

UNDERSTANDING AND TUNING THE HEAT TRANSPORT
AT INTERFACES BETWEEN
METALS AND HIGHLY ANISOTROPIC SEMICONDUCTORS

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ABSTRACT

A complete and accurate description of nanoscale heat transport processes in materials is required to fundamentally understand the energy transfer mechanisms and advance technologically in thermal management applications. Recent advances in nanoscale heat transport have challenged the conventional understanding of Fourier's heat conduction law and energy transfer mechanisms in emerging materials, necessitating further experimental and theoretical research.

In this dissertation, we explore both theoretically and experimentally the fundamental heat transport mechanisms in anisotropic semiconductors and investigate how ultrathin metallic interlayers influence thermal boundary conductance at metal-anisotropic semiconductor interfaces. We first studied how heat transport is modified in metal-isotropic semiconductor systems with ultrathin interlayers. Our results show that the heat transport can be tuned by factors such as phonon frequency overlap and electron-phonon coupling in the metal. The ultrathin interlayer was found to effectively tune thermal transport through its thickness, even with films as thin as 1 nm. This behavior is well captured by a hybrid model based on diffuse mismatch theory, which provides a more comprehensive understanding of thermal transport across interfaces.

Thermal conductivity in semiconductors varies with size when non-diffusive transport ensues. To accurately characterize the metal-anisotropic semiconductor interface and maintain a constant thermal conductivity independent of thickness, we experimentally measured how conductivity evolves with film thickness. We then modeled this behavior using the Boltzmann transport equations. This combined approach allowed us to extract bulk-like thermal conductivities, which is essential for reliable interfacial analysis. Our results show that the thermal conductivities of graphite, MoS₂, and hBN increase with thickness and plateau at ~5 μm for graphite and ~500 nm for both MoS₂ and hBN.

We then analyzed the modification of heat transport in metal-bulk anisotropic semiconductors in the presence of thin metallic interlayers. Our hybrid model predicts the modification of boundary conductance at metal-anisotropic semiconductor interfaces, offering a more accurate representation compared to existing models, and was validated through experimental measurements. Our results provide new insight into the fundamental physics of heat transport as well as offer ways to design materials and devices with tailored thermal properties for applications in nano- and micro-electronics, thermoelectrics, and nanotechnology.

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LIST OF SYMBOLS AND ABBREVIATIONS

a : In-plane lattice constant of the layered material

A_0 : Total laser power

c : Out-of-plane lattice constant of the layered material

C : Volumetric specific heat capacity

C_e : Electron volumetric specific heat capacity

C_p : Phonon volumetric specific heat capacity

C_{TR} : Thermoreflectance coefficient

D : Phonon density of states

D_T : Thermal diffusivity

e : Charge of electron

f_0 : Bose-Einstein distribution function

$f^{j,q}$: Non-equilibrium phonon distribution function for branch j and wavevector q

g : Volumetric electron-phonon coupling constant

G : Thermal boundary conductance

G_a : TBC due to phonon contributions between metal and a-axis of substrate in the DMM model

G_{ani} : Total TBC calculated based on anisotropic DMM model

G_b : TBC due to back transfer of heat from the interlayer to the top metal layer

G_c : TBC due to phonon contributions between metal and c-axis of substrate in the DMM model

$G_{c,ani}$: TBC due to phonon contributions between metal and c-axis of substrate in the anisotropic DMM model

G_{cr} : Total TBC calculated based on crude model

G_{ee} : TBC due to electron contributions in metals

$G_{ep,1}$: TBC due to electron-phonon contributions in top metal

$G_{ep,2}$: TBC due to electron-phonon contributions in interlayer

G_{iso} : Total TBC calculated based on isotropic DMM model
 $G_{pp,1}$: TBC due to phonon contributions between metal and substrate in the DMM model
 $G_{pp,2}$: TBC due to phonon contributions between interlayer and substrate in the DMM model
 $G_{pp,2cr}$: TBC due to phonon contributions between metal and substrate using the crude model
 $G_{pp,AMM}$: TBC due to phonon contributions in the AMM model
 G_{pp} : TBC due to phonon contributions in the DMM model
 $G(L_I)_{pp,1}$: Interlayer thickness dependent TBC
 $G_{pp,accum}$: Accumulated TBC
 $G_{pp,sat}$: Saturated value of accumulated TBC
 G_1 : TBC due to pathway 1 in the thermal model
 G_2 : TBC due to pathway 2 in the thermal model
 h : Planck's constant
 $\hbar$: Planck's constant/ 2π
 i : Phonon polarization
 j : Phonon branch index
 J : heat flux
 k : Total thermal conductivity
 k_B : Boltzmann constant
 k_e : Electronic thermal conductivity
 k_p : Phononic thermal conductivity
 $k_{cumulative}$: Cumulative thermal conductivity
 L_0 : Lorenz number
 L : Sample thickness
 L_I : Thickness of interlayer
 n : Complex refractive index
 n_r : Real part of refractive index

N : Number of atoms per primitive cell
 N_i : Discretized Brillouin zone grid points
 q : Wave vector
 R_{ep} : Resistance due to electron-phonon coupling in metal
 $R_{ep,i}$: Resistance due to interfacial electron-phonon coupling
 R_{pp} : Resistance due to phonon-phonon interaction
 R_1 : Resistance due to pathway 1
 R_2 : Resistance due to pathway 2
 R_T : Total resistance due to pathways 1 and 2
 R : Reflectivity
 S_c : Seebeck coefficient
 S : Suppression function
 t_{echo} : Time taken by the acoustic echo to return to the surface
 T : Temperature
 T_e : Electron temperature
 T_p : Phonon temperature
 V : Amplitude of the lock-in amplifier signal
 V_{in} : In-phase signal of the lock-in amplifier signal
 V_{out} : Out-of-phase signal of the lock-in amplifier signal
 V_{st} : Longitudinal speed of sound
 w_r : Gaussian beam $1/e^2$ radius
 w_o : Pump laser beam $1/e^2$ radius
 w_1 : Probe laser beam $1/e^2$ radius
 Z : Acoustic impedance
 ZT : Thermoelectric figure of merit
 $\alpha_{A \rightarrow B}$: Phonon transmission probability

$\alpha_{A \rightarrow B, an}$: Anisotropic phonon transmission probability
 γ_e : Sommerfeld parameter
 δ : Surface roughness
 θ_D : Debye temperature
 κ : Extinction coefficient
 Λ_p : Mean free path of phonons
 λ : Wavelength of phonons
 λ_{min} : Shortest wavelength phonon at the Brillouin zone edge
 λ_{max} : Longest phonon wavelength limit
 v_p : Group velocity of phonon
 v_e : Fermi velocity of electron
 σ : Electrical conductivity
 τ_B : Boundary scattering rate
 τ_I : Impurity scattering rate
 τ_{p-p} : Phonon-phonon scattering rate
 τ_r : Laser repetition rate
 τ_T : Total relaxation time
 $\tau_0^{j,q}$: Phonon relaxation time for mode j, q obtained from perturbation theory
 ρ : Mass density
 ν_A : Maximum phonon frequencies near the Brillouin zone edge
 ν_L : Maximum longitudinal acoustic phonon frequencies
 ν_T : Maximum transverse acoustic phonon frequencies
 $\nu_{quasi-optical}$: Maximum low-lying optical phonon frequencies in layered material
 φ : Phase of lock-in amplifier signal
 Ω : Unit cell volume
 ω : Phonon angular frequency

ω_c : Maximum phonon angular frequency

ω_D : Debye cut-off frequency

AC: Alternating Current

AMM: Acoustic Mismatch Model

BTE: Boltzmann transport equations

BZ: Brillouin zone

DFT: Density functional theory

DMM: Diffuse mismatch model

EOM: Electro-optic modulator

EPC: Electron-phonon coupling

FDTR: Frequency domain thermoreflectance

IFC: Interatomic force constant

LA: Longitudinal acoustic

MFP: Mean free path

MD: Molecular dynamics

NEGF: Non-equilibrium Green's function

PAW: Projected augmented wave

PBE: Perdew-Burke-Ernzerhof

RTA: Relaxation time approximation

SLG: Single layer graphene

TA: Transverse acoustic

TBC: Thermal boundary conductance

TDTR: Time domain thermoreflectance

TMD: Transition metal dichalcogenide

TTM: Two-temperature model

CHAPTER 1: INTRODUCTION

1.1 Motivation

Understanding heat transport at the nanoscale is crucial for advancing thermal management and energy conversion in an era of ever-shrinking electronic devices. As devices continue to miniaturize, the density of components increases, leading to higher power densities and significant thermal loads. Efficient heat dissipation is required to maintain device performance and longevity. Nanoscale materials exhibit unique thermal behaviors significantly different from their bulk counterparts, such as quantum confinement and non-diffusive transport, which must be understood to prevent hotspots and ensure reliable operation[1]. This knowledge enables the integration of thermal, electrical, and mechanical design considerations, optimizing material selection and cooling strategies. Additionally, understanding heat transport is crucial in enhancing the efficiency of energy conversion technologies, such as thermoelectrics, by allowing precise control over thermal properties[2], [3]. The figure of merit of thermoelectric efficiency, $ZT = \frac{S_c \sigma^2 T}{k}$ (where S_c is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature and $k = k_e + k_p$ is the total thermal conductivity due to electrons (k_e) and phonons (k_p)) can be enhanced by tailored engineering of nanostructures by reducing the thermal conductivity while maintaining the electrical conductivity[2], [4], [5], [6]. Understanding thermal transport helps in designing materials that can either enhance or impede heat flow as required for specific applications.

Heat transfer between metals and semiconductors poses unique challenges due to the difference in predominant heat carriers in the constituent materials and the energy transfer processes between them. Heat transport in anisotropic semiconductors differs from isotropic semiconductors due to the directional dependence of thermal properties arising from the crystal

structure. This is an intrinsic property that is distinct from composite and heterostructure materials, where anisotropy can be engineered by a judicious design. In anisotropic semiconductors, thermal energy can propagate more efficiently along specific axes than others, making them useful for thermal management in devices that require efficient heat dissipation along specific directions to avoid hotspots[7], [8], [9]. Thermal conductivities of layered materials such as graphite or transition metal dichalcogenides (TMD) are highly anisotropic due to the difference in interatomic forces in the in-plane and out-of-plane directions[10]. Most bulk-layered materials have well-known thermal conductivities; nevertheless, at sub-micrometer length scales, their thermal conductivities can show significant material size dependencies[11]. Fundamentally understanding the change in thermal conductivity due to the size effects in these materials is crucial in layered material-based device fabrications. Additionally, the optimized thermal performance of these devices depends upon the efficient heat transfer between the layered material and the various interfaces present in the device, such as those taking place at metallic contacts, the substrate, etc. However, the poor heat conduction across the interfaces involving layered materials is a bottleneck in layered material-based device performance[12], [13]. As dimensions reduce to nanoscale, the thermal resistance at interfaces between different materials becomes a major bottleneck, limiting efficient heat dissipation. In such systems, the resistance at these interfaces can dominate the resistance of the individual layer, making interfacial thermal transport a key factor in determining the overall thermal performance of nanoscale devices. To gain insight into metal-anisotropic semiconductor interfacial thermal transport and its modification, a detailed understanding of metal-isotropic semiconductor interface is a fundamental steppingstone before considering a more complex anisotropic scenario. Nanoscale heat transport in conventional electronics based on isotropic semiconductors such as silicon or germanium has been an active area of research for the

past two decades[14], [15] and modification of the interfacial heat transport at metal-isotropic interfaces by adding a metallic interlayer has been proven experimentally[16], [17], [18], [19]; however, a theory systematically predicting the heat transport modification is still not available. Predicting the modification of interfacial heat transport across metal-isotropic semiconductors requires the identification of the primary factors governing and the modification mechanisms involved in the transport. This work focuses on fundamentally understanding the anisotropic heat transport modification due to the size effects in layered materials and effectively manipulating the heat transport processes across metal-anisotropic semiconductor interfaces.

1.2 Fundamentals of Nanoscale Heat Transfer

Macroscopically, heat transfer occurs in three distinct modes: conduction, convection, and thermal radiation. These modes operate via different mechanisms, yet they all are driven by net transfer of thermal energy from regions of higher temperature to those of lower temperature until thermal equilibrium is achieved. At the microscopic level, conductive¹ heat transfer occurs through a series of inelastic collisions between energy carriers, leading to the exchange and redistribution of thermal energy within the material. Fourier's law of heat conduction, which provides a foundational framework for analyzing classical heat transfer processes, states that the rate of heat transfer through a material is proportional to the negative of the temperature gradient, with the proportionality constant being the thermal conductivity[20]. This relationship is expressed as:

$$J = -k\nabla T \quad (1.1)$$

where J is the heat flux, k is the thermal conductivity and ∇T is the temperature gradient. Thermal

¹This dissertation deals solely with conductive heat transport, so all heat transfer phenomena discussed will be referring to the conduction heat transfer mode without explicitly saying so.

conductivity quantifies a material's ability to conduct thermal energy across a given distance. For bulk isotropic materials, thermal conductivity is an intensive property, remaining constant irrespective of the material's size or geometry which is not true for nanostructures[20], [21]. The total thermal conductivity is the sum of thermal conductivities associated with individual heat carriers, and the energy associated with each energy carrier can be calculated based on quantum mechanical principles[22], [23].

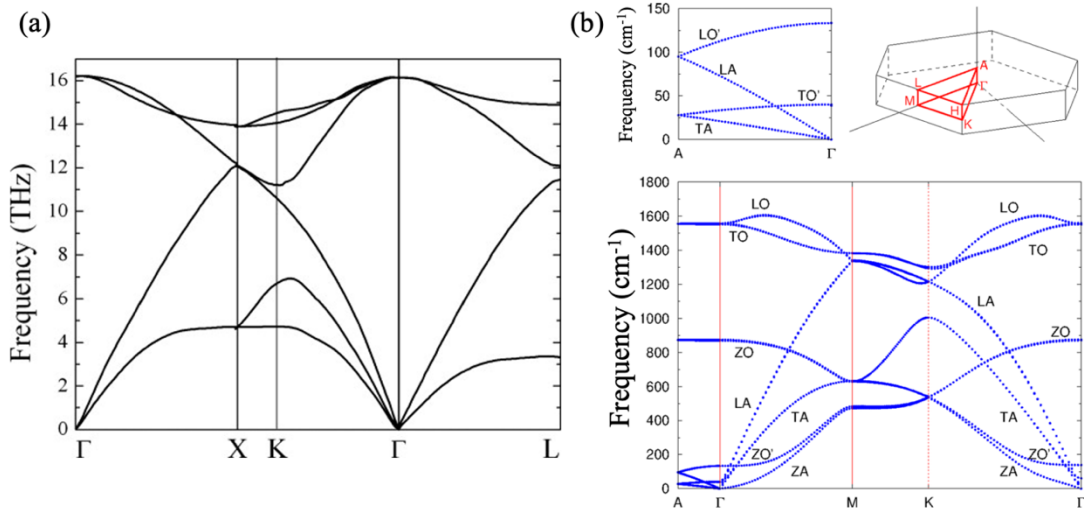


Figure 1.1: Phonon dispersions in (a) Si[26] (an isotropic bulk crystal) and (b) graphite[27] (an anisotropic crystal). The Brillouin zone in reciprocal space and high symmetry points in graphite are shown in the top right. Reprinted with permission from J. Appl. Phys. 107, 083503 (2010) (panel (a)). Copyright 2010, American Institute of Physics. Reprinted with permission from Phys. Rev. B 90, 155448 (2014) (panel (b)). Copyright 2014, American Physical Society.

In most solids, heat is predominantly carried by electrons and phonon so that the total thermal conductivity $k = k_e + k_p$ [24]. Due to the presence of a large density of free carriers, electrons are the primary carriers in metals and in degenerately doped semiconductors. The electronic thermal conductivity k_e can be estimated by measuring the electrical conductivity (σ) using the Wiedemann-Franz law[25]:

$$\frac{k_e}{\sigma T} = \frac{\pi^2 k_B^2}{3e^2} = L_0 = 2.45 \times 10^{-8} \frac{W\Omega}{K^2} \quad (1.2)$$

where T is the absolute temperature, k_B is the Boltzmann constant, e is the charge of electron, and L_0 is the Sommerfeld value of Lorenz number. The electronic thermal conductivity can be readily measured by measuring the electrical resistivity using the four-point probe technique and then applying the Wiedemann-Franz law.

On the other hand, the majority of heat is carried by phonons in semiconductors and insulators. As phonons dominate thermal transport in semiconductors and dielectrics, the terms are used interchangeably. Although these materials differ electronically, the distinction is not relevant here, as we focus only on undoped semiconductors. Phonons are quantized vibrations within a crystal lattice, governed by Bose-Einstein statistics. The relationship between the frequency (ω) of these vibrations and the wavevector (q) is described by the phonon dispersion relation, $\omega(q)$, which reveals the allowable energy levels of phonons based on their wavevector (see Figure 1.1), providing insight into the dynamics of the crystal[23]. Figure 1.1 shows the phonon dispersions in (a) Si[26] (an isotropic bulk crystal) and (b) graphite[27] (an anisotropic crystal). The Brillouin zone (BZ) in reciprocal space and high symmetry points in graphite are shown in the top right. Phonons are categorized into two types: acoustic and optical. Acoustic phonons, which propagate at the speed of sound, are low-frequency vibrations resulting from the in-phase movement of adjacent atoms. They can be further divided into longitudinal acoustic (LA) modes, where atoms oscillate parallel to the wave propagation direction, and transverse acoustic (TA) modes, where atomic displacements are perpendicular to the wave propagation. At long wavelengths, acoustic phonons approach zero frequency at the Brillouin zone center, displaying a linear dispersion relation[23]. Conversely, optical phonons arise from the out-of-phase movement of neighboring atoms and possess higher energies. Optical phonons interact with external

electromagnetic fields and are vital in processes such as optical absorption and scattering. These high-energy phonons exhibit a dispersion relation where frequencies do not converge to zero but instead maintain a relatively constant high value across the *BZ*.

In a three-dimensional lattice, characterized by three degrees of freedom, the total number of phonon modes is $3N$, where N represents the number of atoms per primitive cell and the total number of optical and acoustic phonons for any real lattice is determined by $3N-3$ and 3 , respectively[23]. For example, silicon[28] with a diatomic lattice has 6 phonon dispersion modes with 3 acoustic and 3 optical branches, whereas, with 4 atoms in its unit cell, graphite[29] has 12 phonon branches as shown in Figure 1.1.

The thermal conductivity of solids can be effectively described using kinetic theory, which provides a microscopic understanding of how heat is transported through the particle motion. In the framework of kinetic theory, phononic thermal conductivity can be expressed as[22]:

$$k_p = \frac{1}{3} C_p v_p \Lambda_p = \frac{1}{3} C_p v_p^2 \tau_T \quad (1.3)$$

where C_p is the volumetric specific heat capacity of phonons, Λ_p is the mean free path (MFP) of phonons, v_p is the average group velocity of phonons and τ_T is the total relaxation time of the heat carriers. With a good estimate of specific heat and phonon velocity obtained from the dispersion relation, the thermal conductivity essentially depends on the description of mean free path. Mean free path is described as the average distance travelled by the heat carriers between scattering events and the relaxation time is the average time energy carriers travelled between successive scattering events. The above expression for thermal conductivity calculation assumes that the phonons can be well-characterized by an average velocity and mean free path which is not true for real crystals due to the phonon dispersion relation and large range in mean free paths. Accounting

for the frequency (ω) dependence, phonon thermal conductivity can be expressed as[1]:

$$k_p = \frac{1}{3} \sum_j \int_{\omega_{j,min}}^{\omega_{j,max}} C_p(\omega) v_p(\omega) \Lambda_p(\omega) d\omega \quad (1.4)$$

where j represents the phonon branch index (e.g., acoustic or optical branches) and $\omega_{j,min}$ and $\omega_{j,max}$ are the minimum and maximum frequencies for branch j , defining the spectrum width of that branch. In real materials, the mean free path is limited by various scattering mechanisms in the medium including phonon-phonon scattering, phonon-impurity scattering, phonon-boundary scattering, etc.[1]. Phonon-phonon scattering can be of two types: Normal processes (N-processes) where the phonons conserve the total phonon momentum and typically redistribute energy among phonons without significantly reducing the net heat flow and Umklapp processes (U-processes) where the phonons do not conserve momentum in the same crystal momentum space and effectively reverse phonon momentum, contributing to thermal resistance and reducing the mean free path[22]. Additionally, imperfections, such as vacancies, interstitials, and foreign atoms, disrupt the regular lattice structure, causing phonons to scatter and reducing their mean free path. In nanomaterials, frequent boundary scattering also reduces the mean free path. The total relaxation time (τ_T) can be estimated based on Matthiessen's rule as[22]:

$$\frac{1}{\tau_T} = \frac{1}{\tau_{p-p}} + \frac{1}{\tau_I} + \frac{1}{\tau_B} \quad (1.5)$$

where τ_{p-p} , τ_I , τ_B are relaxation time for phonon-phonon scattering, phonon-impurity scattering and phonon-boundary scattering respectively. Other scattering contributions can be added similarly (such as isotopic scattering), under the assumption that all these contributions to scattering act independently from one another. The dominant scattering process in metals is electron-phonon scattering however, at low temperatures, impurity scattering dominates, and the

total relaxation time is additive based on Matthiessen's rule[22].

In addition to these scattering mechanisms, the behaviour of heat transport in nanoscale is further influenced by confinement effects. As the surface-to-volume ratio of nanomaterials increases, spatial confinement alters the scattering pathways of energy carriers. The confinement modifies phonon properties by changing the velocity, dispersion, and density of states[30]. This effect, often observed in nanowires, superlattices, and other low-dimensional systems, results in changes to the dispersion relations and alters the phonon band structure[30]. As a result, thermal transport in nanomaterials is significantly different from bulk materials, with thermal conductivity typically reduced in nanostructures due to the confinement induced changes. This size effect is particularly beneficial in thermoelectric applications, where reducing thermal conductivity without affecting electrical conductivity can enhance the material's thermoelectric efficiency[1], [2], [3].

1.3 Validity of Fourier's Law of Heat Conduction: Diffusive to Non-diffusive

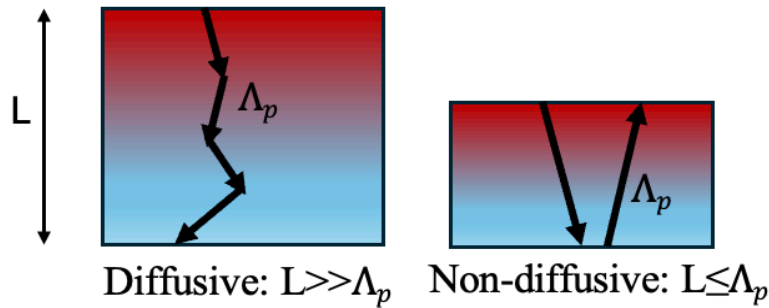


Figure 1.2: Diffusive and non-diffusive heat transfer regimes for different sample thicknesses. L represents the sample thickness and Λ_p represents the phonon mean free path.

As mentioned before, heat transfer results from the random motion of energy carriers and their subsequent scattering with each other or with boundaries until the system reaches thermal

equilibrium. Classically, this diffusive heat transfer process is described using Fourier's law of heat conduction and when the temperature changes over time, the diffusive heat transfer process is governed by the heat diffusion equation, also known as the heat equation, which describes the time evolution of temperature within a material[20]. In differential form, it is given by[15], [22]:

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T \quad (1.6)$$

where $\frac{\partial T}{\partial t}$ is the time rate of change of temperature, $D_T = \frac{k}{C}$ is the thermal diffusivity (with k being the material thermal conductivity and C its volumetric specific heat capacity), and $\nabla^2 T$ is the Laplacian of the temperature, which represents the spatial distribution of temperature across the material. This form assumes that thermal conductivity is constant, i.e., it does not vary with position or temperature. In '*diffusive*' heat transport, the size of the system is much larger than the mean free path of the energy carriers, and the energy carriers undergo a large number of collisions to achieve thermal equilibrium before reaching the physical boundary of the system. However, when the size of the system is reduced (or the distance between locations where the temperature is being measured is reduced), energy carriers undergo few or no scattering events, and the transport deviates from Fourier's law and becomes '*non-diffusive*' [31]. Non-diffusive heat transport can be either '*ballistic*' or '*quasi-ballistic*'. In the ballistic regime, heat carriers, travel without scattering and the mean free path of the heat carriers is much longer than the physical size of the material. The intermediate regime between diffusive and ballistic transport is called quasi-ballistic. The typical mean free paths for phonons range between ~ 1 nm-1 μ m or more in some cases, and at these length scales, the frequent contacts with boundaries that do not exist in bulk material can cause considerable changes in the thermal conductivity of nanomaterials compared to bulk. Note that the MFP for electrons in metals spans a much narrower range that is not longer than a few tens

of nanometers. Figure 1.2 shows the diffusive and non-diffusive heat transfer regimes for different sample thicknesses. L represents the sample thickness and Λ_p represents the phonon mean free path.

In addition, Fourier's law of heat conduction is valid when the timescales of observation are much longer than the relaxation time of the energy carriers, which is the average time between successive scattering events. The relaxation time typically ranges between 10^{-12} - 10^{-10} s. However, when the heat transport process observations occur on timescales shorter than or comparable to the relaxation time, the assumptions underlying Fourier's law break down due to insufficient scattering [22]. This deviation becomes particularly relevant in nanoscale systems or in ultrafast transport processes, such as those induced by femtosecond laser pulses, where the heat carriers have little time to interact and scatter.

To describe heat transport in the non-diffusive regime, more sophisticated models are required, such as the Boltzmann transport equation (BTE), or molecular dynamics (MD). The details of these models will be discussed in Chapter 2.

1.4 Interfacial Heat Transport: Thermal Boundary Conductance

Heat transfer across interfaces involves the movement of thermal energy between two different materials which is hindered by the interface's resistance to heat flow. The presence of high-density interfaces in nano scale devices offers additional scattering channels. When the interfacial resistance accounts for a sizable portion of the device's overall thermal resistance, it becomes crucial to understand the contributions of heat transfer from the interface. This interfacial resistance is characterized by the thermal boundary conductance (TBC, G), also known as the Kapitza conductance. TBC is the measure of an interface's ability to conduct heat and is given by the inverse of the thermal boundary resistance (TBR). Mathematically, TBC can be expressed as

the ratio of heat flux (J) across an interface to the temperature drop (ΔT) at that interface:

$$G = J / \Delta T. \quad (1.7)$$

It quantifies how efficiently heat is transferred across the interface, considering material and interfacial properties.

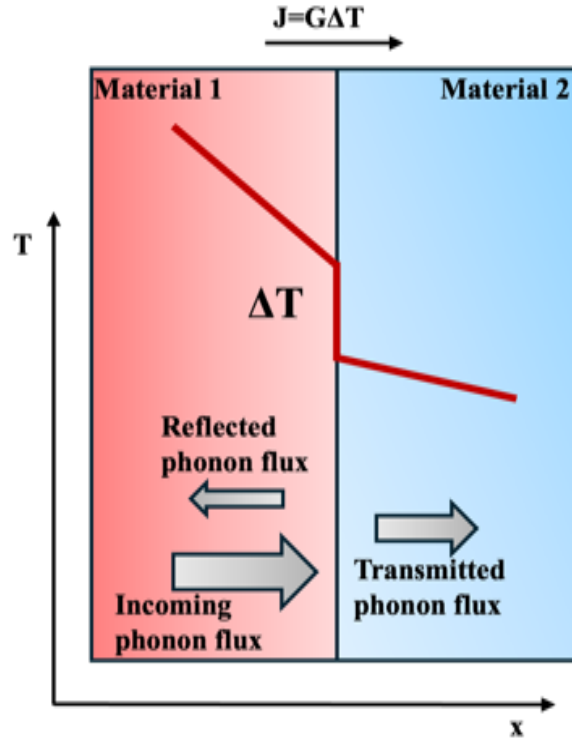


Figure 1.3: Schematic of temperature drop across an interface between material 1 and 2 with illustrations of incoming phonon flux getting transmitted and back-reflected at the interface contributing to TBC.

For a metal-semiconductor interface, heat transfer across the interface happens predominantly via phonon-phonon scattering, as shown in Figure 1.3. This occurs since the electrons do not have means to propagate in the semiconductor. Figure 1.3 shows the schematic of temperature drop across an interface between material 1 and 2 with illustrations of incoming phonon flux getting transmitted and back-reflected at the interface contributing to TBC. In this

process, the incident phonon flux is split into a transmitted flux that crosses the interface and a reflected flux that returns to the original material[22], [32]. The net heat transfer across the interface is determined by the difference between the energy carried by the transmitted phonons and the energy carried by the reflected phonons[32]. High TBC indicates efficient heat transfer, while low TBC signifies a significant thermal bottleneck. The details of the different factors affecting TBC and mathematically quantifying TBC at various interfaces are described in Chapter 2. It is important to point out that non-idealities from this simple model exist here as well. For example, if an interface is selective in terms of the phonon energies that are predominantly transmitted, this will result in near-interface non-equilibrium phenomena, as the thermodynamic distribution of energy carriers can be locally perturbed.

1.5 Objectives and Research Goals

This study aims to investigate the fundamental physics of nano- and micro-scale thermal transport, which could aid in the development of heat dissipation strategies, which are crucial for the thermal management of advanced electronic devices. This dissertation focuses on fundamentally understanding and manipulating heat transport between metal and bulk-anisotropic semiconductor interfaces in the presence of a thin metallic interlayer. This represents a common arrangement in devices that seek to exploit recently discovered layered and two-dimensional materials. For example, such an interface will be found at all electrical contacts. The insights obtained here will also be relevant at other interfaces that are found throughout a wide gamut of devices and composites. In short, the research goals include,

- 1) Predicting theoretically the heat transport mechanisms and pathways in metal/isotropic semiconductor systems in the presence of thin metallic interlayers, in order to validate the experimental data obtained previously.

- 2) Study the size dependent anisotropic thermal conductivities in layered materials to identify the appropriate material thickness required to eliminate any heat transport modifications due to size effects.
- 3) Create a theoretical framework to understand the heat transport due to size effects in layered materials.
- 4) Predict and validate the heat transport mechanisms and pathways at metal/anisotropic semiconductor systems in the presence of thin metallic interlayers.

1.6 Thesis Outline and Scope

The following is the outline of the thesis:

- Chapter 2 discusses the heat transport mechanisms in metal/semiconductor systems and quantifies the thermal boundary conductance at these interfaces. It also reviews the non-diffusive heat transport in layered materials and mathematically models the non-Fourier transport.
- In Chapter 3, we predict the interfacial heat transport modification at metal/isotropic semiconductor interfaces. We examine how the insertion of metallic interlayers with sub-nanometer thickness alters the thermal boundary conductance at metal/isotropic semiconductor interfaces. Further, we validate the results with previously obtained experimental data.
- Chapter 4 contains details about the non-diffusive heat transport in layered materials. We experimentally measured the evolution of anisotropic thermal conductivities in graphite, MoS₂, and hBN. Further, we mathematically modeled the same using Boltzmann transport equations.

- In Chapter 5, we study the modification of heat transport at metal/bulk-anisotropic materials in the presence of a thin metallic interlayer.
- Chapter 6 summarizes the main findings of the research and discusses potential future work, suggesting areas where further research could build on these results and improve our understanding of thermal boundary conductance.

This thesis explores the fundamental heat transport mechanisms at metal/isotropic and metal/anisotropic semiconductor interfaces, with a particular focus on thermal boundary conductance and non-diffusive heat transport. By examining the impact of material anisotropy and the introduction of thin metallic interlayers, this work seeks to enhance the understanding of heat transfer across these interfaces and contribute to the optimization of thermal management and heat spreading in nanoscale systems. Experimental measurements and theoretical modeling are employed to investigate the evolution of thermal conductivities in materials such as graphite, MoS₂, and hBN, aiming to provide insights for designing more efficient thermal interface materials. The research is expected to guide the development of advanced materials and interfaces capable of handling higher power densities, thus improving the performance, reliability, and heat spreading capabilities of next-generation electronics, thermoelectrics, and energy harvesting technologies.

CHAPTER 2: NANOSCALE HEAT TRANSPORT IN METAL-SEMICONDUCTOR SYSTEMS

2.1 Heat Transport Mechanisms in Metal-Semiconductor Systems

Energy transfer from photons to electrons in metals involves several interactions that are determined by the unique electronic structure of metals. When a metal surface is irradiated with photons, the photons are absorbed primarily by the free electrons in the metal. This absorption occurs because metals have a high density of free electrons, which are easily excited by the incident photons. Upon photon absorption, electrons are excited from near the Fermi level to states above it, resulting in a highly non-equilibrium distribution which cannot be represented by a Fermi-Dirac distribution. The excited electrons travelling at the Fermi velocity ($\sim 10^6$ m/s) then undergo rapid scattering processes, such as electron-electron collisions and ballistic electron transport which tend to redistribute the absorbed energy among the electron population, leading to a thermalization of the electrons at a higher effective electron temperature within 500 fs[33]. Following the initial electron excitation and thermalization, the energy is transferred from the hot electron subsystem to the lattice, or the atomic structure of the metal, through electron-phonon interactions. Due to the small volumetric specific heat of electrons ($\sim 10^4$ J/m³K), their temperature reduction will be much higher than the increase in temperature of the lattice and the energy transfer results in modest heating of the lattice which occurs over a longer timescale, typically picoseconds 0.1-10 ps[34]. Within 100 ps, both electron and phonon populations in the metal achieve equilibrium, and the rate of this energy transfer depends on the electron-phonon coupling strength, electron volumetric heat capacity (C_e) and phonon volumetric heat capacity (C_p)[34]. Eventually, the heat is dissipated outside the heated region and across an interface over the course of a few nanoseconds. The interplay of these factors and the dynamics of energy transfer from photons to electrons and then

to the lattice can be modeled using the two-temperature model (TTM). This coupled thermal behavior of the electron and lattice subsystems can be modelled using two nonlinear equations[33], [35]:

$$C_e T_e \frac{\partial T_e}{\partial t} = k_e \frac{\partial^2 T_e}{\partial z^2} - g(T_e - T_p), \quad (2.1)$$

$$C_p T_p \frac{\partial T_p}{\partial t} = k_p \frac{\partial^2 T_p}{\partial z^2} - g(T_e - T_p). \quad (2.2)$$

The above equations represent the one-dimensional temporal and spatial electronic and phononic temperature evolutions in the metal layer. Here, k_e is the electronic thermal conductivity, k_p is the phononic thermal conductivity, g is the electron-phonon coupling (EPC) constant, C_e and C_p are the volumetric heat capacities of electrons and phonons, and T_e and T_p are the electron and phonon temperatures. Note that a source term can be added to either of the two terms of the TTM, depending on the case.

The efficiency of heat transfer between the two materials is determined by the interfacial resistance and the calculation of the total thermal interfacial resistance at these interfaces requires the knowledge of various heat transfer pathways in the materials. At the interface between metal and semiconductor there exist two different pathways to transfer energy from the metal as shown in Figure 2.1. The purple and green arrows represent the direction of heat transport in pathway 1 and pathway 2 respectively. In pathway 1, electrons transfer energy to the phonons in the metal and subsequently the phonons in the metal transfer energy to the phonons in the semiconductor. In pathway 2, electrons in the metal directly couple with the phonons in the semiconductor. The interfacial resistances due to pathway 1 (R_1) and pathway 2 (R_2) is given by:

$$R_1 = R_{ep} + R_{pp} \quad (2.3)$$

$$R_2 = R_{ep,i} \quad (2.4)$$

where R_{ep} is the resistance due to the electron-phonon coupling in metals and R_{pp} is the resistance due to phonon-phonon interaction between the metal and semiconductor. The resistance due to interfacial electron-phonon coupling between the metal and the semiconductor is represented by $R_{ep,i}$. Assuming the resistances from the two channels are parallel to each other, total interfacial resistance can be expressed as:

$$R_T = \frac{R_1 R_2}{R_1 + R_2}. \quad (2.5)$$

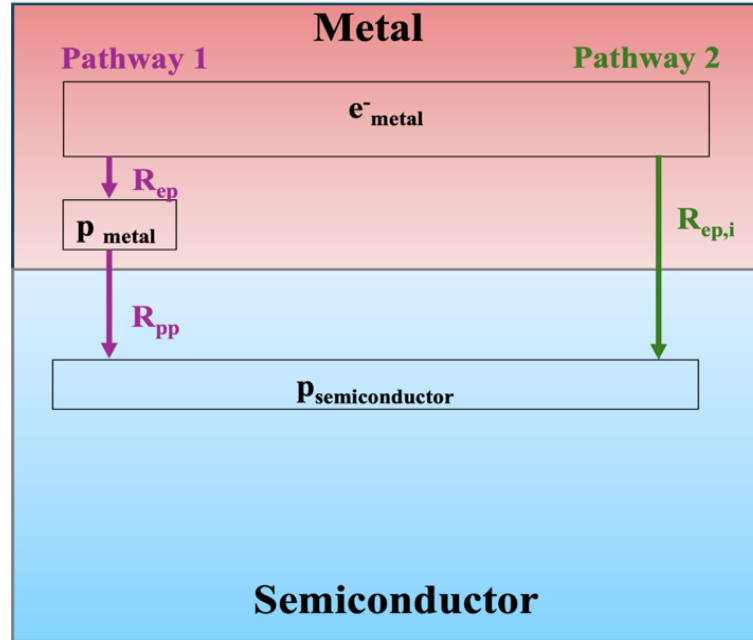


Figure 2.1: Illustration of interfacial heat transfer pathways in metal-semiconductor system. The purple and green arrows represent the direction of heat transport in pathway 1 and pathway 2 respectively.

Several studies have explored the different above-mentioned heat transfer pathways, in metal-isotropic semiconductors[36], [37], [38], [39], [40], [41]. Using the two-temperature model

for electrons and phonons, Majumdar and Reddy[36] investigated the role of electron-phonon coupling at a metal-dielectric interface and suggested that the R_{ep} contribution is given by $1/\sqrt{gk_p}$ where g is volumetric electron-phonon coupling constant and k_p is the thermal conductivity of phonons in the metal. Volumetric electron-phonon coupling constant g , quantifies the strength of the interaction between electrons and phonons in a material. A large value of g indicates a strong coupling between the electron and phonon systems. Typical values for the volumetric electron-phonon constant at room temperature is 10^{16} - 10^{18} $\text{Wm}^{-3}\text{K}^{-1}$. The calculation of R_{pp} based on different phonon scattering assumptions at the interface is explained in detail in the next section. Numerous investigations have been conducted to examine the impact of interfacial electron-phonon coupling ($R_{ep,i}$)[38], [40], [41]. Giri et al. demonstrated that only in situations where the electron temperature is significantly greater than the phonon temperature can electron-phonon scattering at the interface contribute to the interfacial thermal conductance[40]. Given the actual electron temperatures for technical applications are often lower, the interfacial electron-phonon coupling contribution is not as significant. According to Hopkins and Norris[41], direct coupling between electrons in the metal and phonons in the substrate is a major factor in determining interfacial conductance at very high electron-phonon non-equilibria and can be predicted using a three-temperature model. They demonstrated how raising the laser fluence from 1 Jm^{-2} to 15 Jm^{-2} can raise the electron temperature and improve the non-equilibrium electron-phonon interaction. Since our experiments are done at a low laser fluence of $\sim 2 \text{ Jm}^{-2}$ the contribution from $R_{ep,i}$ is negligible in our work.

2.1.1 Quantifying Phonon-Phonon Interfacial Heat Transport

This section focuses on quantifying the thermal boundary conductance based on various

phonon scattering events at interfaces. This is the only contribution at insulator interfaces and one of the factors at metal-insulator interfaces, as explained in the previous section. Two theoretical models, the diffuse mismatch model (DMM) and the acoustic mismatch model (AMM), are frequently employed to predict the phonon contribution of interfacial conductance. The assumptions made on phonon scattering at the interface are different in AMM and DMM, hence they are applicable in different situations. AMM is based on the assumption that the interface between two materials is perfectly flat leading to specular reflection (i.e., in a mirror-like manner)[42]. On the other hand, DMM assumes that the interface between two materials is rough or disordered, which destroys the momentum-space correlations between the incoming and transmitted phonons[42]. Figure 2.2 (a) and (b) shows the specular and diffusive scattering assumptions in AMM and DMM respectively.

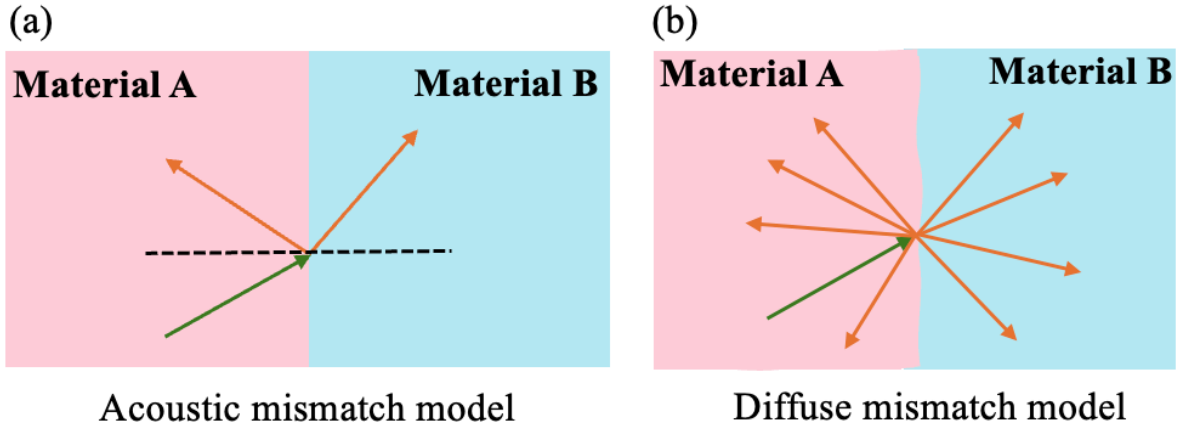


Figure 2.2: (a) Specular scattering based on AMM and (b) Diffuse scattering based on DMM.

2.1.1.1 Acoustic Mismatch model

The AMM posits that when phonons encounter an interface between two materials with different acoustic properties, their transmission depends on the acoustic mismatch between the

materials. This mismatch is quantified by the acoustic impedance, $Z = \rho v_p$ where ρ is the material density v_p is the phonon group velocity. The model assumes that phonons are scattered elastically at the interface, meaning they do not lose energy but may change direction depending on the relative acoustic impedances of the two materials. If the impedances are similar, the phonon is likely to be transmitted; if they are vastly different, the phonon is more likely to be reflected. AMM considers phonons to be plane waves, and transmission probabilities can be calculated using a model analogous to Snell's law for electromagnetic waves. When the phonon wavelength is significantly bigger than the interface roughness, the phonon transmission probability from material A to material B with frequency ω can be described as follows[42]:

$$\alpha_{A \rightarrow B}(\omega, i, q) = \frac{4Z_A Z_B \mu_A \mu_B}{(Z_A \mu_A + Z_B \mu_B)^2} \quad (2.5)$$

where, Z is the acoustic impedance and $\mu_A = \cos \theta_A$ and $\mu_B = \cos \theta_B$, where θ_A and θ_B are the angles of incidence of the phonon, measured from the normal to the surface in materials A and B, respectively. The transmission probability $\alpha_{A \rightarrow B}(\omega, i, q)$ depends on both the phonon polarization i and wavevector q . The thermal boundary conductance is then obtained using:

$$G_{pp,AMM}(\omega, i, q) = \frac{1}{4} \sum_{q,i} \int_0^{\omega_c(i,q)} \hbar \omega_A |v_A(\omega, i, q)| D_A(\omega, i, q) \alpha_{A \rightarrow B}(\omega, i, q) \frac{df_0}{dT} d\omega \quad (2.6)$$

where ω_c is the maximum phonon frequency in material A, $\hbar$ is the reduced Planck's constant, ω_A is the phonon angular frequency in material A, $D_1(\omega, i, q)$ and $v_1(\omega, i, j)$ is the phonon density of states and phonon velocity of material 1 and $f_0 = \frac{1}{\left[\exp\left(\frac{\hbar \omega_{i,A}}{k_B T}\right) - 1\right]}$ is the Bose-Einstein distribution

function where, k_B is Boltzmann's constant, and T is the temperature. The applicability of AMM is limited to low-frequency phonons (less than 100 GHz)[42]. When the phonon wavelengths are short enough to be comparable to that of interfacial roughness, AMM cannot account for them

since it assumes a planar interface and tend to overestimate the TBC. Several tests have demonstrated that, at low temperatures (less than 1 K), AMM can accurately estimate thermal boundary conductance[42]. To put it briefly, AMM is an appropriate model for phonon scatterings at low temperatures[43] (less than 30 K) and at long-wavelengths, when the incident phonon's wavelength is greater than the roughness of the contact.

2.1.1.2 Diffuse Mismatch Model

The DMM was first introduced by Swartz and Pohl in 1987 as an alternative to the acoustic mismatch model, addressing situations where the assumptions of specular reflection and transmission at a smooth interface do not hold[32]. Unlike the AMM, which assumes that phonons reflect and transmit specularly at an interface, the DMM assumes that phonons scatter diffusively. This means that when phonons from material A encounter the interface, they lose the initial acoustic correlations, including their direction and mode of propagation. The scattered phonons can emerge in any direction, regardless of their incident angle[44]. In DMM, the transmission probability of a phonon across the interface is determined solely by the phonon properties of the two materials on either side of the boundary; specifically, the phonon transmission is influenced by the phonon mode energies of the materials. The DMM is particularly effective at predicting interfacial thermal conductance at higher temperatures, typically above 15 K. However, as the temperature approaches room temperature, discrepancies between DMM predictions and experimental measurements often emerge. These discrepancies may result in the DMM either underestimating or overestimating the actual thermal boundary conductance. Due to the limitations of the standard DMM in accurately predicting thermal boundary conductance, particularly at room temperature, several modifications have been proposed to refine the model[36], [44], [45], [46]. Modifications to the DMM have been made by incorporating real phonon dispersion relations

instead of assuming simpler models[44], [45]. This allows for a more accurate representation of phonon modes, especially for complex materials where the phonon dispersion deviates from idealized assumptions such as the Debye approximation. Traditional DMM assumes elastic scattering, where phonons retain their energy (frequency) after scattering. However, modifications that include inelastic scattering, where phonons can change energy due to interactions with other phonons, have been shown to improve agreement with experimental data[46], [47], [48]. In materials with significant electron-phonon interactions, including the strength of the electron-phonon coupling alongside the DMM results can provide a more accurate estimate of thermal boundary conductance[36]. This is particularly important in metals and semiconductors where such interactions influence thermal transport across interfaces. The contribution of optical phonons, which have higher energy and shorter wavelengths compared to acoustic phonons, is often neglected in basic DMM formulations due to their low group velocities; however, including these contributions, especially at higher temperatures, can lead to better predictions of thermal boundary conductance[49]. Anisotropic materials, where properties vary with direction, pose additional challenges for the DMM. Some studies have shown that by incorporating anisotropy into the model, where phonon propagation varies with crystallographic direction, the of DMM predictions can be modified[50], [51], [52]. However, most of the models overpredicts the thermal boundary conductance[50], [51], [52].

Transmission probability can be expressed depending on the elastic and inelastic energy scattering assumption at the interface. The phonon flux at the interface between material A and B is given by[53]:

$$J_{A \rightarrow B} = \frac{1}{16\pi^3} \sum_j \int_{q_{x,A}} \int_{q_{y,A}} \int_{q_{z,A}} \hbar \omega_A f_0 |v_{zj,A}| dq_{x,A} dq_{y,A} dq_{z,A}. \quad (2.8)$$

Here, q is the wavevector, ω_A is the angular frequency of phonons in material A, v_z is the phonon

group velocity perpendicular to the interface, j is the phonon polarization, f_0 is the Bose-Einstein distribution function. The phonon group velocity in the direction of applied thermal gradient is given by $v_{zj,A} = v_{j,A} \cos \theta$ where θ is the elevation angle between the incident phonon and the normal to the interface[53], [54]. Assuming a spherical Brillouin zone for isotropic materials, the volume element in wave vector-space can be converted to spherical coordinates as, $dq_x dq_y dq_z = q^2 \sin \theta dq d\theta d\phi$ where θ is the elevation angle relative to the transport direction and ϕ is the azimuthal angle around the transport direction. The isotropic phonon flux in spherical coordinates is expressed as[53]:

$$J_{A \rightarrow B} = \frac{1}{8\pi^3} \sum_j \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \int_q \hbar \omega_A f_0 v_{j,A} q^2 \sin \theta \cos \theta dq d\theta d\phi. \quad (2.9)$$

In elastic scattering, the incoming phonon flux from material A interact with other phonons without a change in their energy, meaning that phonons with a specific frequency ω in material A can only produce phonons of the same frequency ω in material B as they scatter from the interface. Using the principle of detailed balance and assuming isotropic dispersion the wave vector dependent transmission probability is given by:

$$\alpha_{A \rightarrow B} = \frac{\sum_{j,B} \hbar \omega_{j,B} q_{j,B}^2 v_{j,B} f_0 dq_{j,B}}{\sum_{j,B} \hbar \omega_{j,B} q_{j,B}^2 v_{j,B} f_0 dq_{j,B} + \sum_{j,A} \hbar \omega_{j,A} q_{j,A}^2 v_{j,A} f_0 dq_{j,A}}. \quad (2.10)$$

Inelastic scattering on the other hand involves interactions where phonons change their energy after encountering an interface or interacting with other phonons. Under the inelastic phonon scattering assumption, phonons of all frequencies in material A are involved in the scattering process. Specifically, a phonon with frequency ω_1 in material A can scatter and generate multiple phonons of different frequencies ω_2 and ω_3 at the interface. For instance, in a three-phonon process, this can be represented by $\omega_1 = \omega_2 + \omega_3$ or as $\omega_1 = 2\omega_2$. This indicates that a

high-frequency phonon ω_1 can break down into two lower-frequency phonons ω_2 and ω_3 which may be of equal energy in special cases. The scalar transmission probability is then given by:

$$\alpha_{A \rightarrow B} = \frac{\sum_{j,B} \int_{q_{j,B}} \hbar \omega_{j,B} q_{j,B}^2 v_{j,B} f_0 dq_{j,B}}{\sum_{j,B} \int_{q_{j,B}} \hbar \omega_{j,B} q_{j,B}^2 v_{j,B} f_0 dq_{j,B} + \sum_{j,A} \int_{q_{j,A}} \hbar \omega_{j,A} q_{j,A}^2 v_{j,A} f_0 dq_{j,A}}. \quad (2.11)$$

In the elastic case, the transmission probability is wavevector-dependent because phonon transmission requires matching frequencies across the interface. In the inelastic case, it becomes wavevector-independent, as all phonon states can participate in scattering, and detailed balance is applied over total flux rather than individual frequencies. Thermal boundary conductance due to phonon-phonon interaction is a first order derivative of total heat current density with respect to temperature and can be expressed as:

$$G_{pp} = \frac{1}{8\pi^2} \sum_{j,A} \int_{q_{j,A}} \hbar \omega_{j,A} q_{j,A}^2 |v_{j,A}| \alpha_{A \rightarrow B} \frac{df_0}{dT} dq_{j,A}. \quad (2.12)$$

In equation 2.12 the transmission probability used would be from equations 2.10 or 2.11 depending on whether the model is considering inelastic scattering or not.

2.2 Factors Affecting Interfacial Heat Transport

Thermal transport at a metal-semiconductor interface is influenced by multiple factors, including the quality of the interface (such as roughness, interfacial defects, and bonding), the strength of electron-phonon coupling, and the mismatch between phonon modes across the interface. While extensive research has been conducted to explore how these properties impact interfacial thermal transport, effectively tuning or modifying the interfacial conductance continues to be a significant challenge.

Duda and Hopkins[55] showed that introducing roughness at the Al/Si interface by

chemically etching silicon substrates can lead to a reduction in interfacial conductance due to enhanced phonon scattering at the interface. They demonstrated that at room temperature, even a thin oxide layer (~ 11 nm) at the interface significantly reduces the effective interfacial conductance by more than 50%. Increasing the strength of interfacial bonding can enhance the thermal boundary conductance due to enhanced phonon transmission across the interface[56], [57]. Hopkins suggests that chemically functionalizing a single layer of graphene (SLG) with oxygen enhances the thermal boundary conductance between Al/SLG/SiO₂ layers by 25% due to enhanced covalent bond density.

Some studies have shown that one way to effectively modify the interfacial heat transport is by adding a metallic interlayer between the top metal layer and the isotropic semiconductors[12], [16], [17], [18], [19], [58], [59]. Cheaito et al.'s analysis of TBC over a variety of metal/native-oxide/Si and metal/Al₂O₃ systems revealed that the cut-off frequencies of the materials that make up the interface determine the phonon spectrum contribution to TBC[59]. Jeong et al. showed that TBC can be significantly increased by inserting a thin metal layer between a metal and a semiconductor with an intermediate Debye temperature[16]. They found that adding Cr and Cu interlayers to the Au/Al₂O₃ interface, respectively, resulted in TBC improvements of about 80% and 60%. Wang proposed that interfacial thermal boundary conductance can be increased at a metal-isotropic dielectric interface by inserting an interlayer with an intermediate electron-phonon coupling strength[18]. They investigated the impact of the Al and Pt interlayers, whose thickness ranged from 10 nm to 100 nm, at the Au/Si interface using Boltzmann transport models. Au with lower EPC strength than other common metals experience a high electron-phonon non-equilibrium, increasing the resistance R_{ep} ($R_{ep} = 1/\sqrt{gk_p}$). They suggested that the boundary conductance is improved by interlayers Al and Pt with electron-phonon coupling strengths greater than Au

because they quickly drag electrons and phonons into equilibrium. Chen et al. demonstrated that the high electron-phonon coupling in Ni allows for a 70% reduction in interfacial resistance upon insertion of a 20 nm thick Ni interlayer at the Au/Sapphire contact[60].

Our previous work experimentally analyzed the role of EPC in modifying TBC at metal-isotropic semiconductor interfaces in the presence of ultrathin interlayers (< 2 nm)[16], [58]. We showed that inserting a tantalum interlayer at the Al/Si and Al/sapphire interfaces significantly reduces phonon transmission, with a sharp transition occurring within approximately 1 nm. The sharpness of this transition is strongly influenced by electron-phonon coupling, and when the coupling is strong, the thermal boundary conductance reaches a saturation point within 2 nm. On the other hand, introducing a nickel interlayer results in a local minimum in boundary conductance as the interlayer thickness increases, due to the similar phonon dispersion in Ni and Al. The weaker electron-phonon coupling in Ni causes the boundary conductance to saturate more gradually. Subsequently, we experimentally studied the interplay between the EPC and phonon spectra in modifying heat transfer pathways in metal-interlayer-isotropic semiconductor interfaces[61]. The analysis of heat transport across various metal-isotropic semiconductor interfaces reveals that thermal boundary conductance is influenced by the interaction between phonon vibrational properties and the strength of metal electron-phonon coupling in a non-trivial way. It is now evident that the EPC of the metallic layers and the phonon spectra of the system's constituent materials are important factors influencing the interfacial heat transport in a well-bonded metal-isotropic semiconductor system. Since numerous parallel energy transfer paths exist when interlayers are thin, the interplay between diverse contributions involved in thermal transport to total thermal boundary conductance in the presence of an ultrathin (< 10 nm) metallic interlayer is not well known.

Despite extensive research on understanding and modifying heat transport at metal-isotropic semiconductor interfaces, very few studies have explored heat transfer between metals and highly anisotropic semiconductors such as layered materials. There have been few studies that show how properties of anisotropic semiconductor substrate can be modified to alter (enhance or reduce) the interfacial conductance[56], [62], [63]. As mentioned before, the low TBC between metals and layered materials is a bottleneck for efficient heat management in TMD-based devices[64], [65]. Schmidt et al. have shown that inserting a Ti interlayer at Al/graphite boundary enhanced the conductance by 50%[12]. Koh et al. suggested that for better thermal management and heat conduction across metal/graphene/oxide interfaces, metals (such as Cr, Ni, Ti, and Al) with high Debye temperatures are better choices due to the better phonon energy match between these metals and graphene[62]. They investigated the impact of a 2 nm Ti interlayer and reported TBC values of 52 MW/m²K at the Au/Ti/graphite interface, 25 MW/m²K at the Au/Ti/graphene/SiO₂ interface, and 27 MW/m²K at the Au/graphene/SiO₂ interface. However, our previous experiments on metal-isotropic semiconductors have shown that Debye temperature is not a suitable parameter in determining the TBC improvement across these interfaces[61], [66]. Despite the very low boundary conductance between metals and anisotropic semiconductors that poses severe thermal dissipation issues in device applications, no further studies have analyzed the role of a thin metallic interlayer in modifying the boundary conductance.

2.3 Non-diffusive Heat Transport in Layered Materials

This chapter focuses on interface transport, so it may seem unclear why non-diffusive heat transport in materials is mentioned here. However, it's important to note that, although the primary focus is on interface transport, understanding what constitutes bulk-like behavior is essential for practical analysis of layered materials. In other words, if the thickness of the layered substrate is

not adequate to consider it bulk-like, a significant uncertainty will be introduced when studying the transport at its interface. Therefore, this detour is necessary to establish a clear foundation for determining bulk-like properties, which will be essential for studying interface transport.

Layered materials have been extensively studied over the last decades due to their unique optical, electronic, mechanical, and thermal properties[7], [67], [68]. These materials exhibit large anisotropy in thermal conductivity values in the in-plane and out-of-plane directions; for example, the bulk thermal conductivity values in graphite, hBN, MoS₂ are 2000 W/mK, 490 W/mK, 100 W/mK (in-plane), and 6.5 W/mK, 4.5 W/mK and 3 W/mK (out-of-plane), respectively[65], [69], [70]. Several theoretical and experimental studies have explored the thermal conductivity values in bulk and thin-film layered materials[13], [71], [72], [73], [74]. However, there is still considerable uncertainty in theory and experiments regarding these materials' transition from diffusive to non-diffusive heat transport.

Zhang et al. measured an increasing trend in the out-of-plane thermal conductivity of graphite as a function of thickness (24 nm-22 μ m) with a reported in-plane thermal conductivity value of $\sim$ 2000W/mK[75]. Fugallo et al. using the exact solution of BTE studied the in-plane thermal conductivity evolution as a function of the lateral size of the material and the out-of-plane thermal conductivity evolution as a function of the thickness of the material in graphite[76]. They show that as the lateral size of graphite changes from 10 nm to 1000 μ m, thermal conductivity increases from $\sim$ 100 W/mK and saturates at the bulk value of 2000 W/mK after 10 μ m (see Figure 2.3a), whereas the out-of-plane thermal conductivity changes from 2 W/mK and saturates bulk 6.5 W/mK after 10 μ m. However, it is unclear how the scattered phonons in the out-of-plane direction affect the in-plane thermal conductivity. Minnich used generalized Fuchs-Sondheimer theory with BTE under the relaxation time approximation to show that the anisotropic crystal thin films, such

as graphite, retain their high in-plane conductivity at very low film thicknesses (~ 10 nm) as shown in Figure 2.3b[77]. However, other theories and experiments shows that the at 10 nm graphite thickness, the in-plane thermal conductivity reduces to $\sim 50\%$ of bulk value[76], [78], [79]. Figure 2.3b shows the reported in-plane thermal conductivity of graphite as a function of thickness[13]; experimentally measured conductivity of bulk HOPG (dash-dotted line) by Schmidt et al.[12]; an 87 nm thick graphite on Si (brown-open square) by Zhou et al.[13]; graphite with thicknesses between 25 nm-40 nm on Ni (black-open triangle up) by Zheng et al.[80]; graphite with thicknesses <10 nm encased by a-SiO₂ (blue-triangle down) by Jang et al. [79]; graphite with thicknesses <10 nm on a-SiO₂ (brown-open circle) by Sadeghi et al.[78]. The blue solid line and blue dotted line shows the calculated conductivity for graphite by Jang et al.[79] and Zhou et al.[13] based on a semi-empirical approach. The comparison between different experiments and theories shows that there is still uncertainty regarding the diffusive to non-diffusive transition thickness in graphite. Additionally, a theory that accurately predicts the experimentally observed thermal conductivity changes is currently absent. Furthermore, experimental data for higher thicknesses (above 100 nm) is notably lacking, which makes it difficult to fully understand the behavior of thermal transport in graphite at larger scales[13]. Recently, Machida et al. showed that as the thickness of graphite changes from 8.5 μm to 580 μm , the in-plane thermal conductivity values decrease from 4000 W/mK to 600 W/mK, which is contradictory to the presumed constant bulk graphite thermal conductivity of 2000 W/mK[81]. This clearly shows that new science is still being discovered in layered materials, and the theories describing them are unclear.

Jeong et al. measured the out-of-plane thermal conductivity of MoS₂ as the thickness changed from 100 nm to 1000 nm and observed no particular trend in thermal conductivity variation[82]; however, Sood et al. (20 nm-240 nm) and Jiang et al. (300 nm-1000 nm) reported

an increasing trend experimentally and theoretically in the out-of-plane thermal conductivity of MoS₂[11]. Similar to graphite, there is uncertainty in diffusive to non-diffusive transition in MoS₂. Lindorth et al., using Boltzmann transport equations under relaxation time approximation show an increasing trend in in-plane and out-of-plane thermal conductivity of MoS₂ as a function of boundary scattering length in the corresponding direction (150 nm- 4000 nm)[10] and, it's unclear how the in-plane thermal conductivity would change as a function of thickness theoretically.

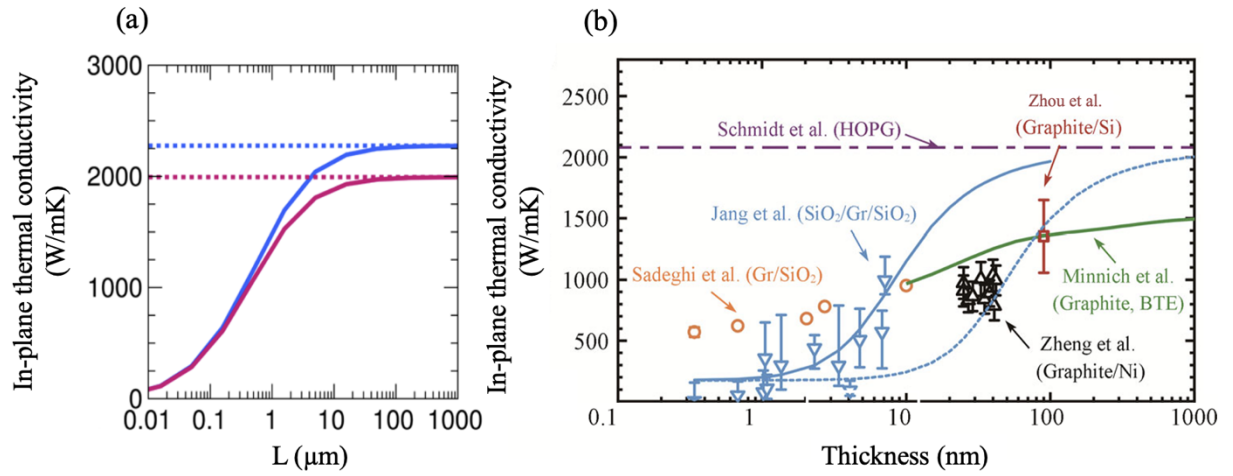


Figure 2.3: Reported in-plane thermal conductivity of graphite as a function of film (a) lateral size[74] and (b) film thickness[13]. (a) In-plane thermal conductivity as a function of lateral film size in graphite[73] (b) Experimentally measured conductivity of bulk HOPG (dash-dotted line) by Schmidt et al.[12], 87 nm thick graphite on Si (brown-open square) by Zhou et al.[13], Graphite with thicknesses between 25 nm-40 nm on Ni (black-open triangle up) by Zheng et al.[80], Graphite with thicknesses <10 nm encased by a-SiO₂ (blue-triangle down) by Jang et al. [79], Graphite with thicknesses <10 nm on a-SiO₂ (brown-open circle) by Sadeghi et al.[78]. The blue solid line and blue dotted line shows the calculated conductivity for graphite by Jang et al.[79] and Zhou et al.[13]. Reprinted with permission from Nano Lett. 14, 11, 6109–6114 (2014) (panel (a)). Copyright 2014, American Chemical Society. Reprinted from J. Therm. Sci. 31, 1008–1015 (2022), with permission of Springer (panel (b)).

Jaffe et al. show an increasing trend in measured out-of-plane thermal conductivity in hBN as thickness changes from 5 nm to 500 nm; however, the reported bulk conductivity value is 8 W/mK, which is unusually higher than the previously reported bulk values[83]. Jiang et al. using

the exact solution of Boltzmann transport equations show that at 300 K, phonons with MFPs between 3 nm to 90 nm contribute to 80% of the out-of-plane conductivity, and phonons with MFPs between 60 nm to 800 nm contribute to 80% of the in-plane conductivity[69]. Recently, Xiao et al. showed that for SnSe₂, both in-plane and out-of-plane conductivities reduce as the thickness of the flake reduces and showed a thickness-independent anisotropy of 8.2 due to the contribution of phonons with long MFP in the in-plane and out-of-plane directions[84]. It is still unclear how the thickness of the flake affects the anisotropy in other layered materials.

2.2.1 Lattice Thermal Conductivity Calculation Using Boltzmann Transport Equations

When modeling thermal transport in materials, especially at the micro and nanoscale, researchers employ two primary categories of simulation methods: continuum simulations and atomistic simulations[85]. Continuum simulations treat materials as continuous media and are particularly effective for modeling heat transfer over larger scales where atomistic details are less critical, whereas atomistic simulations account for the detailed atomic structures of materials, providing a more granular view of thermal transport mechanisms. Atomistic simulations are based on fundamental theories of transport, whereas continuum simulations generally are solely based on the Fourier heat equation. Atomistic simulations are therefore particularly crucial for accurately modeling heat transfer at the micro- and nanoscale, where atomic-level interactions dominate. Some of the widely used atomistic simulation methods for studying heat transfer at these scales include Molecular Dynamics (MD) simulations, the Boltzmann Transport Equation (BTE) and the Non-Equilibrium Green's Function (NEGF) method[85].

The Boltzmann transport equation proposed by Ludwig Boltzmann is a fundamental tool in the study of particle behavior using statistical distribution, particularly when the distribution of

energy carriers (phonons or electrons) is far from thermodynamic equilibrium. Hence, BTE is uniquely suited for describing heat transport under non-equilibrium conditions, which is common in micro- and nanoscale systems. The BTE simulation is informed by parameters such as particle dispersion and scattering rate that are typically calculated from *ab-initio* methods and therefore makes no specific assumption or parametrization on these parameters. The BTE framework allows for the inclusion of various scattering processes, such as phonon-phonon scattering, phonon-electron scattering, and phonon-boundary scattering and by accounting for these interactions, BTE provides a more accurate and detailed description of heat transport.

In this work, we employ BTE to model the non-Fourier phonon heat transport in the layered materials using an open-source software called ShengBTE[86]. Solving the BTE can be challenging due to its complexity, but two common approaches to obtain solutions are iterative methods (to obtain the full solution) and the relaxation time approximation (RTA). The RTA simplifies the scattering term of the BTE by assuming that the time it takes for the system to relax to equilibrium is constant and characteristic for all states (so it is not explicitly dependent on phonon mode or energy). However, assuming a constant relaxation time and may not capture all aspects of phonon scattering as these vary considerably[86]. For our study, ShengBTE is used to predict the thermal conductivities of materials from first principles by iteratively solving the BTE. ShengBTE computes the thermal conductivity and other associated quantities by solving the BTE for phonons, which starts with a set of interatomic force constants (IFCs) and calculates the phonons scattering rates. The details of the density functional theory (DFT) computation used to calculate the IFCs for each study will be explained in more detail in Chapter 4.

In the absence of a temperature gradient ∇T or other thermodynamic forces, the phonons in a material will distribute themselves according to the Bose-Einstein distribution function $f_0^{j,q}$

where j is the phonon branch index and q is the wave vector. The zero subscript refers to an equilibrium distribution. The actual phonon distribution $f^{j,q}$ deviates from $f_0^{j,q}$ in the presence of a temperature gradient and BTE represents the evolution of $f^{j,q}$. This deviation is a result of the combined effects of diffusion (due to the temperature gradient) and scattering processes[86]. In the steady state, the distribution function for phonons no longer changes with time, in other words, the rate of change of distribution function must vanish[86]:

$$\frac{df^{j,q}}{dt} = \left. \frac{\partial f^{j,q}}{\partial t} \right|_{diffusion} + \left. \frac{\partial f^{j,q}}{\partial t} \right|_{scattering} = 0 \quad (2.13)$$

and the rate of change of diffusion can be expressed as[86]:

$$\left. \frac{\partial f^{j,q}}{\partial t} \right|_{diffusion} = -\nabla T \cdot \mathbf{v}^{j,q} \frac{\partial f^{j,q}}{\partial T} \quad (2.14)$$

where $\mathbf{v}^{j,q}$ is the phonon group velocity of mode j, q . $\left. \frac{\partial f^{j,q}}{\partial t} \right|_{scattering}$ is estimated based on different scattering mechanisms involved such as isotope scattering, three-phonon scattering processes and boundary scattering, and is calculated via perturbation theory[86]. Assuming a small temperature gradient, the first order phonon distribution expansion is given by:

$$f^{j,q} = f_0^{j,q} + b^{j,q} \quad (2.15)$$

where $b^{j,q}$ represents the deviation from $f_0^{j,q}$. Assuming a linear dependence of $b^{j,q}$ on the temperature gradient:

$$b^{j,q} = -\mathbf{F}^{j,q} \cdot \nabla T \frac{df_0^{j,q}}{dT}. \quad (2.16)$$

Considering only the three- and two-phonons scattering processes:

$$\mathbf{F}^{j,q} = \tau_0^{j,q}(\mathbf{v}^{j,q} + \mathbf{\Delta}^{j,q}). \quad (2.17)$$

Here, $\tau_0^{j,q}$ represents the phonon relaxation time for mode j, q obtained from perturbation theory. $\mathbf{\Delta}^{j,q}$ is a measure of how much the heat current associated with a specific phonon mode population deviates from RTA solution. As mentioned in Chapter 1, for each phonon mode the total relaxation time is given based on Matthiessen's rule:

$$\frac{1}{\tau_0^{j,q}} = \frac{1}{\tau_{anharmonic}} + \frac{1}{\tau_{isotope}} + \frac{1}{\tau_B} \quad (2.18)$$

The phonon thermal conductivity tensor is then given by[86]:

$$k_p^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{j,q} f_0(f_0 + 1) \left(\frac{\hbar \omega_{j,q}}{2\pi} \right)^2 v_{j,q}^\alpha \mathbf{F}_{j,q}^\beta \quad (2.19)$$

where k_B is the Boltzmann constant T is the temperature, Ω is the unit cell volume, $N = N1 \times N2 \times N3$ q-points is the discretized Brillouin zone grid points and $\hbar$ is the Planck's constant. $\mathbf{F}^{j,q}$ can either calculated using the RTA method, where $\mathbf{\Delta}^{j,q} = 0$ or can be solved iteratively. In the iterative solution, the iteration begins with an initial guess from RTA, $\mathbf{F}^{j,q} = \tau_0^{j,q} \mathbf{v}^{j,q}$ and is repeated until the relative difference in thermal conductivity between successive iterations falls below a certain threshold (typically 10^{-5}).

2.3 Experimental Techniques to Measure Nanoscale Thermal Transport

Experimental techniques for measuring thermal transport properties at the nanoscale can generally be divided into two categories: steady-state and transient methods. Steady-state techniques rely on maintaining a constant temperature gradient over time to measure heat flow, which is ideal for studying bulk materials. These methods, however, often face limitations when applied to thin films, where the size of the sample is much smaller than the scale of conventional

measurement tools. In contrast, transient techniques measure the time-dependent response of a material to a heat pulse, allowing for a more flexible approach in studying nanoscale materials. The 3ω method, thermoreflectance (TR) based techniques such as time domain thermoreflectance (TDTR), and frequency domain thermoreflectance (FDTR) are prominent examples of transient methods that are very versatile and can be applied to the thermal characterization of both bulk and thin film materials. Each of these methods offers distinct advantages for measuring thermal conductivity and thermal boundary resistance.

2.3.1 3ω Method

The 3ω method derives its name from the frequency used to probe thermal transport, where an alternating current (AC) is applied at a frequency ω to a metallic strip that acts as both an electrical heater and a temperature sensor. The voltage response at the third harmonic, 3ω , contains information about the thermal conductivity and thermal boundary resistance of the sample, making it a powerful tool for investigating heat transport at the nanoscale. This method was introduced by Cahill and Pohl in 1987 to measure the thermal conductivities of solids[87].

A typical 3ω measurement setup consists of a thin film deposited on a substrate, with a metallic strip (e.g., Au, Al, or Pt) deposited on top of the film or on the substrate. The metallic strip acts as both an electrical heater and a temperature sensor and the dimensions typically in the range of 10-50 μm in width and 1000-10000 μm in length[88]. An AC current at frequency ω is passed through the strip, generating a periodic heating effect in the sample due to Joule heating in the sensor/heater at a frequency 2ω . The key feature of the 3ω method is the detection of the third harmonic (3ω) of the applied current, which is a result of the nonlinear thermal response of the system. The voltage signal at this third harmonic provides crucial information about the thermal properties of the sample, such as thermal conductivity and thermal boundary resistance. However,

the voltage signal at the 3ω frequency is weak (typically three orders of magnitude smaller than the applied 1ω signal) necessitating the use of a lock-in amplifier to amplify the 3ω signal for accurate measurement[88].

One key advantage of the 3ω method is its ability to measure both in-plane and cross-plane thermal conductivities of thin films, which can differ significantly due to geometric constraints. Recent advancements have enhanced the method's capabilities, including the ability to measure anisotropic thermal conductivity tensors, which is crucial for materials where heat conduction varies with direction. Additionally, the 3ω method is less prone to errors from thermal radiation. Unlike traditional steady-state methods, where radiation heat loss can introduce substantial measurement errors, especially at higher temperatures, the 3ω method is much less sensitive to radiation losses, which tend to increase with the size of the experimental setup.

Despite its many advantages, the 3ω method does have limitations. One challenge is the need for microfabrication to create the metallic heater/sensor, which may require additional time, equipment, and expertise. This can be particularly cumbersome when dealing with materials that are not easily compatible with microfabrication techniques. Additionally, for electrically conductive materials, the requirement to add an insulating layer between the heater and the sample can add additional thermal resistance, which can lower both the sensitivity and accuracy of the measurements. Another limitation of the 3ω method is its dependence on a detailed mathematical model to interpret the voltage signal. This model assumes that the heater is infinitely long and that the sample has uniform thermal properties. However, for materials with complex shapes or varying properties, this assumption might not be valid, potentially leading to errors in the results.

2.3.2 Thermoreflectance Based Techniques

2.3.2.1 Theory of Thermoreflectance

When light strikes the interface between two materials at normal incidence, the reflectivity R (the fraction of light intensity that is reflected back into the first material) can be determined using the complex refractive indices of both materials. The complex refractive index is generally represented as $n = n_r + i\kappa$, where n_r is the real part of refractive index and κ is the extinction coefficient. At normal incidence the reflectivity R is then given by[89]:

$$R = \left| \frac{n_1 - n_2}{n_1 + n_2} \right|^2 \quad (2.20)$$

where n_1 and n_2 are the complex refractive indices of the two materials. The reflectivity is sensitive to changes in the optical constants, and thus, any variation in temperature (ΔT) can lead to a corresponding change in the reflectivity ($\frac{\Delta R}{R}$). This phenomenon, known as the thermoreflectance effect, arises due to various temperature-dependent changes in the material's optical properties, such as shifts in the Fermi level, changes in electron-phonon scattering rates, and alterations in the material's bandgap energy[89]. While it is complex to directly predict the change in reflectivity as a function of temperature, extensive experimental studies have been conducted on metallic[90], [91], [92] and semiconducting materials[93], [94], which have shown that a small temperature fluctuation (on the order of 1 to 10 K) can induce measurable changes in reflectivity across a broad range of photon energies or wavelengths. When the temperature variation is small, the change in reflectivity is directly proportional to the temperature change and can be expressed as:

$$\frac{\Delta R}{R} = \frac{1}{R} \frac{\partial R}{\partial T} \Delta T = C_{TR} \Delta T \quad (2.21)$$

where C_{TR} is the thermorefectance coefficient, a material property that describes how the reflectivity changes with temperature. Both C_{TR} and $\frac{\Delta R}{R}$ are influenced by illumination wavelength since the optical constants vary with wavelength. This linear relationship has been empirically and theoretically validated for a variety of metals, such as Ag, Au, Ta, and Al[89]. Figure 2.4 shows the measured thermorefectance using spectroscopic ellipsometry for Au, Al, Pt, and Ta metal films as a function of illumination wavelength[95]. Within a sufficiently large temperature range, the change in reflectivity scales linearly with the change in temperature, making the thermorefectance effect a useful and reliable tool for temperature measurements in a wide range of materials, especially in the study of metallic and semiconducting systems.

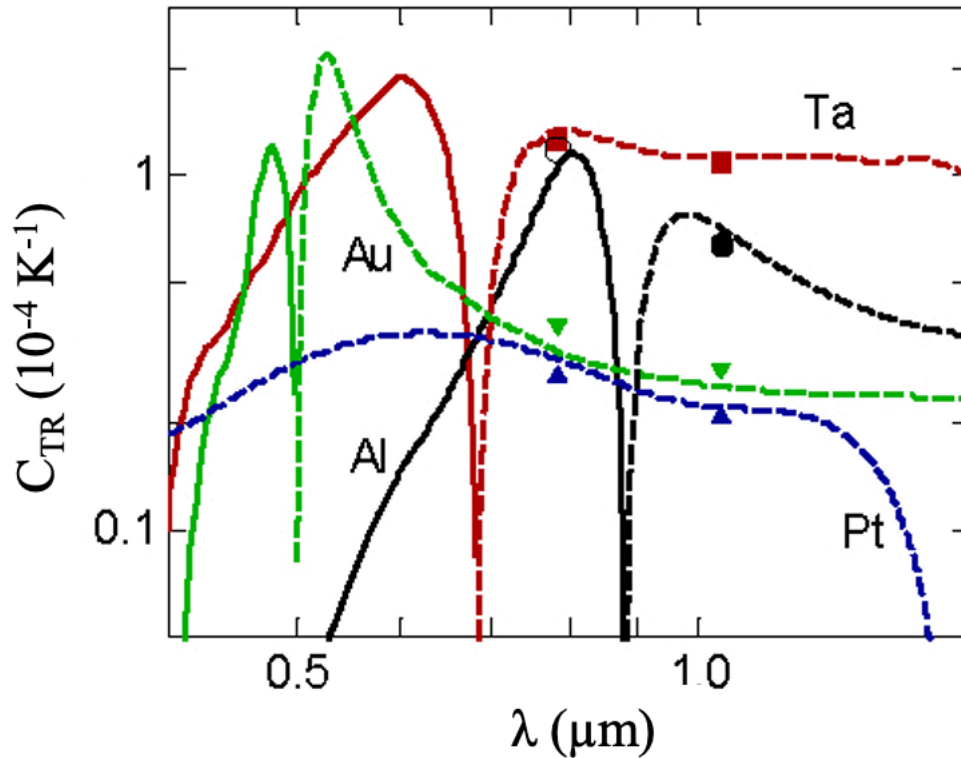


Figure 2.4: Measured thermorefectance for Au, Al, Pt, and Ta metal films as a function of illumination wavelength[92]. The dashed lines indicate a negative coefficient. Reprinted with permission from Opt. Express 20, 28829-28838 (2012) © Optica Publishing Group.

Pump-probe thermoreflectance technique is a non-contact optical method used to measure thermal properties such as thermal conductivity, heat capacity, and interfacial thermal conductance of both bulk and thin film materials. The working principle of a typical pump-probe technique is described here: A thin metallic layer, often referred to as the metallic transducer layer, is deposited on the surface of the sample. When the sample is heated by a pump beam, the temperature rise in the metallic transducer layer leads to a corresponding change in the reflectance of the layer at the laser wavelength. By monitoring this change in reflectance, the thermal response of the sample can be detected and analyzed. In a typical transient thermoreflectance measurement setup, a sample is illuminated with two laser beams: a pump beam and a probe beam. The pump beam is usually modulated either in time (for time-domain methods) or in frequency (for frequency-domain methods). The pump beam heats the sample, while the probe beam measures the thermoreflectance change in the metallic transducer layer, providing a direct correlation to the thermal properties of the material. By combining these measurements with a heat transfer model, thermal transport properties can be inferred. This non-contact approach makes the technique highly valuable for materials that are sensitive to mechanical stress and requires minimal sample preparation. The pump-probe thermoreflectance technique method was pioneered in the 1980s by Maris[96] and Esley[97] using picosecond lasers, and has since evolved into several variants, including time-domain thermoreflectance (TDTR)[34], [98], [99], frequency-domain thermoreflectance (FDTR)[100], [101], transient thermoreflectance (TTR)[82], [102].

2.3.2.2 Frequency-Domain Thermoreflectance

FDTR measures the thermoreflectance response as a function of the modulation frequency of the pump beam. The modulated pump beam in FDTR injects a periodic heat flux that in turn creates a periodic temperature gradient in the sample. This induces a corresponding fluctuation in

the reflectance of the metallic transducer layer. The probe beam is focused directly onto the sample, and the thermorefectance signal is detected using a photodiode and a lock-in amplifier, which allows for high sensitivity to small changes in temperature.

The FDTR set-up implemented in our lab is shown in Figure 2.5. A 515 nm pump laser (Omicron 350) is modulated over a wide range of frequencies (from a few kHz to tens of MHz) using a lock-in amplifier (Zurich Instruments HF2LI), while the probe laser (Omicron 785) operating at 785 nm remains unmodulated. Both beams initially pass through the optical isolators (Conoptics M711A and M712B) to ensure that the laser beams only travel in one direction, preventing back-reflections from destabilizing the laser sources. Similarly, the color filter in front of the probe laser blocks any unwanted back-reflections from the pump beam, preventing noise in the measurements and maintaining signal integrity. A dichroic mirror, which reflects the pump beam while allowing the probe beam to pass through, is used to coaxially align both beams onto the sample surface, where the reflected light from the sample surface is then directed back to the photodetector (Thorlabs PDA8A) and a camera. A neutral density filter before the detector controls the intensity of light entering the detector, preventing sensor saturation. The photodetector converts the reflectivity variations into an electrical signal, which is then fed into a lock-in amplifier. The lock-in amplifier, synchronized with the pump modulation frequency, extracts the

amplitude $V = \sqrt{V_{in}^2 + V_{out}^2}$, (where V_{in} is the in-phase signal and V_{out} is the out of phase signal)

and phase components $\phi = \tan^{-1} (V_{out}/V_{in})$ of the signal, filtering out any noise. The phase measured by the lock-in amplifier is the sum of the phase lag due to the thermophysical properties of the sample and the phase lags contributed by the system components, including optical and electrical components. To extract the thermal phase lag, two measurements are performed: thermal measurement and reference measurement. The first measurement in FDTR, the thermal

measurement, includes contributions from the thermal, optical, and electrical phases. To isolate the thermal phase, a second non-thermal measurement is performed, which removes the thermal contribution and retains only the optical, electrical phases. The color filter before the detector enables selection between measuring the thermorefectance by blocking the pump beam or measuring the reference phase by blocking the probe beam. The reference measurement is usually performed by placing a filter in front of the detector to capture the modulated pump beam instead of the probe, which allows for the extraction of the thermal phase by subtracting the reference measurement from the thermal measurement. The unknown thermal properties are then extracted by fitting an analytical model to the measured phase lag for a range of measured modulation frequencies.

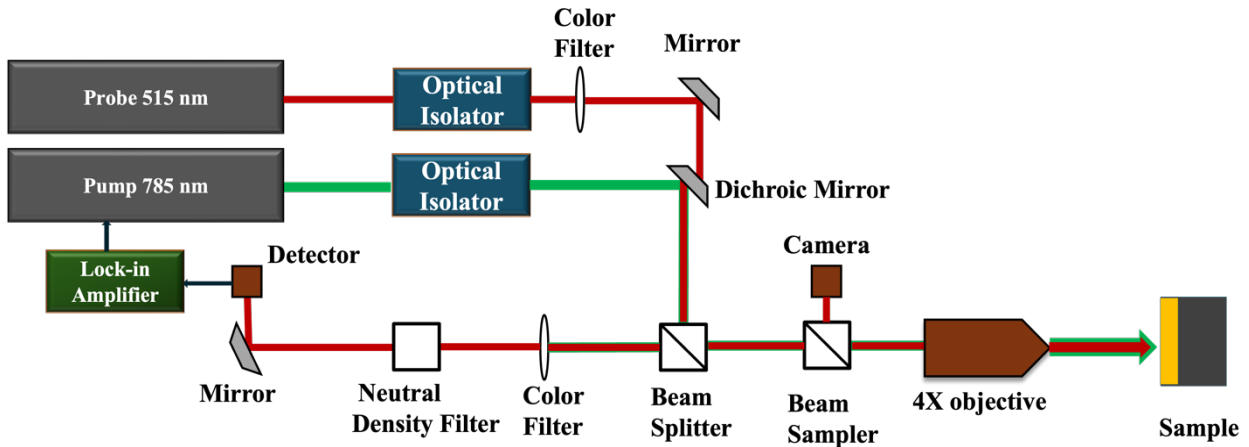


Figure 2.5: Schematic of our FDTR setup.

FDTR is often implemented using continuous-wave laser sources, which are simpler and less expensive compared to the pulsed lasers required for TDTR. Hence, FDTR can be used to measure thermal properties with a similar level of accuracy to TDTR, but at a lower cost. FDTR offers several advantages over TDTR, including lower complexity and the ability to work with

continuous-wave laser sources. It is also less susceptible to beam walk-off and divergence, which can complicate the alignment in TDTR measurements. FDTR has become particularly popular for measuring thermal conductivity in thin films, where the thermal properties are highly anisotropic[103], [104].

2.3.2.3 Time-domain thermorefectance

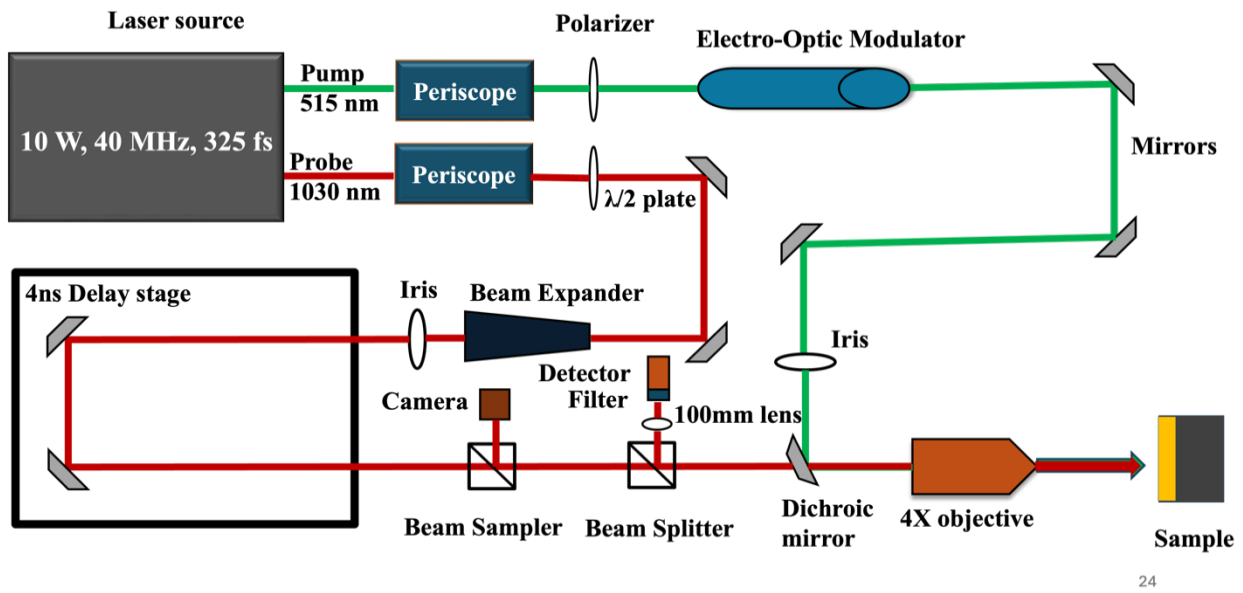


Figure 2.6: Schematic of our TDTR setup.

Similar to FDTR, in a typical TDTR setup, a modulated pump beam heats the sample surface, causing a change in reflectivity that is probed by a second beam directed at the same spot. An ultrafast laser source produces both pump and probe beams and the measurement is done stroboscopically, allowing to capture the reflectivity of the sample by the probe beam at a given time after the arrival of the pump beam. The time delay between the pump and probe beams is controlled by adjusting a delay stage in the pump or probe path, which alters the beam path length, creating a time delay due to the constant speed of light. By varying this delay between the pump

and probe pulses, the pico-second to nano-second time evolution of the surface temperature of the sample can be observed, allowing for precise measurement of the thermorefectance signal and enabling the study of nano-second and pico-second heat carrier dynamics.

Figure 2.6 shows the TDTR setup implemented in our lab. In our TDTR setup, an ultrafast fiber laser (Amplitude Laser, Satsuma HP²) generates pulses at 1030 nm with a pulse width of approximately 300 fs and a repetition rate of 40 MHz. The probe beam is at the same wavelength (1030 nm), while the pump beam is generated by frequency-doubling the source beam to 515 nm. A key component in the pump path is the electro-optic modulator (EOM) (Conoptics model 25DS), which imposes a sine wave modulation at approximately 1 MHz (the modulation frequency can vary, typically around 1-4 MHz in our experiments, and is controlled by a function generator (Stanford Research Systems model DS345)). When the modulated pump pulse is absorbed by the sample surface, it generates a temperature rise at the frequency of the modulation, leading to a transient change in the material's reflectivity. The probe beam, which monitors these changes, passes through a beam expander (Thorlabs GBE05-A) to reduce beam divergence at longer time delays, ensuring minimal variation in the probe radius (less than 5% change over a 4 ns delay stage). A mechanical delay stage (Newport model ESP301), which operates within a 0-4 ns range, is used to control the arrival time of the probe pulse relative to the pump pulse at the sample. The pump and probe beams are then collinearly focused onto the sample surface using a long-working distance 4X objective. The sample is mounted on a movable stage, which ensures that both the pump and probe beams remain in focus on the sample surface throughout the measurement. When the sample is in focus, the reflected probe beam emerges collimated from the objective, capturing changes in reflectivity at the sample surface. A 50:50 beam splitter directs the reflected pump and probe beams to both a camera for visualization and a detector for intensity measurement. The

detector, an InGaAs biased detector (Thorlabs DET10N) with a 5 ns rise time, records the reflected probe intensity. An optical filter placed in front of the detector blocks the reflected modulated pump beam, ensuring accurate probe signal detection. A lock-in amplifier (Zurich Instruments HF2LI) is used to extract the amplitude and phase of the thermorefectance signal. Similar to FDTR, in TDTR, a lock-in amplifier improves the signal-to-noise ratio by isolating the thermorefectance signal at a reference frequency (frequency of EOM) and effectively filtering out background noise.

In our experiments, the phase of the thermorefectance signal is used to extract thermal properties of the sample because it reflects the ratio between the in-phase and out-of-phase signals, eliminating the need for normalization[34]. This approach is particularly advantageous because noise caused by fluctuations in laser power is effectively canceled out in both signal components. In addition to the phase, the ratio of the in-phase and out-of-phase signals, as well as the normalized amplitude, are also used to extract thermal properties[89]. Furthermore, any phase shift introduced by electrical and optical components in the system can be compensated, as the out-of-phase signal remains constant at zero time delay[34]. To obtain the unknown thermal properties in TDTR and FDTR, experimental phase data is compared to a theoretical model based on the heat diffusion equation for a periodic point source on layered media, with fitting parameters adjusted to match the data to the model[99].

2.3.2.4 Modeling Heat Transport for Thermorefectance Experiments

Cahill's thermal model is based on Feldman's algorithm for one-dimensional heat diffusion in layered structures, adapting it to a three-dimensional framework for thermorefectance experiments[99]. Briefly, this approach formulates the transient heat diffusion equation in the frequency domain, accounting for both temporal and spatial variations, to model heat transport in

an n-layer system and the resulting frequency-domain temperature response serves as the basis for computing in-phase and out-of-phase components of the lock-in amplifier signal. The general transient heat conduction can be expressed using heat diffusion equation:

$$\frac{dT}{dt} = D_T \nabla^2 T \quad (2.22)$$

where D_T is the thermal diffusivity and T is the surface temperature. For thermoreflectance experiments with periodic heating, this is transformed into the frequency domain:

$$\frac{i\omega}{D_T} T = \nabla^2 T. \quad (2.23)$$

For an infinite half-space with a sinusoidal heat source in one-dimension (z), the solution is expressed as:

$$T(z, t) = T_0 e^{(i\omega t - pz)}, \quad (2.24)$$

And in the spatial frequency domain:

$$i\omega T = D_T p^2 T \quad (2.25)$$

introducing the thermal wavevector $p^2 = i\omega/D_T$.

Since the co-aligned laser beams in a typical TDTR and FDTR experiment produce cylindrically symmetric heating, the solution for a semi-infinite solid subjected to periodic heating at its surface is given by:

$$g(r) = \frac{\exp(-pr)}{2\pi k r}, \quad (2.26)$$

where k is the thermal conductivity of the solid and r is the radial co-ordinate. To simplify the convolution of the heat solution with the laser intensity distributions, the Hankel transform (s is

the Hankel transform variable) is employed on Eq. 2.26:

$$G(s) = 2\pi \int_0^\infty g(r)J_0(2\pi kr)rdr, \quad (2.27)$$

$$G(s) = \frac{1}{k(4\pi^2 s^2 + p^2)^{1/2}}. \quad (2.28)$$

The pump laser's intensity profile is given by:

$$H(r) = \frac{2A}{\pi\omega_0^2} e^{\left(\frac{-2r^2}{\omega_0^2}\right)}, \quad (2.29)$$

and the Hankel transform of a Gaussian heat source (pump beam) with radius w_0 and amplitude A is given by:

$$H(s) = Ae^{\left(\frac{-\pi^2 s^2 w_0^2}{2}\right)} \quad (2.30)$$

The temperature distribution at the surface is computed by inverse transforming the product of $G(s)$ and $H(s)$:

$$u(r) = 2\pi \int_0^\infty G(s)H(s)J_0(2\pi sr)s ds \quad (2.31)$$

The probe laser measures the surface temperature, weighted by its Gaussian intensity distribution:

$$\Delta T = 2\pi A \int_0^\infty G(s)e^{\left(\frac{-\pi^2 s^2 (w_0^2 + w_1^2)}{2}\right)} s ds \quad (2.32)$$

Eq. 2.32 is valid for a semi-infinite structure and for layered geometries, the heat conduction problem is solved iteratively. The surface temperature of layer n characterized by thickness L_n , diffusivity $D_{T,n}$, and thermal conductivity k_n is related to the adjacent layer $(n+1)$ by:

$$\begin{pmatrix} B^+ \\ B^- \end{pmatrix}_n = \frac{1}{2\gamma_n} \begin{pmatrix} \exp(-u_n L_n) & 0 \\ 0 & \exp(u_n L_n) \end{pmatrix} \begin{pmatrix} \gamma_n + \gamma_{n+1} & \gamma_n - \gamma_{n+1} \\ \gamma_n - \gamma_{n+1} & \gamma_n + \gamma_{n+1} \end{pmatrix} \begin{pmatrix} B^+ \\ B^- \end{pmatrix}_{n+1} \quad (2.34)$$

$$u_n = (4\pi^2 s^2 + p_n^2)^{1/2} \quad (2.35)$$

$$p_n^2 = \frac{i\omega}{D_n} \quad (2.36)$$

$$\gamma_n = k_n u_n \quad (2.37)$$

B^+ and B^- are the amplitudes of the thermal waves propagating in the positive and negative z -directions, respectively, within layer n . The bottom layer is considered infinite since the modulated heats source cannot penetrate through it, resulting in $B^+ = 0$ and $B^- = 1$. The heat transport solution is obtained by recursively propagating this boundary condition from the substrate to the surface layer. For layered materials, the frequency-domain solution $G(s)$ is modified to include the iterative solution for heat conduction through layers and the frequency-domain thermal response is given by:

$$\Delta T = 2\pi A \int_0^\infty \left(\frac{B_1^+ + B_1^-}{B_1^+ - B_1^-} \right) \frac{1}{\gamma_1} e^{\left(\frac{-\pi^2 s^2 (w_0^2 + w_1^2)}{2} \right)} s \, ds \quad (2.38)$$

In TDTR, the lock-in amplifier measures changes in reflectivity $\frac{dR}{dT}$ due to surface temperature oscillations (ΔT) at a given modulation frequency f and time delay t . The signal in-phase and out-of-phase components are derived from the convolution of the thermal response and the probe intensity:

$$Re[\Delta R_M(t)] = \frac{dR}{dT} \sum_{m=-M}^M (\Delta T(m/\tau_r + f) + \Delta T(m/\tau_r - f)) \exp(i2\pi mt/\tau_r) \quad (2.39)$$

$$Im[\Delta R_M(t)] = -i \frac{dR}{dT} \sum_{m=-M}^M (\Delta T(m/\tau_r + f) - \Delta T(m/\tau_r - f)) \exp(i2\pi mt/\tau_r) \quad (2.40)$$

Here, $\frac{dR}{dT}$ is the change in reflectance with respect to temperature, τ_r is the laser repetition rate, t is the delay time between pump and probe beams, ΔT is the frequency-domain solution to the surface temperature distribution (Eq 2.38). In TDTR, data is collected through repeated lock-in measurements at varying time delays. The fitting process in FDTR and TDTR involves using the least squares algorithm to minimize the error between the measured phase data and the modeled phase, allowing for the extraction of thermal parameters by adjusting the values of interest[34], [105]. To assess the accuracy of the fit, the variance of the key parameters is calculated from the variance-covariance matrix, and the standard deviation of the fitted parameters is used to indicate the fit quality.

2.3.2.5 Measurement of Thermal Properties in TDTR and FDTR

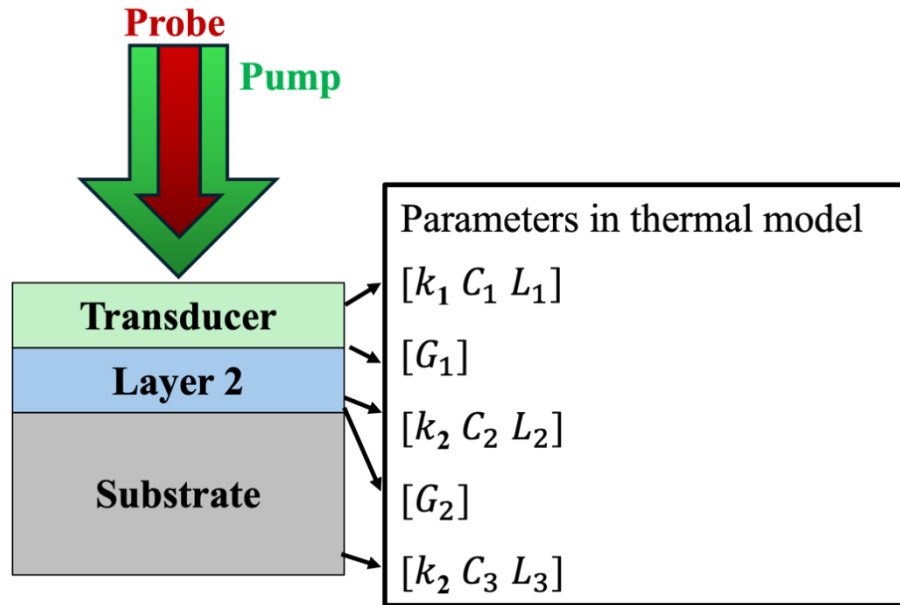


Figure 2.7: Input parameters for a five-layer TDTR and FDTR thermal model. Each layer is represented by a thermal conductivity (k), volumetric heat capacity (C), and a thickness (L). G_1 and G_2 represents the thermal boundary conductances at the two interfaces.

The thermal model requires several thermophysical properties to fit experimental data,

allowing for the extraction of unknown parameters such as thermal boundary conductance and thermal conductivity. The model can vary depending on the number of layers present, with each layer representing a material or an interface. In a typical 5-layer model (comprising three materials and two interfaces), the thermal response at the sample surface depends on various input parameters. These include pump (w_0) and probe (w_1) radii, thermal conductivity (both in-plane (k_r) and out-of-plane (k_z)), volumetric heat capacity (C), and film thickness (L). In TDTR, the thermal response at the sample also depends on modulation frequency (f) and repetition rate of laser (τ_r). Figure 2.7 shows a five-layer model with various input parameters. The thermal boundary conductance is modeled as a 1 nm layer with low heat capacity, where the TBC is the ratio of thermal conductivity to the layer thickness.

In thermoreflectance experiments selecting the appropriate transducer material and thickness is critical for accurate thermal measurements. A good transducer material should have a high thermoreflectance coefficient at the probe wavelength, which improves the signal-to-noise ratio of the measurement[95], [106]. Aluminum (Al) is a commonly used transducer material in TDTR and FDTR experiments due to its large thermoreflectance coefficient in the infrared range (see Figure 2.4). Additionally, transducer needs to be optically thick (typically 50-100 nm) enough so that it is considered opaque to prevent the beam from reaching the substrate, which could interfere with the signal[95], [107]. If the transducer is too thin, part of the laser beam may penetrate through it, reaching the underlying layers and complicating the interpretation of thermal properties since the model would need to account for sub-surface heat diffusion. Conversely, if the transducer is too thick, the temperature gradient across the layer increases, reducing sensitivity to the thermal properties of the underlying material.

The thermal penetration depth refers to the depth within a material at which the temperature

falls to approximately 36.8% ($1/e$) of the temperature at the surface. This concept is crucial in thermoreflectance experiments like TDTR and FDTR because it dictates how deeply the heat from the modulated pump beam penetrates into the material before it is significantly attenuated. In other words, it determines the depth within which the measurement can discern the thermal properties of interest. The thermal penetration depth at a given modulation frequency (f) is given by:

$$d = \sqrt{\frac{k_z}{\pi C f}} \quad (2.41)$$

For example, at a modulation frequency of 1 MHz, the penetration depth in silicon is $\sim 5 \mu\text{m}$ whereas in sapphire it is $\sim 2 \mu\text{m}$.

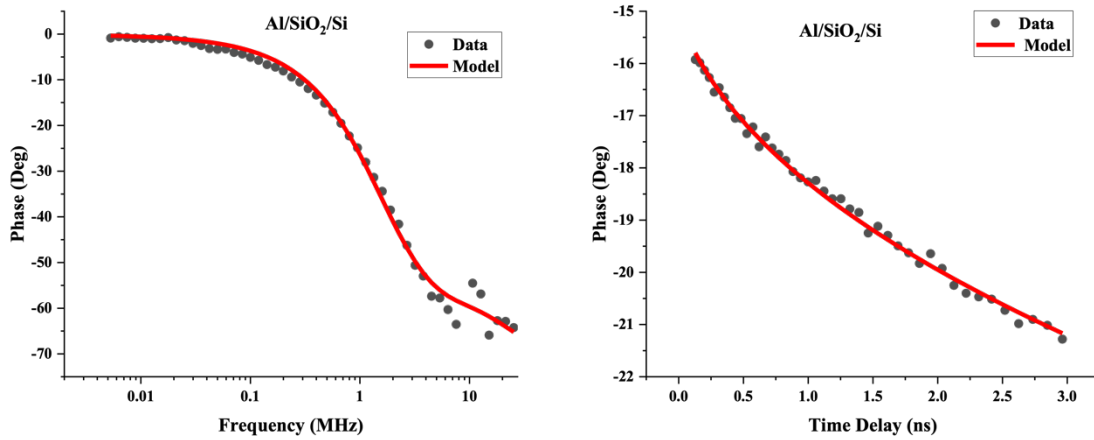


Figure 2.8: Measured phase data (black circles) and the best fit (red line) for Al/a-SiO₂/Si sample using (a) FDTR (b)TDTR.

Figure 2.8 shows an example of the phase data and the best fit on Al/a-SiO₂/Si sample using (a) FDTR and (b) TDTR. The material properties used, and the fit values are given in Table 2.1. The thermal conductivity of a-SiO₂ and TBC between a-SiO₂ and Si were kept as free parameters for the fit. The obtained thermal conductivity and TBC using FDTR and TDTR are in good agreement with the literature. As mentioned before, the uncertainties in our results are

derived solely from the goodness of fit, specifically the standard deviation of the fitted parameters, which reflects the quality of the fit based on the least squares algorithm.

Table 2.1: Material properties used for fitting Al/a-SiO₂/Si sample.

	TDTR	FDTR
k_z (W/mK)	Al=242 a-SiO ₂ = Unknown Si= 145	Al=242 a-SiO ₂ = Unknown Si= 145
C (MJ/m ³ K)	Al=2.42 a-SiO ₂ =1.59 Si= 1.64	Al=2.42 a-SiO ₂ =1.59 Si= 1.64
L (nm)	Al = 46 a-SiO ₂ = 300 Si= 10 ⁶	Al = 46 a-SiO ₂ = 300 Si= 10 ⁶
k_r (W/mK)	Al=71 a-SiO ₂ = Unknown Si= 145	Al=71 a-SiO ₂ = Unknown Si= 145
G at Al/a-SiO ₂ interface (MW/m ² K)	150	150
G at a-SiO ₂ /Si interface (MW/m ² K)	Unknown	Unknown
f (MHz)	1	0.005-30
Spot sizes (μm)	Pump= 6.5 Probe= 3.6	Pump= 5.8 Probe= 2.5
Fit results	$G_{\text{a-SiO}_2/\text{Si}} = 21.7 \pm 1.6 \text{ MW/m}^2\text{K}$ $k_z = k_r = 1.35 \pm 0.03 \text{ W/mK}$	$G_{\text{a-SiO}_2/\text{Si}} = 24.2 \pm 8.3 \text{ MW/m}^2\text{K}$ $k_z = k_r = 1.23 \pm 0.12 \text{ W/mK}$

2.3.3 Other characterization techniques

2.3.3.1 Four-Point Probe Technique

We employ four-point probe measurements (Ossila Four-Point Probe) to assess the in-plane electrical conductivity of thin metallic films and utilize the Wiedemann-Franz law to calculate their thermal conductivity. A current is supplied by two outer probes, while the voltage drops across the material is measured by the two inner probes. The voltage measured between the inner probes is directly related to the current injected, and the sheet resistance. The Wiedemann-

Franz Law states that the ratio of thermal conductivity to electrical conductivity for a metal is proportional to temperature (Eq. 1.2) and for a thin film with thickness L and sheet resistance R_{sh} it can be expressed as:

$$k_e = L_0 T / R_{sh} L \quad (2.42)$$

where L_0 is the Lorenz number, approximately equal to $2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ and T is the temperature.

2.3.3.2 Picosecond Acoustics

Picosecond acoustics is a precise technique for measuring the thickness of thin films, and in this case, it is applied to accurately determine the thickness of the transducer layer. Picosecond acoustics relies on the generation and detection of acoustic waves through rapid thermal expansion induced by a short, intense laser pulse. When a pulsed laser is absorbed by a thin film, the rapid heating causes the material to expand. This expansion generates a strain pulse or an acoustic wave that travels through the material. The properties of this wave, such as its speed and reflections, can be detected by measuring changes in optical reflectivity at the surface. At short time delays (~ 10 -100 ps), TDTR signal contains the acoustic echoes resulting from the initial absorption of laser energy as shown in Figure 2.9. As the laser pulse heats the material, the resulting lattice expansion causes the propagation of sound waves through the sample. These waves are partially reflected at interfaces between layers with different acoustic impedances, which include materials like metal films, substrates, oxide layers, etc.

The acoustic impedance z of a material is a product of its density and the speed of sound. When an acoustic wave encounters an interface between two materials with different impedances, part of the wave is reflected, and the remainder continues into the second material. The key point here is that the reflected wave can undergo a phase shift. If the wave reflects from a material with

a lower impedance, the phase shift is π , while reflecting from a material with a higher impedance result in no phase shift[108], [109], [110]. This phase change is crucial for understanding the shape of the echo peaks in the thermoreflectance signal, which is directly linked to the thickness of the layers in question. The shape and sign of the acoustic peaks depend on the material properties and the interfaces involved.

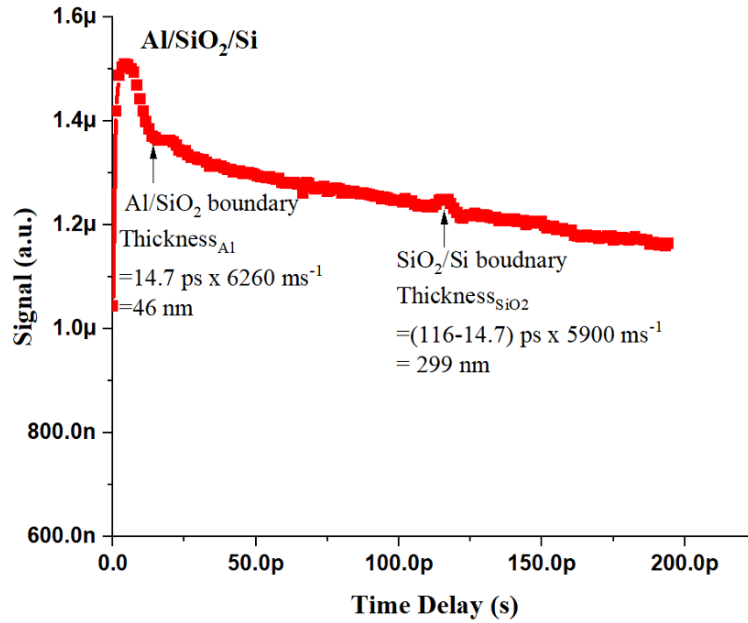


Figure 2.9: Acoustic echoes on a ~50 nm Al film on a Si wafer with 300 nm oxide layer.

Figure 2.9 shows the acoustic echoes on a ~50 nm Al film on a Si wafer with 300 nm thermally grown oxide layer. Here, the acoustic impedance of the aluminum [111] ($Z=1.7 \times 10^7$ kg/(m²s)) is higher than that of the a-SiO₂ [111] ($Z=1.4 \times 10^7$ kg/(m²s)) and this difference causes the acoustic wave to undergo a phase shift at the Al/a-SiO₂ interface. Specifically, the first echo peak is negative due to a π phase change at the interface. Subsequently at a-SiO₂/Si interface, the acoustic impedance of Si[112] ($Z=1.9 \times 10^7$ kg/(m²s)) is larger than that of a-SiO₂ and the acoustic

wave undergoes no phase shift, resulting in a positive peak as shown in Figure 2.9. The speed of sound in Al is 6260 m/s and hence the thickness of Al layer is 46 nm given by:

$$\text{Film thickness} = \frac{1}{2} t_{echo} V_{sl} \quad (2.43)$$

t_{echo} is the time taken by the acoustic echo to return to the surface and V_{sl} is the longitudinal speed of sound of the material. The second peak at the a-SiO₂/Si boundary is a combination of two layers Al and a-SiO₂ ($t_{echo,Al} + t_{echo,SiO_2}$) and subtracting the thickness of Al gives the a-SiO₂ thickness as ~300 nm.

2.3.3.3 Knife-Edge Method

We use the knife-edge technique to measure the radii of the pump and probe beams in FDTR and TDTR experiments. Assuming the laser beam is in the TEM₀₀ mode with a Gaussian intensity profile, the beam intensity distribution can be expressed as[34]:

$$I(r) = \frac{2A_0}{\pi w_r} \exp\left(\frac{-2r^2}{w_r^2}\right) \quad (2.45)$$

where A_0 is the total beam power, r is the radial distance from the center of the beam, and w_r is the beam's 1/e² radius. This 1/e² radius, also called the beam waist (also spot size), is a key parameter that defines the beam size at the focal point. By moving a sharp edge (e.g. a razor blade) across the beam and recording the change in intensity as a function of position, the knife-edge technique captures the gradient of the Gaussian profile. The spot size is then determined by fitting the measured data to a Gaussian function. This is typically done by analyzing the derivative of the intensity profile, as the sharp edge causes a rapid intensity change, making the derivative measurement more accurate and providing a clearer representation of the beam's spatial characteristics.

In this technique, a power meter is used to collect the light that is either transmitted (in TDTR) through or reflected (in FDTR) from the sharp edge, typically the edge of a sample with a silicon wafer substrate). As the sample moves through the focused laser beam in x-direction, it progressively cuts across the beam, which causes the detected intensity to change at each location and the total light intensity at the power meter is given by[34]:

$$I(x) = \frac{2A_0}{\pi w_r} \int_{-\infty}^{\infty} \exp\left(\frac{-2y^2}{w_r^2}\right) \int_{-\infty}^x \exp\left(\frac{-2x^2}{w_r^2}\right) \quad (2.46)$$

A Gaussian fit is applied to the data, which involves fitting the derivative of the measured intensity curve to a Gaussian function, from which the beam's spot size along the direction of the scan can be determined. Since a Gaussian profile is symmetric, this spot size is typically the same along both the x and y axes if the beam is circular. However, if the beam is elliptical, separate measurements along both axes are required.

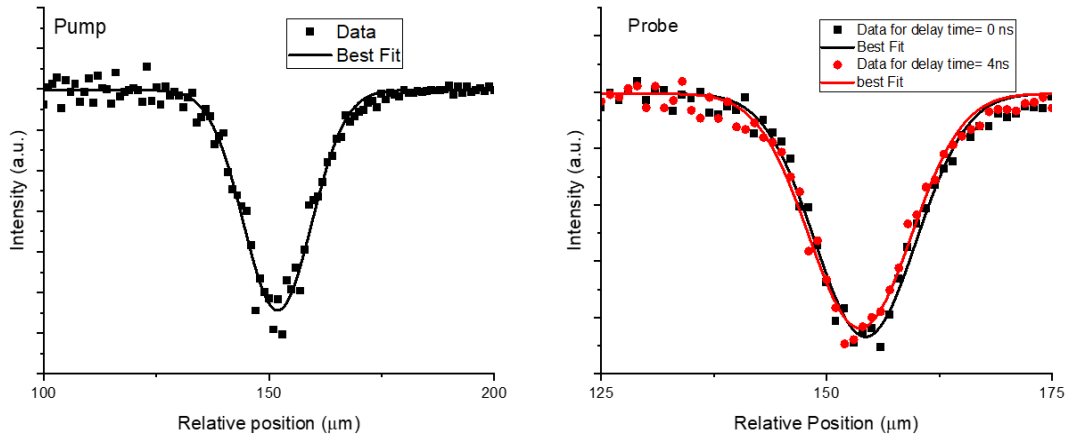


Figure 2.10: Measured (a) pump and (b) probe intensity profiles along with their Gaussian fit respectively for TDTR measurements.

Figure 2.10 (a) and (b) shows an example of the measured pump and probe intensity

profiles along with their Gaussian fit respectively for TDTR measurements. The measured pump spot size was 15.11 μm and the probe spot sizes at the maximum and minimum time delays were 11.30 μm and 11.24 μm respectively, demonstrating negligible beam shift and expansion in spite of the delay stage motion.

CHAPTER 4: PREDICTING HEAT TRANSPORT IN METAL-ISOTROPIC SEMICONDUCTOR SYSTEMS WITH ULTRATHIN INTERLAYERS

Chapter 3 has been partially adapted from:

Oommen, Shany & Pisana, Simone (2021). Role of the electron-phonon coupling in tuning the thermal boundary conductance at metal-dielectric interfaces by inserting ultrathin metal interlayers. *Journal of Physics: Condensed Matter*. 33. 10.1088/1361-648X/abcdbd8.

Oommen, Shany & Fallarino, Lorenzo & Heinze, J & Hellwig, Olav & Pisana, Simone (2022). Role of vibrational properties and electron-phonon coupling on thermal transport across metal-dielectric interfaces with ultrathin metallic interlayers. *Journal of Physics: Condensed Matter*. 34. 10.1088/1361-648X/ac926a.

* All the experiments in this study were done during master's study (2017-2019)

3.1 Introduction

Understanding the various interfacial heat transport mechanisms in materials provides numerous ways to tune the heat transport, which can lead to engineering novel micro- and nano-electronic devices with optimal thermal performance. It is often possible to tune the heat transport at interfaces by inserting a thin additional layer with specific thermophysical properties, where it is generally accepted that the interlayer should bridge the vibrational properties of the adjacent materials to increase the interface conductance. Typically, layers of intermediate Debye temperatures are chosen, whereas the electron-phonon coupling is less often considered as a dominant factor. However, these mechanisms are not well understood particularly for ultrathin (< 10 nm) interlayers, and the general approach of using materials with intermediate Debye temperatures can fail. This regime is of technological importance, since the overall performance

of devices may depend on a compromise between thermal transport and other metrics, such as electrical or optical performance. As an example, plasmonic devices used in heat-assisted magnetic recording should include a low-loss plasmonic material but also dissipate heat effectively[113]. Ultra-thin interlayers can therefore facilitate heat dissipation at the interface between a plasmonic metal and a dielectric heat sink provided that its thickness is small enough to not introduce additional plasmonic losses. This work focuses on developing a thermal model to predict the modification of thermal boundary conductance at metal-isotropic semiconductors in the presence of ultrathin interlayers (5 nm).

3.2 Interlayer Selection Rationale

The thermal transport between a metal and a semiconductor is primarily controlled by phonons, as these carry energy in both materials. When the phonon energies in these materials are different, phonon transmission is hindered due to lack of available phonon states, though inelastic phonon scattering can somewhat increase phonon transmission. It has been argued that phonon interaction at a metal-semiconductor interface can be enhanced by adding an interlayer with intermediate vibrational properties in order to bridge the vibrational spectra mismatch of metal and semiconductor layers[19], [59]. The vibrational overlap can be expressed in terms of phonon density of states overlap, which determines the number of available phonon states in a determined energy interval. Neglecting momentum conservation or inelastic processes, matching the spectral distribution of the phonon density of states yields a high boundary conductance, since phonons states of the same energy coexist in both materials. Alternatively, since the shape of the spectral density of states for acoustic phonons share common features, one can simply consider the overlap between phonon acoustic cut-off frequencies (ν_A)- these are the maximum phonon frequencies near the Brillouin zone edge. Again, neglecting momentum conservation and inelastic processes,

materials with matching acoustic phonon cut-off frequencies would have similar phonon energies and group velocity, yielding a high boundary conductance. Optical phonons are usually neglected, since acoustic phonon modes have larger group velocities and hence carry most of the heat. Furthermore, high-energy optical phonon modes are not populated in large numbers near or below room temperature, but this is generally true only for materials with high optical phonon frequencies. However, there has been evidence to show that optical phonons indeed carry a non-negligible amount of heat[45], and there are some cases where low-lying optical phonons should be considered, as we will also see below.

The Debye approximation assumes linear phonon dispersions ($\omega = V_s q$), and the phonon density of states is given by:

$$D(\omega) = \frac{3\omega^2}{2V_s^3\pi^2} \quad (3.1)$$

where ω is the phonon angular frequency and V_s is the speed of sound. This is valid up to ω_D , which is the Debye cut-off frequency[114]. ω_D is directly proportional to the Debye temperature θ_D ($\omega_D = \hbar\theta_D/k_B$), where $\hbar$ is the reduced Planck's constant and k_B is the Boltzmann constant. Thus, under the linear approximation, the Debye temperature is a direct measure of phonon density of states. Jeong et al.[16] shows that inserting interlayers with intermediate θ_D enhances the overall thermal boundary conductance at a highly mismatched metal-dielectric interface, thanks to the presence of phonon states with intermediate energies. The availability of more phonon modes enhances the phonon flux across the system, resulting in an enhancement in the overall boundary conductance. The use of the Debye approximation is debatable, since realistic phonon dispersions are associated with maximum phonon frequencies near the Brillouin zone edge that are lower than ω_D of the Debye model. This lowers the group velocities near the Brillouin zone edge and the

phonon flux through an interface for a specific phonon mode, since the flux is directly proportional to the group velocity and the number of available phonons in that mode. A mismatch in phonon cut-off frequency ν_A lowers the phonon transmission across an interface due to the limit in the available high-energy phonons for transmission[59]. This is not easily captured by comparing Debye temperatures, since realistic phonon dispersions are not simple linear extrapolations of the behaviour near the Brillouin zone center. The difference can be further highlighted by considering the following examples. Crystalline SiO₂ has values for θ_D and ν_A of 470 K and 2.5 THz, respectively. For Al, θ_D is 428 K (91% the value of quartz), and ν_A is 7 THz (280% the value of quartz). So, the values don't scale linearly as expected in the linear Debye model. Similarly, c-Al₂O₃ and Cr have similar cut-off frequencies (7.9 THz each), however the c-Al₂O₃ Debye temperature is 166% that of Cr. We proposed that the phonon cut-off frequency should be a better measure of phonon transport across an interface, as it explicitly gives a limit to the phonon energies involved in the transport. Our previous experimental results agrees that phonon cut-off frequency is a better predictor than Debye temperature [61], [66], however theoretical predictability is missing due to lack of proper understanding of the heat transfer mechanisms involved.

For the case of metal-semiconductor interfaces, it is also important to consider the role of electron-phonon energy transfer because electrons are the primary heat carriers in metals. The electron-phonon coupling constant g of a metal determines the rate of energy exchange between electrons and phonons. Upon the establishment of a temperature gradient, the non-equilibrium between electrons and phonons can be long-lived if the metal has a weak g . This increases the resistance to heat transport across a metal-semiconductor interface, since energy transfer needs to bridge the electron system (which dominates transport in a metal) and the phonon system (which is the sole energy carrier in a dielectric), yielding an overall reduction of the thermal boundary

conductance G . Adding an interlayer with higher g at the metal-dielectric interface can decrease the non-equilibrium by rapidly dragging the electron and phonon systems into equilibrium. It is not clear, however, whether g of the interlayer can be arbitrarily large or whether it plays a role with respect to other thermophysical properties of the system. Our experiments suggest that depending on the EPC strength of the top metal layer, the interlayer EPC may play a role in determining the overall TBC.

In order to understand the role of these parameters and determine the driving mechanisms for the modification of G at a metal-dielectric interface, we experimentally analyzed a series of interfaces in the presence of various interlayers with a thickness of 5 nm[61], [66]. The thickness was chosen based on our previous work, so that the thickness-dependence of the interlayer would not be a factor even when considering materials with differing g , allowing us to focus on the material properties and decouple any effects of the interlayer thickness[58]. Interlayers were selected based on the assumption that adding an interlayer with intermediate vibrational properties and higher electron-phonon coupling constant should enhance the overall thermal boundary conductance. It should be noted that for the interlayer thickness used in this work (5 nm), the rationale of using an intermediate Debye temperature is less applicable, as we show that at this thickness the interlayer material properties dominate the transport, and the properties of the top metal are less important. However, we will show that material choices based on the Debye picture are still less reliable in determining the thermal boundary conductance. We consider three material parameters in our analysis: Debye temperature (θ_D), acoustic phonon cut-off frequencies (ν_T and ν_L for transverse and longitudinal modes, respectively), and volumetric electron-phonon coupling constant (g). The various thermophysical properties of materials used in this study are given in Table 3.1.

The values for Debye temperature or phonon cut-off frequency may not be readily available for the materials of interest. The Debye temperature can be determined experimentally from the longitudinal & transverse speeds of sound or bulk modulus & Poisson ratio, or theoretically from the phonon dispersion curves. Knowledge of the phonon dispersion curves is required to determine the phonon cut-off frequencies, and this can be obtained experimentally through neutron or X-Ray scattering or theoretically through ab-initio methods or lattice dynamics. Generally speaking, the accessibility of lattice dynamics simulations facilitates the determination of phonon dispersions, so that accessing values for phonon cut-off frequencies is relatively straightforward even for materials that are not well characterized in the literature.

Table 3.1: Thermophysical properties of different materials of interest in this work. θ_D is the Debye temperature, ν_L , ν_T , ν_A and $\nu_{optical}$ are highest phonon frequencies for the longitudinal acoustic modes, two transverse acoustic modes, polarization-averaged acoustic modes and optical modes, respectively. g is the volumetric electron-phonon coupling constant.

Top Metal	Interlayer	Substrate
Al $\theta_D = 428$ K [115] $\nu_L = 9.6$ THz [116] $\nu_T = 5.7$ THz [116] $\nu_A = 7$ THz $g = 0.24 \times 10^{18}$ W/(m ³ ·K) [115]	Al $\theta_D = 428$ K [115] $\nu_L = 9.6$ THz [116] $\nu_T = 5.7$ THz [116] $\nu_A = 7$ THz $g = 0.24 \times 10^{18}$ W/(m ³ ·K) [115]	AlN $\theta_D = 1150$ K [117] $\nu_L = 17.6$ THz [118] $\nu_T = 10.3$ THz [118] $\nu_A = 12.7$ THz $\nu_{optical} = 27$ THz [118]
Au $\theta_D = 165$ K $\nu_L = 4.6$ THz [119] $\nu_T = 2.8$ THz [119] $\nu_A = 3.4$ THz $g = 0.023 \times 10^{18}$ W/(m ³ ·K) [115]	Cr $\theta_D = 630$ K [120] $\nu_L = 10$ THz [121] $\nu_T = 6$ THz, 7.7 THz [121] $\nu_A = 7.9$ THz $g = 0.42 \times 10^{18}$ W/(m ³ ·K) [122]	c-Al ₂ O ₃ $\theta_D = 1047$ K [123] $\nu_L = 10$ THz [124] $\nu_T = 6.9$ THz [124] $\nu_A = 7.9$ THz $\nu_{optical} = 26$ THz [124]

	Ni $\theta_D = 450 \text{ K}$ [115] $\nu_L = 9.1 \text{ THz}$ [125] $\nu_T = 4.5 \text{ THz}$ [125] $\nu_A = 6 \text{ THz}$ $g = 0.36 \times 10^{18} \text{ W}/(\text{m}^3 \cdot \text{K})$ [115]	$\alpha\text{-SiO}_2$ $\theta_D = 470 \text{ K}$ [126] $\nu_L = 4 \text{ THz}$ [127] $\nu_T = 1.8 \text{ THz}$ [127] $\nu_A = 2.5 \text{ THz}$ $\nu_{\text{optical}} = 37 \text{ THz}$ [127]
	Ta $\theta_D = 225 \text{ K}$ [128] $\nu_L = 5.5 \text{ THz}$ [121] $\nu_T = 2.6 \text{ THz}, 3.7 \text{ THz}$ [121] $\nu_A = 3.9 \text{ THz}$ $g = 3.1 \times 10^{18} \text{ W}/(\text{m}^3 \cdot \text{K})$ [129]	Si $\theta_D = 640 \text{ K}$ [130] $\nu_L = 12 \text{ THz}$ [131] $\nu_T = 4.6 \text{ THz}$ [131] $\nu_A = 7.1 \text{ THz}$ $\nu_{\text{optical}} = 16 \text{ THz}$ [131]

3.3 Modeling of TBC in Metal-Interlayer-Isotropic Semiconductor System

At metal-semiconductor interfaces both phonon and electron transport channels should be considered, together with the electron-phonon coupling which governs the rate at which energy is transferred between these channels[36] and affects the overall thermal boundary conductance. In the presence of an interlayer, several energy transfer pathways exist among the channels. Following the approach of Blank and Weber[17], we consider the total G involving two parallel pathways: *pathway 1* and *pathway 2* as shown in Figure 3.1. The energy transfer begins with the laser-excited electrons in the top metal and ends with phonon transport in the dielectric substrate. We ignore interfacial electron-phonon coupling, as this was shown to play a role only at high electron temperatures, a regime not reached in these experiments[40]. Indeed, estimates of electron temperature rise in our experimental conditions using a two-temperature model reveal that the electron temperature rise is well below 50 K, which is a small perturbation of the lattice temperature (300 K). This is opposite the requirement of electron temperature rise being much greater than the lattice temperature in order to observe an appreciable influence of interfacial electron-phonon coupling[40].

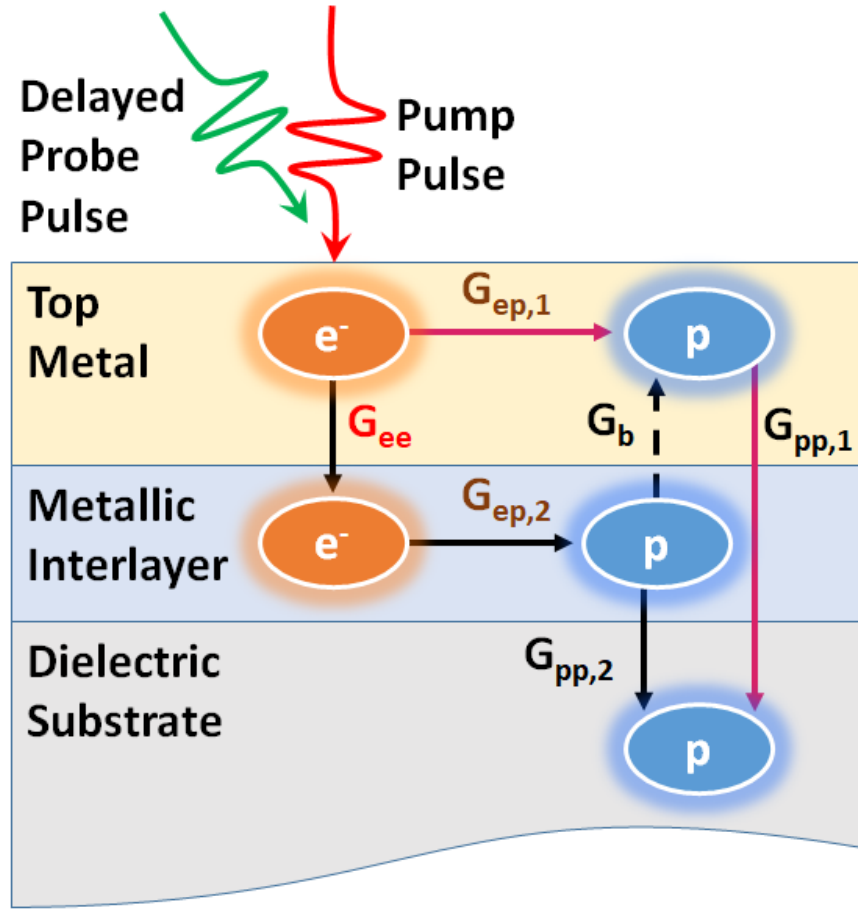


Figure 3.1: Thermal transport mechanisms at a metal-dielectric interface in the presence of an interlayer. Pink and black solid arrows represent heat transport *pathway 1* and *pathway 2*, respectively. The black dashed arrow represents heat backflow from the interlayer to the top metal. In this work, *pathway 2* dominates transport, since the interlayers studied are 5 nm thick.

Figure 3.1 shows the thermal transport mechanisms at a metal-dielectric interface in the presence of an interlayer. Pink and black solid arrows represent heat transport *pathway 1* and *pathway 2*, respectively. The black dashed arrow represents heat backflow from the interlayer to the top metal. In this work, *pathway 2* dominates transport, since the interlayers studied are 5 nm thick. In *pathway 2* the electrons in the top metal interact with the electrons in the metallic interlayer to transfer energy (G_{ee}). After this, the interlayer electrons transfer their energy to the lattice via electron-phonon coupling ($G_{ep,2}$). Finally, the phonons in the interlayer transfer energy

to phonons in the substrate ($G_{pp,2}$). Given the nanometric thickness of the interlayer, we only consider phonons with wavelength smaller than the interlayer thickness to participate in this pathway[16], [17]. This is because phonons with wavelength larger than the interlayer thickness would conceptually extend beyond the layer's physical size and would have hybrid characteristics determined by the vibrational properties of the interlayer and adjacent materials. This would make the vibrations spectrally varied and the concept of a phonon would be meaningless. Therefore, only phonons with sufficiently small wavelength are considered in this layer, with their properties determined by the composition of the interface material. Note that this assumption does not entirely exclude phonons with wavelength larger than the interlayer size in the overall interface transport, as long wavelength phonons will be considered in *pathway 1* as described below. The addition of an interlayer with an electron-phonon coupling constant higher than that of the top metal layer can result in back transfer of heat from the interlayer to the top metal layer (G_b). This occurs because the phonon temperature in the interlayer is larger than that of the top metal. This effect however only lasts for a few picoseconds, as the electron and phonon temperatures equilibrate in both the top metal and interlayer. We analyze the system response starting from 100 ps after the arrival of the pump pulse, thus the contribution of G_b to the overall conductance measured can be ignored[40]. The total interfacial conductance due to *pathway 2* can be expressed assuming the resistance due to all three energy transfer steps are in series as:

$$\frac{1}{G_2} = \frac{1}{G_{ee}} + \frac{1}{G_{ep,2}} + \frac{1}{G_{pp,2}} \quad (3.1)$$

In *pathway 1*, electrons couple with the phonons in the metal ($G_{ep,1}$), and subsequently the phonons exchange energy with the substrate ($G_{pp,1}$). Phonons from the metal layer pass directly to the substrate if the phonon wavelength is larger than the interlayer thickness, as done

previously[16], [17]. This assumption is based on the idea that phonons with wavelengths longer than the interlayer thickness can tunnel through it, effectively bypassing the interlayer as if it were transparent. This treatment is justified by the fact that, in this case, the phonons with longer wavelengths are able to pass through the thin interlayer without significant scattering. Although this model simplifies the complexities of phonon tunneling, it provides a reasonable approximation, given that a more rigorous treatment would need to account for the varied bonding and local vibrational states at the interface, which would complicate the analysis[16], [132]. The total interfacial conductance due to *pathway 1* can again be expressed assuming the resistances are in series as:

$$\frac{1}{G_1} = \frac{1}{G_{ep,1}} + \frac{1}{G_{pp,1}} \quad (3.2)$$

In the following we will outline how the components of Eqs. (3.1 and 3.2) can be treated, including considerations for finite size effects, and finally we will combine the results into a total value for G for both pathways.

To model the phonon thermal transport at the interface between metal and dielectric ($G_{pp,1}$ and $G_{pp,2}$) we use a modified diffuse mismatch model[37]. We consider realistic phonon dispersion relations to calculate the phonon transmission coefficient and G [133], and assume an isotropic phonon dispersion along the crystal growth direction[16]. Assuming an isotropic phonon dispersion makes the computation less time consuming and is a good enough approximation of the three-dimensional phonon dispersion for cubic structures[37]. We use different DMM scattering models (in the limits of purely elastic scattering or considering all elastic and inelastic scattering processes) and the role of optical phonons to check the importance of this assumption on the systems studied here[45]. For elastic scattering, the phonon transmission probability from material

1 to 2 can be expressed using Eq. 2.10. On the other hand, for the case of all elastic and inelastic scattering processes, the phonon transmission probability from material 1 to 2 can be expressed using Eq. 2.11. The phonon dispersion of each branch $\omega_j(q)$ is obtained by using a polynomial fit to the experimental dispersion curves along the preferential growth direction reported for our substrates. The summation is performed either over all phonon branches or for the acoustic branches only, to determine the relative importance of optical phonons. We note that although various expressions have been presented in the literature to treat elastic and inelastic scattering, the choice of which to use is not trivial. We will comment on this choice further in the Results and Discussion section below and propose a hybrid elastic/inelastic treatment of interfaces with interlayers based on the relative phonon mismatch among the materials.

The total thermal boundary conductance can be expressed using Eq. 2.12, which is used to calculate the total G_{pp} at interfaces. However, this expression does not directly allow to limit the calculation to only a fraction of the phonon spectrum. Based on the discussion above, we would like to consider the fraction of phonons with wavelength λ less than or equal to the interlayer thickness L_I , thus we would like to limit the integration to $\lambda_{max} = L_I$. This is more easily accomplished by changing the integration variable from q to λ using the relation $q = \frac{2\pi}{\lambda}$. The accumulation of thermal boundary conductance[16], [59] as a function of phonon wavelength can then be expressed as:

$$G(\lambda < \lambda_{max})_{pp,accum} = -\frac{1}{8\pi^2} \sum_{j,A} \int_{\lambda_{min}}^{\lambda_{max}} \hbar \omega_{j,A} q_{j,A}^2 |v_{j,A}| \alpha_{A \rightarrow B} \frac{df_0}{dT} \frac{2\pi}{\lambda^2} d\lambda_{j,A} \quad (3.3)$$

where λ_{min} represents the shortest wavelength phonon at the Brillouin zone edge, λ_{max} is the limit to phonon wavelength we would like to impose, j is the phonon polarization, q is the phonon wavevector $\hbar$ is the reduced Planck's constant, $\omega_{j,A}$ is the phonon angular frequency in material

A, $v_{j,A}$ is the phonon group velocity in material A, $\alpha_{A \rightarrow B}$ is the phonon transmission probability from material A to B and f_0 is the Bose-Einstein distribution function. The thickness dependent $G(L_I)_{pp,1}$, which for pathway 1 should not include phonons with wavelengths that can exist in the interlayer (those are considered in pathway 2) can therefore be calculated using[16]:

$$G(L_I)_{pp,1} = G_{pp,sat} - G(\lambda_{max} = L_I)_{pp,accum} \quad (3.4)$$

where $G_{pp,sat}$ is the saturated value of $G_{pp,accum}(\lambda < \lambda_{max})$ as $\lambda_{max} \rightarrow \infty$. The shape of the $G(L_I)_{pp,1}$ curve decreases with increasing interlayer thickness, since the contribution to the total G from phonons originating in the metal and transmitting into the substrate decreases as more of the phonons are cut-off. Figure 3.2 shows the contribution from pathway 1 (red line) and pathway 2 (black line) as the interlayer thickness increases in Al(50 nm)/Ni/Sapphire. Al/Sapphire and Ni/Sapphire have similar G_{pp} due to the similar vibrational properties of Al and Ni. Hence, at higher and lower interlayer thicknesses the G values are similar and approach the bulk value of the Ni/Sapphire and Al/Sapphire interfaces, respectively.

In a similar way, for *pathway 2*, where the contribution of phonon conduction from the interlayer into the substrate increases with interlayer thickness as more phonon wavelengths are allowed, the thickness dependence is given by:

$$G(L_I)_{pp,2} = G(\lambda_{max} = L_I)_{pp,accum} \quad (3.5)$$

The expressions above account for finite size effects by forbidding interlayer phonon wavelengths longer than the interlayer thickness, but this phenomenological treatment does not account for changes in phonon band structure in thin slabs and still assumes a bulk-like phonon dispersion. We have modeled by lattice dynamics the changes to the phonon band structure in Silicon ultra-

thin slabs due to phonon confinement and have found that the phonon band bending near the Brillouin zone center or the creation of quasi-optical bands in slabs as thin as 0.54 nm alter the value for G_{pp} obtained by the DMM by only 6% in a Silicon/Germanium interface. Figure 3.3 shows phonon band structure in slabs of Si calculated from lattice dynamics for different slab thicknesses. This allowed us to isolate the effect of nanostructure band structure modification and estimate its importance. While this treatment is not as complete as those reported by molecular dynamics, non-equilibrium Green's function or Boltzmann transport approaches, it provides us some confidence that in our DMM framework the tunneling and accumulative effects in phonon transport outlined above are more dominant than phonon confinement effects.

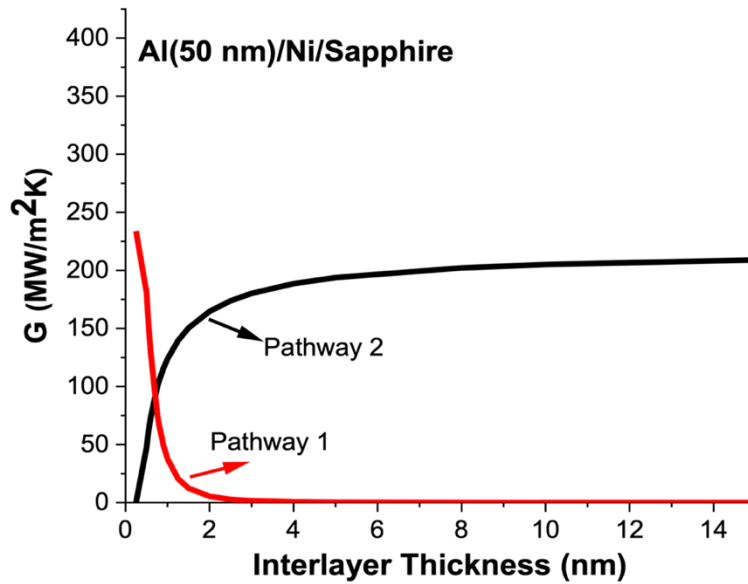


Figure 3.2: Contribution from pathway 1 (red line) and pathway 2 (black line) as the interlayer thickness increases in Al(50 nm)/Ni/Sapphire.

We now turn to the remaining terms contributing to the heat conduction pathways. The thickness-dependent resistance due to the electron-phonon coupling g in an interlayer with

thickness L_I can be evaluated by[134]:

$$G_{ep,2} = L_I g. \quad (3.6)$$

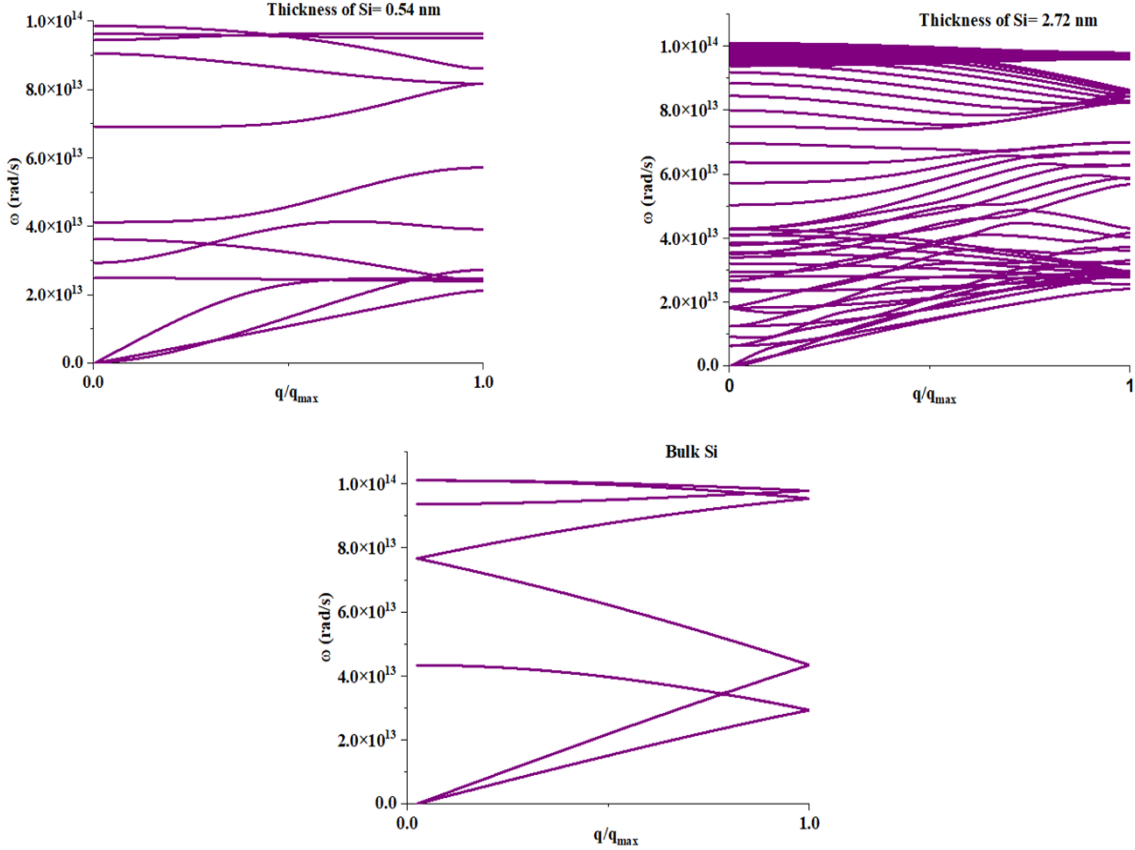


Figure 3.3: Phonon band structure in slabs of Si calculated from lattice dynamics for different slab thicknesses.

This expression is valid for sub-nanometer thick layers, where electron-phonon coupling is incomplete. The contribution from electron-phonon coupling in the top metal layer (~ 50 nm thick) can be calculated using $G_{ep,1} = \sqrt{k_p g}$, where k_p is the phonon contribution to the thermal conductivity of the metal[36]. In our work the contribution of $G_{ep,1}$ is negligible, since Al has a high value for g , and there is small electron-phonon non-equilibrium (negligible resistance) in the top Al layer. The thermal boundary conductance at the interface between two metals due to

electron-electron interaction can be expressed as[135]:

$$G_{ee} = \frac{\gamma_{e,A} \nu_{e,A} \gamma_{e,B} \nu_{e,B}}{4(\gamma_{e,A} \nu_{e,A} + \gamma_{e,B} \nu_{e,B})} T \quad (3.7)$$

where $\gamma_{e,A} = C_{e,A}/T$ is the Sommerfeld constant for metal A, $C_{e,A}$ is the electronic heat capacity, T is the temperature, $\nu_{e,A}$ the Fermi velocity of electrons in material A.

The total interfacial conductance predicted by this framework in the presence of an interlayer can be calculated assuming the resistances due to the two pathways are parallel to each other. The total contribution is therefore:

$$G_{model} = G_1 + G_2 \quad (3.8)$$

As the interlayer thickness increases and becomes comparable to the largest phonon wavelength in interlayer, the contribution from G_1 in pathway 1 becomes negligible. On the other hand, the contribution from G_2 in pathway 2 becomes larger with interlayer thickness, with the growth rate being dominated by $G_{pp,2}$ and $G_{ep,2}$, since the values for G_{ee} are typically large. To model the phonon-phonon transmission when evaluating the conductances $G_{pp,1}$ and $G_{pp,2}$ in the system, we used a modified version of the DMM. Given that the inelastic contribution to phonon transmission is only likely to take place for low-n phonon processes[45] during the calculations of the transmission coefficients we employ a hybrid approach where we consider elastic processes for the energetically mismatched (e.g.: Au/Sapphire) interface (where high-n phonon processes are unlikely) and inelastic processes for the better matched (e.g.: Ni/Sapphire) interface (where low-n phonon processes are likely). Here we refer to low-n phonon processes as inelastic scattering processes involving few (3-4) phonons. In practice, we distinguish our hybrid DMM model in three cases: (1) when acoustic modes of materials across the interface have energies within a factor

of 2, (e.g.: Al/Si system as shown in Figure 3.4 (a)), we consider inelastic scattering, since these would involve few-phonon processes and are more likely; (2) when acoustic modes differ by more than a factor of 2 (e.g.: Ta/Si as shown in Figure 3.4 (b)) (the cut-off frequency of the LA mode of Si is more than 2X that of the LA mode of Ta), we consider elastic scattering, since it is not as likely to have many inelastic processes involving phonons that could span large energy differences; (3) when the acoustic modes of the metal are comparable to those of the dielectric, but there are low-lying optical modes of comparable energies, (e.g.: Al/Sapphire as shown in Figure 3.4 (c)) system, we consider inelastic scattering as in case (1) but also include low-lying optical modes of the dielectric that have comparable frequencies to those of the metal. Figure 3.4 shows phonon dispersions for (a) Al/Si (b) Ta/Si (c) Al/Sapphire. The green, purple, red, and blue curves represent Al, Si, Ta, and sapphire respectively. In Al/Si, we consider inelastic scattering and exclude optical phonons. In Ta/Si, we consider elastic scattering and exclude optical phonons. In Al/sapphire, we consider inelastic scattering and include low-lying optical phonons which have energies comparable to those of Al.

Elastic versus inelastic scattering is considered as described previously in Chapter 2. Briefly, the transmission probability in the elastic case is calculated as the fraction of heat flux across the interface as function of the wave-vector (Eq. 2.10), thereby forcing the correspondence of phonon energies on either side of the interface at each wave-vector for transmission to occur. In the inelastic case the fraction of heat flux across the interface is calculated by integrating over all the heat flux contributions (Eq. 2.11), thereby considering all possible carrier scattering initial and final states. We note that this hybrid approach to treat elastic and inelastic scattering by limiting it to more likely low-n phonon processes has not been reported before, and we believe is an important feature that allows to more accurately model interfacial heat transfer.

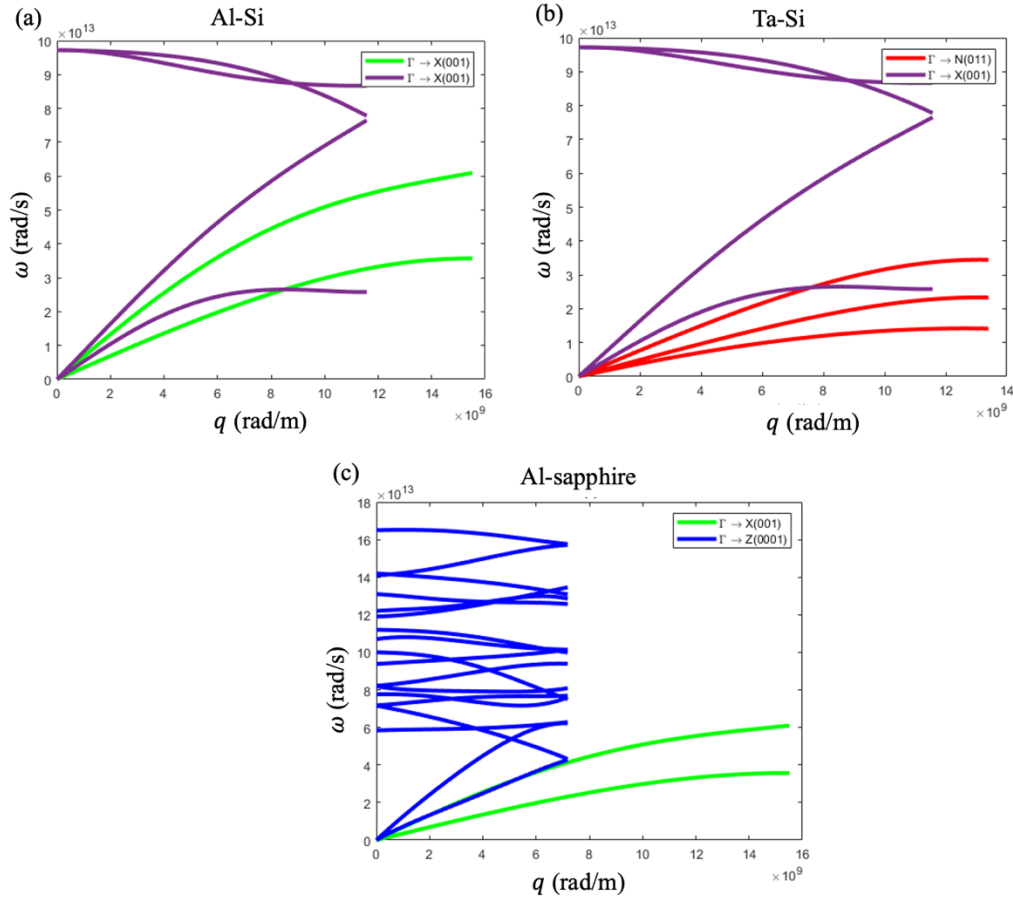


Figure 3.4: Phonon dispersions for (a) Al/Si (b) Ta/Si (c) Al/Sapphire. The green, purple, red, and blue curves represents Al, Si, Ta, and sapphire respectively. In Al/Si, we consider inelastic scattering and exclude optical phonons. In Ta/Si, we consider elastic scattering and exclude optical phonons. In Al/Sapphire, we consider inelastic scattering and include low-lying optical phonons which have energies comparable to those of Al.

3.4 Results and Discussion

3.4.1 Thickness Dependence of the Interlayer

In this study, we investigate the interlayer thickness dependence of the thermal boundary conductance for the Au (50 nm)/Ni/c-Al₂O₃ system to confirm that it reaches saturation at a thickness of 5 nm, as expected. The thickness-dependent analysis also serves to validate our theoretical model, demonstrating its ability to predict the saturation thickness for interlayers. Experimentally, ultrathin Ni layers (ranging from 0.5 nm to 5 nm) were inserted at the Au/c-Al₂O₃

interface, and the thermal boundary conductance was measured using the TDTR technique. Film thickness was measured using X-ray reflectivity (XRR), which simultaneously evaluates interfacial roughness. The measured roughness was minimal, indicating that the films were uniform and continuous. Detailed information about the experiment, including sample preparation and thermal properties, can be found in Refs. [61], [66]. Our previous study[58], [61] shows that the thickness dependent thermal boundary conductance at a metal-dielectric interface reaches a saturation before ~ 5 nm if the interlayers have a sufficiently strong electron-phonon coupling constant.

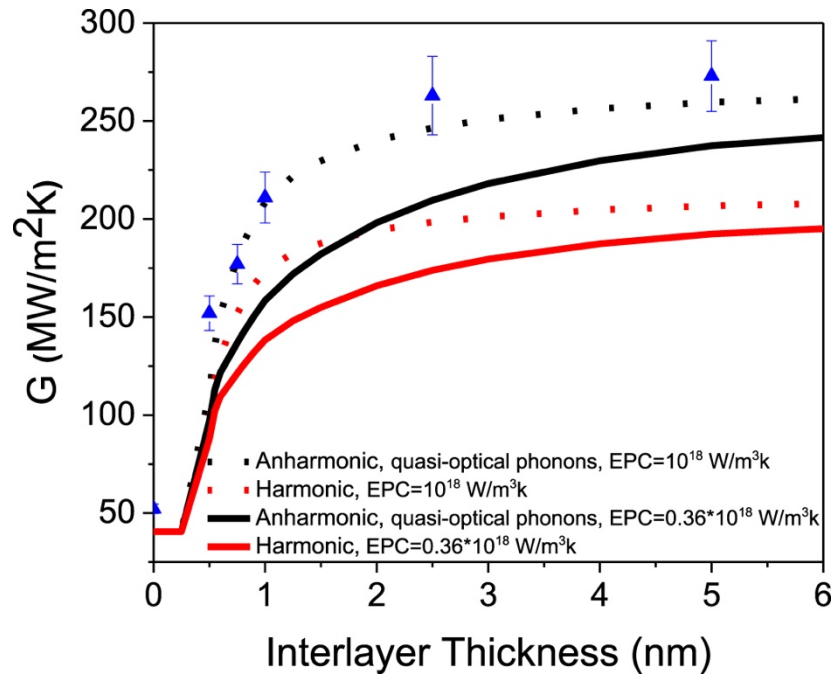


Figure 3.5: Comparison of experimental G with the model as function of interlayer thickness for the Au (50 nm)/Ni/c-Al₂O₃ system. Experimental results are represented as filled symbols. The red solid curve represents the total G evolution based on the hybrid model including only acoustic phonons in c-Al₂O₃ with Ni EPC = 0.36×10^{18} W/(m³K). The black solid line denotes the hybrid model considering low-frequency quasi-optical phonon modes in c-Al₂O₃ with Ni EPC = 0.36×10^{18} W/(m³K). The dotted lines represent the G evolution with Ni EPC value of 10^{18} W/(m³K).

Figure 3.5 shows the comparison of experimental G with the model as a function of interlayer thickness for Au/Ni/c-Al₂O₃ system. The blue triangular symbols represent the measured G , and the black and red curves show the G calculated from the model above, with and without the contribution of the low-frequency quasi-optical phonons in c-Al₂O₃, respectively. We plot two sets of curves: the solid lines use the EPC of Ni of 0.36×10^{18} W/(m³K), but for reference we include in the dashed lines the EPC value of 1.03×10^{18} W/(m³K). This is because previous studies have reported multiple values for g of Ni in the above range [136]. From the figure, we can conclude that only low-frequency quasi-optical phonons in c-Al₂O₃ contribute to the thermal boundary conductance, as it is unlikely that high n-phonon processes would be involved or that high-energy optical phonon modes would be occupied near room temperature. The experimental G evolution trend saturates at 5 nm as expected. Other interlayers used later in this study are Al, Cr and Ta, the first two having a similar EPC value to Ni, and Ta having a much higher value. Cr and Ta interlayers are expected to have a thickness dependence that saturates similarly to or even more quickly than Ni, but for Al in the Au/Al/Substrate systems, more attention is needed since Al has a smaller EPC. The results so far tell us that for most materials studied here a 5 nm interlayer thickness is sufficient to saturate the value for G due to the sufficiently high electron-phonon coupling values of the interlayers.

3.4.2 Comparison of Calculated and Measured TBC

In this section we to compare the calculated and measured TBC for various metal-interlayer-isotropic semiconductor systems. Table 3.2 shows the comparison of measured TBC ($G_{\text{experiment}}$) and predicted TBC ($G_{\text{predicted}}$) values based on the hybrid model for various metal-interlayer-semiconductor combinations along with several intermediate boundary conductance values that break down the relative contributions. At the interface between Al and c-Al₂O₃, the

acoustic phonon cut-off frequencies of c-Al₂O₃ ($\nu_A = 7.9$ THz) are closer to Cr ($\nu_A = 7.9$ THz) followed by Al ($\nu_A = 7$ THz) and Ni ($\nu_A = 6$ THz). This better match of phonon cut-off frequencies between the metals and the substrate leads to higher thermal boundary conductance in the Al/Cr/c-Al₂O₃ system, followed by Al/Ni/c-Al₂O₃, and Al/c-Al₂O₃. This trend is consistent with the predicted and measured thermal boundary conductance values presented in Table 3.2. On the other hand, Al/Ta/c-Al₂O₃ showed a decrease in predicted and measured G due to the highly mismatched acoustic phonon cut-off frequencies in Ta ($\nu_A = 3.9$ THz) and Al₂O₃. For α -SiO₂ ($\nu_A = 2.5$ THz), one might at first expect a lower G , because the phonon cut-off frequencies are lower than those of most metals. However, α -SiO₂ has several low-lying optical phonon branches below 10 THz, and these may match well the phonon modes of the metals through elastic or low-order inelastic scattering. The agreement between predictions and experiment for the metal/ α -SiO₂ samples shows that low-lying optical modes can significantly contribute to heat transport and must be taken into account. Our results show that inserting metals with intermediate phonon cut-off frequency can enhance the TBC significantly while noting that low-lying optical modes must be considered where present, and that for most cases involving interlayers thicker than ~ 5 nm, one may simply disregard the influence of a top metal layer.

Inserting Cr and Ni interlayers at the Au/AlN interface, which have a better cut-off frequency match to AlN and a higher EPC than Au, enhanced the thermal boundary conductance, with both experimental and theoretical results in agreement. The lower thermal boundary conductance observed in the metal/AlN system can be attributed to the reduced phonon flux and transmission, which arise from the weak spectral overlap between the metal's phonon modes and those of AlN. This poor phonon match can be deduced from the differences in acoustic phonon cut-off frequencies in Table 2.

To understand the role of electron-phonon coupling, we compare the samples with Al in contact with c-Al₂O₃: Al/c-Al₂O₃ with G of 197 MWm⁻²K⁻¹, and Au/Al/c-Al₂O₃ with G of 94 MWm⁻²K⁻¹. One might expect identical results, because the metal-dielectric interface is the same. However, Au possesses a very low EPC, with g of 2.3×10^{16} Wm⁻³K⁻¹, and Al is only 10X larger, causing the electron and phonon thermal baths to remain out of equilibrium over a long distance, decreasing the conductance. This can be illustrated through a simple numerical example. Let us first consider the Al/c-Al₂O₃ interface. Modeling the transport as a series of two resistors modeling the electron to phonon transfer in the Al layer, followed by the phonon-phonon interface, with conductances of $G_{ep,Al} = \sqrt{k_p g} \cong 1.5$ GWm⁻²K⁻¹ and $G_{pp,Al-Sub} = 235$ MW m⁻²K⁻¹, we would predict $G_{Al-Al_2O_3} = 203$ MWm⁻²K⁻¹, very close to our measured value. The Au/Al/c-Al₂O₃ interfaces can similarly be modeled by a series of resistors modeling the electron to phonon transfer followed by the phonon transport. The length scale for electron-phonon equilibration in the Al layer is $\sqrt{k/g} \sim 30$ nm, and since this is greater than the Al layer thickness, we can assume that not all electrons would be thermalized. Therefore, one must consider electron-phonon coupling in the Au layer. This leads to considering the following conductances, from top to bottom : $G_{ep,Au} = \sqrt{k_p g} \cong 245$ MWm⁻²K⁻¹, $G_{pp,Au-Al} = 266$ MWm⁻²K⁻¹ (evaluated by the DMM), $G_{p,Al} = k_p/h \cong 2$ GWm⁻²K⁻¹ and $G_{pp,Al-Sub} = 300$ MW m⁻²K⁻¹, yielding a predicted $G_{Au-Al-Al_2O_3} = 86$ MWm⁻²K⁻¹, again close to our measurement. Thus, it is clear that the low EPC in Au and Al causes significant resistance. For comparison, the Au/Cr/c-Al₂O₃ has an interlayer with an EPC almost 2X that of Al. Assuming that this is sufficient to equilibrate the electron and phonon temperatures in the Cr layer, the conductance predicted for the Al/Cr/c-Al₂O₃ interfaces would be given by $G_{e,Au} = k_e/h \cong 6$ GWm⁻²K⁻¹, $G_{ee,Au-Cr} \cong 4$ GWm⁻²K⁻¹, $G_{ep,Cr} = hg = 2$ GWm⁻²K⁻¹ and $G_{pp,Cr-Sub} = 344$ MW m⁻²K⁻¹, yielding $G_{Au-Cr-Al_2O_3} = 263$ MWm⁻²K⁻¹, which matches well our experiment. These

considerations, while employing approximations in modeling the overall transport, show a good degree of agreement with our experimental data, and can explain why the Au/Al/c-Al₂O₃ sample has a lower conductance than the Al/c-Al₂O₃ interface, and why the Au/Al bilayer is the interface that is more importantly affected by the value of the EPC.

Table 3.2: Comparison of measured TBC ($G_{\text{experiment}}$) and predicted TBC ($G_{\text{predicted}}$) values based on the hybrid model for various metal-interlayer-semiconductor combinations along with several intermediate boundary conductance values.

System	Top metal-interlayer transport (MW/m ² K)	Interlayer transport (MW/m ² K)	Interlayer-substrate transport (MW/m ² K)	$G_{\text{predicted}}$ (MW/m ² K)	$G_{\text{experiment}}$ (MW/m ² K)	Notes
Al/c-Al ₂ O ₃	N/A	$G_{ep} - 1,150$	$G_{pp} - 300$	226	197 ± 7	Anharmonic scattering, quasi-optical phonons
Al/Ta/c-Al ₂ O ₃	$G_{ee} - 10,500$	$G_{ep,2} - 15,500$	$G_{pp,2} - 63$	62	70 ± 5	Harmonic scattering, no optical phonons
Al/Cr/c-Al ₂ O ₃	$G_{ee} - 8,600$	$G_{ep,2} - 2,100$	$G_{pp,2} - 344$	269	285 ± 20	Anharmonic scattering, quasi-optical phonons
Al/Ni/c-Al ₂ O ₃	$G_{ee} - 6,900$	$G_{ep,2} - 1,800$	$G_{pp,2} - 288$	228	257 ± 15	Anharmonic scattering, quasi-optical phonons
Au/c-Al ₂ O ₃	N/A	$G_{ep} - 245$	$G_{pp} - 45$	38	52 ± 2	Harmonic scattering, no optical phonons
Au/Al/c-Al ₂ O ₃	$G_{ep} - 245$ $G_{pp,Au/Al} - 266$	$G_{p,Al} - 2,000$	$G_{pp} - 300$	86	94 ± 1	Anharmonic scattering, quasi-optical phonons, e-p equilibration in top metal

Au/Cr/ c- Al₂O₃	$G_{ee} - 4,000$	$G_{ep,2} - 2,100$	$G_{pp,2} - 344$	263	249 ± 20	Anharmonic scattering, quasi-optical phonons
Au/Ni/ c- Al₂O₃	$G_{ee} - 5,350$	$G_{ep,2} - 1,800$	$G_{pp,2} - 288$	228	273 ± 18	Anharmonic scattering, quasi-optical phonons
Al/ α- SiO₂	N/A	$G_{ep} - 1,150$	$G_{pp} - 183$	153	227 ± 27	Anharmonic scattering, quasi-optical phonons
Al/Cr/ α-SiO₂	$G_{ee} - 8,600$	$G_{ep,2} - 2,100$	$G_{pp,2} - 186$	162	242 ± 31	Anharmonic scattering, quasi-optical phonons
Al/Ni/ α-SiO₂	$G_{ee} - 6,900$	$G_{ep,2} - 1,800$	$G_{pp,2} - 175$	151	270 ± 40	Anharmonic scattering, quasi-optical phonons
Au/Al N	N/A	$G_{ep} - 245$	$G_{pp} - 88$	64	32 ± 7	Harmonic scattering, no optical phonons
Au/Cr/ AlN	$G_{ep} - 245$ $G_{pp,Au/Cr} - 234$	$G_{p,Cr} - 2,000$	$G_{pp,2} - 189$	71	54 ± 1	Harmonic scattering, no optical phonons, e-p equilibration in top metal
Au/Ni/ AlN	$G_{ep} - 245$ $G_{pp,Au/Al} - 204$	$G_{p,Ni} - 2,000$	$G_{pp,2} - 166$	64	88 ± 2	Harmonic scattering, no optical phonons, e-p equilibration in top metal
Al/Si	N/A	$G_{ep} - 1,150$	$G_{pp} - 328$	242	250 ± 2	Anharmonic scattering, no optical phonons
Al/Ta/ Si	$G_{ee} - 10,500$	$G_{ep,2} - 15,500$	$G_{pp,2} - 98$	95	70 ± 2	Harmonic scattering, no optical phonons
Al/Ni/S i	$G_{ee} - 6,900$	$G_{ep,2} - 1,800$	$G_{pp,2} - 316$	245	268 ± 13	Anharmonic scattering, no

						optical phonons
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To further understand the role of EPC, we compare the Au/c-Al₂O₃ and Al/Ta/c-Al₂O₃ interfaces. Au/c-Al₂O₃ interface is highly resistive due to both large phonon mismatch but also due to the resistance incurred by the low EPC of Au. In comparison, the Al/Ta/c-Al₂O₃ system includes larger EPC materials, and thus one would expect a larger conductance G . The Al/Ta/c-Al₂O₃ interface shows a comparable value for G both experimentally and theoretically. Although Ta has a very high EPC, the electron-phonon non-equilibrium is not an important factor in the overall interface conductance. Rather, the very large mismatch in phonon frequencies between Ta and c-Al₂O₃ is responsible for the similar value for G to the Au/c-Al₂O₃ interface. This highlights that a high EPC won't by itself lower the boundary conductance.

Based on these observations, we suggest that when the electron-phonon non-equilibrium in the top layer is strong for its thickness (such as 50 nm of Al), the overall thermal boundary conductance is primarily governed by phonon frequency overlap between interlayer and substrate. However, when the top metal layer has a weak electron-phonon coupling constant (such as 50 nm of Au), the modification of thermal boundary conductance involves an interplay between phonon spectra overlap and coupling strength of interlayer. Figure 3.6 illustrates a comparison between the predicted thermal boundary conductance from the hybrid DMM model and the measurements obtained in this study. A straight-line representing $x=y$ is shown, indicating agreement between the predictions and the experimental results.

Models based on the DMM typically can estimate the order of magnitude of G but as the complexity of the models have grown, so did their prediction ability. Generally speaking, however, prediction models based on the DMM have their limitations, as they include simplifying

assumptions such as the way scattering is modeled at the interface and phonon dispersion. More sophisticated theories such as those based on the Landauer formalism or atomistic Green's function with input from density functional theory can be more accurate if the interfaces are well-controlled but require much more computational investment and are therefore still seldomly used. Despite its limitations, the hybrid DMM model used in our work is able to capture the most dominant aspects affecting the value of G , and therefore can provide reasonable predictability. As we have shown here, even a relatively simple comparison of acoustic cut-off frequencies can provide a first indication of what interlayers should produce the desired change in G in metal-semiconductor systems.

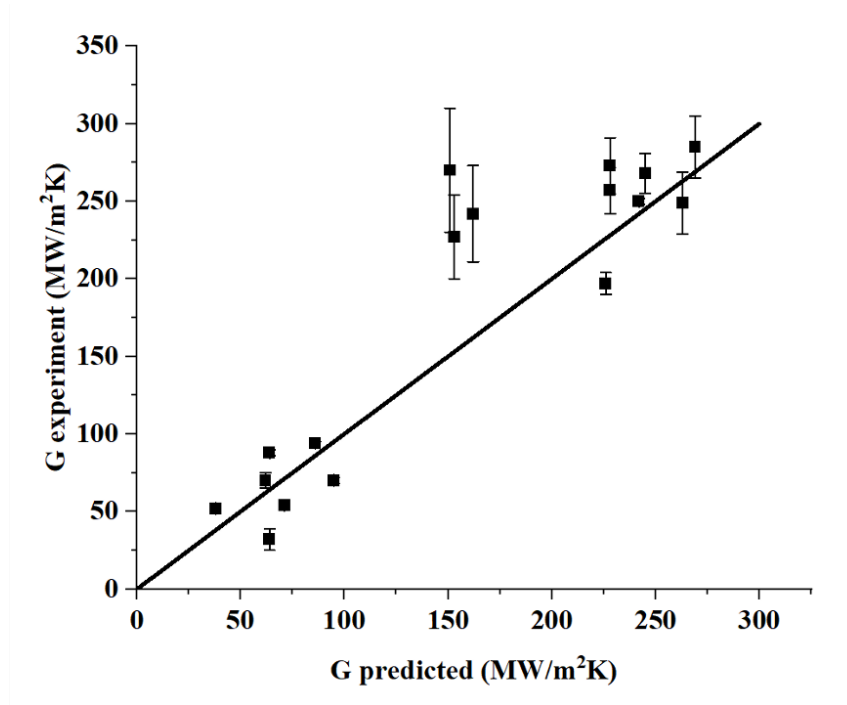


Figure 3.6: Comparison between the predicted thermal boundary conductance from the hybrid DMM model and the measurements obtained in this study.

3.5 Conclusion

We studied the interfacial mechanisms that affect the thermal boundary conductance in metal-dielectric systems in the presence of an interlayer. The two important interlayer properties that determine the modification of G at metal-semiconductor interfaces are phonon spectra and electron-phonon coupling strength. Better overlap between phonon spectra of the interlayer and substrate enhances the overall G due to the increase in phonon flux at the interface. The enhancements can be very sizeable, above 3X in the materials studied in this work. The influence of the top metal is not important in most cases (where the top metal EPC is at least as strong as Al) for interlayer thickness of only 5 nm. However, for top metals with very weak EPC such as Au, the overall value for G involves an interplay between phonon spectra overlap and coupling strength of interlayer. The EPC strength of the interlayer determines the thermal boundary conductance saturation thickness in the presence of an interlayer in all metal/dielectric systems. However, the EPC alone cannot be used as a quantity to predict the modification of thermal boundary conductance in the presence of an interlayer. This work advances the state of the art by demonstrating that relatively simple, non-atomistic models like the hybrid DMM can predict thermal boundary conductance with high accuracy, often within 10% of experimental results, offering a more efficient approach compared to traditional atomistic simulations, while still capturing the essential physics of phonon scattering and electron-phonon coupling.

CHAPTER 4: SIZE DEPENDENT ANISOTROPIC THERMAL CONDUCTIVITIES IN LAYERED MATERIALS

Understanding the size-dependent anisotropic thermal conductivities in layered materials is crucial for advancing fundamental knowledge of heat transport in nanoscale materials. Despite the progress to understand the size dependent heat transport in layered materials, significant gaps remain in both theory and experiments regarding the transition from diffusive to non-diffusive heat transport in these materials. In this study, the anisotropic thermal conductivities of layered materials are analyzed using the frequency domain thermorefectance technique on graphite, MoS₂, and hBN samples of varying thickness. The experimental data for in-plane thermal conductivity and cross-plane thermal conductivity are compared with values obtained from a computational model for further analysis and discussion. We found that both in-plane and out-of-plane thermal conductivities increases in layered materials as a function of thickness until it plateaus depending on the phonon mean free paths of the material. Our modeling suggests that changes in thermal conductivity for the out-of-plane direction is not solely determined by phonons traveling along the out-of-plane direction. Although there is a difference between our experimental results and the theoretical models, this points to the complexities of thermal transport in layered materials and suggests that the models may need further refinement to more accurately reflect the behavior at different thicknesses. Additionally, we have added a wider range of data points, especially for higher thicknesses, which were previously lacking in the literature, allowing for a more comprehensive understanding of thermal conductivity trends and filling gaps in current knowledge. The results are crucial for understanding thermal size effects in layered materials, particularly in heat-spreading applications for advanced thermal management technologies.

4.1 Introduction

In layered materials, such as graphite, hexagonal boron nitride, or transition metal dichalcogenides, the atomic bonding is much stronger within the crystalline basal planes than between the planes, where weak van der Waals forces dominate. This stark difference in bonding strength leads to highly anisotropic thermal conductivity, where heat flows much more easily in-plane compared to the cross-plane direction. For example, at room temperature, in bulk graphite, the in-plane thermal conductivity is over 300 times higher than the out-of-plane thermal conductivity, while in hBN and MoS₂ the anisotropy is around 100-fold and 50-fold respectively. This anisotropic behavior is a defining characteristic of layered materials and plays a critical role in their thermal management applications, especially in fields like nanoelectronics and thermoelectrics, where directional heat dissipation is crucial. Figure 4.1 shows the lattice structures for the materials used in this study (a) graphite (b) hBN (c) MoS₂ along with the first Brillouin zone (hexagonal) for these materials[137]. Graphite crystalizes in AB stacking while hBN and 2H-MoS₂ exhibits AA' stacking. The in-plane and out-of-plane lattice constants are given by a and c respectively.

Non-diffusive heat transport phenomenon in layered materials becomes prominent as the thickness of individual layers is reduced, especially to the nanoscale[10], [11], [13], [69], [74], [76], [77], [80]. In conventional diffusive heat transport, heat carriers, such as phonons, undergo frequent scattering events which can be effectively described by Fourier's law of heat conduction. However, in layered materials, when the layer thickness approaches or becomes smaller than the phonon mean free path, the nature of heat transport shifts from diffusive to non-diffusive or ballistic. In this regime, phonons can travel across the layer without scattering, meaning their transport is constrained more by the boundaries of the material than by internal scattering processes.

As the thickness decreases, phonons with long MFPs become more sensitive to boundary scattering, scatter more frequently, and their ability to contribute to the overall thermal conductivity diminishes. This leads to a reduction in the thermal conductivity compared to bulk materials, where long-MFP phonons contribute fully. The boundary scattering may be diffuse or specular, further complicating the heat transport behavior, as specular reflection at smooth interfaces allows phonons to retain their momentum, while diffuse scattering randomizes their direction.

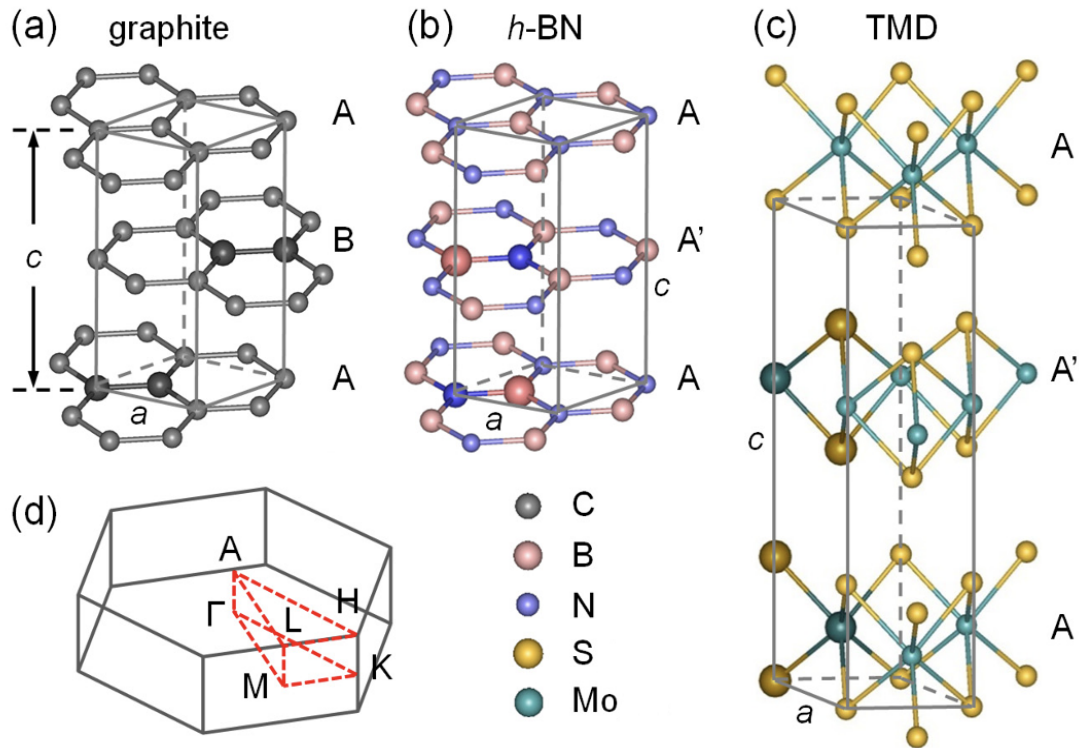


Figure 4.1: Lattice structures for the materials used in this study (a) graphite (b) hBN (c) MoS₂ along with the first Brillouin zone (hexagonal) for these materials[137]. Graphite crystallizes in AB stacking while hBN and 2H-MoS₂ exhibits AA' stacking. The in-plane and out-of-plane lattice constants are given by a and c respectively.

The interplay between layer thickness and the phonon MFP leads to size effects, where the thermal conductivity becomes dependent on the layer thickness in a manner that deviates from bulk behavior. The transition from ballistic to diffusive heat transport is often assumed to occur

when the sample size is on the order of the phonon MFP, where heat carriers begin to scatter more frequently, leading to a shift from ballistic (boundary-dominated) to diffusive (intrinsic scattering-dominated) transport. However, this transition is not as straightforward as it might seem, and the characteristic length scale at which it occurs is often inconsistently estimated in the literature. Casimir initially introduced the idea that thermal conductivity is proportional to the size of system, also known as Casimir limit[138]. In real materials, phonons exhibit a wide range of MFPs, from a few nanometers to several micrometers, depending on their frequencies and modes. The transition from ballistic to diffusive transport does not happen at a single, well-defined length scale, but over a range of sample sizes as phonons with different MFPs transition at different rates. Different materials have varying phonon dispersion relations, group velocities, and scattering mechanisms (e.g., boundary, impurity, or Umklapp scattering), which affect how and when the transition occurs. Even in materials with similar atomic structures, variations in crystal quality, defects, and boundary conditions can shift the observed MFP and transition point. Additionally, different experimental techniques (e.g., time-domain thermoreflectance, steady-state techniques) and theoretical models (Boltzmann transport equation, molecular dynamics) often report different values for the phonon MFP due to variations in how they treat phonon interactions and heat transport. This leads to discrepancies in the reported sample size where the transition is expected to occur. For example, the MFP of Si from the Debye heat capacity model is 40 nm and ~ 300 nm from modeling real phonon dispersion; however, Henry et al. using equilibrium molecular dynamics show that phonons with MFPs greater than 1 μm contributes significantly, around 40% to the total thermal conductivity[139]. Jeong et al. using the Landauer approach found that boundary scattering leads to a reduction in both the in-plane and cross-plane thermal conductivities of silicon thin films[21]. Only recent advancements in modeling have begun to fully capture the

long MFP contribution to the total thermal conductivity of Si[140]. On the other hand, experimental techniques for measuring thermal transport in silicon also have evolved significantly over the years, improving our understanding of phonon-mediated heat transport. The laser-induced transient thermal grating technique, for example, has enabled the direct observation of non-diffusive phonon-mediated transport at room temperature in silicon membranes[141]. This method has proven effective for studying thickness-dependent thermal conductivity in suspended silicon membranes, providing data that align closely with first-principles theories. This observation highlights the critical role of long-MFP phonons in heat conduction in Si.

Several models and techniques have been developed to understand and quantify how boundary effects modify the MFP and, consequently, the thermal conductivity in nanostructures. Matthiessen's rule and the suppression function are two common methods used to account for boundary effects on the mean free path in nanostructures[142]. Matthiessen's rule assumes that different scattering mechanisms, such as intrinsic scattering (due to impurities or defects) and boundary scattering, are independent of each other. It calculates the total MFP by summing the inverse of the individual MFPs for each scattering process, resulting in a simpler model. On the other hand, the suppression function, S directly incorporates the nanostructure's size and geometry, adjusting the bulk MFP with a size-dependent factor that reduces the MFP due to increased boundary scattering ($MFP_{nanostructure} = S.MFP_{bulk}$). Suppression function was initially introduced by Minnich relating phonon MFP and thermal length[143]. S is typically a function of the size of the nanostructure (e.g., geometry, size, etc.) hence the derivation of suppression function for a particular geometry is a difficult task[144]. Suppression function can be predicted using phonon BTE[145] or through simpler analytical models by simplifying the geometry of the system[144]. However, it is important to note that the BTE alone cannot directly provide the

suppression function unless it incorporates the correct physics. Most BTE models, in their standard form, do not account for all the necessary boundary effects and geometric considerations, which are essential for accurately determining S . The total phonon thermal conductivity can be expressed as $k_p = \int_0^\infty f(\Lambda_p) d\Lambda_p$, where $f(\Lambda_p)$ is the differential contribution to the thermal conductivity from phonons with MFP Λ_p and the integration is over all possible MFPs from 0 to infinity, reflecting all phonon contributions. The cumulative thermal conductivity function represents how thermal conductivity builds up as phonons with increasing MFPs are considered and it's the integral of $f(\Lambda_p)$ from 0 to Λ_p , representing the contribution to thermal conductivity from all phonons with MFPs up to Λ_p :

$$k_{cumulative}(\Lambda_p) = \int_0^{\Lambda_p} f(\Lambda') d\Lambda' \quad (4.1)$$

When calculating the thermal conductivity in a system with finite size L , the suppression function $S(\Lambda, L)$ is used to adjust the contribution of each phonon mode to account for boundary scattering. The thermal conductivity of a finite-size film can be calculated as:

$$k_p(L) = \int_0^\infty S(\Lambda_p, L) f(\Lambda_p) d\Lambda_p \quad (4.2)$$

The main advantage of the suppression function over Matthiessen's rule is that it provides a more comprehensive and material-specific description of boundary effects. It accounts for the fact that the suppression of thermal conductivity is not uniform across all phonon modes but varies with the phonon's mean free path and the scale of the system. In contrast, Matthiessen's rule treats boundary scattering as just one of many independent scattering processes, often overlooking the more intricate details of phonon transport in low dimensions or crystal anisotropy[146]. On the other hand, it offers simplicity, efficiency, and widespread applicability in systems with multiple

scattering mechanisms. While the exact nature of the interactions between different scattering processes, such as boundary scattering and phonon-phonon interactions, may not be fully known, Matthiessen's rule provides a practical approach by assuming these mechanisms are approximately independent. This assumption is commonly made in many materials systems and serves as a reasonable starting point when more detailed information about the system is unavailable. Additionally, Matthiessen's rule offers computational efficiency, making it ideal for quick estimates of thermal conductivity in complex systems.

Most of the available literature on the variation of thermal conductivity in anisotropic semiconductors to date focuses on how the conductivity changes with the lateral size in the in-plane direction and with the thickness in the out-of-plane direction. So far, no work has focused on the directional dependence of phonons in modifying anisotropic conductivities, i.e. does the substrate thickness matter for the in-plane thermal transport? Casimir's original work applied to nanowires indeed considered a similar scenario, where the nanowire diameter affected the transport along the wire length. Additionally, recent studies on thermal grating measurements in silicon membranes demonstrate variations in in-plane thermal transport as a function of thickness, emphasizing the significance of dimensional effects on thermal conductivity[141]. In our work, we try to understand the variation in thermal conductivities in some of the common anisotropic semiconductors as a function of the thickness for both the in-plane and out-of-plane directions, and theoretically, we will also explore how phonons moving in the out-of-plane direction affect the anisotropic thermal conductivity. This is crucial in fundamentally understanding the physics of low-dimensional materials.

In this work, to include the effect of thickness, we introduced a directional boundary scattering term (Eq. 4.4) and consider the total scattering rate as the summation of different

scattering processes according to Matthiessen's rule (Eq. 2.18). The boundary scattering rate can be expressed as [10], [147]:

$$\frac{1}{\tau_B} = \frac{|v|}{L} (1 - p) \quad (4.3)$$

where, $|v| = \sqrt{v_x^2 + v_y^2 + v_z^2}$ is the magnitude of phonon group velocity vector, L is the thickness of the film and p is the specularity parameter. This formulation treats the scattering isotropically, as the film thickness L applies regardless of the direction of propagation of the phonons. The specularity parameter, which represents the probability of a phonon's specular reflection at the boundaries, takes a value of $p = 1$ for purely specular scattering and $p = 0$ in the diffusive limit (Casimir limit), where phonons experience diffuse scattering. It should be noted that to determine the probability of diffusive or specular scattering, other comprehensive forms of specularity parameter exists, such as Ziman's specularity parameter, $p = \exp(-16\pi^2\delta^2/\lambda^2)$, where δ is the surface roughness and λ is the phonon wavelength [147]. Ziman's approach improves upon simpler models that assume a constant p by incorporating the momentum dependence of scattering, but it still fails to account for the incident angle dependence of phonon surface scattering [146]. Here we do not consider Ziman's specularity, as at room temperature $\frac{\delta}{\lambda} \sim 0$. To understand the direction dependence of phonons traveling in the out-of-plane direction in modifying anisotropic conductivities, we added a direction dependence to the boundary scattering term.

Assuming z-axis is along the direction perpendicular to the plane of layered materials, the distance traveled by a phonon ballistically before getting scattered is $L/\cos\theta$ where, L is the thickness of the film, θ is the angle between the phonon wave vector and z-axis. In this work, assuming a fully diffusive scattering ($p = 0$) we introduce a modified boundary scattering rate, which is given by:

$$\frac{1}{\tau_B} = \frac{|v_z|}{L}, \quad (4.4)$$

where, v_z is the magnitude of phonon group velocity in z-axis. The purely diffusive ($p = 0$) assumption is justified by the fact that our experiments are conducted at room temperature and the interfaces under consideration are not atomically smooth, making specular reflection unlikely. Under these conditions, phonon reflections at the interface are expected to be random, rather than mirror-like, hence the use of the fully diffusive limit. It should be noted that another common definition of boundary scattering rate in literature is $\frac{1}{\tau_B} = \frac{v}{L/2}$ where the factor of 2 reflects the average normal distance from a random point in the layer to a boundary[148]. While both formulations serve as rough approximations, they both are widely used for modeling boundary scattering and do not alter the fundamental conceptual framework of the scattering process itself. In other cases, a form factor is introduced to account for aspects such as material shape and specularity, and under this definition, Eq. 4.4 can be obtained assuming a specularity parameter $p = 0.5$. Thermal conductivities obtained without the directional dependence in the work are labelled as ‘*isotropic model*’ and the thermal conductivity with directional dependence is labeled as ‘*anisotropic model*’. In other words, the isotropic model assumes that phonons scatter in all directions in the same way or there’s no preferred scattering direction. The anisotropic model, on the other hand, considers that phonons scatter differently depending on the direction, just like phonons moving in the out-of-plane direction travel with a different group velocity differently than those moving in the in-plane direction. For films thinner than the bulk mean free path, boundary scattering will play a role, meaning the phonons are limited by the film’s thickness. This directional boundary scattering leads to a suppression of the phonon contributions to the film’s thermal conductivity. Phonons with mean free paths much longer than the film thickness are strongly

suppressed, while phonons with shorter mean free paths are less affected by the boundaries.

4.2 Computational Modeling

The non-Fourier phonon heat transport in the layered materials can be modeled using Boltzmann transport equations as phonons obey Bose-Einstein statistics. ShengBTE (open-source software) is used to solve the BTE using the iterative approach [75], with the phonon thermal conductivity expressed using Eq. 2.19.

The essential input files in ShengBTE for scattering rate calculations are the harmonic (second-order) and anharmonic (third-order) interatomic force constants (IFCs). The second-order terms correspond to the harmonic approximation, where atomic interactions are modeled as linear springs, while the third-order terms account for anharmonic effects, which are important for capturing phonon-phonon interactions and nonlinear behaviors. The IFCs are obtained by density functional theory (DFT)². For hBN and MoS₂, calculations were performed using the Quantum Espresso package[149] with a projected augmented wave (PAW) pseudopotential and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Electronic wave functions were expanded using plane waves with an energy cutoff of 110 Ry (hBN) and 80 Ry (MoS₂). A fully converged k-point mesh of $12 \times 12 \times 3$ was employed for Brillouin zone integration. The convergence thresholds for geometry relaxation were set to 10^{-5} a.u. and 10^{-3} Ry/a.u. for forces. Harmonic (second-order) interatomic force constants (IFCs) for each structure were then obtained using the finite displacement method as implemented by the Phonopy package[150] on a $6 \times 6 \times 3$ supercell for hBN and $5 \times 5 \times 2$ supercell for MoS₂. Cubic anharmonic IFCs were calculated to determine phonon lifetimes, constrained by three-phonon scattering processes. The harmonic and

² The DFT calculations were courtesy of Dr. Armin Taheri (hBN) and Dr. Simone Pisana (MoS₂).

anharmonic force constants for graphite were obtained directly from the almaBTE database[132]. To ensure convergence of the thermal conductivities we utilized a q-mesh size of $22 \times 22 \times 13$. van der Waals interactions were included in the DFT calculations for MoS₂ using the Grimme-D3 method, but were not included for the hBN and graphite calculations. Following a convergence test, the thirdorder.py script of the ShengBTE package was used to generate supercells of $5 \times 5 \times 3$ for hBN and $4 \times 4 \times 3$ for MoS₂, with interatomic interaction cutoffs set to the 6th nearest neighbors for hBN and 3rd nearest neighbors for MoS₂. The lattice constants obtained this way are $a=2.478 \text{ \AA}$, $c=6.435 \text{ \AA}$ for hBN and $a=3.169 \text{ \AA}$, $c=12.51 \text{ \AA}$ for MoS₂. These are within 0.9% and 3.4% (for a and c axes for hBN) and 0.6% and 1.7% (for a and c axes for MoS₂) of experimental data[151], [152]. Thermal conductivity calculations were performed via ShengBTE using the following converged q-point meshes: $26 \times 26 \times 14$ for hBN and $14 \times 14 \times 6$ for MoS₂.

4.3 Experiment and Characterization

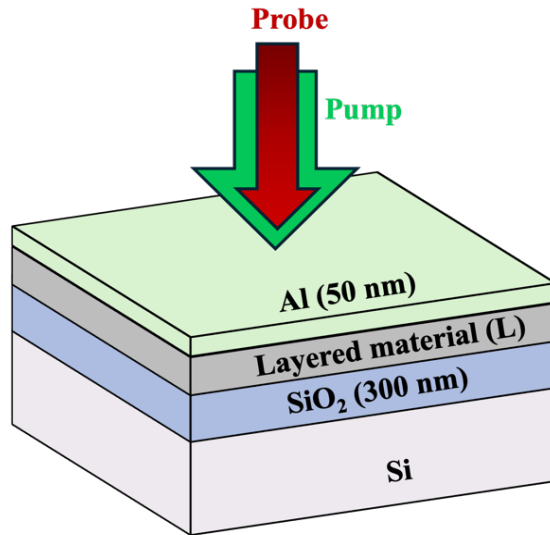


Figure 4.2: Schematic of the samples in this study. The layered materials used are graphite, MoS₂ and hBN varying thickness L.

Samples for this study were prepared by mechanically exfoliating the layered crystals (purchased from 2D semiconductors - graphite, MoS₂, and h-BN) using low-temperature thermal release tape onto Si wafer pre-deposited with 300 nm thermally grown a-SiO₂. Subsequently, a ~45 nm Aluminum layer was deposited onto the fresh surface using electron-beam deposition. The schematic of the sample in this study is shown in Figure 4.2. The layered materials used are graphite, MoS₂ and hBN with varying thickness L.

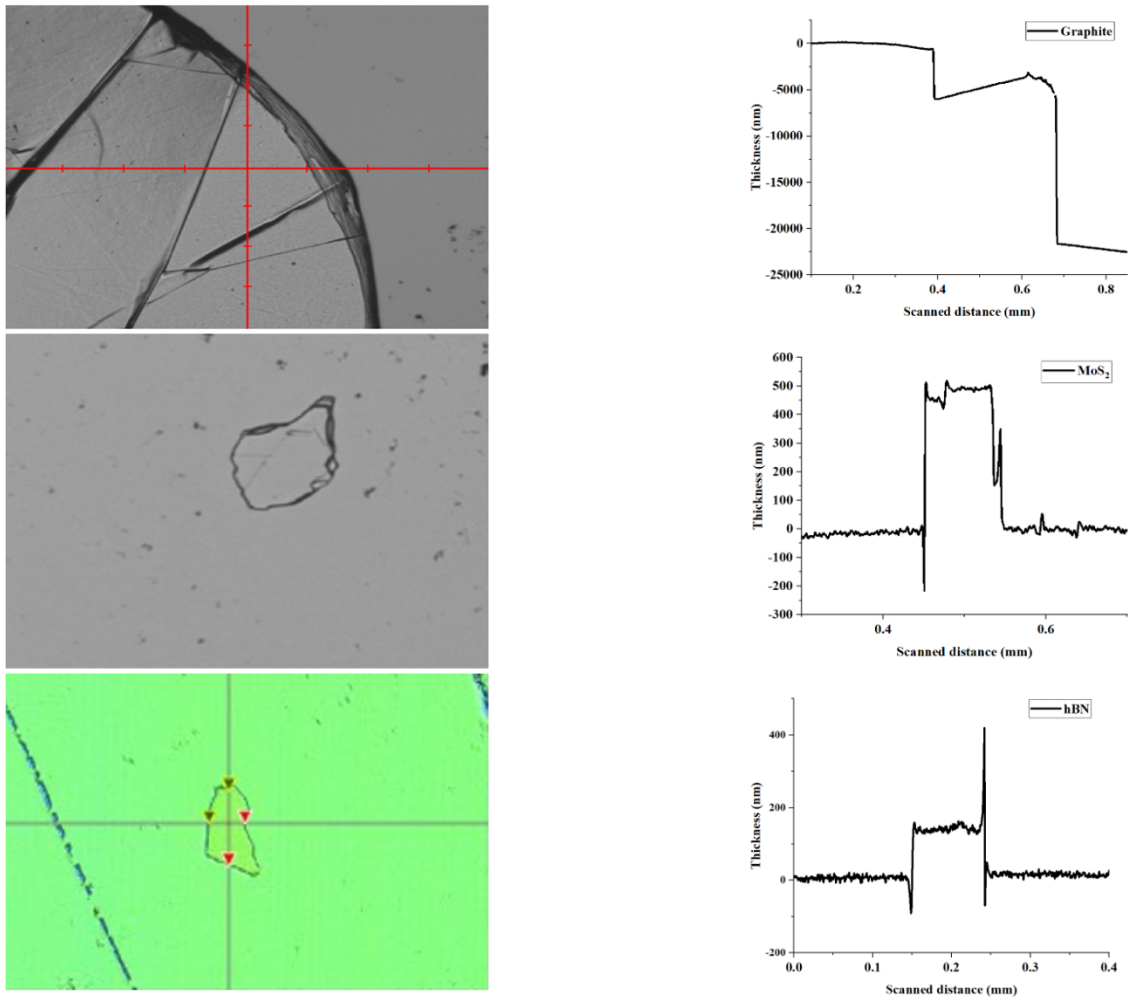


Figure 4.3: Optical Microscope image of flakes of (a) Graphite (b) MoS₂ (c) hBN and the corresponding thickness of the flakes measured using optical profilometry for (d) Graphite (e) MoS₂ (f) hBN.

The thickness of the semiconductors was characterized using an optical profilometer (Bruker Contour GT-K 3D) with measurements for graphite, MoS₂, and hBN flakes shown along with their optical microscope images in Figure 4.3. Figure 4.3 shows the optical Microscope image of flakes of (a) Graphite (b) MoS₂ (c) hBN and the corresponding thickness of the flakes measured using optical profilometry for (d) Graphite (e) MoS₂ (f) hBN. The lateral sizes of the exfoliated flakes ranged from 50 μm to 200 μm . The thickness of the metallic layer was determined using picosecond acoustics technique as described in section 2.3.3.2. The exfoliated flakes were characterized using Raman spectroscopy (Bruker Senterra dispersive Raman microscope) at 532 nm using a 50X objective for a power of 20 mW. Figure 4.4 shows the Raman spectra for (a) MoS₂ and (b) graphite. For graphite (red curve), the G-band and 2D-band are observed at 1595 cm^{-1} and 2732 cm^{-1} respectively, agreeing with previous reports[153]. For MoS₂ (blue curve), the in-plane and out-of-plane peaks were observed at 393 cm^{-1} and 418 cm^{-1} respectively. The difference between the peaks $\sim 25 \text{ cm}^{-1}$ confirms the presence of bulk-MoS₂[153]. For hBN, at the excited wavelength, the Raman peaks were non-resonant and hence showed weaker spectra. To characterize the thermal properties, we used frequency domain thermoreflectance technique and the details of the setup have been previously described in Chapter 2. The pump (515 nm) and the probe (785 nm) beam were focussed on to the sample using a 10x objective lens with a $1/e^2$ radii of 5.8 μm and 2.5 μm respectively. To obtain the anisotropic thermal conductivity, the experimentally measured thermal phase response of the sample obtained was fitted to a thermal transport model based on the solution of the heat diffusion equation in cylindrical symmetry for layered anisotropic media.

The in-plane thermal conductivity of the metallic layers was calculated using the Weidmann-Franz law by measuring the electrical conductivity using four-point probe technique.

The thermal conductivity of the Si substrate and the volumetric heat capacities of the layers were taken from literature. The thermal boundary conductance between Al/graphite, Al/hBN and Al/MoS₂ were fixed at 50, 40 and 15 MW/m²K respectively[11], [12], [69], [154]. The thermal boundary conductance between a-SiO₂/Si was obtained from fitting for conductance in a sample without the layered material and was fixed at ~20 MW/m²K. The in-plane and out-of-plane thermal conductivities of layered materials were obtained by fitting for the thermal phase of the sample. Table 4.1 shows the various thermophysical properties of the samples in this study.

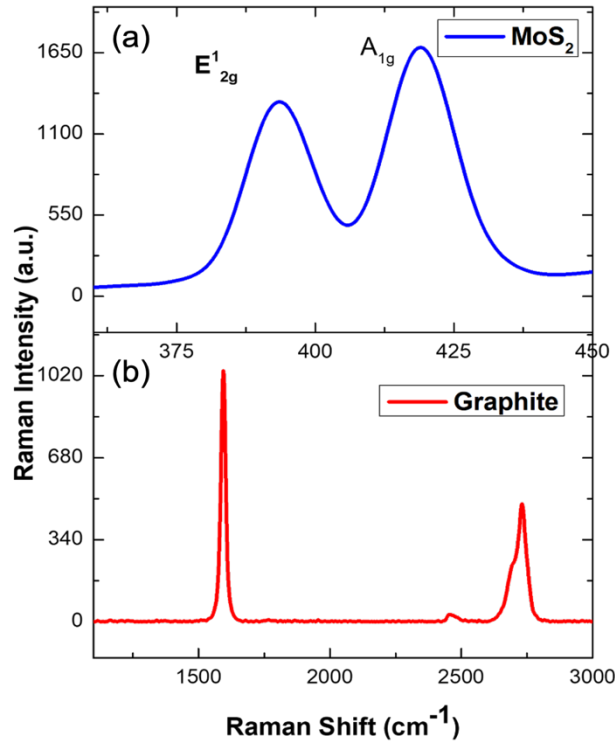


Figure 4.4: Raman spectra for (a) MoS₂ and (b) graphite.

Table 4.1: Thermophysical properties of the samples in this study.

	k_z (MW/m ² K)	k_r (MW/m ² K)	C (MW/m ² K)	L (nm)
Al	Same as k_r	~70-130	2.42	46

Graphite	Fitted	Fitted	1.62	L
MoS ₂	Fitted	Fitted	1.89	L
hBN	Fitted	Fitted	1.85	L
a-SiO ₂	1.4	1.4	1.59	300
Si	145	145	1.64	Semi-infinite

4.4 Results and Discussion

4.4.1 Graphite

Figure 4.5(a) shows the in-plane thermal conductivity as a function of thickness for graphite. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles represent the experimental data points in the work and the yellow triangles, and the dark-cyan triangle represent the experiments by Sadeghi et al[78] and Zhou et al[13]. The brown line represents the BTE calculation by Minnich et al[77]. Green and Purple dashed lines represent the calculations by Pop et al.[137] and Fugallo et al.[76] as a function of *lateral size* of the graphite flake. The figure shows that the in-plane conductivity increases and gradually plateaus as thickness increases (in-plane conductivity reaches 83% of bulk conductivity (~ 2000 W/mK) at 450 nm.) in both experiment (blue symbols) and theoretical predictions (red and black curves). The black curve (isotropic model) underestimates the experimental values at small thicknesses but aligns well at intermediate and large thicknesses, suggesting that it may have overestimated boundary scattering effects by assuming phonons contribute equally in all directions at smaller thicknesses. The red curve (anisotropic model), on the other hand, consistently overestimates thermal conductivity, particularly at smaller thicknesses, indicating that it may have underestimated the boundary scattering effects. The comparison of these models suggests that in addition to the contribution of out-of-plane phonons, the phonons moving in other directions also

contributes to the in-plane thermal conductivity, but in a non-trivial way. In the anisotropic model, since only the normal component (along the thickness direction) of the MFP is responsible for boundary scattering, phonons with MFPs oriented along the in-plane are not affected much by the boundary. Due to the small MFP in the out-of-plane direction or the thickness direction[77], the in-plane conductivity stays elevated even for very thin films as seen in the anisotropic model in Figure 4.5(a). The experimental data (blue points) fall between the two models, suggesting that the actual phonon transport behavior is not just only determined by phonons in the out-of-plane direction. Additionally, adjusting the specularity parameter influences the boundary scattering rate, effectively shifting the thermal conductivity curves in the x-axis. A higher specularity parameter (e.g., $p = 0.5$) reduces boundary scattering by allowing more specular reflections, leading to a delayed suppression of thermal conductivity as the thickness decreases. At lower thicknesses (below 150 nm) Minnich's model shows a better agreement with data. Minnich used generalized Fuchs-Sondheimer theory with BTE solution under relaxation time approach to get the in-plane thermal conductivity of graphite as[77]:

$$k_r(L) = \sum_{q>0} k_{in,q} S(\xi) \quad (4.5)$$

where L is the thickness of graphite, $k_{in,q}$ is the intrinsic thermal conductivity of graphite, $\xi = L/\Lambda_c$ is the non-dimensional thickness where, Λ_c is the component of MFP along c-axis (out-of-plane) and $S(\xi)$ is the boundary scattering function that describes the boundary scattering-induced decrease in thermal conductivity. This again points to the need for refined models that better account for both in-plane and out-of-plane phonon contributions and boundary scattering.

Figure 4.5(b) shows the out-of-plane thermal conductivity as a function of thickness for graphite. The red and black curves represent the anisotropic and isotropic model in this work

respectively. The blue triangles represent the experimental data points in the work and the yellow triangles, pink triangle and the cyan triangle represent the experiments by Zhang et al.[75], Zheng et al.[80], and Wei et al.[155]. The brown line represents the BTE calculation by Minnich et al.[77]. Green and Purple lines represent the calculations by Pop et al.[137] and Fugallo et al.[76]. The figure shows the out-of-plane TC reaches 85% of the bulk TC (~ 6.5 W/mK) at 450 nm. Here, the different theoretical models including ours consistently overestimates thermal conductivity as a function of thickness. This could be due to the presence of stacking faults in the sample which introduces additional scattering mechanisms in the experiment and depending on the sample quality, different experiments show different trends.

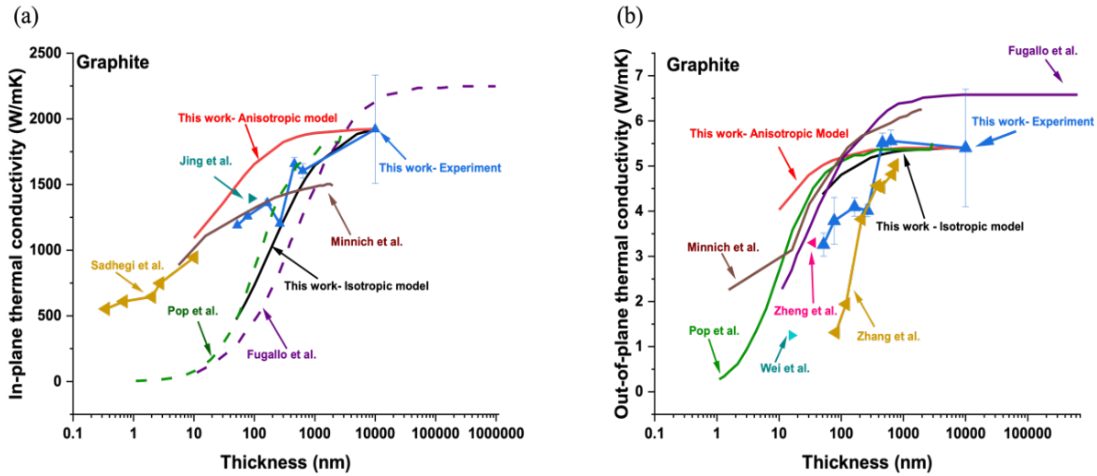


Figure 4.5: (a) In-plane thermal conductivity as a function of thickness of graphite. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles represent the experimental data points in the work and the yellow triangles, and the dark-cyan triangle represent the experiments by Sadeghi et al.[78] and Zhou et al.[13]. The brown line represents the BTE calculation by Minnich et al.[77]. Green and purple dashed lines represent the calculations by Pop et al.[137] and Fugallo et al.[76] as a function of *lateral size* of the graphite flake. (b) Out-of-plane thermal conductivity as a function of thickness of graphite. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles represent the experimental data points in the work and the yellow triangles, pink triangle and the cyan triangle represent the experiments by Zhang et al.[75], Zheng et al.[80], and Wei et al.[155]. The brown line represents the BTE calculation by Minnich et al. [77]. Green and Purple lines represent the calculations by Pop et al.[137] and Fugallo et al.[76].

4.4.2 hBN

Figure 4.6(a) shows the in-plane thermal conductivity as a function of thickness of hBN. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles represent the experimental data points. The experimental data matches with the isotropic model implying that the effect of directional dependence in boundary scattering is negligible. In the isotropic model, all directions of phonon motion are treated equally, meaning there is no preferential direction of heat transport. This implies that in-plane phonons dominate the thermal transport, and the effect of out-of-plane phonons (which would be more prominent in the anisotropic model) may be negligible or less significant in hBN.

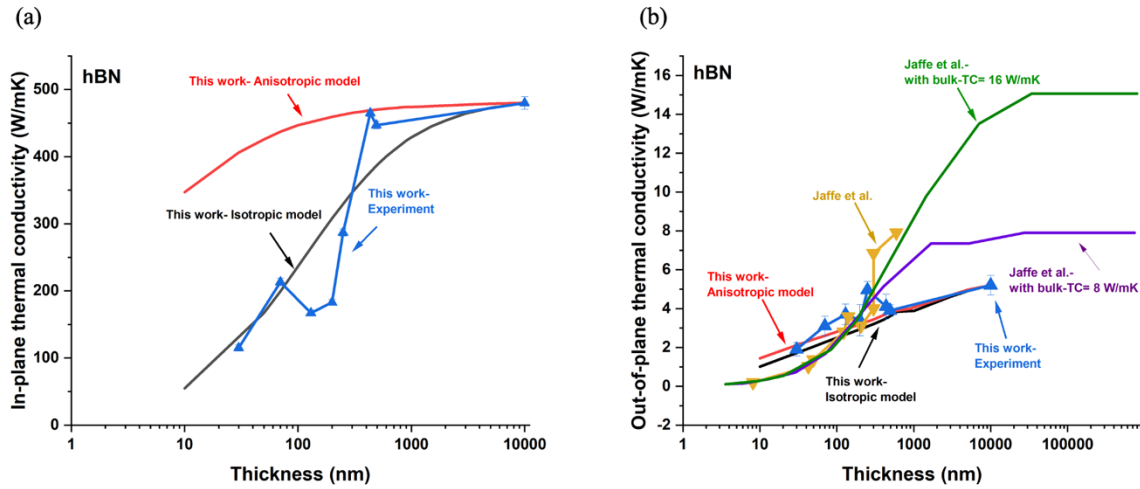


Figure 4.6: (a) In-plane thermal conductivity as a function of thickness of hBN. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles represent the experimental data points in the work. (b) Out-of-plane thermal conductivity as a function of thickness of hBN. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles represent the experimental data points in the work. The yellow triangles represent the experiments by Jaffe et al[83]. The purple and the green lines represent the phonon MFP contribution fits to the data assuming a maximum bulk thermal conductivity of 8 W/mK and 16 W/mK respectively[83].

Figure 4.6(b) shows the out-of-plane thermal conductivity as a function of thickness of hBN. The red and black curves represent the anisotropic and isotropic model in this work

respectively. The blue triangles represent the experimental data points in the work. The yellow triangles represent the experiments by Jaffe et al[83]. The purple and the green lines represent the phonon MFP contribution fits to the data assuming a maximum bulk thermal conductivity of 8 W/mK and 16 W/mK respectively[83]. Here, the experiment agrees with both the models. When the experimental data matches both the isotropic and anisotropic models, it suggests that the phonons in all directions contribute equally to thermal transport, but their velocities are almost entirely aligned with the z-axis, causing the system to behave like an isotropic material in this case. Jaffe et al. predicted and measured the out-of-plane conductivity as a function of hBN thickness[83]. Similar to Minnich[77], they used a suppression function to account for boundary scattering. At lower thicknesses experiments and theory agree with each other; but at higher thicknesses they deviate significantly, reporting very large values of out-of-plane thermal conductivity[83].

4.4.3 MoS₂

Figure 4.7(a) shows the in-plane thermal conductivity as a function of thickness of MoS₂. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles and the yellow triangles represent the experimental data points in the work for synthetic crystal-MoS₂ and natural crystal-MoS₂. Green and purple dashed lines represent the calculations by Pop et al.[137] and Lindroth et al.[10] as a function of *lateral size* of the MoS₂ flake. Similar to graphite, the experimental data falls between the isotropic and anisotropic models, indicating that both in-plane and out-of-plane phonons contribute to thermal conductivity. In-plane phonons are partially influenced by boundary scattering, while out-of-plane phonons have a greater impact. This intermediate behavior suggests that the models need refinement to more accurately account for boundary scattering and phonon contributions in both directions.

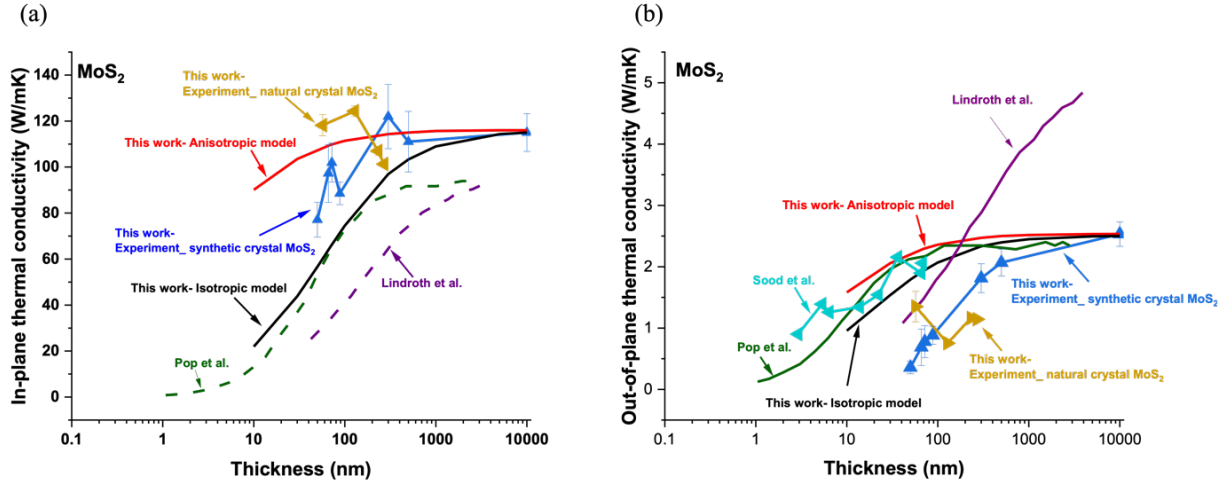


Figure 4.7: (a) In-plane thermal conductivity as a function of thickness of MoS₂. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles and the yellow triangles represent the experimental data points in the work for synthetic crystal-MoS₂ and natural crystal-MoS₂. Green and Purple dashed lines represent the calculations by Pop et al.[137] and Lindroth et al.[10] as a function of lateral size of the MoS₂ flake. (b) Out-of-plane thermal conductivity as a function of thickness of MoS₂. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles and the yellow triangles represent the experimental data points in the work for synthetic crystal-MoS₂ and natural crystal-MoS₂. Green and Purple lines represent the calculations by Pop et al.[137] and Lindroth et al.[10].

Figure 4.7(b) shows the out-of-plane thermal conductivity as a function of thickness of MoS₂. The red and black curves represent the anisotropic and isotropic model in this work respectively. The blue triangles and the yellow triangles represent the experimental data points in the work for synthetic crystal-MoS₂ and natural crystal-MoS₂. Green and Purple lines represent the calculations by Pop et al.[137] and Lindroth et al.[10]. Similar to graphite, in the out-of-plane direction, thermal conductivity is more suppressed in theory than in practice indicating that sample faults could introduce additional scattering mechanisms.

There is a marked inconsistency in experiments regarding the out-of-plane thermal conductivity evolution as a function of film thickness in MoS₂. As shown in Figure 4.8, Jeong et al.[82] observed no thickness dependence while Sood et al.[11] observed an increase in thermal

conductivity as a function of thickness. We analyzed the thickness dependence of synthetic crystal-MoS₂ and compared it with the natural crystal-MoS₂. Figure 4.7 shows the measured thermal conductivities in the (a) in-plane and (b) out-of-plane directions in synthetic-MoS₂ and natural-MoS₂ crystals. The figure shows that thermal conductivities do not show any thickness dependence in natural-MoS₂ crystals. These inconsistencies can be reconciled by noting that natural crystals have markedly smaller crystallite sizes, which can dominate the scattering. The experimentally measured bulk thermal conductivities of the synthetic crystal-MoS₂ were 2.5 ± 0.3 W/mK and 114 ± 8 W/mK in the out-of-plane and in-plane directions, respectively.

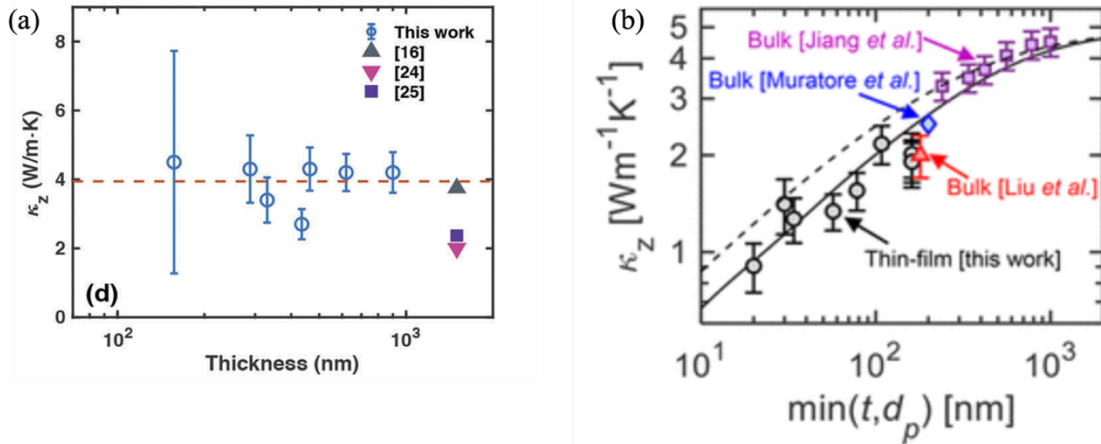


Figure 4.8: Comparison of out-of-plane MoS₂ as a function of film thickness as reported by the works of (a) Jeong et al.[82] © copyright [2019], reprinted by permission of Informa UK Limited, trading as Taylor & Francis Group, (b) Sood et al.[11]. Reprinted with permission from Nano Lett. 2019, 19, 4, 2434–2442. Copyright 2019 American Chemical Society.

4.5 Conclusion

In conclusion, our study reveals that both in-plane and out-of-plane thermal conductivities in layered materials increase with thickness before plateauing, which is influenced by the phonon mean free paths. Our modeling highlights that changes in out-of-plane thermal conductivity are not solely governed by phonons traveling in the out-of-plane direction. The discrepancy between

experimental results and theoretical models points to the complexities of thermal transport in layered materials, suggesting that current models may require further refinement. Additionally, by incorporating a broader range of data, particularly for thicker materials, our work provides a more comprehensive understanding of thermal conductivity trends and addresses gaps in existing literature.

CHAPTER 5: MODIFICATION OF HEAT TRANSPORT AT METAL-ANISOTROPIC SEMICONDUCTORS ON ADDITION OF ULTRATHIN INTERLAYERS

This study extends the work from Chapter 3, where the thermal boundary conductance at metal-isotropic semiconductor interfaces was modified by adding thin metallic interlayers. In this work, we focus on predicting and validating the modification of thermal boundary conductance at metal/layered material interfaces through the insertion of thin metallic interlayers. Given that the thickness of layered materials significantly affects their thermal conductivity, we build on the work in Chapter 4 showing that flakes thicker than approximately 10 μm exhibit bulk-like thermal conductivity, which allows us to maintain a constant thermal conductivity independent of thickness and precisely isolate the effects of the interface modification for accurate predictions and validations of the thermal boundary conductance at these interfaces.

To accurately model these effects, we apply our hybrid diffuse mismatch model that predicts TBC modifications at metal/anisotropic semiconductor interfaces. We validate these predictions with experimental measurements, ensuring the model's reliability and accuracy. Our results show that inserting thin metallic interlayers can alter interfacial thermal transport depending on the phonon properties of the materials and the electron-phonon coupling constants of the metal layers. We also find that a simplified isotropic DMM is sufficient for predicting TBC modifications, offering a more efficient alternative to the complex anisotropic DMM. Furthermore, the study emphasizes the importance of considering full phonon dispersion, the role of low-lying optical phonons, and the strength of electron-phonon coupling in improving traditional models of thermal boundary conductance. By integrating these factors, we demonstrate that conventional models can be significantly enhanced to provide more accurate predictions of heat flow at metal-layered

material interfaces. This work contributes to improving thermal management in nanoscale devices, where effective heat dissipation is essential for the performance of layered material-based electronics.

5.1 Introduction

In recent years, layered materials such as transition metal dichalcogenides, and graphite have gained significant attention for applications in nanoelectronics, optoelectronics, and thermoelectrics[156], [157], [158]. These materials are characterized by exceptional electronic, thermal, optical, and mechanical properties, which are strongly influenced by the number of layers and their structural arrangement. Their thermal transport behavior is anisotropic, with significantly higher thermal conductivity in-plane (within the layers) compared to the out-of-plane (perpendicular) direction. This anisotropy enables precise heat management, allowing for controlled heat flow in specific directions, which is crucial for effective heat dissipation, such as in heat spreaders, to maintain performance and longevity in high-density electronic systems[8]. However, while the in-plane thermal conductivity of these materials is often very high, the thermal transport properties across the interfaces between metal and layered materials ultimately determine overall heat dissipation. The interfacial thermal conductance which governs the rate of heat transfer at metal/layered material interfaces plays a critical role in the thermal management capabilities of these materials. Understanding and controlling the boundary conductance in metal/layered material structures is therefore critical for optimizing thermal performance in advanced electronic and optoelectronic devices.

One of the challenges in optimizing heat management in metal/layered material structures is typically the low interfacial thermal conductance observed at the metal/layered material interfaces. Specifically, the TBC between Al/graphite is reported to be around 35-60 MW/m²K,

while the Al/MoS₂ interface has a lower value of 25-40 MW/m²K[11], [34], [145], [159]. These low TBC values are primarily due to the mismatch in phonon spectra between metals and layered materials. The low thermal conductance at the interface impedes efficient heat flow, leading to thermal bottlenecks that can limit the overall thermal performance of devices, especially in densely packed electronic systems. This makes it crucial to develop strategies for enhancing the interfacial thermal conductance, such as through surface treatment[160], interfacial engineering, or using intermediate materials to better match the thermal properties of the two interfaces[62]. In this work, we aim to enhance the interfacial thermal conductance between metal and layered materials by introducing intermediate materials that can bridge the phonon transport. By selecting suitable intermediate materials, it may be possible to facilitate more efficient phonon transmission across the interface, thereby improving heat dissipation. Through careful material selection, we hope to achieve a significant increase in TBC, which would be crucial for advancing thermal management in high-performance electronic and optoelectronic devices.

To achieve this, accurate prediction of the thermal boundary conductance is essential, and the diffuse mismatch model provides a robust framework for estimating TBC between metals and layered materials. Schmidt et al. applied the diffuse mismatch model under the Debye approximation to predict the thermal boundary conductance across a series of metal/graphite interfaces[12]. Their study focused on both the metal/c-axis and metal/a-axis graphite configurations. While the DMM underpredicted the TBC for the metal/c-axis graphite interface, it overpredicted the values for the metal/a-axis graphite interface. To improve the prediction, Schmidt et al. modified the model by replacing the c-axis group velocity with a weighted-average group velocity that accounts for the fraction of phonons traveling in the a-axis direction. This adjustment again led to an overprediction of TBC at metal/graphite interfaces. This highlights the

challenges in accurately modeling thermal transport at such interfaces, particularly when considering the anisotropic nature of graphite's thermal properties and the complexity of phonon scattering. Subsequently, Liu et al. extended the DMM framework by employing a mode-to-mode comparison to predict the thermal boundary conductance across a series of metal/graphite and metal/MoS₂ interfaces[161]. Unlike traditional DMM approaches that rely on simplified phonon spectra, their method involved a mode-to-mode comparison, which directly analyzes the phonon modes in material A and determines which ones are transmitted across the interface into material B. While this approach improves upon the standard DMM by incorporating full phonon dispersion, it tends to overpredict the TBC values. For example, their model predicts the TBC for Al/graphite and Cr/graphite interfaces to be 93 MW/m²K and 89 MW/m²K, respectively[161]. Similarly, for Al/MoS₂ and Cr/MoS₂, the predicted values are 56 MW/m²K and 49 MW/m²K[161]. Subsequently, the same group predicted the TBC between above materials using the same mode-to-mode comparison approach but by decreasing the frequency interval while matching the phonon frequencies in two materials[159]. The predicted TBC for Al/graphite, Cr/graphite, Al/MoS₂ and Cr/MoS₂ interfaces were 77 MW/m²K, 77 MW/m²K, 48 MW/m²K and 39 MW/m²K respectively[159]. These overpredictions highlight the continued challenge of accurately modeling the interfacial thermal conductance.

In this work, we aim to extend the DMM framework by examining the role of electron-phonon coupling, anisotropy, optical phonons, and inelastic scattering, which have been overlooked in previous works, to more accurately predict the thermal boundary conductance at metal/layered material interfaces. Additionally, we consider the presence of an interlayer between the metal and the layered material, which can further influence thermal transport. By accounting for these factors, we aim to improve the accuracy of TBC predictions, addressing the limitations

of traditional models and providing a more comprehensive understanding of heat flow at these complex interfaces. Table 5.1 shows the thermophysical properties of materials of interest in this work.

Table 5.1: Thermophysical properties of materials of interest in this work. θ_D is the Debye temperature, ν_L , ν_T , ν_A and $\nu_{optical}$ are highest phonon frequencies for the longitudinal acoustic modes, two transverse acoustic modes, polarization-averaged modes and optical modes, respectively. g is the volumetric electron-phonon coupling constant.

Top Metal	Interlayer	Substrate
Al $\theta_D = 428$ K[115] $\nu_L = 9.6$ THz [116] $\nu_T = 5.7$ THz [116] $\nu_A = 7$ THz $g = 0.24 \times 10^{18}$ W/(m³·K)[115]	Cu $\theta_D = 343$ K[162] $\nu_L = 7.5$ THz[163] $\nu_T = 3.5$ THz[163] $\nu_A = 4.8$ THz $g = 0.1 \times 10^{18}$ W/(m³·K)[162]	Graphite $\theta_D = 1575$ K [164] $\nu_L = 2.88$ THz $\nu_T = 0.8$ THz $\nu_{quasi-optical} = 1.2$THz, 4 THz $\nu_A = 1.8$ THz $\nu_{optical} = 27$ THz
Au $\theta_D = 165$ K $\nu_L = 4.6$ THz [119] $\nu_T = 2.8$ THz [119] $\nu_A = 3.4$ THz $g = 0.023 \times 10^{18}$ W/(m³·K)[115]	Ti $\theta_D = 380$ K[165] $\nu_L = 5.9$ THz $\nu_T = 3.1$ THz $\nu_A = 4$ THz $g = 1.3 \times 10^{18}$ W/(m³·K)[115]	hBN $\theta_D = 1500$ K [164] $\nu_L = 2.7$ THz $\nu_T = 1.21$ THz $\nu_{quasi-optical} = 1$THz, 4 THz $\nu_A = 2$ THz $\nu_{optical} = 27$ THz
	Ni $\theta_D = 450$ K[115] $\nu_L = 9.1$ THz [125] $\nu_T = 4.5$ THz [125] $\nu_A = 6$ THz $g = 0.36 \times 10^{18}$ W/(m³·K)[115]	MoS₂ $\theta_D = 260$ K-320 K $\nu_L = 1.2$ THz $\nu_T = 0.07$ THz $\nu_{quasi-optical} = 1.2$THz, 1.75 THz $\nu_A = 0.92$ THz $\nu_{optical} = 27$ THz

5.2 Predicting G at metal-interlayer-anisotropic semiconductors

To understand the heat transport modification in the presence of an interlayer, we are using the previously developed thermal model for metal-interlayer-isotropic semiconductors as shown in Figure 3.1. Two parallel heat transport channels are included in the overall interfacial

conductance. The thermal conductance that results from the first electron-phonon energy exchange ($G_{ep,1}$) in the top metal layer and the subsequent phonon-phonon energy transfer ($G_{pp,1}$) between phonons in the substrate and phonons in the top metal layer is described by Pathway 1 (Eq. 3.2). Here, we assume that phonons with wavelengths longer than the interlayer thickness can directly tunnel to the substrate and as the interlayer thickness increases, the phonon flux reduces due to the reduction in phonon flux contribution from the long wavelength phonons. We use an interlayer with thickness 10 nm in this work hence the contribution from pathway 1 is negligible. Pathway 2 involves energy transfer between electrons in the top metal layer and the metallic interlayer (G_{ee}), consequently allowing the interlayer electrons to transmit their energy to its lattice ($G_{ep,2}$). Depending on the interlayer's electron-phonon coupling constant and the system's time-dependent temperature dynamics, heat from the interlayer may then move to the substrate ($G_{pp,2}$) or return to the top metal (G_b). Since this back transfer mechanism (G_b) is only significant for time scales smaller than the ones we examine in the TDTR response (<10 ps), back-propagation can be disregarded. Pathway 2 can be mathematically expressed using Eq. 3.1.

To understand the contribution due to the anisotropy of the substrate, we modeled the interlayer-substrate phonon-phonon ($G_{pp,2}$) heat transport in few different methods as described below.

5.2.1 Crude Model

In anisotropic materials like graphite, where phonon properties along different crystallographic directions varies greatly, it is unclear in which proportion the total thermal boundary conductance would involve the heat flow along both the a-axis (in-plane) and c-axis (out-of-plane). Due to the stronger atomic bonds in the a-axis direction, heat flows more efficiently in-plane, resulting in a higher conductance magnitude compared to the c-axis conductance.

However, pure in-plane transport does not contribute to the net heat flux in the direction the transport is being measured (across the interface), so the relation between these effects is unclear. The overall TBC is not a simple average but can be expressed as a weighted sum that reflects the proportion of heat flowing along each axis.

In order to calculate the TBC, we start with a crude model that assumes a spherical BZ for both metal and substrates, and then use a hybrid DMM approach, as outlined in Section 3.3. Figure 5.1 shows the phonon dispersions for Al (green solid line) and Au (blue solid line), comparing them to (a) the c-axis graphite (black solid line) and c-axis MoS₂ (red solid line), and (b) the a-axis graphite (black dashed line) and a-axis MoS₂ (red dashed line). Graphite consists of graphene monolayers (two atoms per unit cell) held together by weak van der Waals forces, with six phonon branches in each monolayer, which split into two branches per mode in graphite (four atoms per unit cell), resulting in twelve branches in total. The three acoustic branches of graphene—longitudinal acoustic (LA), transverse acoustic (TA), and out-of-plane acoustic (ZA) split into three acoustic branches (ZA, TA, LA) and three quasi-optical branches (ZO', TO', LO') in graphite, along with remaining six optical branches[166]. Since graphite is three-dimensional, it allows phonons to propagate in both the in-plane and out-of-plane directions, with the ZA branch behaving as longitudinal acoustic and the ZO' branch as longitudinal optical when the wave vectors are along the Γ -A direction of the Brillouin zone as shown in Figure 1.1[29], [167]. In the Brillouin zone, most of the branches are double degenerate, except for the ZA and ZO' branches[167]. Similar to graphite, bulk hBN also has four atoms per unit cell, resulting in twelve phonon branches, including three acoustic branches, three quasi-optical branches, and six remaining optical branches. On the other hand, MoS₂ has 6 atoms per unit cell leading to eighteen total phonon branches including three acoustic branches, three quasi-optical branches, and remaining twelve optical

branches.

In the metal/c-axis layered material systems (see Figure 5.1a), elastic scattering is considered due to the acoustic modes differing by more than a factor of 2, making inelastic processes involving large energy differences less likely. Additionally, the low-lying quasi-optical modes along the c-axis are included in the calculation because their frequencies overlap with those of metals. For metal/a-axis layered material systems, we consider elastic scattering for Al/a-axis graphite, Al/a-axis MoS₂, and Au/a-axis graphite since the acoustic modes differ by more than a factor of 2. Inelastic scattering is considered for Au/a-axis MoS₂, while optical branches are excluded along the a-axis for all the substrates due to the large energy differences between metals. The phonon dispersions in hBN are similar to those in graphite, so they follow the same logic.

For an anisotropic system where G_c is the conductance along the c-axis and G_a is the conductance along the a-axis, the total weighted thermal boundary conductance from the crude model ($G_{pp,2cr}$) is expressed as:

$$G_{pp,2cr} = \frac{1}{3}G_c + \frac{2}{3}G_a \quad (5.1)$$

This crude model effectively represents the parallel nature of heat flow in anisotropic systems, capturing the relative contributions of the in-plane and out-of-plane conductances. Table 5.1 shows the predicted TBC for various metal/layered semiconductor systems. For samples with no interlayer, the conductance due to electron phonon coupling is given by $\sqrt{gk_p}$ where g is volumetric electron-phonon coupling constant and k_p is the thermal conductivity of phonons in the metal and for Al, Au, and Ti these values are 1163 MW/m²K, 260 MW/m²K, and 2674 MW/m²K respectively. The total conductance (G_{cr}) in this case is calculated based on Eq. 2.5. For all other cases with interlayers, G_{cr} represents the total boundary conductance in the structure after

accounting for different mechanisms involved and is described by Eq. 3.1. Table 5.2 shows the calculated TBC for various metal-layered material systems. Here, G_c , G_a , $G_{pp,2cr}$ and G_{cr} represents the TBC between metal/c-axis layered material, metal/a-axis layered material, phonon TBC based on Eq. 5.2, and total TBC including other pathways respectively. Table 5.3 reports the calculated TBC due to electron-electron interaction between metal/interlayer (G_{ee}) and electron-phonon coupling in the interlayer ($G_{ep,2}$) in pathway 2 in hybrid model.

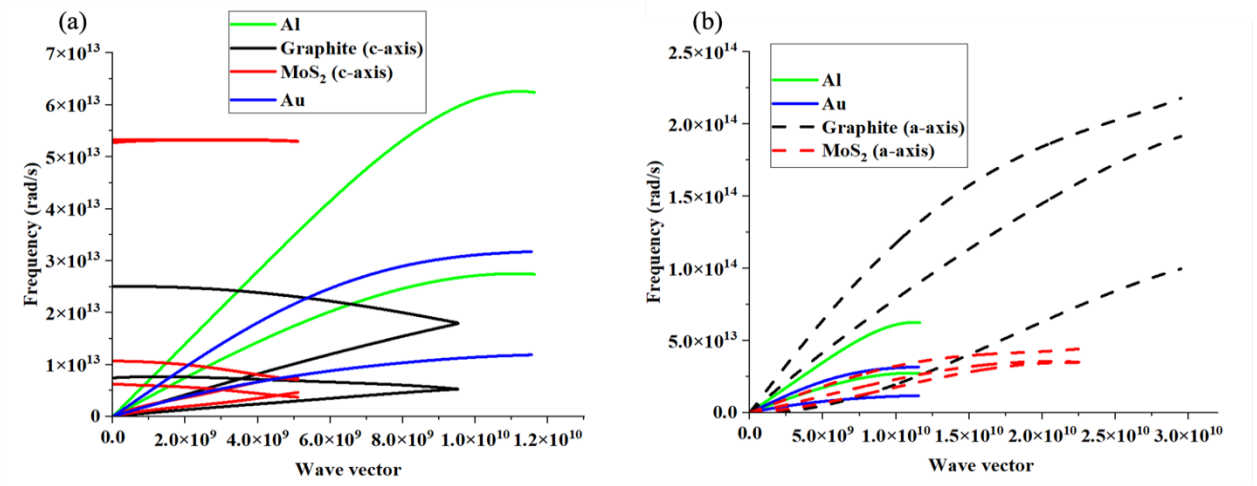


Figure 5.1: Phonon dispersions for Al (green solid line) and Au (blue solid line), comparing them to (a) the c-axis graphite (black solid line) and c-axis MoS₂ (red solid line), and (b) the a-axis graphite (black dashed line) and a-axis MoS₂.

Table 5.2: Calculated TBC for various metal-layered material systems. G_c , G_a , $G_{pp,2cr}$ and G_{cr} represents the TBC between metal/c-axis layered material, metal/a-axis layered material, phonon TBC based on Eq. 5.2, and total TBC including other pathways respectively.

	G_c (MW/m ² K)	G_a (MW/m ² K)	$G_{pp,2cr}$ (MW/m ² K)	G_{cr} (MW/m ² K)
Al (50 nm)/HOPG	49.3	258	188	154
Al (50 nm)/Ni (10 nm)/HOPG	46.7	257	187	173
Au (50 nm)/HOPG	72.7	43.9	53.5	44.4
Au (50 nm)/Ni (10 nm)/HOPG	46.7	257	187	172

Al (50 nm)/MoS ₂ (only including first 3 quasi-optical branches)	0.507	287	191	164
Al (50 nm)/MoS ₂ (including all low-lying optical branches)	30.1	287	201	171
Al (50 nm)/Ni (10 nm)/MoS ₂ (only including first 3 quasi-optical branches)	0.387	348	232	211
Al (50 nm)/Ni (10 nm)/MoS ₂ (including all low-lying optical branches)	31.9	348	243	220
Au (50 nm)/MoS ₂ (only including first 3 quasi-optical branches) (in-elastic)	12.6	196	135	88.9
Au (50 nm)/MoS ₂ (including all low-lying optical branches) (in-elastic)	32.4	196	141	91.4
Au (50 nm)/Ni (10 nm)/MoS ₂ (only including first 3 quasi-optical branches)	0.387	348	232	209
Au (50 nm)/Ni (10 nm)/MoS ₂ (including all low-lying optical branches)	31.9	348	243	218
Al (50 nm)/hBN	56.2	310	225	188
Al (50 nm)/Ni (10 nm)/hBN	51.7	301	218	197
Au (50 nm)/hBN	73.3	50.6	58	47.4
Au (50 nm)/Ni (10 nm)/hBN	51.7	301	218	198

Table 5.3: Calculated TBC due to electron-electron interaction between metal/interlayer (G_{ee}) and electron-phonon coupling in the interlayer ($G_{ep,2}$) in pathway 2 in hybrid model.

	G_{ee} (MW/m ² K)	$G_{ep,2}$ (MW/m ² K)
Al/Ni (10 nm)	6900	3600
Au/Ni (10 nm)	5350	3600
Al/Cu (10 nm)	5600	1000
Al/Ti (10 nm)	9100	13000
Au/Ti (10 nm)	6550	13000

As observed from Figure 5.1, the phonon dispersions along the c-axis exhibit much lower energy compared to those along the a-axis, resulting in a lower total flux across the interface between metal and the c-axis phonons. This, in turn, leads to a lower thermal boundary

conductance in metal/c-axis layered materials. These calculations show that the crude model significantly overestimates the TBC predictions in the cases presented above, when compared to available literature values for metal/layered material interfaces[12], [62], [161]. Table 5.4 presents the experimentally measured TBC values from the literature for metal/layered material interfaces.

Table 5.4: Experimentally measured TBC values from the literature for metal/layered material interfaces.

	G (MW/m ² K)
Al/graphite	34.6[168] 45[12] 40-80[75]
Ti/graphite	120[12]
Al/Ti/graphite	100[12]
Au/graphite	30[12]
Au/Ti/graphite	52[62]
Al/MoS ₂	25[70] 38[169]
Au/MoS ₂	21[170]

Additionally, existing experimental data are better aligned with the boundary conductance values (G_c) derived from the c-axis phonon dispersion in a spherical Brillouin zone except for Au/layered material systems. This observation provides a hint into the dominant heat transport mechanisms in metal/layered material systems. The weak interlayer bonding in layered materials causes phonon focusing to occur predominantly in the in-plane (ab-plane) direction, where phonons travel with higher velocities due to the strong covalent bonds as shown in Figure 5.2[161]. Figure 5.2 shows the phonon group velocity vectors for (a) graphite and (b) Al. In panel (a), the green arrows indicate a concentration of vectors within the ab-plane indicating that phonons in graphite predominantly propagate along the in-plane direction leading to a very high thermal conductivity in the in-plane direction. The less concentration of phonon group velocity vectors in the c-axis direction indicates that phonons propagate less efficiently along the out-of-plane

direction in layered materials like graphite. This is primarily due to the weaker interlayer bonding between the graphene sheets, which reduces the velocities of phonons traveling perpendicular to the layers. As a result, fewer phonons contribute to heat transfer along the c-axis, leading to lower thermal conductivity in the out-of-plane direction. In contrast, for aluminum (panel b), the group velocity vectors are uniformly distributed across all directions, reflecting the isotropic nature of the material. The transparent envelope surrounding the group velocity vectors visually highlights the difference between the anisotropic behavior of graphite and the isotropic behavior of aluminum.

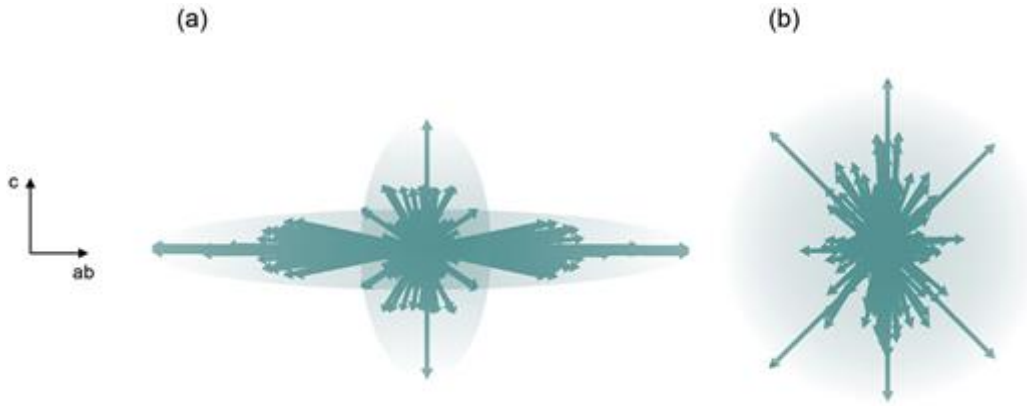


Figure 5.2: Phonon group velocity vectors for (a) graphite and (b) Al are shown. In panel (a), the green arrows represent the direction of the group velocity vectors, with a noticeable concentration of vectors within the ab-plane in graphite[161]. This indicates that phonons in graphite predominantly propagate along the in-plane direction. In contrast, for aluminum (panel b), the group velocity vectors are uniformly distributed across all directions, reflecting the isotropic nature of the material. The transparent envelope surrounding the group velocity vectors visually highlights the difference between the anisotropic behavior of graphite and the isotropic behavior of aluminum[161].

This indicates that, for heat transfer across the metal/layered material interface, c-axis phonons are primarily responsible for out-of-plane thermal transport, and the reduced concentration of group velocity vectors along the c-axis reflects the more limited heat transport capacity in this direction. While both in-plane and out-of-plane phonons contribute to the overall

thermal conductivity in layered material, it is the c-axis phonons that predominantly control the heat transfer across the metal-layered material interface, as these phonons are the ones that can primarily travel between layers. Therefore, by considering only the c-axis phonons, we are better aligning with the experimental conditions, where we measure heat dissipation across metals and layered material in c-axis direction. This approach simplifies the model without sacrificing the accuracy of TBC predictions, while appropriately accounting for the weak interlayer coupling. In the next section we therefore focus on TBC predictions in materials using the c-axis phonon dispersion assuming the Brillouin zone is isotropic in both metal and the layered material.

5.2.2 Isotropic DMM with c-axis phonon dispersion

To understand the heat transport mechanisms in metal/layered material systems, in this model we calculate the thermal boundary conductance assuming a spherical BZ for both metal and layered material. Table 5.5 shows the calculated TBC for various metal/layered material systems. Here, G_c represents TBC between metal/c-axis layered material and G_{iso} the total boundary conductance including all other pathways.

Table 5.5: Calculated TBC for various metal-layered material systems using isotropic DMM. Here, G_c represents TBC between metal/c-axis layered material and G_{iso} represents the total boundary conductance including all other pathways.

	G_c (MW/m ² K)	G_{iso} (MW/m ² K)
Al (50 nm)/HOPG	49.3	47.3
Al (50 nm)/Ni (10 nm)/HOPG	46.7	45.8
Al(50 nm)/Cu (10 nm)/HOPG	119	104
Al(50 nm)/Ti (10 nm)/HOPG	147	143
Au (50 nm)/HOPG	72.7	57
Au (50 nm)/Ni (10 nm)/HOPG	46.7	45.7
Au (50 nm)/Ti (10 nm)/HOPG	147	142
Al (50 nm)/MoS ₂ (only including first 3 quasi-optical branches)	0.507	0.507
Al (50 nm)/MoS ₂ (including all low-lying optical branches)	30.1	29.3

Al (50 nm)/Ni (10 nm)/MoS ₂ (only including first 3 quasi-optical branches)	0.387	0.387
Al (50 nm)/Ni (10 nm)/MoS ₂ (including all low-lying optical branches)	31.9	31.0
Au (50 nm)/MoS ₂ (only including first 3 quasi-optical branches) (in-elastic)	12.6	12.0
Au (50 nm)/MoS ₂ (including all low-lying optical branches) (in-elastic)	32.4	28.8
Au (50 nm)/Ni (10 nm)/MoS ₂ (only including first 3 quasi-optical branches)	0.387	0.386
Au (50 nm)/Ni (10 nm)/MoS ₂ (including all low-lying optical branches)	31.9	28.4
Al (50 nm)/hBN	56.2	53.6
Al (50 nm)/Ni (10 nm)/hBN	51.7	49.5
Au (50 nm)/hBN	73.3	57.2
Au (50 nm)/Ni (10 nm)/hBN	51.7	43

The calculations indicate that the predicted thermal boundary conductance values from the model align well with those reported in the literature for various metal/layered material systems. For example, the predicted TBC value for Al/HOPG, Al/MoS₂ systems are ~ 47 MW/m²K, ~ 29 MW/m²K respectively, which are consistent with published data. Our results show that inserting Cu and Ti interlayers with better phonon cut-off frequency overlap with HOPG, enhances the TBC by factors of two and three respectively. On the other hand, Ni interlayer with similar cut-off frequency as Al has no effect in TBC enhancement at Al/HOPG interfaces. Although Au has a better cut-off frequency overlap with HOPG compared to Al or Ni, the low EPC strength of Au further brings down the TBC at Au/HOPG interface making it similar to Al/HOPG or Ni/HOPG interfaces in the model and when a Ti interlayer is introduced at the Au/HOPG interface, the TBC increases by a factor of two. However, when comparing the model predictions to experimental data from literature[12], [62], the predicted TBC values for Au/HOPG systems are higher,

suggesting that the model may slightly overestimate the TBC in these cases. This will be discussed further in the Results and Discussion section. The model also reveals that due to the similar phonon frequencies in HOPG and hBN, the TBC values for metal/hBN and metal/HOPG systems are comparable. In contrast, for MoS₂, the TBC between metal/MoS₂ is much lower than metal/HOPG or metal/hBN systems due to poor phonon frequency cut-off overlaps. The model also shows that including all low-lying optical phonons with overlapping frequencies with metal in the model is necessary for accurately predicting TBC, reinforcing the validity of our hybrid model approach.

To understand the role of anisotropy in predicting TBC, our next model accounts for the anisotropy in the crystal structure of the layered material by considering both the cylindrical Brillouin zone and phonon focusing effects, which are particularly significant in anisotropic layered materials.

5.2.3 Anisotropic DMM with c-axis phonon dispersion

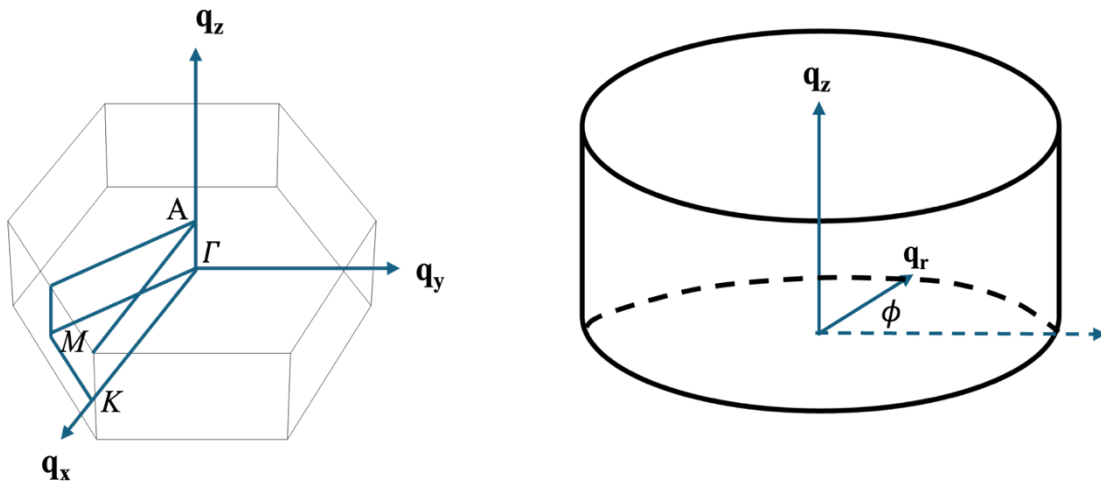


Figure 5.3: First Brillouin zone of graphite, hBN, and MoS₂ (a) hexagonal first Brillouin zone and (b) cylindrical approximation of the first Brillouin zone.

In isotropic materials, the phonon properties exhibit no directional dependence due to the

uniform atomic structure and bonding interactions throughout the material. Consequently, the Brillouin zone can be approximated as spherical, reflecting the isotropic nature of the material where phonons propagate equally in all directions. In contrast, anisotropic materials, such as layered materials with a hexagonal crystal structure, show direction-dependent phonon propagation. Therefore, the Brillouin zone in these systems is more accurately represented by a cylindrical shape, reflecting the anisotropic phonon dispersion. Figure 5.4 shows the hexagonal first Brillouin zone of graphite, hBN, and MoS₂ (a) and (b) cylindrical approximation of the first Brillouin zone.

Assuming a cylindrical symmetry with $q_x = q_y$ we can introduce a cylindrical coordinate system in the q_x - q_y plane, with the radial component $q_r = \sqrt{q_x^2 + q_y^2}$. The volume element $dq_x dq_y dq_z$ in Eq. 2.8 becomes $q_r dq_r dq_z d\phi$ and the phonon flux can now be expressed as:

$$J_{A \rightarrow B} = \frac{\hbar}{8\pi^3} \sum_j \int_0^{2\pi} \int_{k_z} \int_{k_r} \omega_A f_0 v_{j,A}(q_z) q_{r,A} dq_{r,A} dq_{z,A} d\phi \quad (5.2)$$

here, q is the wavevector, ω_A is the angular frequency of phonons in material A, $v_{j,A}$ is the phonon group velocity perpendicular to the interface, j is the phonon polarization, f_0 is the Bose-Einstein distribution function. The phonon group velocity in the direction of applied thermal gradient is given by $v_{j,A}(q_z) = v_{j,A} \cos \theta$ where θ is the elevation angle between the incident phonon and the normal to the interface and $\cos \theta = q_z / \sqrt{q_z^2 + q_r^2}$. The directionality dependence collapses assuming diffuse scattering and the phonon flux can be written as:

$$J_{A \rightarrow B} = \frac{\hbar}{4\pi^2} \sum_j \int_{k_z} \int_{k_r} \omega_A f_0 v_{j,A} \cos \theta q_{r,A} dq_{r,A} dq_{z,A} \quad (5.3)$$

We obtained the phonon frequency by fitting a fourth-order polynomial to the previously published phonon dispersions in the crystallographic direction of interest. The group velocity in

the direction of transport is obtained by taking the gradient of phonon dispersion in z-direction. For layered materials, we consider q_r oriented in the Γ -K direction and q_z oriented in the Γ -A direction as shown in Figure 5.2. Assuming elastic scattering with isotropic phonon dispersion for metals (given by Eq. 3.3) and anisotropic phonon dispersion for the layered materials, the anisotropic transmission probability $\alpha_{A \rightarrow B, an}$ can be determined using the principle of detailed balance,

$$\alpha_{A \rightarrow B, an} = \frac{\frac{\hbar}{4\pi^2} \sum_{j,B} \omega_{j,B} q_{r,B} v_{j,B} f_0 dq_{r,B} dq_{z,B}}{\frac{\hbar}{4\pi^2} \sum_{j,B} \omega_{j,B} q_{r,B} v_{j,B} f_0 dq_{r,B} dq_{z,B} + \frac{\hbar}{8\pi^2} \sum_{j,A} \omega_{j,A} q_{j,A}^2 v_{j,A} f_0 dq_{j,A}} \quad (5.4)$$

The phonon-phonon thermal boundary conductance can be obtained with the anisotropic transmission probability calculated above as:

$$G(\lambda)_{pp, an} = -\frac{1}{8\pi^2} \sum_{j,A} \int_{\lambda_{min}}^{\lambda_{max}} \hbar \omega_{j,A} q_{j,A}^2 |v_{j,A}| \alpha_{A \rightarrow B, an} \frac{df_{BE}}{dT} \frac{2\pi}{\lambda^2} d\lambda_{j,A} \quad (5.5)$$

This equation is similar Eq. 3.3, with the isotropic phonon transmission coefficient replaced by the anisotropic transmission coefficient. The total anisotropic thermal boundary conductance of the metal/interlayer/anisotropic semiconductor is calculated using Eq. 3.1, accounting for other mechanisms based on hybrid model. Table 5.4 shows various calculated anisotropic thermal boundary conductance ($G_{c, ani}$) and total thermal boundary conductance including other heat transfer mechanisms (G_{ani}) in various metal/layered material interface. For comparison, the last column shows the TBC calculated from the isotropic model (G_{iso}).

Table 5.6: Calculated TBC for various metal/layered material systems using anisotropic DMM. For comparison, the last column represents the TBC calculated from the isotropic model (G_{iso}).

	$G_{c, ani}$ (MW/m ² K)	G_{ani} (MW/m ² K)	G_{iso} (MW/m ² K)
Al (50 nm)/HOPG	55.9	53.3	47.3

Al (50 nm)/Ni (10 nm)/HOPG	49.9	48.9	45.8
Al (50 nm)/Cu (10 nm)/HOPG	144	123	104
Au (50 nm)/HOPG	140	91.0	57
Al (50 nm)/MoS ₂ (only including first 3 quasi-optical branches)	4.39	4.37	0.507
Al (50 nm)/Ni (10 nm)/MoS ₂ (only including first 3 quasi-optical branches)	3.72	3.71	0.387
Au (50 nm)/MoS ₂ (only including first 3 quasi- optical branches)	79.2	60.7	12.0
Al (50 nm)/hBN	61.7	58.6	53.6
Al (50 nm)/Ni (10 nm)/ hBN	55.8	54.5	49.5
Au (50 nm)/ hBN	278	134	57.2

The results show that TBC between metals and layered materials are nearly the same for both isotropic and anisotropic DMM except for Au/layered material combination. The Au/layered material system is expected to show higher TBC due to better phonon cut-off frequency match between the materials involved. Despite the good phonon frequency match, the weak EPC strength of Au in the Au/layered material system reduces the effectiveness of phonon transmission across the interface, leading to the models overestimating the TBC compared to the experiments.

While both the isotropic and anisotropic models provide useful insights into TBC between metals and layered materials, the discrepancies observed in the Au/layered material combination underscore the complexity of accurately predicting interfacial heat transfer. The cylindrical model, while capturing the directional phonon propagation effects, tends to overestimate TBC in cases where weak EPC strength limits the efficiency of phonon transmission, as seen in the Au/layered system. The isotropic model, by assuming more uniform phonon behavior, offers a more conservative and often more accurate estimate in these cases. This simplification helps reduce the

overestimation associated with complex phonon interactions, particularly in cases of weak interlayer bonding, where phonon scattering effects are more difficult to capture accurately. The isotropic model's efficiency and accuracy make it a practical alternative, especially when predicting TBC modifications at interfaces where detailed directional phonon data is not easily accessible.

5.3 Experimental Procedures

The samples were fabricated by mechanically exfoliating the bulk layered material onto a a-SiO₂ (300 nm)/Si substrate. The metallic bilayers were deposited onto the substrate using magnetron sputtering for Al/Cu and e-beam evaporation for all other bilayers. We employed time-domain thermoreflectance technique to measure the thermal transport properties of the samples mentioned above. A detailed description of the experimental setup can be found in Chapter 3. The thickness characterization of bilayers was done using picosecond acoustic technique and stylus profilometer. Four-point probe technique was used to measure the in-plane thermal conductivity of the metallic bilayers. TBC between bilayers and substrate was obtained by fitting the experimental data using a thermal transport model based on the solution of the heat diffusion equation in cylindrical symmetry for layered media. For fitting purposes, the metallic bilayer is modeled as a single layer, with a thickness equal to the combined thickness of the bilayers and a volumetric heat capacity calculated as the thickness-weighted average.

5.4 Comparison of Experimental and Calculated TBC

Table 5.5 shows a comparison of experimental TBC (G_{expt}) with TBC G_{iso} from model based on isotropic DMM. The measured Al/HOPG TBC is consistent with previously reported values[12]. Our results demonstrate that inserting thin metallic interlayers at Al/HOPG interface,

with intermediate phonon cut-off frequencies, can enhance the TBC significantly and this enhancement can be accurately predicted using the hybrid model. Specifically, inserting Cu and Ti interlayers leads to a two- and three-fold increase in TBC, respectively, while a Ni interlayer, with a similar cut-off frequency to that of Al, shows no significant effect. Schmidt et al. measured the Al (90 nm)/Ti (5 nm)/HOPG TBC using TDTR and the change in TBC at this interface was well predicted by the hybrid model. The measured TBC for Au/HOPG is in agreement with the previously reported values[12]. The lower experimental value of Au/HOPG can be attributed to the weak adhesion of Au to the HOPG[12]. Additionally, experiments are designed to work as of the heat is deposited at the surface and EPC doesn't play a role, but, in case of gold it's a convolution of phonon-phonon and EPC effects and we need to extract the phonon-phonon sufficiently. Koh et al. reported the TBC at Au (50 nm)/Ti (2 nm)/HOPG interface $\sim 52 \text{ MW/m}^2\text{K}$, showing that Ti enhances the TBC at metal/HOPG interface. For, Au/HOPG and Au/Ti/HOPG systems, the hybrid model over predicts the TBC at the interface. However, it predicts a 2.5-fold increase in TBC with the presence of the Ti interlayer, which aligns well with experimental results. hBN with similar phonon properties as that of graphite shows similar trends as metal/graphite systems.

For metal/MoS₂ systems, the experiments agree well with the theory. The hybrid model was able to predict the changes at the metal/MoS₂ interfaces better than other models previously published confirming the importance of accounting for various heat transfer pathways in the system[12], [62], [161].

So far, no other models have been able to accurately predict the TBC at these interfaces, both with and without interlayers. This highlights that, despite its limitations, the hybrid DMM provides a reasonable estimate of TBC modifications at these interfaces, offering a more reliable

approach compared to previously published models. These findings suggest that a more nuanced model, incorporating material-specific interfacial characteristics and phonon scattering mechanisms, could improve TBC predictions and help better understand heat transport in metal-layered material interfaces.

Table 5.7: Comparison of experimental TBC (G_{expt}) with TBC G_{iso} from model based on isotropic DMM

	G_{expt} (MW/m ² K)	G_{iso} (MW/m ² K)
Al (50 nm)/HOPG	39±3.4	47.3
Al (50 nm)/Ni (10 nm)/HOPG	54.7±2.1	45.8
Al (50 nm)/Cu (10 nm)/HOPG	107±7.4	104
Al (90 nm)/Ti (5 nm)/HOPG	100±20[12]	137
Ti (90 nm)/HOPG	120±20[12]	139
Au (50 nm)/HOPG	21.3±1.2	57
Au (50 nm)/Ti (2 nm)/HOPG	52[62]	141
Al/MoS ₂	20.2±1.1	29.3
Al (50 nm)/Ni (10 nm)/MoS ₂	25.4±2.1	31.0
Au (50 nm)/MoS ₂	29.3±0.9	28.8
Al (50 nm)/hBN	40.1±1.5	53.6
Au (50 nm)/ hBN	25.1±2.3	57.2

5.5 Conclusion

In summary, this work analyzes the mechanisms of heat transport at metal-layered material systems. Our studies show that interface conductance can be modified by introducing an appropriate metallic interlayer, and these modifications can be accurately predicted using the hybrid diffuse mismatch model (DMM). Furthermore, our results indicate that a simple isotropic hybrid DMM is sufficient to predict TBC modifications accurately, allowing us to avoid the complexity of anisotropic DMM theories. The study also emphasizes the importance of incorporating full phonon dispersion, the role of optical phonons, and the strength of electron-phonon coupling in metals. By considering these factors, we demonstrate that traditional models

of thermal boundary conductance can be significantly improved, leading to more precise predictions of heat flow at metal-layered material interfaces.

CHAPTER 6: CONCLUSION AND FUTURE WORK

6.1 Summary

This dissertation investigates the fundamental principles behind heat transport at metal-semiconductor interfaces, particularly when thin metallic interlayers are introduced. As heat dissipation becomes more critical for the performance and reliability of advanced electronic devices, especially those incorporating layered and two-dimensional materials, understanding the mechanisms driving thermal boundary conductance is essential. The work in this study provides a theoretical framework, validated with experimental data, to predict and analyze heat flow in these systems.

A key focus of this research was to explore how the introduction of metallic interlayers impacts the TBC at interfaces between metals and conventional isotropic semiconductors. The results demonstrate that the phonon spectra of the interlayer and the strength of electron-phonon coupling play critical roles in determining the TBC at these interfaces. Specifically, when the phonon spectra of the interlayer align well with that of the substrate, the TBC can be significantly enhanced, sometimes by more than three times. However, for metals with weak EPC (like gold), the relationship between the phonon spectra overlap and EPC strength becomes crucial. This suggests that while EPC strength is important, it cannot be solely relied upon to predict changes in TBC, as the overall interface behavior is governed by a complex interplay of factors.

In addition to exploring interfacial heat transport, this dissertation also examines the role of material thickness in thermal conductivity of anisotropic semiconductors. The study reveals that both in-plane and out-of-plane thermal conductivities in layered materials increase with thickness until they plateau. However, the behavior of heat transport is more complex than previously thought, as out-of-plane thermal conductivity is influenced by more than just phonons traveling in

the out-of-plane direction. This finding highlights the need for refining existing theoretical models to account for the complexities involved in heat transport in layered materials, particularly when considering thinner structures.

When considering metal/layered material systems with thin metallic interlayers, the study further shows that a simplified, isotropic diffuse mismatch model can accurately predict TBC modifications, avoiding the complexity of anisotropic models. This is a significant contribution, as it suggests a more efficient approach for predicting TBC changes without sacrificing accuracy. Additionally, the work emphasizes the importance of incorporating factors like full phonon dispersion, the role of optical phonons, and electron-phonon coupling in improving traditional models of thermal boundary conductance. By accounting for these factors, the study shows how TBC predictions can be significantly enhanced, offering a more precise understanding of heat transfer at metal-layered material interfaces.

6.2 Future Work

While this dissertation has contributed to understanding the role of material thickness and phonon scattering mechanisms in anisotropic semiconductors, several areas remain open for further exploration to refine and improve the models of heat transport. Future research could focus on refining models to more precisely predict the diffusive to non-diffusive transition point and the thermal conductivity behavior in thin films or nanostructures of varying sizes. This could involve using techniques, such as the suppression function approach, which offers a more comprehensive description of boundary effects than traditional models like Matthiessen's rule. Although the suppression function approach provides a material-specific description of boundary effects, more work is needed to predict these functions for different geometries and material systems. These

models could be particularly useful for designing materials for thermoelectric applications, where controlling the heat transport directionality is crucial.

Another area for future improvement is enhancing TBC predictions by moving beyond the Diffuse Mismatch Model (DMM). While models based on the DMM can provide estimates for the order of magnitude of thermal boundary conductance, they rely on simplifications that limit their accuracy. For instance, DMM typically makes assumptions about scattering at the interface, Brillouin zone, and phonon dispersion, which may not capture all the complexities of real-world interfaces. Atomistic models, such as molecular dynamics, the atomistic Green's function method, and the Boltzmann transport equation coupled with first-principles calculations, offer a more detailed and accurate description of TBC by accounting for the atomic-level interactions at the interface. Despite the advantages, challenges remain, such as the high computational cost of large-scale simulations and the difficulty in modeling complex interfacial structures with defects and impurities.

To further enhance TBC predictions between metals and anisotropic semiconductors, future work will focus on employing the Boltzmann transport equation to model heat transport in metal/layered material systems. For this, we plan to utilize the open-source software called almaBTE, which allows for the calculation of phonon transport and thermal boundary conductance in multilayered materials using properties obtained from density functional theory [132]. almaBTE (steady_montecarlo1d module) utilizes a Monte Carlo-based simulation approach to model steady-state thermal transport in one-dimensional multilayered systems[132], [171]. Figure 6.1 shows a schematic diagram of the simulation model for thermal boundary conductance calculation. By imposing a temperature gradient across the sample, the resulting heat flux can be measured, enabling predictions of the thermal boundary conductance. The thermal boundary conductance can

be calculated using:

$$G = \frac{T_L - T_R}{J} \quad (6.1)$$

where T_L and T_R are the temperatures on either side of the interface and J is the heat flux across the sample. For predicting TBC, least-squares linear regression is applied to the temperature profile along each part of the material by fitting a straight line to the data, and the temperature drop across the system is calculated based on the linear fits at the interface[171]. The thermal conductivity can be calculated using:

$$k = \frac{J}{dT/dz} \quad (6.2)$$

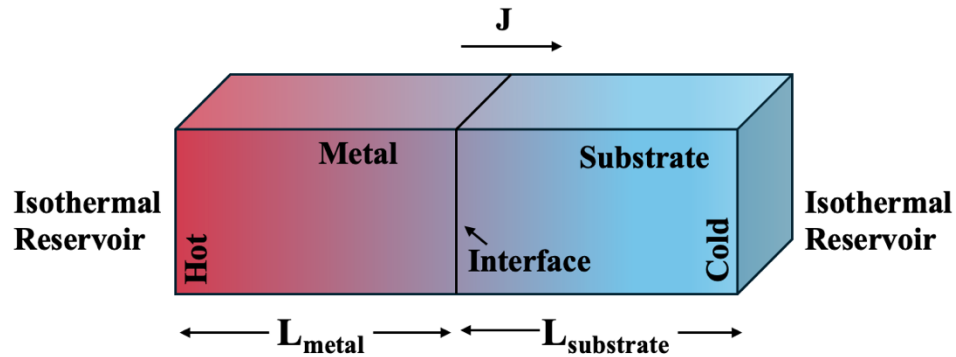


Figure 6.1: shows a schematic diagram of the simulation model for thermal boundary conductance calculation.

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