the theoretically calculated, direction-specific phonon dispersion characteristics that determine thermal conductivity, such as heat capacity and group velocity. $\kappa$ is often considered a scalar quantity, which implicitly assumes three-dimensional isotropic behavior, e.g., $\kappa$ of wurtzite (hexagonal) aluminum nitride at room temperature is considered to be 320 W/m.K. Although, simultaneously, it is acknowledged that the phonon transport characteristics within crystalline materials varies non-negligibly with direction; we calculate
the a-axis and c-axis heat capacity and group velocity at room temperature to be different by approximately a factor of 10 and 2.5, respectively, favoring basal-plane heat conduction. Experimental measurements may elucidate these phenomena, but fabrication of large single crystals in multiple orientations is impractical for most materials, and in those samples which are commonly single crystal, such as thin films, nanowires, or nanodots, it is difficult to measure the full thermal conductivity tensor.

This dissertation then develops two experimental techniques to measure $\kappa$ anisotropy of two substrate-supported thin film systems. An optical technique called thermoreflectance thermometry was utilized to measure the heat transport that takes place only within the plane of Si films, ranging in thickness from 70 nm to 255 nm, atop thermally insulating substrates. The use of an optical method was deployed to preclude possible heat losses from contacted thermometer structures and enabled temperature measurements with sub-miliKelvin resolution, with 4 um spatial resolution. Additionally, heater/thermometer structures, in a $3\omega$ measurement configuration, were used to simultaneously probe the cross-plane and in-plane heat transport characteristics of aluminum nitride thin films, between 500 nm and 750 nm thick, deposited by molecular beam epitaxy on sapphire substrates. Finite element models were applied to fit the measured data, using the thin film thermal conductivity as a free parameter. Finally, the results are discussed with respect to calculations of the heat capacity and group velocity based on phonon dispersion relations, and scattering mechanisms specific to the thin film samples.
1 Introduction

The theoretical framework of transient heat conduction equation (HCE) was first published by Jean Baptiste Joseph Fourier in 1807, introducing the classical form of heat transport which has come to be well understood. Consideration of the differential form of the HCE, written in equation 2.1, is useful to develop a basic intuition of how thermal energy, heat, conducts through bulk materials coerced by temperature or heat flux boundary conditions.

\[
\nabla^2 T + \frac{P}{\kappa} = \frac{1}{D} \frac{\partial T}{\partial s}.
\]

(1.1)

Most notably, heat flow is only dependent on the experimental geometry and thermal properties of its constituents, comprised of thermal conductivity, \( \kappa \), density, \( \rho \), and heat capacity, \( C \). The terms \( P \) and \( D \) refer to the internally generated thermal power and the thermal diffusivity, respectively, where \( D = \frac{\kappa}{\rho C} \). The variable \( s \) represents time. The thermal conductivity parameter, while straightforward to understand in this context, contains a rich and complex set of relationships that govern how the behavior of quantized energy packets that carry heat, phonons and electrons, is transduced into a net flow of thermal energy. This dissertation focuses on the behavior of phonons and the role they play in heat conduction through solid, semiconductor materials fabricated on the nanoscale.

Phonons are the quantum analog of coordinated atomic vibrations. They are also bosons that, when present in a crystal lattice, allow the description of their collective behavior to be made through definitions of their wavevector determined energy levels, \( i.e. \) they follow a dispersion relation. In parallel fields of study where dispersion relations are used to describe physical phenomena, namely electrical and
optical engineering, there have been significant technological breakthroughs in the last half-century which have enabled the characterization of the wavevector or frequency dependent behavior of solitary ‘particles.’ For example, the bandgap in semiconductor materials, in conjunction with the ability to control at the single electron level through doping methods and novel device structures, make the control of charge transport in crystalline solids exceptionally tunable. Additionally, unprecedented control of electron flow is accomplished using materials whose electrical conductivity values span over ten orders of magnitude. In optical studies, single mode, narrow-band lasers make computational prediction using Maxwell’s equations accurate and experimental verification relatively straightforward. The field of thermal transport has not yet had similar luxuries and continues, without alternative, to characterize broadband ensembles of phonons.

There is a smaller contrast between thermally insulating and conducting materials than their electrical analogs, exhibiting roughly four orders of magnitude variation. It is common in nanoscaled thermal conductivity experiments to use creative geometries, such as suspended bridges, in order to surround the material of interest in vacuum to avoid parasitic, conductive and convective heat losses inherent in the diffusive nature of heat. Yet, this is replacing one difficulty with another; advanced processing techniques are needed to fabricate these structures. Another solution, one example of which is explored in this work, is to account for the parasitic heat losses through numerical methods. Although careful estimations and confirmatory experiments are needed, this numeric technique has been proven to be accurate and useful in gaining intuition about physical behavior.

It would also be of value to measure phonon propagation properties for individually specified wavevectors and energies, but no phonon equivalent of an optical laser has yet been developed thus limiting most measurements to probe broadband behavior. Phonon ‘filters’ have been developed to negate the long-wavelength tail of the phonon spectrum from contributing to heat transport through variation of the heating pulse time [1], and to measure the conduction of phonons with shorter mean free paths through control of the probe size [2]. Interface phonon scattering behavior can span from diffusive to specular, which has been considered theoreti-
cally through the diffusive mismatch and acoustic mismatch models, respectively [3, 4]. Understanding scattering behavior is complicated by how the mechanism is wavelength dependent and, in practice, the finite thermal resistances present at the interface between two materials can become non-negligible [5] and the quality of these interfaces is typically difficult to predict and control.

Nonetheless, characterization and understanding thermal transport in microstructured materials remains paramount from both an applied and a fundamental perspective and the work presented in this dissertation was pursued in order to address some of the current issues faced by the thermal measurement community: thermal conductivity anisotropy in thin films. In this work a new thermal measurement is proposed to probe the direction-dependent heat transfer properties of crystalline, semiconducting thin films adhered to solid substrates. The method is optical and non-contact, precluding one issue common in thermal measurements – heat leakage from the test volume by way of the temperature probes. The high sensitivity of the optical measurement supports sub-millikelvin temperature resolution and micron-scale spatial resolution, with scanning capability allows for detailed temperature mapping. Finite element modeling software is then implemented to correlate the temperature measurement with the thermal conductivity of the film. Extraction of the thermal behavior of the film from the substrate system is successfully performed for a variety of heater-film-substrate geometric configurations. The accuracy of this technique is confirmed through measurement of the in-plane thermal conductivity, \( \kappa_{ip} \), of Si thin films in the Silicon-On-Insulator (SOI) substrate configuration. The measured \( \kappa_{ip} \) values are analyzed with respect to phonon-boundary scattering mechanisms, and are very well matched with previously measured values [6, 7, 8, 9]. Further characterization of heat transport in substrate supported thin films is carried out on single crystal epitaxial AlN thin films deposited on sapphire substrates using a modified version of the commonly used 3\( \omega \) method. AlN belongs to a unique class of ionic, wide band-gap semiconductor materials, such as BeO, diamond, and SiC, that simultaneously exhibit high thermal conductivity and electrically insulating properties [10, 11, 12, 13]. The single crystal bulk has been measured to have a room temperature \( \kappa \) of up to
319 $\text{W.m}^{-1}\text{K}^{-1}$ [10], which is comparable to one of the most widely used heat sink materials, Cu ($\kappa_{\text{Cu}} = 401 \text{W.m}^{-1}\text{K}^{-1}$). This combination of properties may be useful if integrated into microelectronic devices to serve as passive heat spreading layers while electrically isolating one device from another, in order to mitigate the ever-present issue of self-heating. Using the presented techniques, the $\kappa_{ip}$ and cross-plane thermal conductivity, $\kappa_{cp}$, is determined for single-crystal and polycrystalline AlN thin films and the effects of grain boundary and defect scattering are discussed.

1.1 Heat transport in solids

Heat transport is mediated by a combination of radiative, convective, or conductive mechanisms, which are commonly characterized through measurement of the spatially dependent thermal potential energy, $k_b T$, defined through temperature, $T$. Conduction is the dominant heat transfer mechanism in solid materials: a lack of mass transport prevents convective heat transport and intrabody radiative effects are negligible. In a steady-state condition of a homogenous, axisymmetric material heated at one end and thermally grounded at the other, the thermal conductivity of an undefined solid is determined through Fourier’s law of heat conduction for one dimension,

$$\frac{\dot{Q}}{A} = -\kappa \frac{\partial T}{\partial x},$$

(1.2)

where the heat flux, $\dot{Q}$, per unit area, $A$, is sustained by the temperature gradient, $\frac{\partial T}{\partial x}$, with the relative magnitudes determined by the thermal conductivity, $\kappa$.

Acknowledging that the rate of heat transfer is defined by not by the thermal energy differential, $\Delta T$, but by the gradient, implies that heat transport is a diffusion limited process. The classical kinetic theory of gases has been used to approximate the relation of the material thermal conductivity to its energy-carrying quasi-particles,

$$\kappa = \frac{1}{3}Cvl,$$

(1.3)
where the values of heat capacity, $C$, velocity, $v$, and mean free path, $l$, are identical for all particles, and the product of $Cvl$ must normalized by three degrees of freedom to arrive at the average value in a given direction. The mean free path is defined as average distance travelled by a particle before colliding with another particle. This nomenclature is known as the “gray approximation,” in which all particles contribute to heat conduction equally and, hence, are indistinguishable, or ‘gray.’ Of course, it is well known that thermal energy in solids is transported by ensembles of quantitatively unique phonons and electrons, such that $\kappa = \kappa_{ph} + \kappa_{el}$ [14]. In the work presented here, we analyze these phenomena in crystalline, intrinsic or large band-gap semiconductors and, thus, neglect the contribution of electrons, $\kappa_{el} \rightarrow 0$, and focus on the mechanisms by which phonon transport is influenced by crystal structure and quality, as well as sample geometry.

1.2 Heat as phonons

The propagation of phonons in a crystal lattice is a well-posed problem of wave propagation in a periodic potential. Phonon dispersion curves can be calculated when the crystal morphology, lattice and elastic constants, and atomic masses are known, and is shown to agree with experimental results for the heat capacity of Si [15, 16], AlN [17, 18, 19, 20] and pyrolytic graphite [21] systems. The phonon dispersion relation contains the information of the first two parameters in equation 1.3, $C$ and $v$. The mean free path remains relatively difficult to characterize through both ab initio and experimental approaches, and is typically used as a fitting parameter to match thermal conductivity theory to data. Nonetheless, the behavior of phonons as heat-carrying particles can be captured mathematically by rewriting equation 1.3 with respect to all permissible wavevectors, $b$, in crystallographic direction indexed by, $b_{ij}$, with longitudinal and transverse polarizations, and acoustic and optical modes, encapsulated in subscript $p$,

$$\kappa_{ij} = \sum_p \int_{b_{ij}} C(b_{ij}, \omega_p)v(b_{ij}, \omega_p)l(b_{ij}, \omega_p)db,$$

where $\kappa_{ij}$ is defined through,
\[ \dot{Q}_i = \kappa_{ij} \nabla T_j. \quad (1.5) \]

In this formulation, the thermal conductivity is proportional to the product of \( C_{vl} \), which is wavevector and polarization dependent, and matches the bulk value when integrated over all permissible wavevectors.

### 1.2.1 Heat capacity

The bulk heat capacity, \( C \), defines the amount of thermal energy that must be transferred to a material before it rises one unit of temperature (degree Kelvin), per unit volume (cubic meter). In the case of an electrically insulating crystalline solid, it is defined as the temperature derivative of the total internal energy harnessed as phonons, \( U \),

\[ C = \frac{dU}{dT}, \quad (1.6) \]

where \( U \) is equal to the sum of the energy contained in each phonon polarization, \( p \), over all wave vectors for a given crystallographic direction, \( b_{ij} \),

\[ U = \sum U(b_{ij}, \omega_p). \quad (1.7) \]

The total energy per mode is determined the sum of the energy of each phonon whose population density is fixed by the dimensionality of the system and the energy distribution, specified by the Boltzmann distribution, integrated over all permissible wavevectors,

\[ U(b_{ij}, \omega_p) = \int_0^{b_{ij,0}} D(b) n_B(\omega_p(b_{ij})) \hbar \omega_p(b_{ij}) db. \quad (1.8) \]

In equation 1.8, \( b_0 \) is the maximum wavevector allowed, corresponding to the edge of the 1st Brillouin Zone (BZ). \( \omega_p(b) \) is the phonon frequency of mode \( p \) at wavevector \( b_{ij} \). \( D(b) \) is the Density of States (DOS) in three dimensions, and \( n(\omega_p(b)) \) is the Boltzmann distribution.

With an assumed three-dimensional lattice, the derivation of DOS is as...
follows,

\[ N(b) = \left( \frac{L}{2\pi} \right)^3 \frac{4\pi}{3} b^3 = \frac{L^3 b^3}{6\pi^2}. \]  

(1.9)

\[ D(b) = \frac{dN}{db} = \frac{L^3 b^2}{2\pi^2}. \]  

(1.10)

The Boltzmann distribution is,

\[ n_B(\omega_p(b)) = \frac{1}{\exp \left( \frac{h\omega_p(b)}{k_B T} \right) - 1}. \]  

(1.11)

Thus, through substitution of the relevant terms into equation 1.8, the total phonon energy *per unit volume* is,

\[ U = \frac{1}{2\pi^2} \sum \int_0^{b_{ij}} \frac{b_{ij}^2 h\omega_p(b_{ij})}{\exp \left( \frac{h\omega_p(b_{ij})}{k_B T} \right) - 1} db, \]  

(1.12)

and the temperature derivative of equation 1.12 provides the final form of the bulk heat capacity,

\[ C = \frac{dU}{dT} = \frac{\hbar^2}{2\pi^2 T^2 k_B} \sum p \int_0^{b_{ij}} \frac{b_{ij}^2 (\omega_p(b_{ij}))^2 \exp \left( \frac{h\omega_p(b_{ij})}{k_B T} \right)}{\left( \exp \left( \frac{h\omega_p(b_{ij})}{k_B T} \right) - 1 \right)^2} db. \]  

(1.13)

The crystallographic direction chosen to define the phonon dispersion and, accordingly, \( C \), is considered in predicting \( \kappa \). Previously attempted theoretical analysis of the bulk specific heat of Si [22, 23] has assumed an isotropic phonon dispersion relation equivalent to that established for the (100) crystallographic direction. We have replicated the Si heat capacity calculation from equation 1.13.
and plotted the values simultaneously with experimental values measured by others [22], shown in figure 1.1. The close match between the heat capacity values calculated using the isotropic phonon dispersion approximation, and the measured data, suggest that the thermal behavior of Si can be accurately predicted with such an approximation. However, this simplified method does not address the efficiency of heat conduction in the (111) or (110) directions, which has been measured at low temperatures to vary significantly from the behavior in the (100) direction [24], nor does it provide insight on how it might be applied to non-cubic crystals. In practice, $C$ should be evaluated in three dimensions to account for the entirety of the crystal geometry and a method to perform this analysis is proposed through the investigation of a hexagonal-close-packed (HCP), wurtzite crystal structure of AlN in chapter 4.
1.2.2 Phonon group velocity

In the kinetic theory of heat conduction, the phonon velocity is commonly assumed to be equal to the acoustic velocity of sound. With respect to the wavevector and polarization dependence of phonons, this is an equivalent assumption to all phonons having velocity equal to that of phonons populating the longitudinal acoustic band near zero wavevector. This inherently velocity characteristics of phonons at short wavelengths in both the acoustic bands and the optical bands. Instead, the dispersion relation can be used to specify the velocity by which an ensemble of phonons, with identical wavevector and polarization, propagate through a lattice; this group velocity is defined by the slope of the frequency-wavevector dispersion curve: \( v_g \equiv \frac{\partial \omega_p}{\partial b} \).

Phonon dispersion curves of real materials reveal complex propagation behavior. For example, in crystalline Si, many bands are occupied by a non-negligible number of phonons that have group velocities which significantly deviate from the acoustic velocity [16, 25, 15]. The calculated Si phonon DOS is concurrently shown with the calculated full phonon dispersion in figure 1.2, with plotted experimental values obtained by inelastic neutron scattering in agreement. In the regime of 13 to 15 THz, the optical phonon bands exhibit the capacity to store a significant amount of thermal energy evidenced by the large DOS. However, the \( v_g \) values in this energy region are near zero at the major critical points (\( \Gamma, L, K, \) and \( X \)) suggesting these phonons contribute to thermal energy storage, not conduction. For many ranges of wavevectors in between the critical points, the \( v_g \) is negative implying that optical phonons even oppose heat conduction, or propagate in the direction of the temperature gradient, at high energies.

The variation of \( v_g \) in both magnitude and sign suggests that phonons may be categorized into two types: those that contribute to thermal energy transport with non-negligible group velocity and thus contribute to \( \kappa \), and those with small \( v_g \) which store heat. G. Chen made this distinction in an effort to calculate a more accurate phonon mean free path in bulk Si, by first assuming the usual value for \( \kappa \), and then calculating an average value for \( v_g \) based on the phonon dispersion and neglecting the contribution of the optical phonons to the total heat...
capacity, resulting in a reduction of $C$ by $\sim \frac{1}{3}$ and $v$ by $\sim \frac{1}{2}$. This technique has been labeled in the literature as the “semi-gray approximation.” Analysis within this work refines the accuracy of the semi-gray approximation one step further by calculating the product of $Cv$ as it is being summed over all wavevectors and polarizations, as opposed to using the product of the independently calculated $\bar{C}$ and $\bar{v}_g$, thus scaling the amount of energy carried by a phonon to its corresponding group velocity. It is then appropriate to define the bulk $\bar{v}_g$ as follows,

$$
\bar{v}_{g,ij} = \left[ \sum_p \int_{b_{ij}} C(b_{ij}, \omega_p) v_g(b_{ij}, \omega_p) db \right] \left[ \sum_p \int_{b_{ij}} C(b_{ij}, \omega_p) db \right]^{-1}.
$$

(1.14)

Using this methodology to calculate the average phonon velocity yields significantly different values than that of the acoustic sound velocity assumption. The speed of sound in Si in the [100] direction is approximately 6400 m.s$^{-1}$, while $\bar{v}_g$ has been calculated to be closer to 2500 m.s$^{-1}$ [26, 22], further delineating the discrepancy between the gray and semi-gray approximations.
1.2.3 Phonon wavelength and mean free path

There are two length-scale specific phenomena that affect how phonons contribute to thermal conduction: the wavelength, $\lambda_p$, which governs how wave-like the phonon behaves when interacting with structural and material features, and the mean free path, which determines to what degree phonon propagation is ballistic or diffusive. The heat conduction process uses phonons of all wavelengths, provided $\lambda_p$ does not exceed an upper limit either spatially fixed by the characteristic length scale, $L$, of the sample under test, or temporally limited by the distance to which heat has time to propagate as it conducts through a material. Additionally, the maximum $\lambda_p$ changes the effective $\kappa$ by specifying the minimum $\omega_p$ in the integral that calculates $C$. Phonons propagating in an infinitely large, perfect crystal at 0 K would propagate in a purely ballistic fashion, but as physical and energetic perturbations are introduced, phonon-system interactions that interfere with ballistic transport are a statistical certainty. The quality of the interaction is determined by the relative scales of $\lambda_p$ and the system imperfection. For example, in the case of phonon interactions with solid-solid interfaces and $\lambda_p$ is much greater than the roughness of the interface, phonons propagating through the interface behave specularly and follow the acoustic mismatch model (AMM) [27]. This behavior follows directly with an optical analog, where the acoustic reflection for a normally incident phonon traveling from material 1 through an interface into material 2 is defined by,

$$R_p = \frac{Z_1 - Z_2}{Z_1 + Z_2},$$  \hspace{1cm} (1.15)

and the acoustic impedance is $Z(=\rho v_g)$.

Conversely, when $\lambda_p$ is on a similar length-scale as the interface roughness, or smaller, it will likely scatter according to behavior roughly approximated by the diffuse mismatch model (DMM) [4], which assumes that phonons absorbed and re-emitted from interfaces, and do so irrespective of their initial state. In this approximation of phonon scattering, it is useful to reintroduce the mean free path parameter, described by an average phonon scattering time, $\tau_p = \frac{L}{v_g}$. The $\omega_p$ and $T$
dependence of the three dominant scattering effects in crystalline solids, boundary scattering, impurity scattering and phonon-phonon (or umklapp) scattering, are sequentially defined in equation 1.16 [28].

\[
\frac{1}{\tau_p} = \frac{F_s v_g}{L} + F_1 \omega_p^4 + F_2 e^{-\left(\Theta_D/F_3 T\right)} T^3 \omega_p^2 \tag{1.16}
\]

The boundary scattering term contains the characteristic length scale of the sample, \(L\), and a fitting parameter, the shape factor, \(F_s\). Impurity scattering is analogous to Rayleigh scattering in that the impurity size is typically much smaller than \(\lambda_p\), leading to a \(\omega_p^4\) dependence with fitting factor \(F_1\). Finally, the umklapp process, which introduces a unique transform of the phonon momentum vector as it is scattered into a new Brillouin zone, dictated by the Debye temperature of the material, \(\Theta_D\), and two fitting factors, \(F_2\) and \(F_3\), has both temperature-cubed and frequency-squared dependence which make this mechanism dominant at room temperature.

Intrinsic semiconducting materials, where electrons play an insignificant role in heat conduction, typically exhibit a \(\kappa\) vs \(T\) behavior similar to that of Si, shown in figure 1.3. The regime at low temperatures is characterized by large average \(\lambda_p\) and large \(l\), where geometric boundary scattering is dominant. This is commonly called the ‘Casimir’ regime, after H. B. G. Casimir who discussed nearly ballistic phonon transport at low temperatures [29]. The gradual increase in \(\kappa\) is due to an increase in heat capacity correlated with the rise in the density of states with temperature; fewer and fewer phonon are ‘frozen.’ This trend is rapidly offset near 25 K by increasing impurity and defect scattering and is eventually dominated by phonon-phonon scattering at high temperatures.

Myriad types of semiconductor processing introduce modifications to \(\kappa\) through the scattering term. For example, dopant implantation for carrier density engineering in SOI thin films [32] introduces defects and impurities which increase phonon scattering in the bulk of the film. In other, epitaxial superlattice structures, intra-film domains are introduced that are thought to introduce mini-Brillouin zones and could be used for simultaneous phonon and electron bandgap engineering. In most cases, however, the interfaces between these domains diffu-
Figure 1.3: The measured $\kappa$ of Si [30] with characteristic parabolic response with respect to temperature fit by Yang et al. [31].

Singly scatter cross-plane travelling phonons due to similar characteristic length between the nanometer-scale interface roughnesses and small wavelength phonons that contribute to heat conduction [33, 22, 34], most strongly influencing $\tau_p$ over the original intension of modifying $C$ or $v_g$. Thin film growth mechanisms and conditions commonly lead to non-equilibrium crystal states, with grain boundaries and defects, which also lead to increased phonon scattering. The cumulative effects of scattering mechanisms add in parallel, justified phenomenologically by the scattering mechanism that leads to the shortest scattering times dominates the magnitude of the mean free path.

$$\tau_p^{-1} = \tau_{\text{phonon-phonon}}^{-1} + \tau_{\text{impurity}}^{-1} + \tau_{\text{defect}}^{-1} + \tau_{\text{boundary}}^{-1} + \tau_{\text{interface}}^{-1} + ...$$

(1.17)
1.3 Determination of thin film thermal conductivity

Analysis of the factors that determine bulk thermal conductivity, as described above, do not inherently differ from that which can be used to describe heat conduction in thin films; what may vary between systems is which scattering terms are most influential. Note: An exceptional case which will not be discussed here, would be a thin film with thickness on the order of a few nanometers that may confined phonon effects, if its thermal behavior is not dominated by boundary scattering introduced by surface roughness. In systems where the thin film is a single crystal with few defects, \( e.g. \) industrially available silicon-on-insulator wafers, the heat transfer characteristics intrisic to the material do not differ from the bulk, but geometric factors introduced by the thin film top and bottom planar boundaries may become influencial. For example, as the length scale of the film thickness, \( t \), approaches the phonon mean free path, \( l \), as defined for the bulk material, the boundary interface scatters phonons within the material to a greater degree, thus, reducing heat conduction. This thin film effect is conveniently quantified by defining the cross-plane and in-plane thermal conductivity, \( \kappa_{cp} \) and \( \kappa_{ip} \), which are the effective thermal conductivity values with respect to heat conduction parallel to the film surface normal vector, and in the plane of the film, respectively, and by claiming that measured, or predicted, difference between the two values must be explained by the boundary scattering. Of course, this effect quickly vanishes if features in the crystal, such as grain boundaries in polycrystals, are more densely spaced in the bulk of the film in comparison to the film thickness. The other way that thin films often differ from bulk manifestations of the same material is how they are manufactured and processed. For example, sintered AlN manufactured for low temperature cofired ceramic modules will likely have a drastically different crystal structure, and possibly modified stoichiometric composition, in comparison to sputter or evaporation deposited AlN films. These microstructural differences are understood through the \( \tau \) term in the thermal conductivity integral (equation 1.4) and are not dependent on the nature of the material being a ‘thin film’.
As the few fundamental differences between heat transport in bulk and thin film materials are elucidated, the remaining efforts in characterizing thin film thermal conductivity must be devoted to experimental measurement. The primary challenge in this endeavor is inherent to the characteristics of the film/substrate system, where thin films are typically fabricated on, and supported by, substrates with thicknesses $10^2$ to $10^5$ greater than $t$. As heat from a measurement probe interacts with both domains, the resulting temperature profile (the most commonly measured quantity) may be overwhelmingly dependent on the substrate $\kappa$ due to their relative sizes, making determination of the thin film $\kappa$ difficult. In the next chapter, experimental methods developed to extract the small contribution that reveals the thermal conductivity of the thin film will be discussed and critiqued.
2 The art of thermal conductivity measurements

The design of any experimental technique must come through exploitation of the appropriate physical parameters, and their relations, to maximize the contrast in the measurable result, which (hopefully!) returns the unknown value of interest. The HCE is represented in equation 2.1,

$$\nabla^2 T + \frac{P}{\kappa} = \frac{1}{D} \frac{\partial T}{\partial s},$$

(2.1)

where parameters \( P \) and \( D \) refer to the internally generated thermal power and the thermal diffusivity, respectively, with \( D = \frac{\kappa}{\rho C} \) in which \( \rho \) is the density of the material, and the variable \( s \) represents time. This relationship shows that the diffusivity term is the dominant physical parameter that relates the temporal and spatial components of thermal transport. Thus, an intuitive understanding of the effects of \( D \) on the variation of \( T \) with respect to space and time will aid in achieving better experimental design. Case in point: The behavior of the diffusivity term for solids commonly found in semiconductor manufacturing, is typically decided by the thermal conductivity, as \( \kappa \) can vary two orders of magnitude between materials (\( \kappa_{SiO_2} \sim 1.4 \text{ W.m}^{-1}\text{K}^{-1}, \kappa_{Cu} \sim 401 \text{ W.m}^{-1}\text{K}^{-1} \)), whereas \( \rho \) varies by a factor of two (\( \rho_{Si} \sim 2330 \text{ kg.m}^{-3}, \rho_{GaAs} \sim 5320 \text{ kg.m}^{-3} \)), and \( C \) trends inversely with \( \rho \), on the same order (\( C_{Si} \sim 705 \text{ J.kg}^{-1}\text{K}^{-1}, C_{GaAs} \sim 330 \text{ J.kg}^{-1}\text{K}^{-1} \)). It then follows that the contrast in measured values of \( T \) will correlate most to changes in \( \kappa \), geometry, or time scale, rather than the other materials properties. In this chapter, heat conduction within solids will be examined and discussed with respect
to the advantages and challenges inherent in many common thermal conductivity measurements, specifically those used to measure nanoscaled thin films. Then, we then propose and implement modifications that improve upon spatial-domain thermoreflectance (TR) techniques and the $3\omega$ method.

### 2.1 Heat flow in time and space, and the electro-thermal analogy

There are three independent experimental avenues to probe $D$: (1) a time invariant steady-state measurement, leaving $\kappa$ as the only free material parameter; (2) the use of a transiently powered heat source with a spatially localized temperature probe, which may be highly sensitive to $D$ or $\kappa$, dependent on the AC heating period; (3) a measurement of the linear superposition of both the transient and the spatially varying $T$. It can be useful to qualitatively classify the various heat transfer regimes through a commonly used analogy between electrical and thermal transport. In the cases where thermal and electrical conduction operate within the diffusive regime, the following equivalencies can be made,

1. $\sigma \Leftrightarrow \kappa,$
2. $I_{el} \Leftrightarrow \dot{Q},$
3. $\Delta V_{el} \Leftrightarrow \Delta T.$

The formulation of Fourier’s law of steady-state heat conduction can then be derived from Ohm’s law,

$$I = \Delta V \left[ \frac{L}{\sigma A} \right]^{-1} \Leftrightarrow \dot{Q} = \Delta T \left[ \frac{L}{\kappa A} \right]^{-1}. \quad (2.2)$$

To complete the electro-thermal analogy with the three experimental conditions listed above, they describe the direct-current (DC) case, alternating-current (AC) case, and the linear sum of the DC and AC phenomena. Further elaboration on the conductivity analogy permits the definition of a one dimensional thermal ‘resistivity,’ $R_{th} = \frac{L}{\kappa A}$, that applies in both AC and DC. For the AC condition, a
thermal capacitance, $C_{th} = \rho C$, can be used to define a thermal time constant, $\tau_{th} = R_{th} C_{th}$. For a Dirichlet temperature boundary condition (BC) at a fixed point, the solution to the heat conduction equation of the surrounding body will be of the form $T(s) \propto e^{\frac{s}{\tau_{th}}}$, mimicking the behavior of a discharging capacitor, as thermal potential $T$ and electrical potential $V_{el}$ both decay with the characteristic exponential curve. While the electro-thermal analogies do not aid in solving the HCE, understanding heat transport with respect to easily conceptualized circuit models helps in developing intuition and the design of thermal experiments; these terms will be used throughout the rest of the chapter to describe the reviewed measurement techniques.

### 2.2 Measuring thin film thermal conductivity

The heat stimuli used in thermal conductivity measurements of substrate supported thin films fall into one of three temporal BC regimes, DC, AC, and AC + DC. In the latter two states, the purely transient (AC) case is ensured when the AC period $\gg \tau_{system}$ such that the system relaxes to thermal equilibrium after each pulse, and 'quasi' steady-state (AC + DC) case occurs when the AC period $< \tau_{system}$ and the signal is measured after $s >> \tau_{system}$. Each measurement time scale has distinct trade-offs. The convenience of DC measurements manifests in both the theoretical and experimental domains: steady-state solutions of the HCE are more straightforward to solve for complex geometries, and only basic electrical instrumentation is needed for temperature measurement, commonly implemented by thermocouple or thermally resistive detector. Steady-state measurements on thin films must be carried out in vacuum to prevent convective heat losses; convection can be especially confounding in thin film measurements due to the large surface area to volume ratio. AC thermal experiments provide a variety of advantages over steady-state measurements. Convective heat losses in non-vacuum environments on the time scale of the measurement are precluded when the heating and probe periods are much smaller than the heat loss transient. Additionally, modern instrumentation used to acquire AC signals include advanced filters, allowing for
the detection of AC signals over five orders of magnitude smaller than background noise. Finally, control over the thermal diffusion length, also called the ‘thermal penetration depth’ (TPD), during a single heating period, is possible. The physical basis for this claim can be explained if the sample is perceived an thermal RC network, which will have a lumped thermal time constant. Accordingly, the heat will conduct from source to sink, more quickly through the paths of least resistance. If the heating time is smaller than the RC time constant, the heat will not have time to flow all the way to the sink during a single pulse, leaving it trapped in the earlier elements. This transient response has been used, for example, to restrict heat flow in thin film materials to probe $\kappa$ through short time-scale surface heating in order to contain the TPD to the film, but not the underlying substrate, thus significantly increasing the sensitivity of the experimental method.

Concomitantly with transient heat flow behavior, the characteristic length scale of the heating area relative to the geometric parameters of the sample volume can be used to enhance anisotropic heat flow, thus probing individual components of the thermal conductivity tensor. For example, if a uniform heat flux is applied to the entire surface of a thin film on a substrate, with the substrate bottom grounded, one-dimensional heat conduction takes place with only the film $\kappa_{\text{cp}}$ and $\kappa_{\text{sub}}$ influencing heat conduction. Instead, if the sample dimensions remain fixed while the heat flux is systematically reduced in area, heat will escape by a continually increasing amount in the plane of the film near the edges of the heating area. The distance that the heat will travel through the film before it passes into the substrate depends on the relative $\kappa$ values of the two domains, and the thickness of the film. Alternatively, the substrate influence can be completely avoided through the suspension of the thin film structure to restrict heat conduction to the in-plane direction and solely probe $\kappa_{\text{ip}}$. Current thin film thermal conductivity measurement techniques, regarded as either cross-plane, in-plane, or a mixture of both, are discussed in the following sections.
2.2.1 Cross-plane measurement techniques

The “flash” method embodies the basic mechanisms used to extract the cross-plane thermal conductivity of a substrate or multilayer stack. In the earliest version of the technique implemented by Parker, et al., a modulated heat lamp was used to impart a thermal pulse on the front side of axially symmetric sample and a thermocouple is used to monitor the subsequent heating on the back [35]. In this experimental geometry, one dimensional heat transport through the thickness of the sample is maintained, allowing for fitting of the diffusivity through the equation,

\[ D \propto \frac{F \times L^2}{s^{\frac{1}{2}}}, \]  

(2.3)

where \( F \) is a geometrically determined factor, \( L \) is the length of the sample, and \( s^{\frac{1}{2}} \) is the amount of time that passes before the sample temperature rises to half of its peak value. The experimental requirement of the heat passing through the entirety of substrate thickness makes adaptation of this method to study thin films difficult, as the effective thermal diffusivity of the sample is likely dominated by the substrate. Instead, other measurement techniques have been developed using localized thermal pump and probe geometries to make the heat transport behavior sensitive to nearby features, like nanowires and thin films.

One of the most widely used thermal measurement techniques is the \( 3\omega \) method, based on a method developed by Birge and Nagel to measure the specific heat of liquids [36], was first introduced by Cahill to measure the thermal conductivity of solids [37], and further expanded to characterize thin films [38]. The \( 3\omega \) method utilizes a long, narrow metal line deposited on the surface of the sample which simultaneously acts as a heater and thermometer, whose schematic cross section is featured in figure 2.1. Sinusoidal AC heating is induced in the metal line through Joule heating through an electrical current at angular frequency \( \omega = (2\pi f) \). The current signal is rectified by the \( I^2 \) Joule heating term, which drives a temperature dependent resistance change of the metal line at \( 2\omega \). Finally, the heating is monitored through the voltage at \( 3\omega \), \( V_{el,3} \), that arises from the
product of the $1\omega$ voltage and $2\omega$ resistance variation. In this configuration, radial heat flow is assured when the TPD $\sim \sqrt{\frac{\kappa}{\omega \rho C}}$ is much greater than the heater width, and if the TPD is much less than the substrate thickness, to heated volume may be approximated as semi-infinite. With these geometric constraints, an analytic solution to the HCE can be used to relate the $\kappa$ of the substrate to the frequency dependence of the self heating,

$$\kappa \propto F \times \frac{\ln(f_2/f_1)}{V_{el,3.1} - V_{el,3.2}}. \quad (2.4)$$

**Figure 2.1:** Schematic cross section of the $3\omega$ sample geometry, perpendicular to the long dimension of the heater [37].

The thin film $\kappa$ may be extracted from a differential version of the $3\omega$ method, where the self heating of the heater structure is compared between a bare substrate and film/substrate system. In this method, the heater width and TPD must be much greater than the film thickness such that the thermal characteristics of the film can be included in the model as a one dimensional $R_{th}$. An example of the self heating ($\Delta T$) as a function of $f$ used to measure the $\kappa_{cp}$ of a SiO$_2$ thin film on a Si substrate is shown in figure 2.2 [38]. The precision of the method diminishes when the sensitivity of the heater cannot measure the influence of the thin film with the self-heating effect, as in cases with very thin films, or in films with much higher thermal conductivity than the substrate. Additionally, if the geometric restrictions of the method that enable the analytic fitting cannot be met, alternative methods, such as finite element modeling, must be used.

Time-domain thermoreflectance (TDTR) technique pioneered by Paddock and Eesley [39] addresses the issues associated with the geometry and implemen-
Figure 2.2: Example of data obtained using the $3\omega$ method. The offset of the two curves were used to measure the thermal resistance of a 45 nm SiO$_2$ thin film $\kappa$ [38].
tation issues associated with the $3\omega$ method and, essentially, can measure predominantly the cross-plane thermal conductivity of any sample that has a smooth, reflective surface and is at least a few tens of nanometers thick. In principle, it is identical to the $3\omega$ method: the surface of the sample is heated, and the rate at which the heat escapes into the bulk of the sample is correlated to the $\kappa$ of the sample through fitting to a solution of the HCE. Heating and measurement is accomplished by a ‘pump,’ using a single high energy, excimer laser pulse with width on the order of picoseconds to heat the surface of the film in an area of about a few square microns as the optical energy is absorbed. Thin metal overlayers are deposited on the surface of transparent samples to ensure uniform heating at the top of the film. The phenomena of thermoreflectance, which derives from the temperature dependence of the refractive index of a material, is used to ‘probe’ the temperature of the heated surface via a reflectance measurement to investigate how quickly the heat diffuses cross-plane. The temporal probe pulse width is less than 10 picoseconds, which correlates to an effective TPD on the order of nanometers, thus directly measuring the thermal conductivity of a thin film, irrespective of substrate. Improvements by Capinski, et al., reduced the error in the timing in the probe pulse by replacing the previously used mechanical stage which introduced the optical delay, with an optical fiber setup [40]. Alternative pump/probe methods have also been developed, such as the thermal wave-mirage technique [41]. Very similar to the TDTR method, the thermal response of the material is measured not through a surface-reflected signal, but deduced from the ‘mirage,’ or thermally modulated refractive index, of the heated air above the sample hot spot.

2.2.2 In-plane measurement techniques

Measurements of the in-plane thermal conductivity of substrate supported thin films can only be accomplished when $\kappa_{\text{sub}} << \kappa_{\text{film}}$ and sufficient heat is confined to the film such that the measured temperature profile is $\kappa_{\text{film}}$ dependent. This has been implemented in Si films on SOI substrate using electrical resistance thermometry in the steady state [42, 9], where temperature variation at two distinct
points (via \textit{in situ} fabricated highly doped areas in the Si films as shown in figure 2.3) was measured using an electrical resistance change. Subsequently, the $\kappa$ was fit using an approximate solution to the two-dimensional, steady-state HCE. In other efforts, the film can be suspended by removing a sacrificial layer in between the film of interest and the substrate, effectively implementing a ‘zero’ thermal conductivity substrate. Liu and coworkers performed measurements on suspended Si thin film membranes, fabricated through wet etching techniques using a geometry shown in figure 2.4 [7]. This methodology requires comparison of a metal heater deposited on a suspended bridge, with and without the Si device layer present, and thermal contact issues related to the sensors could still be significant in the characterization of $\kappa_{ip}$.

![Figure 2.3: Schematic cross section of sample geometry to measure $\kappa_{ip}$ of Si films using electrical heating and temperature probe structures [42].](image)

Some $\kappa_{ip}$ measurements evolved from $\kappa_{cp}$ measurements as the accuracy and precision of the methods were improved to include additional terms to the solution of the HCE, accounting for effects from heat flow in-plane and cross-plane simultaneously. A few corrections in the measurement of the $\kappa_{cp}$ in the $3\omega$ method, to capture the degree heat flow parallel to the surface, have been described by Borca-Tasciuc, \textit{et al.}, to understand the relative influences of the TPD, heater width, underlying layer thickness, and thermal conductivity anisotropy, and other geometry dependent correction factors [43]. While the updated formulations could
be used to investigate thin film thermal conductivity anisotropy, the experimental restrictions inherent in the $3\omega$ method remain. Alternatively, in TDTR and frequency domain thermoreflectance (FDTR) methods, the effects of heat accumulation (**e.g.**, when the material does not reach its unperturbed state between two successive laser heating pulses) on radial heat transfer have been probed and used to accurately extract the $\kappa_{ip}$ and $\kappa_{cp}$ values of highly oriented pyrolytic graphite [44].

The above state-of-the-art methodologies yield a good measure of the thermal conductivity anisotropy but, nonetheless, they remain to be indirect and approximate. For example, in TDTR techniques that employ pulse accumulation to enhance radial heat flow to probe $\kappa_{ip}$, isotropic thermal conductivity in the plane of the sample is assumed. However, typically, the materials under test are crystalline with non-radial axes of symmetry. It would be desirable to develop a simpler method for measuring the anisotropy in any material, which is the primary aim of this work. Through an extensive survey, we were convinced that correlating the
changes in the optical reflectance to the temperature [45] would be most suitable, as it provides a non-contact method and mitigates issues such as boundary resistances and heater capacitances [43]. The collateral difficulties are the sensitivity of the measured signal to surface conditions and wavelength [46]. Nevertheless, we use the SOI structure as a practical platform to consider thermal conductivity anisotropy through thermoreflectance (TR) measurement.

The $\kappa$ of Si thin film systems has already been extensively studied, making it ideal for proof-of-concept, and calibration, of the new TR measurement technique. Previous measurements of the lateral thermal conductivity of Si thin films in SOI structures mainly used electrical resistance thermometry in the steady state [42, 9], where temperature variation at two distinct points (via \textit{in situ} fabricated highly doped areas in the Si films) was measured using an electrical resistance change. Subsequently, the $\kappa$ was fit using two-dimensional heat conduction models. In another effort [7], measurements on suspended Si thin film membranes, fabricated through wet etching techniques, were performed. However, this methodology requires comparison with a metal heater deposited on a suspended bridge, with and without the Si device layer present, and thermal contact issues related to the sensors could still be significant in the characterization of $\kappa_{ip}$. A scanning thermoreflectance technique was also suggested [47] to monitor the transient temperature distribution along the drift region of a SOI power transistor. However, a discrepancy in the trend of values in the earlier data [42, 9, 8] with values in later measurements and theory [7] was noted.

2.3 A new approach to a modern method: thermoreflectance thermometry

Thermoreflectance (TR) is an experimental method that allows for non-interactive interrogation of the relative or absolute temperature of a surface or interface of a metallic or semiconducting material, enabled through the temperature dependence of the dielectric constant. Heating shifts the Fermi level in metals, and induces band bending in semiconductors, modulating the reflectivity in a lin-
ear fashion with respect to temperature when the temperature perturbation is small. Hence, the temperature of an electrically active material can be measured optically. When the phenomena of thermoreflectance is implemented to measure temperature, it must be assured that the temperature excursion is relatively small, typically on the order of a few degrees Kelvin, such that the proportionality of change in reflectance to the change in temperature can be approximated as linear. Under these conditions, a coefficient of thermoreflectance \((C_{TR})\) may be defined in a similar manner as the temperature coefficient of electrical resistance, or linear coefficient of thermal expansion, where \(R = R(T_0), \Delta R = R(T_1) - R(T_0),\) and \(\Delta T = T_1 - T_0,\)

\[
\frac{\Delta R}{R} = C_{TR}\Delta T.
\] (2.5)

The earliest applications of thermoreflectance to measure semiconductor properties was initially focused on probing the band structure, but, at present, this method is most commonly exploited for the study of heat transport. One advantage of this technique is derived the utilization of imaging or scanning optics, which allows for temperature mapping of arbitrary sample surface geometries. This feature has great utility in understanding thermal transport in microelectronics and MEMs, where ‘hot spots’ commonly develop and pose a reliability issue. Additionally, as this optical method is non-interacting, it allows for thermal measurement of sensitive, nanoscale devices such as nanowires or suspended structures without thermally perturbing the system. One challenge is associated with measuring the TR intensity, in the presence of the total reflected intensity, as it is typically two to five orders of magnitude smaller, thus requiring highly sensitive detection techniques. The TR response is also highly dependent on the wavelength of light used, surface conditioning, and the existence of transparent overlayers [46]. Using modified microscopes, or other custom optics, to focus visible light onto the sample, temperature resolutions of 10 mK and diffraction limited spatial resolutions of 250 nm [48] are fundamentally possible and have nearly been achieved [49, 50].
2.3.1 Physical basis

Thermoreflectance is the manifestation of a reflectivity perturbation from the change in refractive index or, equivalently, the change in dielectric constant due to a change in temperature. The reflectivity of the surface of a material in contact with air ($n_{air} = 1$) with respect to a normal, incident electromagnetic wave is defined as,

$$R = \left( \frac{\tilde{n} - 1}{\tilde{n} + 1} \right)^2$$

(2.6)

where $\tilde{n}$ is the complex refractive index, $\tilde{n} = n + ik$. By expanding (2.6) with respect to the real part of the refractive index, $n$, and attenuation constant, $k$, the reflectivity is expressed as,

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}. \quad (2.7)$$

Differentiating the reflectivity with respect to $n$ and $k$, and normalizing to the total reflectivity, gives the contribution of both the change in refractive index, $\Delta n$, and attenuation constant, $\Delta k$, and yields the normalized modulation of $R$,

$$\frac{\Delta R}{R} = \frac{4(n^2 - k^2 - 1) \Delta n + 8nk\Delta k}{[(n + 1)^2 + k^2] [(n - 1)^2 + k^2]}.$$

(2.8)

In the special case where $k \ll n$, which occurs in semiconductors near or below the fundamental absorption edge, the normalized, modulated reflectance can be simplified to,

$$\frac{\Delta R}{R} = \frac{4\Delta n}{n^2 - 1}. \quad (2.9)$$

The refractive index is related to the dielectric constant by way of Maxwell’s equations. The complex dielectric constant, $\tilde{\epsilon}$, (in a non-magnetic material) is related to $\tilde{n}$ such that $\tilde{\epsilon} = \tilde{n}^2$. By separating the real and imaginary parts, the relations are,

$$\epsilon_1 = n^2 + k^2, \quad (2.10)$$

$$\epsilon_2 = 2nk. \quad (2.11)$$

Similar to a line of work by Willardson, et al., [51], solving equations (2.10) and
(2.11) for \(n\) and \(k\) obtains,

\[
n = \left[ \frac{1}{2} (\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} + \frac{1}{2} \epsilon_1 \right]^{\frac{1}{2}},
\]

(2.12)

\[
k = \left[ \frac{1}{2} (\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} - \frac{1}{2} \epsilon_1 \right]^{\frac{1}{2}}.
\]

(2.13)

By substituting (2.12) and (2.13) into (2.8), the relation between the reflectivity modulation and the dielectric constant modulation, is clear,

\[
\frac{\Delta R}{R} = \frac{2A}{A^2 + B^2} \Delta \epsilon_1 + \frac{2B}{A^2 + B^2} \Delta \epsilon_2,
\]

(2.14)

where,

\[
A = n(n^2 - 3k^2 - 1),
\]

(2.15)

\[
B = k(3n^2 - k^2 - 1),
\]

(2.16)

and, if the dielectric constant is a function of temperature,

\[
\Delta \tilde{\epsilon} = \frac{\partial \tilde{\epsilon}}{\partial T} \Delta T,
\]

(2.17)

then the mathematical basis for thermoreflectance has been established.

### 2.3.2 Correlating thermo-electro-optic properties

From the definitions in section 2.3.1, monitoring the optical properties of a thermally perturbed material through the measured reflected intensity can yield information about its electronic properties. In previous work, thermoreflectance measurements have been used to characterize the fine features of electronic band structure in metals [52, 53, 54] and semiconductors [55, 56, 51]. In a study on the optical properties of alkalai metals performed by Matatagui et al. [52], thermoreflectance was used to characterize the plasmon resonance features in Cs, K, and Rb as a function of spectral energy. Using the Kramers-Kronig relations, \(\epsilon_1\) and \(\epsilon_2\) of Rb were found simultaneously by fitting \(\frac{\Delta R}{R}\) vs. \(\hbar \omega\) data, shown in figure 2.5, with the Drude-Lorentz formulation of the dielectric constant near the plasmon
frequency, $\omega_{pl}$,

$$\tilde{\varepsilon} = 1 - \frac{\omega_{pl}^2}{\omega^2 + i\omega\gamma},$$  \hspace{1cm} (2.18)

where $\gamma$ is a damping constant, and the relation from equation 2.17 is assumed.

Figure 2.5: Experimentally measured (dots) and fitted (line) TR spectra of Rb at $T = 100$ K [52].

In addition, TR spectra behavior can be correlated to other electronic band structure features, such as rapid changes in the density of states, exemplified from measurements performed on Au. Au reflectance and TR spectra over an energy range between 2 to 10 eV [53] revealed a rapid drop in $R$ near 2.5 eV which manifests a dispersion-like curve in the TR response, shown in figure 2.6. This is due to a combination of two physical phenomena. First, the plasmon frequency of Au is near 2.5 eV, decreasing the TR intensity with increasing energy, as described by equation 2.18. Simultaneously, the rapid positive increase in the TR intensity at slightly higher energies is caused by a rapid increase in the imaginary component.
of the dielectric constant [54]. This is quantitatively described by the definition of $\epsilon_2$ with respect to interband transitions in this energy regime,

$$
\epsilon_2 = \frac{e^2}{2\pi m^*} \frac{1}{E^2} \int d^3b \frac{2}{m^*} |P_{ul}|^2 \delta (E_{ul} - E) \\
\propto \frac{1}{E^2} D_{ul}(b, E),
$$

where the subscript ($ul$) refers to the upper and lower energy levels associated with the transition and $P_{ul}$ is the momentum matrix. The calculations accomplished by Cooper, et al., show that the magnitude of the Fermi surface at this transition is rapidly changes, leading an increase in $N$, and thus $\epsilon_2$ as well, explaining this anamolously large transition in the spectra [54].

![Figure 2.6](image)

**Figure 2.6:** Reflectance and thermoreflectance spectra of Au from 2 to 10 eV [53]. A notable dispersion-like behavior occurs near 2.2 eV.

Features in TR spectra of semiconductors are also primarily governed by the dependence of $\epsilon_2$ on the available transitions between the valence band and
the conduction band, described by,

\[ \epsilon_2 = \frac{4e^2 \hbar^2}{\pi m^* E^2} \int db |P_{cv}|^2 \delta(E_{cv} - E) \propto \frac{1}{E^2} D_{cv}(b, E). \]  

(2.20)

It can be shown [51] that \( D_{cv} \propto \frac{1}{|\nabla b E|} \), i.e. the slope of the electron dispersion. When \( \nabla_b E \) goes to zero at critical points in the first Brillouin zone, a Van Hove singularity is generated, where \( D_{cv} \) goes to infinity. These spikes in \( \epsilon_2 \) can give rise to absorption peaks at many energy transitions, exemplified in the GaAs spectra shown in figure 2.7.

![Figure 2.7](image)

**Figure 2.7**: TR spectra of GaAs at (a) liquid-nitrogen temperature and (b) room temperature [55].

The physical behavior that manifests the variable magnitude of the TR intensity serves as a reminder that the optical probe energy for a given material must be carefully chosen to ensure a high signal to noise ratio; a significant fraction of the TR spectra yields near zero intensities. In the next chapter, the practical
considerations of maximizing the TR intensity through choice of probe wavelength, material, and layer thickness are discussed, as well as experimental tools that can be used to acquire very small signals in the presence of a large noise background.
3 Characterization of Si thin film thermal conductivity using thermoreflectance thermometry

With the evident need to characterize the $\kappa$ tensor in crystalline materials, we have developed a new thermal conductivity measurement technique and verify its efficacy through an investigation of silicon thin films. In addition to its immense technological usage, silicon can be configured industrially in silicon-on-insulator (SOI) structures, where Si thin films can be prepared with varying thickness on an underlying layer of SiO$_2$ with low $\kappa_{\text{SiO}_2} \sim 1.4 \text{ W.m}^{-1}\text{K}^{-1}$. The advantage of the SOI manifold is that the Si thin films can be considered to be approximately thermally independent of the underlying structure. However, it should be noted that while the Si films are typically close to single-crystalline, processing could introduce random defects/impurities. In addition to enabling easier experimentation (the alternative would be to suspend the Si through complicated etching procedures), the SOI structure is commercially used in electronic devices with feature lengths $< 100$ nm, where it has been indicated that up to a 25% increase in switching speed concomitant with a 50% reduction in the consumed power is achievable [57]. However, enhanced electronic switching performance is typically coupled with increased heat production [58], the dissipation of which is a major issue with SOI based structures.

In this chapter, we expand on the utility of the TR technique to monitor the $\kappa_{ip}$ of Si thin films (in the 68 - 258 nm range) in SOI based structures. The experimental method is aimed to avoid thermal contact related issues through
the use of the thermoreflectance based temperature sensing. While the details will be exemplified later, briefly, the surface temperature gradient in the thin film induced through on-layer heating is monitored. It is then generally observed that the thermoreflectance, in the visible wavelength range, on SOI structures must be carefully calibrated and understood considering the optical interactions and interferences due to reflections from multiple interfaces, i.e., air-Si, Si-SiO$_2$ (the buried oxide layer - BOX), and the SiO$_2$ - Si substrate, all of which are involved in the correlation of the measured TR intensity to the actual sample temperature. The optical characteristic matrix (OCM) [59] is then calculated to predict the device layer thickness at which the TR response is optimal, considering the probe wavelengths [60, 46] and overlayer thicknesses [60, 46, 47, 61, 62]. A finite-element model based physics solver is used to estimate the temperature profile in the SOI structure with the $\kappa_{ip}$ of the device layer as the only free parameter to fit the calculated surface temperature to the measured data. Finally, the determined $\kappa_{ip}$ are compared to theoretical predictions [22, 63, 30, 64].

3.1 The thermoreflectance measurement

A schematic of the experimental setup used to perform TR scans is displayed in figure 3.1. In short, a visible laser source projects a collimated beam through a series of conditioning and focusing optics to generate a spot on the sample. A surface temperature gradient (dependent on the $\kappa_{film}$) is induced on-chip via deposited heater structures subjected to Joule heating, and the spatially variant TR intensity (proportional to the temperature gradient) is measured from the reflected beam, as the sample is rastered underneath the focused spot. Then, finite element modeling (FEM) is used to fit the measured $T$ vs $x$ plot using $\kappa_{ip}$ as a free parameter.

More specifically, a normally incident, linearly polarized He-Ne laser (633 nm, 10 mW, from Thorlabs, Inc.) was focused onto a heated sample through a 36x, objective lens (Ealing Inc., with Numerical Aperture = 0.5). The spot size was determined through a knife-edge technique, where the beam was scanned over the
**Figure 3.1:** Schematic of the arrangement of apparatus used for the scanning thermoreflectance thermometry.
metal heater edge onto the Si film surface. Assuming a Gaussian beam profile, with intensity variation given through \( I(x) = I_0 \exp \left( \frac{-x^2}{2r^2} \right) \), the spot radius, \( r \), was found to be \( \sim 4 \) \( \mu \)m. The effect of deviations from normal incidence on the OCM was characterized and it was seen that there was a small upwards shift of the TR curve. For recording the spatial variation of the TR, the sample was translated using a remotely controlled stage propelled by a stepper motor, with \( 0.2 \) \( \mu \)m resolution, rastering the focused laser spot across the surface. The reflected intensity was diverted through a non-polarized beam splitter onto a diode detector (ThorLabs DET110A PIN), amplified by a preamplifier (Stanford Research Systems SR 570) connected to a lock-in amplifier (Stanford Research Systems SR 830). Both the amplitude (proportional to the temperature fluctuations of the surface) and the phase (related to the sign of the \( C_{TR} \) and the temporal shift of the heat wave as it propagates through the material) of the signal were recorded as a function of distance from the heater.

The configuration of each node in the chain of equipment used to acquire and amplify the optical TR signal was critical in achieving an adequate signal to noise ratio. The photodetector transduced the optical intensity into a current with an efficiency of approximately 0.4 A.W\(^{-1}\). It had a rise time of 20 ns when properly impedance matched to 50 \( \Omega \) with the coupling BNC cable and following equipment. Deviations in the rise time due to impedance mismatch were unlikely to affect the measurement, as the relevant signal frequencies never exceeded more than 10 kHz. The listed dark current, \( i.e. \) current due to thermally excited carriers at room temperature, was 10 nA, but experimental measurements have shown that AC coupled signals may be measured down to 1 nA, or less. The photocurrent was amplified by the preamplifier, which transduced the current into an output voltage. The output bandwidth was found to be highly dependent on the signal frequency due to the RC characteristics inherent in the system, that can act as filters; consequently, the preamplifier was not suitable for frequency dependent measurements, such as the \( 3\omega \) method. When acquiring at a single frequency, use of the built in bandpass filter typically reduced the noise of the signal. The ‘low noise’ gain mode was selected to minimize noise and drift of the signal, as the drift
of the lock-in signal was determined to be due to difficulty of maintaining locked-in to the small signal, not actual signal drift. The sensitivity setting was chosen to be as large as possible without triggering the input or output overload, and was typically near $1 \mu\text{A.V}^{-1}$. It was found that the ‘input offset’ feature could be used to cancel the large optical signal background of $R$, in order to further amplify the $\frac{dR}{dT}$ signal without causing an output overload. The configuration of the lock-in amplifier input was for a single voltage input (A), in AC coupled mode to block the DC offset from $R$, with the machine input outer conductor grounded; no line filters were used. The time constant was set to be at least 100x greater than the period of the acquired signal, although a 1000x $\tau$ ratio was preferred. The notch filter was required to have a slope of 24 dB per octave, or else the signal-to-noise ratio was unacceptably low, and the ‘high reserve’ setting typically prevented input overload.

### 3.2 Performing TR on multilayer systems

The discussed measurement depends highly on the sensitivity of the heater induced temperature distribution in the sample on the material properties, such as $\kappa_{ip}$. The temperature change ($\Delta T$) could be measured through an optical reflectance ($\Delta R$) change [50], with the normalized TR response expressed through a coefficient, $C_{TR} = \frac{1}{R} \frac{dR}{dT}$. There are few published values of $C_{TR}$, even for bulk materials, as the sign and magnitude can vary significantly with the wavelength of incident light and sample surface quality. For example, the measured $C_{TR}$ of Au is typically less than $10^{-4}$ K$^{-1}$ in the visible wavelength regime, except in the 450 nm to 575 nm range where there are peaks (up to $6 \times 10^{-4}$ K$^{-1}$) and zeros at $\sim 500$ nm [60, 65, 66]. In addition to surface roughness and contamination effects, any overlayer could also modify the spectral response of the TR, due to internal reflections and interference effects [60, 46, 47]. Consequently, it is often preferred in practice, to predict the $C_{TR}$ using analytical methods, through knowledge of the temperature variation of the refractive index ($\tilde{n}$) and thermal coefficient of expansion. For example, in the pertinent case of a Si substrate with a SiO$_2$ over-
layer, the $C_{TR}$ has been derived as a function of thickness of the overlayer [47]. The reasonable agreement of the calculated values with experimentally measured results suggests that the former can be sufficient for estimation of the overlayer and spectral dependence of the $C_{TR}$.

The typical challenges associated with experimental TR measurements on SOI based structures are related to the (1) adequate signal to noise ratio, given typical $C_{TR}$ values of $< 10^{-3} \text{ K}^{-1}$, (2) deconvoluting the TR contribution of the top Si film/device layer from the underlying layers/substrate, and subsequently (3) correlating the TR intensity to the relative/absolute temperature modulation. While the issues associated with (1) could, in principle, be overcome through averaging or amplification. We consider (2) by calculating the sensitivity of the TR intensity with respect to the thickness and temperature of the top device layer. We then show that the TR signal intensity could be maximized through deliberate selection of a device layer thickness through evaluating the OCM of the SOI structure.

We choose an interrogation wavelength ($\lambda$) corresponding to visible light, i.e., at $\lambda = 633$ nm, and geometry, as specified in figure 3.2 with appropriate parameters for the Si ($\tilde{n} = 3.92 + 0.022i, \frac{dn}{dT} = (4.5 + 0.073i) \times 10^{-4} \text{ K}^{-1}$) [67, 68, 69] and SiO$_2$ ($\tilde{n} = 1.457, \frac{dn}{dT} \sim 10^{-5} \text{ K}^{-1}$) [67, 70]. The device layer is single crystalline Si (with thicknesses, $t_{dev}$, in the range of 68 - 258 nm, and resistivity $\sim 1$-$10 \text{ \Omega.cm}$), with an underlying 1 $\mu$m SiO$_2$ (BOX) layer, supported by a 675 $\mu$m thick single crystal substrate. From an optical standpoint, the electromagnetic skin depth of silicon, $d_{Si}$, at $\lambda = 633$ nm, is 2.3 $\mu$m [59] which indicates that incident radiation would penetrate through the Si device layer. The BOX layer is transparent and was modeled with only a real component to $\tilde{n}$, while the substrate is much thicker than $d_{Si}$ and is optically opaque.

If the incident radiation, modeled as a electromagnetic plane wave and represented through $Q_0 = [E_0 \ H_0]$, with $E_0$ and $H_0$ as the free-space amplitudes of the electric and magnetic fields, is incident upon a slab of material with refractive index $n$, the resultant amplitude at depth $z$ within the slab is given by $Q = [E(z) \ H(z)]$ where $Q_0 = M_sQ$. The electric and magnetic fields are taken to be of the forms:
Figure 3.2: Schematic of the SOI samples studied in this work. The optical parameters governing the beam-material interactions, \( n \): refractive index and \( t \): the material thickness, are indicated.

\[ E_x = E(z)e^{i(kz-\omega t)} \]

\[ H_y = H(z)e^{i(kz-\omega t)} \]

\( M_s \) is the OCM of the layered slab, comparing the amplitude of the propagated wave to that of the initial state, and for normal incidence, is,

\[
M_s(z) = \begin{bmatrix}
m_{11}^s(z) & m_{12}^s(z) \\
m_{21}^s(z) & m_{22}^s(z)
\end{bmatrix} = \begin{bmatrix}
\cos \left( \frac{2\pi n_s z}{\lambda} \right) & -\frac{i}{n_s} \sin \left( \frac{2\pi n_s z}{\lambda} \right) \\
-i n_s \sin \left( \frac{2\pi n_s z}{\lambda} \right) & \cos \left( \frac{2\pi n_s z}{\lambda} \right)
\end{bmatrix}.
\] (3.1)

For SOI structures, the \( M_{SOI} \), is equal to the product of the individual OCMs of each optically active layer, \( i.e. \), the top Si device layer (\( dev \)) and the SiO\(_2\) (\( BOX \)),

\[
M_{SOI}(z) = M_{dev}(z)M_{BOX}(z).
\] (3.2)

It can then be shown [59] that the total reflectance of the SOI structure, \( R_{SOI} \), is,

\[
R_{SOI} = \left| \frac{(m_{11}^{SOI} + m_{12}^{SOI}n_{air})n_{sub} - (m_{21}^{SOI} + m_{22}^{SOI}n_{sub})}{(m_{11}^{SOI} + m_{12}^{SOI}n_{air})n_{sub} + (m_{21}^{SOI} + m_{22}^{SOI}n_{sub})} \right|^2.
\] (3.3)
A plot of $R_{SOI}$ as a function of the device layer thickness ($t_{dev}$) at $\lambda = 633$ nm is shown in figure 3.3, along with obtained experimental results, and the close correspondence for the chosen thicknesses (the reason for the choice is explained later in this section) indicates the accuracy of our modeling and experimental calibration. The peaks and troughs in the $R_{SOI}$ are due to interference effects of the incident radiation from the device layer boundaries. The shape of the variation, i.e., broad peaks and narrow troughs, are due to a large refractive index contrast ($\tilde{n}_{dev} - \tilde{n}_{BOX} \sim 2.5$) between the Si device layer and the underlying oxide, and the periodicity is determined by one quarter of the optical path length ($t_{dev}\tilde{n}_{dev}$), due to constructive and destructive interference interactions.

![Figure 3.3: The calculated and measured optical reflectance ($R_{SOI}$) of the SOI samples, with varying device layer thickness ($t_{dev}$).](image)

It can then be inferred from the $R_{SOI}(t_{dev})$ variation, that the $C_{TR}$ (or $\frac{dR}{dT}$) could be increased at an optimal $t_{dev}$. Generally, when any layer of thickness $t$ has a temperature variation $\Delta T$, the change of the refractive index and thickness would be $\Delta \tilde{n} = \frac{dn}{dT} \Delta T$ and $\Delta t = \zeta \Delta T$, respectively, where $\zeta$ is the linear thermal coefficient of expansion. For a given SOI sample with a specified $t_{dev}$ and an initial temperature, $T^0$, with reflectance $R(T^0, t_{dev})$, the net change in the reflectance,
\[ \Delta R = \frac{dR}{dT} \Delta T = R \left( T^0 + \Delta T, t_{\text{dev}} + \Delta t \right) - R \left( T^0, t_{\text{dev}} \right). \tag{3.4} \]

For a unit rise in \( \Delta T \) (= 1 K), and using equation 3.4, a plot of \( \Delta R \) as a function of \( t_{\text{dev}} \) was formulated (as in figure 3.4), to show the individual \((j= \text{dev}, \text{BOX}, \text{or sub})\) due to the uniform temperature rise for the \( j^{th} \) layer. From an experimental point of view, we model the observed \( \frac{dR}{dT} \) of the SOI structure as arising due to a linear superposition of the individual layers as follows,

\[ \frac{dR_{\text{SOI}}}{dT} = \frac{dR_{\text{dev}}}{dT} + \frac{dR_{\text{BOX}}}{dT} + \frac{dR_{\text{sub}}}{dT}. \tag{3.5} \]

Such a model is necessary as the individual contributions of the layers of the SOI are not measurable and is justified on the basis of our observation, through computational simulations using MATLAB®, that the difference of \( \frac{dR_{\text{SOI}}}{dT} \) between (1) that found by considering and summing the individual contributions from each layer (each with a \( \Delta T = 1 \text{K} \)) and (2) assuming that that SOI structure, as a whole has \( \Delta T = 1 \text{K} \), is less than 1%.

The following are then observed from the \( \frac{dR}{dT} \) vs \( t_{\text{dev}} \) plot: (1) there is a pronounced modulation of the \( \frac{dR_{\text{dev}}}{dT} \) which could be either positive/negative, and which is proportional to the slope of \( R_{\text{SOI}} \), (2) the \( \frac{dR_{\text{dev}}}{dT} \) dominates that of the other layers by two orders of magnitude (\( \sim 10^{-3} \text{ K}^{-1} \) vs. \( \sim 10^{-5} \text{ K}^{-1} \)) resulting from both the position of the device layer, and the much larger \( \frac{\tilde{d}_n}{dT} \), and would be the chief contributor to the TR intensity; (3) The modulation of the \( \frac{dR_{\text{dev}}}{dT} \) increases in amplitude with \( t_{\text{dev}} \) and exhibits a maxima whenever there is a minimum in the \( R \) (cf., figure 3.3), with the experimental implication that there are select values of \( t_{\text{dev}} \) where the \( \frac{dR_{\text{dev}}}{dT} \) is maximum/minimum with corresponding effect on the TR intensity. Consequently, \( t_{\text{dev}} \) must be chosen carefully for maximal signal to noise ratio in the TR measurements, to enabling more accurate determination of the \( \kappa \). We have then chosen Si thin films with \( t_{\text{dev}} = 68, 151, 235, \) and 258 nm corresponding to thicknesses near the maxima of the absolute \( \frac{dR_{\text{dev}}}{dT} \) as indicated in figures 3.3 and 3.4.
Figure 3.4: The variation of the temperature derivative of the reflectance ($\frac{dR}{dT}$) with device layer thickness ($t_{dev}$) for the Si device layer, underlying buried oxide (BOX) and Si substrate. The values corresponding to the $t_{dev}$ of the measured samples (Sample) and the minima ($R_{min}$) – from figure 3.3, are indicated.
Knowledge of the approximate value of \( \frac{dR}{dT} \) and the limitations of the experimental equipment allows for a calculation of the temperature resolution of the measurement technique. It is expected from the calculations above that for samples of the chosen \( t_{dev} \), \( \frac{dR}{dT} \sim 10^{-3} \). Additionally, it was experimentally measured that ratio of the TR intensity, compared to \( R \), was on the order of \( 10^{-6} \) to \( 10^{-8} \), implying that the measured temperatures were between \( 10^{-3} \) to \( 10^{-5} \) K, i.e. sub-milliKelvin thermal resolution was accomplished.

### 3.3 Sample design and fabrication

Si thin films of optimal \( t_{dev} \) thickness, following the discussion of the previous section, were fabricated on SOI based wafers (from SOITEC, made using a Bond and Etch-Back (BESOI) technique) through Reactive Ion Etching (RIE, using the Oxford Plasmalab®100) of the as-received structures. The Si crystalline device layer (258 nm thick) was (100) oriented, p-type (1-10 \( \Omega \cdot cm \)), with an underlying BOX layer of 1 \( \mu \)m thickness. The electrical dopant density of \( \sim 10^{15} \) atoms.cm\(^{-3}\) [71], is not expected to much affect the \( \kappa \) [32]. Measurement and calibration of film thickness was done through spectral reflectance (Filmetrics F20) and error in the measurement was estimated to be less than 5 nm. The surface roughness introduced during the RIE was of the order of a few nanometers. A metal line was then deposited on the Si film surface to serve for an electrical resistance based heater. For this purpose, the heater pattern was transferred through a double-layer photolithographic technique, employing the following procedures: (1) 400 nm of photoresist (Nano PMGI SF8) was spun onto the sample and baked for 5 minutes at 180\( ^\circ \)C, (2) 2 \( \mu \)m of another photoresist (Shipley 1818) was then spun on top and baked for 3 minutes at 110\( ^\circ \)C. The photoresist was then exposed, through a suitably designed mask (using a Karl Suss MA6 mask alignment platform) for 10 s at \( \sim 300 \) W. The heater line was constituted of a multilayer of Cr (10 nm)/Au (200 nm) deposited through electron beam evaporation (Temescal BJD 1800), and was typically 10 mm long and 6 \( \mu \)m wide. Use of a double layer photolithography process seems to ensure better contact between the heater and the
device layer along the entire width. To characterize possible current leakage from the heater into the substrate, 30 nm of SiO$_2$ was deposited underneath the heater line. However, measurements did not indicate any leakage effects precluding the need for such an oxide. Subsequent to the fabrication of the optimal $t_{dev}$ films, the samples were mounted and wire-bonded to ceramic chip-carriers. Thermal epoxy was used to bond the substrate bottom to the sample holder. The overall sample configuration is schematically shown in figure 3.5.

Figure 3.5: Schematic of the sample cross-section, mounted on a chip carrier. The lateral heat flow, in the $x$-direction, in the region delineated by the dotted box, is sensitive to the in-plane thermal conductivity ($\kappa_{ip}$) and the corresponding temperature variation along the surface has been measured.

A sinusoidal current $I(f)$, at a given frequency $f$, was passed through the deposited metal line and induces Joule heating (with a harmonic component of $2f$, as derived from the $I^2$ component of the heating). Thermal losses, due to convection or radiation heat transfer, were rendered negligible through the use of
time constants (and $f$ values) not overlapping with the characteristic time scales associated with such loss mechanisms. Using lumped thermal analysis [72], we estimated that for the device layer thicknesses considered in our experiments, the time scales were of the order of magnitude of 0.01 - 0.1 s. Consequently, we use a heating current frequency, $f$, of $\sim 2.5$ kHz, and we could consider only the conductive heat transfer. Also, the estimated change in the surface temperature due to convective/radiative heat loss was estimated to be less than 1%, through elementary calculations using Newton’s law of cooling and the Stefan-Boltzmann Law.

At the chosen $f$, the thermal wave propagates into the Si substrate, through the top device layer and the BOX. Considering the cross-plane thermal resistances ($= \frac{t}{\kappa_{cp}}$) of the device and buried oxide layers, it can be assumed that there is a much larger temperature drop across the oxide. Hence, the top device layer is essentially isothermal through the thickness at any given distance from the heater. However, there seems to be significant lateral heat conduction in the BOX near the heater, which modifies the temperature profile of the device layer, and precludes the use of analytic expressions for the temperature distribution, as was done in earlier studies [9]. Consequently finite element modeling was used to understand such variations.

### 3.4 Finite Element Modeling

As noted earlier, the SOI geometry along with the large aspect ratio of the heater width ($\sim 40$) vis-à-vis the device layer thickness ($t_{dev} < 260$ nm) implies a decaying temperature profile from the heater edge in the $x$-direction, as defined in figure 3.5. Consequently, a two-dimensional analysis of the heat conduction along the cross-section of the sample, perpendicular to the heater axis (i.e., the $x$-$z$ plane), was to correlate the measured amplitude and phase of the TR signal to the thin film $\kappa$. The HCE was solved through a finite element model constructed in the COMSOL Multiphysics @ software environment to determine the time varying temperature along the surface of the device layer in the proximity of the heater
and for analyzing the sensitivity of the device layer $\kappa_{ip}$. By choosing appropriate free parameters, the calculated temperature profiles could be fit to the measured TR data to elucidate the thermal properties of the device layer.

In accordance with experimental conditions, the following assumptions were used in the model: (1) the heat sink fixes the bottom substrate surface to room temperature, $T_{bottom} = 293.15$ K, (2) sample surfaces exposed to air were taken to be insulating, $i.e.$, $(\frac{dT}{dx})_{side\ surface} = (\frac{dT}{dz})_{top\ surface} = 0$, (3) the power per unit area dissipated by the heater at the heater/device layer interface is equal to Joule heat generated by the heating current, and (4) the BOX and Si substrate have bulk thermal properties. The sensitivity of the model solution was examined with respect to the cross-plane thermal conductance, heating power, and frequency. It was found that the surface temperature was unperturbed by variation of the device layer $\kappa_{cp}$ considered in this work, as well as from the introduction of thermal boundary resistances at the device layer/BOX and BOX/substrate interfaces, with commonly accepted values [5]. This result was expected, as the cross-plane thermal resistances, from the film ($R_{th} < 5 \times 10^{-9}$ m$^2$K.W$^{-1}$) and interfaces ($R_{th} \sim 2 \times 10^{-8}$ m$^2$K.W$^{-1}$), were much smaller than that of the BOX ($R_{th} \sim 7 \times 10^{-7}$ m$^2$K.W$^{-1}$).

The thermal epoxy between the substrate bottom and the sample holder could introduce a resistance ($\sim 10^{-3}$ m$^2$K.W$^{-1}$) in series with the sink. However, this resistance had no effect on the transient component of the surface temperature as the chosen $f$ limits the thermal penetration depth to $\sim 75$ µm in Si, precluding the interaction of the thermal wave with the bottom of the substrate. Finally, variation of the heating power and frequency were found to be within the limits of specified machine error, $\sim 0.1\%$, did not yield a change in the surface temperature greater than the obtained precision. An example of the calculated temperature profile along the sample cross section near the peak of the heating cycle is shown in figure 3.6.

Extracting the temperatures that phenomenologically correlate with the TR intensity from the model was a multi-step process. Verified by the optical calculations, the TR intensity corresponded to temperature at the surface of the thin film. The signal was acquired by the lock-in amplifier which, by design,
measures the amplitude and phase of each sinusoidal harmonic component of the input, starting with the base reference frequency; the DC component is filtered out. The actual temperature in the sample was expected to have a steady-state (DC) and transient (AC) component, as defined in section 2.2. In actuality, the DC component is transient when the heater is initiated, then, after a time much longer than the $\tau_{th}$ of the chip, it reaches quasi steady-state, with a time-invariant DC component with an AC component. The model generates a full temperature map for the entire geometry at each time step, with the temperature profile at the peak of a heating cycle exemplified in figure 3.6. The black curve in figure ?? shows the temporal evolution of the temperature at a point on the surface of the film at the heater edge. The variation of the DC component of the temperature with time replicates the expected chip-heating behavior before quasi steady-state is reached. The data extracted from the simulation, to match the TR intensity (lock-in measured amplitude), was half the peak-to-peak amplitude of the temperature at a point in time when DC component was constant, which was typically found to be after 10 – 30 transient heating cycle periods. Figure 3.8 reveals the near-synchronous temperature behavior of points along the surface of the film, 0, 10, 20, 30, and 60 µm away from the heater edge. The amplitude is shown to exponentially decrease with distance, while the time-offset between temperature peaks at increasingly large distances from the heater correspond to the lag in the lock-in measured phase, phenomenologically linked to the thermal diffusitivity, implying that $\kappa$ may also be found through fitting of the phase.

To further elaborate on the importance of fitting the measured temperature oscillation with the simulated peak-to-peak temperature, as opposed the peak temperature, the temperature profiles along the film surface at the maximum and minimum of the heating cycle, are plotted concurrently with the ambient (heat sink) temperature, in figure 3.9. Basically, the peak-to-peak temperature as a function of location, is the approximately difference between the ‘maximum’ and ‘minimum’ curves, whereas the peak temperature must have a reference, which defaults as the ambient value and thus overestimates the actual temperature fluctuation a small, but non-negligible amount.
Figure 3.6: An example of the simulated temperature rise along the SOI sample cross-section, at the peak of a given heating cycle. The $x = 0 ~\mu$m point bisects the heater width.

Figure 3.7: An example of the simulated, AC + DC components of the transient Si film temperature fluctuation, 0 $\mu$m away from the heater edge ($x = 3 ~\mu$m c.f. figure 3.6), with the DC component schematically drawn for comparison.
**Figure 3.8:** An example of the simulated, transient Si film temperature at locations 0, 10, 20, 30, and 60 µm away from the heater edge.

**Figure 3.9:** An example of the simulated Si film temperature at times where the maximum and minimum heating occurs, with the ambient temperature profile at the heat sink.
3.5 Experimental results

A typical TR scan, across the surface of the device layer ($t_{\text{dev}} = 258$ nm), indicating the experimental data superposed on calculated temperature profiles with varying $\kappa_{ip}$ is shown in figure 3.10. Each datum represents the maximum amplitude variation of the TR intensity as it varies in time at frequency $2f$, and whose $x$-coordinate coincides with the center of the probe beam. The error bars due to variation of the TR intensity are also labeled, but are too small to be visible. The magnitude of the TR intensity was scaled such that the values in the limit of $x \to \infty$, e.g., when $x \sim 40$ $\mu$m in figure 3.10, match the calculated temperature. While the total TR intensity was an average of the temperature profile convoluted with the spatially distributed intensity of the beam, the resulting measurement was still an accurate indication of the actual temperature at the center of the beam spot [73]. The solid curves represent equivalent, time-variant temperature amplitudes as a function of distance from the heater edge at various modeled $\kappa_{ip}$. The goodness of fit between the measured results and simulated curves was determined in the range of spatial values where modeled temperature profiles diverged by more than 10%, i.e., at $4 \mu$m $< x < 30 \mu$m. The largest correlation coefficient ($\Re$) between the scaled TR measurements and calculated temperature values was $\Re^2 = 0.9999$, corresponding to the fit with $\kappa_{ip} \sim 100$ W.m$^{-1}$K$^{-1}$. It was noted that the values of $\kappa_{ip}$, matching 60 and 148 W.m$^{-1}$K$^{-1}$, have $\Re^2$ values of 0.9955 and 0.9978, respectively. While correlation remains high for the given calculated temperature profiles, their relative values could be used to indicate the most appropriate $\kappa_{ip}$ so as to closely match experimental data.

Figure 3.11 shows the measured TR signal phase of the heat wave peak as a function of the distance from the heater, where decreasing phase indicates greater lag with respect to the heating frequency reference. The phase was a direct indication of the difference in sign of $\frac{dR_{ip}}{dT}$ between samples of different thickness (cf., figure 3.4). More specifically, comparing the signs of the $\frac{dR_{ip}}{dT}$ for $t_{\text{dev}} = 258$ nm to other device thicknesses, i.e., $t_{\text{dev}} = 68$, 151 and 235 nm, the former has a positive value while the latter have negative values. Consequently, the lock-in measurement of two TR signals with identical phase but opposite sign would be
Figure 3.10: A typical TR scan across the surface of the device layer ($t_{dev} = 258$ nm) indicating the experimental data superposed on modeled temperature profiles with varying $\kappa_{ip}$. The error bars are too small to be visible.
manifested in a $\pi$ radians phase shift, as indicated in figure 3.11. It was also noted that the TR signal phase did not indicate a $\pi$ phase shift as the beam was rastered from the Au heater line to the device layer, implying that $\frac{dR_{dev}}{dT}$ and $\frac{dR_{Au}}{dT}$ are of the same sign for samples with $t_{dev} = 68, 151$ and $235$ nm. As it was previously established that the $\frac{dR_{Au}}{dT}$ is negative at $\lambda = 633$ nm [60, 65, 66] the $\frac{dR_{dev}}{dT}$ of these SOI samples at these thickness must be negative as well, further supporting the OCM predictions plotted in figure 3.4.

![Figure 3.11](image)

**Figure 3.11**: The measured TR signal phase of the heat wave peak as a function of the distance from the heater ($x=0$ marks the center of the heater) is a direct indication of the difference in sign of TR intensity between samples of different thickness (*cf.* Figure 3).

### 3.6 Theoretical analysis of specific heat, phonon group velocity, and boundary scattering

A suitable value for the density ($\rho$) and the specific heat ($C$) constituting the thermal diffusivity ($D = \frac{\kappa}{\rho C}$) of the device layer was necessary prior to
modeling and solving the transient heat conduction equation. While the density was assumed to be that of the bulk [67], $\rho_{Si} = 2329 \text{ kg.m}^{-3}$, the bulk value of $C \sim 1.67 \times 10^6 \text{ J.m}^{-3}\text{K}^{-1}$ associated with the ‘gray’ approximation of phonons [74]. A more appropriate value of $C$ which does account for the phonon dispersion was derived through previously developed methods [22, 63, 30, 64]. To illustrate, a simplified version of the methods to calculate $C$ and $v_g$ put forward in chapter 1 was used. Instead of using the complete phonon dispersion, it was assumed that only the acoustic phonons contribute to heat conduction, while the optical phonons do not, due to their small group velocity, and that the $C$ associated with heat conduction would be that appropriate for the former group. The full acoustic phonon dispersion in Si, consisting of one longitudinal and two degenerate transverse modes, was considered. Using polynomial fitting functions to analytically describe the experimentally measured acoustic phonon dispersion [25], we calculated a $C \sim 0.95 \times 10^6 \text{ J.m}^{-3}\text{K}^{-1}$ under the Debye model formulation [64]. We also estimated an average phonon group velocity, $\bar{v}_g$, by including the dispersion and normalizing, as follows,

$$\bar{v}_g = \frac{C_{LA}v_{g,LA} + 2C_{TA}v_{g,TA}}{C}. \quad (3.6)$$

The resulting analysis yields $\bar{v}_g = 2274 \text{ m.s}^{-1}$, which is notably smaller than the value typically considered for bulk, i.e., $\sim 6000 \text{ m.s}^{-1}$. Taking a $\kappa$ value for Si $(148 \text{ W.m}^{-1}\text{K}^{-1})$, $\bar{v}_g$, and $C$, we obtain an effective value of the mean free path, $l \sim 200 \text{ nm}$, implying more phonon-boundary interaction in thin films than traditional thermal analysis suggests. Thus, a reduction of $\kappa_{ip}$ at film thickness near or less than $l$ would be expected. Such a framework to understand the reduction of the in-plane thermal conductivity, $\kappa_{ip}$, in Si thin films [23, 7, 75] and the device layer in SOI substrates [9, 8] has been previously established and agreed well with our calculations. Our experimental results [73] also indicated that considering the full phonon dispersion was more accurate.

The principles outlined above were used to determine the values of the and compare with the $\kappa_{ip}$ results obtained by other previous measurements [8, 73, 6, 7, 9] and have been plotted in figure 3.12. Generally, a decreasing $\kappa_{ip}$ is observed with
respect to $t_{dev}$. The high accuracy and precision of the data obtained in this work - as in figure 3.10 - stems from the accuracy in modeling as well as improved spatial resolution. Most notably, there seems to very good agreement between our measured $\kappa_{ip}$ and those obtained through measurements with suspended Si structures fabricated from SOI substrates [7]. Generally, suspended beam geometry greatly simplifies thermal analysis due to the restriction on heat conduction paths. However, fabrication of such geometries is elaborate and non-trivial involving highly controlled wet etching and is often not easily implemented for many thin films of interest, e.g., those lacking a sacrificial intermediate layer. The comparison of the $\kappa_{ip}$ previously measured through electrically resistive elements of suspended [7] and supported [42, 9, 8] Si films show that measurements of supported samples seem to be less sensitive to the film properties [8] or have high variability [9].

![Figure 3.12: A comparison of the thermal conductivity values (obtained from the TR intensity fits in the present work) with those obtained previous literature (Aubain, et al. [73], Liu, et al. [6, 7], Ju, et al. [8], and Asheghi, et al. [9]).](image-url)
3.7 Summary

The $\kappa_{ip}$ of single crystal silicon thin films was successfully measured using the proposed scanning thermoreflectance thermometry technique. In principle, this technique can be used to probe the $\kappa_{ip}$ of any substrate-supported thin film system when the following requirements are met: $\kappa_{sub}$ must be sufficiently small when compared to $\kappa_{film}$, such that the lateral heat flow contained within the film ensures a measureable thermal conductivity dependence in the surface temperature profile; the temperature profile spans a distance larger than the probe spot diameter; the optical and thermal properties of the film are uniform; the film is thermo-optically active and the $C_{TR}$ is sufficiently large. In the next chapter, an attempt to use this TR technique to measure $\kappa_{ip}$ aluminum nitride films, epitaxially grown on sapphire substrates, is made, and the measured thermal conductivity values are discussed.
4 Characterization of AlN thin film thermal conductivity

The inexorable miniaturization and eventual 3-D integration of electronic devices continues to drive the development of localized thermal dissipation solutions to mitigate self-heating and related reliability issues. Active heat sinks, such as thermoelectric coolers [76], have been used to reduce the temperature rise in ‘hot spots,’ but are unlikely to be implemented en-masse due to added cost from additional processing required for their on-chip integration. One method to cheaply reduce device operating temperatures is through the integration of highly thermally conductive thin films deposited near where power is dissipated. Aluminum nitride is one such material suitable for heat spreading applications when considered for its thermal and electrical properties. AlN is an ionic material with wurtzite crystal symmetry, expected to have an exceptionally high thermal conductivity of $\kappa_{\text{AlN}} = 319 \text{W.m}^{-1}\text{K}^{-1}$ [10] at room temperature, and has a relatively wide bandgap of 6.28 eV [77].

In this chapter, we present the $\kappa_{\text{ip}}$ and $\kappa_{\text{cp}}$ of single crystal AlN thin films of two thicknesses, determined through measurements accomplished by a modified version of the $3\omega$ method and fitting with FEM models. It was found that $\kappa_{\text{ip}} \neq \kappa_{\text{cp}}$, and both parameters where dependent on the thin film thickness, $t$. The measured thermal conductivity anisotropy is classified on two bases. First, the effects of intrinsic thermal conductivity anisotropy arising from the crystallographic direction dependent $C$ and $\bar{v}_g$ was computed using the phonon dispersion relation. Then, the effects of phonon scattering at the thin film boundaries and intra-film defects are considered, investigated through analysis of transmission electron microscopy
(TEM) micrographs and x-ray spectroscopy data, each of which show a measure of the quantity and type of crystallographic defects found in the crystal. A discussion of the relative influences of these factors is then given with respect to the measured results.

4.1 Fabrication and structural characterization

The AlN films studied in this work were deposited by molecular beam epitaxy (MBE) by a confidential third party. In this deposition technique, source materials are effused in a ultra-high vacuum environment \((10^{-7} \text{ to } 10^{-10} \text{ torr})\) onto a substrate that is heated to a significant fraction of the melting temperature of the deposited material. Deposition of highly crystalline thin films is possible when the rate of surface-diffusion-incorporation of the adsorbing atoms is much faster than the monolayer deposition rate, given that the substrate temperature allows for sufficient surface diffusion for equilibrium bonding formation \([78]\). AlN thin films of two thicknesses were deposited under identical deposition conditions, near 900 °C, with the chamber pressure less than \(10^{-7}\) torr, on \([0001]\) oriented, 6” sapphire wafers. \([0001]\) oriented substrates were expected to be a satisfactory template to grow \([0001]\) oriented films with moderate amounts of strain-induced defects as there was a significant difference between a-axis lattice constants of sapphire, 0.467 nm \([79]\), and AlN, 0.3112 nm \([80]\), but both crystals have hexagonal lattice geometry in the basal plane.

The thicknesses of the films investigated here was measured using ellipsometry and found to be 486 nm and 733 nm. Atomic force microscopy (AFM) was used to scan a 2 \(\mu\text{m}^2\) area of each film, an example of which is shown in figure 4.1, with this 733 nm film exhibiting \(R_a\) (RMS roughness) of 0.219 nm, and \(R_q\) (height standard deviation) of 0.279 nm. The \(R_a\) and \(R_q\) values indicate that macro-scale crystal defects, such as grain boundaries, hillocks, or voids, are unlikely at the top part of the film. TEM micrographs taken of nominally identical films as the ones studied here show the characteristics of the internal film structure in figure 4.2. Imperfections in the crystal indicated by the dark striations are seen to run
relatively vertically throughout a majority of the film thickness, with a greater density near the film/substrate interface. X-ray diffraction (XRD) 2Θ scans were used to determine the crystal orientation of the film, locating the dominant Bragg peak which was found near 36°, corresponding to the AlN (0002) plane.

Figure 4.1: AFM scan of a 2 µm² of the 733 nm thick AlN film, characteristic of the film surface quality of all samples. For this particular sample, the $R_q = 0.279$ nm and the $R_a = 0.219$ nm.

4.2 Thermal conductivity characterization

The TR thermal conductivity measurement technique from chapter 3 was an ideal platform to study the effects of phonon-interface scattering on $\kappa_{ip}$ in single crystal thin films due to its high precision and solution fitting insensitivity to $\kappa_{cp}$. However, TR scans on AlN, an example of which is shown in figure 4.3, had unavoidable noise inherent in the sample that made the curve fitting errors with FEM analysis too large to provide a meaningful $\kappa$. The signal variation, which seemed to randomly oscillate around the expected curve, was systematically repeatable.
Figure 4.2: TEM micrographs of AlN films, at varied magnifications (A, B, C), that show characteristic length scales of crystal defects.
with multiple scans across the same location, implying that the noise could be attributed to a structural feature of the sample itself. With the smoothness of the surface confirmed by the AFM scans, it was concluded the noise was caused by variation in the refractive index due to the TEM identified defects distributed throughout the film, which would also influence $C_{TR}$. Without a way to locally calibrate the spatially dependent $C_{TR}$, the TR measurement could not be used to quantitatively measure the thin film temperature profiles. Additionally, the geometric factors in the AlN thin film system, namely its vertically oriented defects and crystal structure anisotropy, required the characterization of both $\kappa_{ip}$ and $\kappa_{cp}$. We measured both simultaneously using on-chip heater/thermometer structures with varied widths.

![Figure 4.3](image)

**Figure 4.3:** A TR scan across the surface of a 733 nm film. The peak intensity near $x = 5 \, \mu m$ corresponds to a 1 $\mu m$ wide heater, with characteristic exponential decay of the temperature profile shown to evolve with increasing $x$. 
4.2.1 Implementation of a modified $3\omega$ method

4-point probe Al heater structures were deposited, 300 nm thick, on the AlN film surface with varied geometries similar to those used for $3\omega$ measurements, as shown in figure 4.4. The total heater length measured 2050 $\mu$m with the two central voltage probe leads located 550 $\mu$m apart. The leads at each end of the heater were designed to be 200 $\mu$m wide to minimize the $I^2R_{el}$ Joule heating, while the heater width varied from 0.5 $\mu$m to 10 $\mu$m. The inner leads, which are used to only measure voltage, were 10 $\mu$m to minimize the heat escaping through lateral conduction. Electrical contact was made through either gold wire-bonding from the pads to adjacent electrodes on a chip carrier, in which the sample was mounted, or by using needle probes in a probe-station. It was experimentally verified that measurements taken with either configuration produced identical results on a given sample.

Figure 4.4: Schematic of $3\omega$ heater structure used for electrical measurement of the thin film $\kappa$. ‘I+/-’ and ‘V+/-’ designate the current source and voltage probe connections, respectively.

The utility of the $3\omega$ method is derived from the analytic solution of the frequency dependence of the heater self-heating; if the geometric requirements of the relative heater width/sample thickness/TPD length scales can be met, then the thermal conductivity of the substrate may be determined using a linear fit. However, the simultaneously present drawback is apparent when more complex
systems must be characterized, such as a film with anisotropic thermal conductivity on a substrate. A more flexible data analysis method that takes these parameters into account is finite element modeling.

We determined the thermal conductivity of the AlN films through an iterative process of measurement and FEM analysis, building confidence in each parameter used in the model. The data acquired in the measurement is identical to the $3\omega$ method: the amplitude and phase of the $3\omega$ voltage, $V_{el,3}$, across the two inner contacts of the 4-point probe heater is measured as a function of heating current frequency, sourced at the $1\omega$ frequency, where $f = \frac{1}{2\pi}$ ranges between 500 Hz and 1000 Hz. This frequency range was chosen to preclude convective heating effects, as described in section 3.3, and to limit the TPD in sapphire ($\sim 60 \mu$m at 500 Hz) such that $(5 \times \text{TPD}) < t_{sub} = 500 \mu$m to ensure no interaction with the bottom substrate/chip-carrier interface.

In the $3\omega$ method [37], the determination of the material thermal conductivity requires data fitting with an equation similar to,

$$\kappa \propto F \times \frac{\ln(f_2/f_1)}{V_{el,3,1} - V_{el,3,2}}, \quad (4.1)$$

with the factor $F$ containing information about the geometric scaling factors from the radial solution of the HCE and dissipated electrical power. The frequency and $3\omega$ voltages with subscripts (1) and (2) refer to experimental values taken at a (1) lower frequency and (2) a higher frequency. The implicit assumption in this frequency regime is that the response of $V_{el,3}$ is approximately linear with $\ln(f)$ such that $\kappa$ is inversely proportional to the slope of the data. The data fitting method in this work is considered a ‘modified’ $3\omega$ method because instead of using the analytically derived $F$, the geometric effects are accounted for in the FEM and the requirement of using the power scaling factor $(F_{\text{power}} \propto \frac{P_{el}}{L})$ is precluded through a data normalization scheme. The entire $V_{el,3}$ data set, for a given $t$ and heater width, is normalized to the voltage value at the lowest frequency, which in this case happens to be 500 Hz, exemplified in figure 4.5. Since $V_{el,3,1} \propto T \propto P_{el}$, the normalization removes the dependence of the actual temperature on the slope of the data set. Then, the $T$ vs. $\ln(f)$ data obtained from the FEM is normalized in the
same way (to the temperature at 500 Hz), and the two slopes are compared. The thermal conductivity parameter used in the simulation that adequately matches the slopes from the measured and simulated data sets is considered to be the actual $\kappa_{\text{film}}$.

![Figure 4.5: Normalized 3\(\omega\) voltage plotted as a function of ln\(f\). The frequency response is approximately linear, enabling slope fitting with simulated FEM values.](image)

### 4.2.2 Experimental results

The thermal conductivity of the substrate, $\kappa_{\text{sapphire}}$, was expected to have properties identical to that of the bulk single crystal. However, the room temperature values found in the literature vary significantly: Belyaev measured 23 W.m\(^{-1}\)K\(^{-1}\) parallel to the c-axis and 25 W.m\(^{-1}\)K\(^{-1}\) perpendicular to the c-axis [81], while data from D. Cahill [82] measure an isotropic value of 35 W.m\(^{-1}\)K\(^{-1}\), and Kyocera Inc. specifies 42 W.m\(^{-1}\)K\(^{-1}\) [83]. The actual value of $\kappa_{\text{Sapphire}}$ of the sample substrate is essential to the accuracy of the model to determine $\kappa_{\text{film}}$, however, a sapphire substrate sample without a deposited film was unavailable, and $\kappa_{\text{sapphire}} = 35$ W.m\(^{-1}\)K\(^{-1}\) was assumed.

The AlN thin film $\kappa$ was first characterized by implementing the modified 3\(\omega\) method with 1 \(\mu\)m a and 10 \(\mu\)m wide heaters and finite element models were
used fit the data using an *isotropic*, $\kappa_{iso}$, fitting parameter; to the zeroth order, the self-heating of the heaters is equally dependent on the $\kappa_{ip} = \kappa_{cp}$. In actuality, as the heater width increases, a greater fraction of heat flux exiting the center of the heater is forced to conduct only in the cross-plane direction, due to the heater width/film thickness anisotropy. Therefore, if the wider heater measures a larger $\kappa_{iso}$ than its narrower counterpart on a given sample, then it is expected that $\kappa_{cp} > \kappa_{ip}$. Using the $\kappa_{iso}$ as initial values, the $\kappa_{ip}$ and $\kappa_{cp}$ were fit simultaneously using the FEM until two chosen values matched the data taken using both heater widths. In essence, the problem consisted of two (heat conduction) equations and two (unknown) fitting variables, which were solved for simultaneously. All matched $\kappa$ values have been listed in table 4.1. The thermal conductivity follows two trends, (1) $\kappa$ decreases with $t_{AlN}$, and (2) $\kappa_{cp} > \kappa_{ip}$, the physical justification of which will be discussed in the following section.

**Table 4.1:** Fitted values of direction dependent $\kappa$ for AlN films. $\kappa_{iso}$ values were found assuming a single, isotropic thermal conductivity and single heater width in the model, whereas $\kappa_{ip}$ and $\kappa_{cp}$ were solved for simultaneously using data obtained with both heater widths.

<table>
<thead>
<tr>
<th>$t$ (nm)</th>
<th>$K_{iso}^{1\mu m}$ (W.m$^{-1}$K$^{-1}$)</th>
<th>$K_{iso}^{10\mu m}$ (W.m$^{-1}$K$^{-1}$)</th>
<th>$K_{ip}$ (W.m$^{-1}$K$^{-1}$)</th>
<th>$K_{cp}$ (W.m$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>486</td>
<td>125</td>
<td>145</td>
<td>100 +/- 30</td>
<td>175 +/- 30</td>
</tr>
<tr>
<td>733</td>
<td>210</td>
<td>230</td>
<td>200 +/- 30</td>
<td>275 +/- 30</td>
</tr>
</tbody>
</table>

### 4.3 Theoretical analysis of thermal conductivity anisotropy

Crystalline aluminum nitride forms with zinc-blende (face-centered cubic) or wurtzite (hexagonal) symmetry. The films under study here are epitaxial with the underlying hexagonal symmetry of the sapphire and are wurtzite, with the equivalent crystal geometry schematically shown in figure 4.6. As AlN is a two constituent system, each sphere in the figure represents an Al and N atom pair. Previous thermal conductivity measurements performed on single crystal bulk,
wurtzite AlN by Slack and coworkers [10], were conducted parallel to the a- and c-axes. The measured temperature dependent $\kappa$ favored a-axis over c-axis by up to 20% at temperatures below 100 K, the differentiation of the values diminished near RT. At 300 K, the measured c-axis $\kappa = 285 \text{ W.m}^{-1}\text{K}^{-1}$ and the theoretical value for pure AlN, calculated by omitting the oxygen impurity scattering term, was 319 W.m$^{-1}$K$^{-1}$. The measured thermal conductivity anisotropy is generally attributed to the difference in elastic constants and, equivalently, acoustic velocities in the two crystallographic directions. Slack discusses comparisons with similar ionic crystals, such as BeO, which also has a hexagonal crystal structure [11]. TEM images from the reference qualitatively show that the ‘single-crystal’ sample has defects that run parallel to the direction of heat flow (c-axis), but no quantitative analysis of determination of the defect type/density was made. The total BeO $\kappa$ anisotropy was found to be less than 20% with $\kappa_{c-axis} < \kappa_{a-axis}$. Slack’s measurements of ZnO [84], also with hexagonal geometry, also revealed a 20% increase of $\kappa$ in the a-axis, over the c-axis, at temperatures less than 300 K. In summary, experimental results suggest that heat transport in the basal plane of hexagonal crystals is greater than along the c-axis, but lack of acknowledgement of phonon scattering at defects and in-depth analysis of the effects due to crystallographic anisotropy leaves the question of inherent thermal conductivity anisotropy unresolved.

4.3.1 Crystal structure

Two of the three terms that govern the thermal conductivity of a crystalline material can be analytically calculated if the phonon band structure is known, $C$ and $v_g$. The heat capacity, given by equation 1.13, is determined by the temperature, the phonon DOS, and the phonon dispersion relation. The bulk heat capacity of AlN has been previously characterized by direct measurement [85], molecular dynamics simulations [86], and phonon dispersion calculations [18], with the phonon dispersion itself found using the ‘rigid-ion’ model [20, 18, 19] and density-functional perturbation theory [17]. These investigations have considered the crystallographic nature of the AlN structure, which can take the form of wurtzize or zinc-blende, but none have discussed the individual contributions of the crystallographic direction
Figure 4.6: Schematic representation of wurtzite crystal structure unit cell with two atomic species.
dependent phonon bands to the bulk heat capacity value, nor the phonon velocity. In this work we calculate the respective contributions to the specific heat and average phonon velocity using the phonon dispersion of the crystal lattice in the [0001], [1100], and [11̅20], which in reciprocal space is referred to the Γ-A (GA), Γ-M (GM), and Γ-K (GK) directions, respectively. Refer to appendix B for the derivation of the Brillouin zone geometry of the AlN wurtzite crystal structure.

Using the phonon band structure from Davydov, et al., [19] shown in figure 4.7, the dispersion curves for all 12 phonon bands were ‘digitized’ by first plotting the values, and then generating a polynomial equation fit to mathematically represent the continuous frequency variation as a function of wavevector. An example plot of the phonon band polynomial fitting equations in the GK direction is shown in figure 4.8, in which all acoustic and optical bands with both longitudinal and transverse polarizations are represented. The numerical band labeling in the legend of figure 4.8 corresponds to bands of increasing frequency range, such that ‘Band 1’ represents the lowest energy, acoustic, transverse mode. The 12 bands in the AlN wurtzite dispersion relation arise from the two pairs of Al-N atoms (4 in total) per unit cell and three possible vibrational modes, one longitudinal and two transverse. From the plots, three general types of \( v_g \) behavior are present. The acoustic bands, which reside at frequencies of \( \omega_p < 10 \times 10^{13} \text{ rad.s}^{-1} \), typically have a positive \( v_g \) and are largest in magnitude, with group velocities at \( b = 0 \text{ m}^{-1} \) as high as \( 1.2 \times 10^4 \text{ m.s}^{-1} \). A number of optical phonon bands with frequencies \( 10 \times 10^{13} \text{ rad.s}^{-1} < \omega_p < 13 \times 10^{13} \text{ rad.s}^{-1} \) exist with \( v_g \) remaining relatively close to zero. These bands contribute to the \( C \) of the material, but do not significantly contribute to heat conduction due to negligible \( v_g \).

Quantitatively elucidating the effect of the crystal structure on the specific heat and phonon group velocity is performed by assuming that the band structure for a given direction is the isotropic phonon dispersion. In this way, equation 1.13 can be used to calculate the equivalent three-dimensional bulk heat capacity for a given band structure, defined by the characteristics of the crystal in one dimension. Calculated \( C \) values are shown in figure 4.9, with the values corresponding to room temperature listed in table 4.2. The relative magnitudes of the actual bulk value
Figure 4.7: AlN phonon dispersion calculated using a rigid ion model by Davydov, et al. [19].

Figure 4.8: Digitized phonon band structure data of wurtzite AlN in the Γ-K direction from data set measured by Davydov, et al. [19].
and the calculated values draws a distinction between the out-of-plane (c-axis) and basal plane directions; the $C_{GK}$ and $C_{GM}$ values are within a factor of 2 of, and greater than, the bulk value, while $C_{GA}$ is approximately a factor of 5 less than the experimental bulk value, at RT. It is difficult to directly compare the calculated $C$ to the bulk measured value because of the assumptions used in the calculation (one dimensional dispersion relation representing isotropic phonon behavior). To calculate a more accurate bulk value, an average $C$ over all crystal directions would have to be implemented. However, the governing trends seen here are explained by the wurtzite bonding arrangement and constituent atomic species, which gives rise to the exact character of the band structure (determined by the elastic constants), and the range in k-space over which the heat capacity integral is defined (set by the lattice constants and lattice geometry). The cumulative effect gives rise to the large descrepancy between $C_{GA}$ and the in-plane equivalent values; the relatively large c-axis bond length reduces the heat capacity integral substantially, which makes the phonon band structure inherently less thermally capacitive.

The calculation used to find the average group velocity, $\bar{v}_g$, has been previously defined by equation 1.14, with calculated values listed in table 4.2. The temperature dependence of $\bar{v}_g$ is governed by the behavior of $C$, which is a function of temperature due, in part, to the phonon Boltzmann distribution, and is proportional to prefactor which contains the term $T^{-2}$. The thermal energy weighting distribution (as a function of frequency) included in the heat capacity terms of $\bar{v}_g$ modulate their values relative to the group velocity (as a function of frequency), and therefore introduce a temperature dependence in $\bar{v}_g$, plotted in figure 4.10. At 300 K, $\bar{v}_g$ is equal to 1720 m.s$^{-1}$, 1500 m.s$^{-1}$, and 661 m.s$^{-1}$, for the GM, GK, and GA directions, respectively. The $\bar{v}_g$ values of the basal plane crystallographic directions (GM and GK), are greater than that of the c-axis (GA) direction by a factor of 2 to 3, further increasing the anisotropy in heat transport in hexagonal AlN, but in this case due to speed with which phonons carry heat.

Comparison of the calculated values of heat capacity and average group velocity, and their $C\bar{v}_g^2$ product, which most directly corresponds to the final value of $\kappa$ ($= C\bar{v}_g^2\tau$), suggests significant thermal conductivity anisotropy in AlN thin films
Figure 4.9: Heat capacity of AlN calculated through equation 1.13 as a function of temperature, with experimentally measured bulk values from Koshchenko, et al., co-plotted [85].

Table 4.2: Calculated heat capacity, average group velocity, and $C\bar{v}_g^2$ product, at 300 K as a function of crystallographic direction.

<table>
<thead>
<tr>
<th>Direction</th>
<th>$C$ (J.m$^{-3}$K$^{-1}$)</th>
<th>$\bar{v}_g$ (m.s$^{-1}$)</th>
<th>$C\bar{v}_g^2$ (W.m$^{-1}$K$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma K$</td>
<td>$4.06 \times 10^6$</td>
<td>1500</td>
<td>$9.14 \times 10^{12}$</td>
</tr>
<tr>
<td>$\Gamma M$</td>
<td>$2.45 \times 10^6$</td>
<td>1720</td>
<td>$7.28 \times 10^{12}$</td>
</tr>
<tr>
<td>$\Gamma A$</td>
<td>$4.57 \times 10^5$</td>
<td>903</td>
<td>$3.73 \times 10^{11}$</td>
</tr>
</tbody>
</table>
Figure 4.10: Average group velocity of AlN calculated as a function of temperature in the GK, GM, and GA crystallographic directions.
due to crystal structure, up to a factor of $\sim 40$. However, discussing anisotropy of the $\kappa$ tensor at RT due to crystal lattice characteristics typically has not been discussed previously in the study of heat transfer in thin films. One reason is the dominating effect of phonon scattering by other phonons at room temperature, as well as the diffusive nature of heat propagation making direction-specific heat flux measurements in thin films difficult. Another complication is the implementation of a three-dimensional BZ to most accurately calculate $C$ and $v_g$. Recent thermal conductivity measurements performed on single crystal samples, such as those from Si wafers and SOI thin films, used analysis to predict phonon behavior that assumed the [100] dispersion relation was representative of the isotropic thermal conductivity of the crystal [23, 7, 75, 9, 8, 73, 26], as the calculated bulk heat capacity matched well with measured values, as shown in figure 1.1. A review of older literature quickly reveals the inaccuracy of this approximation, as the heat-flow in the [100], [110] and [111] directions of Si is quantitatively and significantly different at low temperatures [24] due to ‘phonon focusing’ [87, 88, 89] or, equivalently, from enhanced transport in certain directions that enhance $\kappa$ due to larger $C$ and $v_g$, as described above.

In this vein, pyrolytic graphite (PG) is a well characterized material that can be used for ‘proof of concept’ of room temperature $\kappa$ anisotropy. Schmidt, et al., developed a FDTR technique to probe the behavior of radial and one-dimensional cross-plane heat conduction from the PG surface through the implementation of two spot size, and heating frequency, regimes [90]. The experimental method was verified by measurements of PG at room temperature, which yielded values of $\kappa_{cp} \sim 6 \text{ W.m}^{-1}\text{K}^{-1}$ and $\kappa_{ip} \sim 2000 \text{ W.m}^{-1}\text{K}^{-1}$, matching previous measurements [67]. Using similar arguments that determine $C$ and $v_g$ as explained above, the phonon dispersion curves for PG [21] shown in figure 4.11 suggest that $\kappa$ anisotropy is not due only to phonon scattering. The large relative difference between slopes and curve shapes of the acoustic bands of the c-axis, [001], and basal plane, [100] and [110], directions, in addition to the unit wavevector inverse lengths differences, suggest large anisotropy in $C$ and $v_g$. 
Figure 4.11: Phonon dispersion relation of pyrolytic graphite in the c-axis, [001], and basal plane, [100] and [110], directions calculated by Nicklow, et al. [21].
4.3.2 Deposition methods and conditions, crystal defects, and thin film boundaries

Significant efforts have been devoted to measuring $\kappa$ of AlN thin films and, for a comparison of $\kappa_{cp}$ values, all the thin films discussed in this section have a c-axis, (0001) out-of-plane orientation. Kuo, et al., deposited 1 $\mu$m thick films on (0001) oriented sapphire substrates by plasma source molecular beam epitaxy (PSMBE) near 1000 $^\circ$C. The thermal diffusivity was characterized using a thermal wave-mirage technique and it was found that $\kappa_{cp} = 25.2$ W.m$^{-1}$K$^{-1}$ [91]. Other physical vapor deposition (PVD) methods rely on the ablation of an Al metal target held in a high purity nitrogen atmosphere, in which the Al and N react as deposition occurs. A 310 nm thick film deposited Jacquot, et al., by pulsed laser deposition (PLD) was fabricated on a (100) oriented Si wafer heated to a temperature between 200 – 400 $^\circ$C. The 3$\omega$ method was used to measure $\kappa_{cp} = 0.8$ W.m$^{-1}$K$^{-1}$, with thermal conductivity temperature dependence show phonon scattering behavior indicative of an amorphous solid [92]. Zhao and coworkers measured very similar $\kappa_{cp}$ values, less than 2 W.m$^{-1}$K$^{-1}$, for film thicknesses ranging from 100 nm to 1 $\mu$m, that had been deposited by RF sputtering at RT [93].

Duquenne, et al., was the first group to make progress with highly thermally conductive, sputtered AlN thin films using an ‘unbalanced’ magnetron sputtering method [94, 95]. The optimal nitrogen to argon ratio present during deposition was empirically determined and tuning of the magnetic field generated by the target cathode was used to enhance the plasma characteristics. The $\kappa_{cp}$ of films with thicknesses between 150 nm and 3.5 $\mu$m were measured using a ‘hot-strip’ technique, in which the self-heating effects similar to that of the 3$\omega$ measurement are harnessed, but a square-wave heating pulse is utilized. The films in this study generally showed that the effective thermal conductivity of the entire film increased with film thickness, while the columnar, ‘bulk’ part of the film, that grows over thin amorphous/polycrystalline seed layers near the substrate surface, exhibited a consistent $\kappa_{cp}$ of 170 W.m$^{-1}$K$^{-1}$ [96]. Belkerk, et al., summarizes the quality of crystal formation seen in DC sputtered films on (001) oriented Si substrates by designating three conditions: (I) balanced cathode, (II) unbalanced cathode with
20% nitrogen atmospheric content and 0.26 Pa pressure, and (III) unbalanced condition with 35% nitrogen atmospheric content and 0.4 Pa pressure. It is shown that as the deposition conditions change from (I) to (III), the films become more dense, have larger grain sizes, lower oxygen content and reduced amorphous layer thickness, all leading to increased $\kappa_{cp}$ [97]. A summary of the measured $\kappa_{cp}$ values from the references and this work is plotted in figure 4.12.

![Figure 4.12](image_url)

**Figure 4.12:** Measured $\kappa_{cp}$ values for c-axis oriented AlN bulk (Slack, et al.) [10] and thin film samples deposited by MBE (Kuo, et al.) [91], and this work), PLD (Jacquot, et al.) [92] and reactive sputtering (Zhao, et al.) [93], (deposition conditions (I), (II), (III) in Belkerk, et al.) [97].

While an in-depth explanation of the mechanisms of thin film sputtering and MBE deposition techniques is outside of the scope of this dissertation, coarse, but representative, observations can be made about the trends between thermal conductivity and crystal quality through discussion of dominant scattering mechanism. It is shown in figure 4.12 that the transition between near amorphous films (Kuo, et al.) and defected single crystal films (this work) enhances the positive
trend that relates the thermal conductivity to the film thickness. The two primary phenomena that justify the increase of $\kappa_{cp}$ with $t_{AlN}$ are: (1) grain growth, or defect density reduction, typically occurs with film growth such that the upper sections of thin films conduct heat more efficiently than the lower section due to reduced scattering at defects and grain boundaries, thus increasing thickness leads to an overall increase in effective $\kappa_{cp}$ [98, 97]; (2) interface scattering may also play a roll in the thickness dependence of $\kappa$ through limiting the phonon mean free path if the crystal near the film/substrate interface exhibits amorphous behavior, or simply offers an additional specular/diffuse scattering boundary, the exact mechanisms of which have been extensively studied in Si thin films [23, 7, 75, 9, 8, 73, 26].

The measured thermal conductivity anisotropy, in which $\kappa_{cp}$ is larger, is likely due to, not the crystal structure itself, which already has been established to have enhanced thermal conduction in the basal plane of the film, but how the location and geometric orientation of the microstrucal defects (that act as phonon scattering mechanisms) are dependent on the crystal lattice geometry. A common sputter growth mode of (0002) oriented AlN thin films occurs by formation of hexagonally shaped islands that impinge upon each other as they grow outward, to form vertically aligned grain boundaries as they grow upward [94, 95]. In the case of epitaxial MBE growth, the grain boundaries may not have the identical character as those found in sputtered films, but the defect are still vertically oriented, as shown in TEM micrograph in figure 4.2. Vertically aligned defects would have different effective scattering volumes with respect to in-plane and cross-plane propagating phonons, having a much greater effect on the former. It may then be expected that at a certain defect density threshold, in-plane phonon scattering increased to such a degree that the predicted thermal conductivity anisotropy for a single crystal would no longer be representative, e.g. when $\kappa_{cp} > \kappa_{ip}$. 
5 Conclusions

5.1 Summary

In order to study the inherent anisotropy in \( \kappa \) of crystalline solids resulting from their specific atomic arrangements, direction specific thermal conductivity measurement techniques for thin films have been developed. One method relied on the thermo-optic effect of thermoreflectance to scan temperature profiles along the surface of heated thin films in order to characterize how heat flow took place in the plane of the film. The \( \kappa_{ip} \) values of single crystal Si thin films, on SOI substrates, of thicknesses ranging between 68 nm and 255 nm, were measured to test the utility of the measurement. The \( \kappa \) values were extracted through fitting of the measured temperature profiles with a finite element model and it was found that the measured thermal conductivity, as a function of thin film thickness, was in good agreement with those from literature.

The second method was developed from the commonly utilized 3\( \omega \) method and implemented electrically with deposited thermometer structures of varied widths in order to extract the thin film \( \kappa_{ip} \) and \( \kappa_{cp} \) simultaneously. This was an advancement from the basic technique as it implemented finite element modeling which enabled the measurement of thin films with anisotropic \( \kappa \), on an insulating substrate, with arbitrary heater geometries. This method was used to probe (0002) oriented AlN films that were deposited epitaxially on single crystal sapphire substrates, that were thought to exhibit thermal properties similar to that of a single crystal. Calculations of the heat capacity and group velocity were performed using the direction dependent phonon dispersion relation and it was found that the \( C\bar{v}_g^2 \) product in the basal plane was approximately 40x greater than that along
the c-axis, suggesting significant, room temperature $\kappa$ anisotropy. However, it was found experimentally that $\kappa_{ip} < \kappa_{cp}$, likely due to the nature of the defected crystal structure, which was essentially a series of adjacent columnar grains, separated by vertically oriented defect boundaries.

5.2 Future Work

The quantitative correlation between $\kappa$ and the crystallinity, characterized by the defect density, grain size, etc., and the thickness, of the AlN thin film system is still largely uncharacterized. Using the modified 3$\omega$ method, as described previously, to measure $\kappa$, while exploring the quality of the crystal structure using XRD rocking curve scans of the (0002) and (10-12) peaks to quantify the magnitude and orientation of defect density would provide insight on the dominant phonon scattering mechanisms in the film. The number of defects may be controlled through film thickness, deposition conditions, and substrate type, as both sapphire and (111) oriented Si are both candidates. If the relevant phonon scattering mechanisms can be quantified as a function of temperature, then the experimental measurement may be used to confirm the predicted $\kappa$ found through the phonon dispersion analysis.
A Definition of symbols

Variables and Parameters

\[ a = \text{in-plane lattice constant} \]
\[ \dot{a} = \text{lattice basis vector} \]
\[ A = \text{area} \]
\[ \hat{b} = \text{reciprocal lattice basis vector} \]
\[ b = \text{wavevector} \]
\[ b_{TD} = \text{threading dislocation Burger vector} \]
\[ \beta = \text{rocking curve FWHM} \]
\[ c = \text{out-of-plane lattice constant} \]
\[ C = \text{heat capacity} \]
\[ C_{TR} = \text{thermoreflectance coefficient} \]
\[ C_{th} = \text{thermal capacitance} \]
\[ d = \text{electromagnetic skin depth} \]
\[ \delta = \text{Dirac delta function} \]
\[ D = \text{thermal diffusivity} \]
\[ D(b) = \text{density of states} \]
\[ D_{dis} = \text{dislocation density} \]
\[ e = 1.602 \times 10^{-19} \text{C}, \text{electron charge} \]
\[ E = \text{electron energy} \]
\[ \tilde{\epsilon} = \text{complex dielectric constant} \]
\[ \mathcal{E} = \text{electric field magnitude} \]
\[ f = \text{frequency} \]
\[ F = \text{factor/fitting parameter} \]
γ = damping constant
Γ = Brillouin zone center
H = magnetic field magnitude
\( \hbar = 6.626 \times 10^{-34} \text{ J.s, Planck's constant} \)
\( \hbar = \frac{h}{2\pi} \)
\( i = \sqrt{-1} \)
I = optical intensity
\( I_{el} = \) electrical current
k = imaginary part of refractive index
\( k_B = 1.381 \times 10^{-23} \text{ J.K}^{-1}, \) Boltzmann’s constant
\( \kappa = \) thermal conductivity
\( \lambda = \) optical wavelength
\( \lambda_p = \) phonon wavelength
l = phonon mean free path
\( L = \) length, or characteristic length
\( m = \) optical characteristic matrix element
\( m^* = \) electron effective mass
\( M = \) optical characteristic matrix (OCM)
\( \tilde{n} = \) complex refractive index
\( n = \) real part of refractive index
\( n_B = \) Boltzmann distribution
\( N = \) density of states
\( \omega = \) angular frequency
\( \omega_{pl} = \) plasmon frequency
p = polarization
\( P = \) generated heat
\( P_{ul} \) or \( P_{cv} = \) momentum matrix
\( \dot{Q} = \) heat flux
\( r = \) gaussian beam radius
\( R = \) optical reflectance
\( R_p = \) phonon reflectance
\( R_{th} = \) thermal resistance
\( R_{el} = \) electrical resistance
\( R_q = \) profilometric height standard deviation
\( R_a = \) profilometric RMS roughness
\( \rho = \) density
\( s = \) time
\( S = \) thermoelectric power factor
\( \sigma = \) electrical conductivity
\( t = \) thickness
\( T = \) temperature
\( \tau = \) time constant
\( \tau_p = \) phonon scattering time constant
\( \theta = \) vector angle
\( \theta_d = \) Debye temperature
\( U = \) total internal energy
\( v = \) velocity
\( V = \) volume
\( V_{el} = \) electrical voltage
\( W = \) prefactor
\( \xi = \) electromagnetic plane wave vector
\( x = \) spatial coordinate
\( y = \) spatial coordinate
\( z = \) spatial coordinate
\( Z = \) acoustic impedance
\( \zeta = \) linear coefficient of thermal expansion

**Acronyms**

AC: Alternating current
AFM: Atomic force microscopy
AMM: Acoustic mismatch model
BC: Boundary condition
BZ: Brillouin zone
DC: Direct current
DMM: Diffuse mismatch model
DOS: Density of states
FEM: Finite element modeling
FWHM: Full width at half maximum
GA: Γ-A direction in reciprocal space
GK: Γ-K direction in reciprocal space
GM: Γ-M direction in reciprocal space
MBE: Molecular beam epitaxy
NA: Numerical aperture
PSMBE: Plasma source molecular beam epitaxy
PG: Pyrolytic graphite
RMS: Root mean squared
RT: Room temperature
SEM: Scanning electron microscopy
TCR: Thermal coefficient of resistance
TEM: Transmission electron microscopy
TPD: Thermal penetration depth
TR: Thermoreflectance
XRD: X-ray diffraction
B Derivation of the wurtzite crystal structure Brillouin zone

AlN Lattice Constants [80]: $a = 3.112$ Å; $c = 4.982$ Å

Lattice vector definition for a hexagonal crystal:

\[ \hat{a}_1 = \frac{a}{2} \hat{x} - \frac{\sqrt{3}a}{2} \hat{y} \]  
\[ \hat{a}_2 = \frac{a}{2} \hat{x} + \frac{\sqrt{3}a}{2} \hat{y} \]  
\[ \hat{a}_3 = c \hat{z} \]

Reciprocal lattice vector derivation:

\[ \hat{b}_1 = 2\pi \frac{\hat{a}_2 \times \hat{a}_3}{\hat{a}_1 \cdot \hat{a}_2 \times \hat{a}_3} \]
\[ = \frac{2\pi}{\frac{\sqrt{3}}{2} a^2 c} \]
\[ = \frac{2\pi \left( \frac{1}{a} \hat{x} - \frac{1}{\sqrt{3}a} \hat{y} \right)}{\sqrt{3}a} \]
\[ = \frac{2\pi}{\sqrt{3}a} \left( \sqrt{3} \hat{x} - \hat{y} \right) \]  
\[ (B.4) \]
\[
\hat{b}_2 = 2\pi \frac{\hat{a}_3 \times \hat{a}_1}{\hat{a}_1 \cdot \hat{a}_2 \times \hat{a}_3}
\]
\[
= 2\pi \frac{\sqrt{3}a \hat{x} \hat{c} + \frac{a \hat{c}}{\sqrt{3}} \hat{y}}{\sqrt{3}a^2 c}
\]
\[
= 2\pi \left( \frac{1}{a} \hat{x} + \frac{1}{\sqrt{3}a} \hat{y} \right)
\]
\[
= \frac{2\pi}{\sqrt{3}a} \left( \sqrt{3} \hat{x} + \hat{y} \right) \quad \text{(B.5)}
\]

\[
\hat{b}_3 = 2\pi \frac{\hat{a}_1 \times \hat{a}_2}{\hat{a}_1 \cdot \hat{a}_2 \times \hat{a}_3}
\]
\[
= 2\pi \frac{\sqrt{3}a^2}{\sqrt{3}a^2 c} \hat{z}
\]
\[
= \frac{2\pi}{c} \hat{z} \quad \text{(B.6)}
\]

**Table B.1:** Reciprocal lattice vector definitions with respect to the three inverse space directions of interest: \( \Gamma A \), \( \Gamma K \), and \( \Gamma M \).

| Direction | \( \hat{b} \) | \( ||\hat{b}|| \) formula | \( ||\hat{b}|| \) (m\(^{-1}\)) |
|-----------|---------------|----------------------------|---------------------------------|
| \( \Gamma K \) | \( \langle \frac{1}{3}, \frac{1}{3}, 0 \rangle \) | \( \frac{4\pi}{3a} \) | \( 1.346 \times 10^{10} \) |
| \( \Gamma M \) | \( \langle \frac{1}{2}, 0, 0 \rangle \) | \( \frac{2\pi}{\sqrt{3}a} \) | \( 1.166 \times 10^{10} \) |
| \( \Gamma A \) | \( \langle 0, 0, \frac{1}{2} \rangle \) | \( \frac{\pi}{c} \) | \( 6.306 \times 10^{9} \) |
Figure B.1: Schematic of $x$-$y$ plane, hexagonal close packed lattice, demarcated with $x$ and $y$ axes orientation and chosen basis vectors.

\[
\hat{a}_1 = \frac{a}{2} \hat{x} + \frac{\sqrt{3}}{2} \hat{y}
\]

\[
\hat{a}_2 = \frac{a}{2} \hat{x} - \frac{\sqrt{3}}{2} \hat{y}
\]

Figure B.2: Schematic of $x$-$y$ plane, hexagonal close packed reciprocal lattice, demarcated with $x$ and $y$ axes orientation, derived basis vectors, first Brillouin Zone and points M and K.

\[
\hat{b}_1 = \frac{2\pi}{\sqrt{3}a} (\sqrt{3} \hat{x} - \hat{y})
\]

\[
\hat{b}_2 = \frac{2\pi}{\sqrt{3}a} (\sqrt{3} \hat{x} + \hat{y})
\]
Figure B.3: Brillouin zone of a wurtzite crystal lattice. The directions in inverse space most relevant to thermal conductivity anisotropy analysis were $\Gamma A$, $\Gamma K$, and $\Gamma M$. 
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