Thermal boundary conductance accumulation and interfacial phonon transmission: measurements and theory

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Abstract

The advances in phonon spectroscopy in homogeneous solids have unveiled extremely useful physics regarding the contribution of phonon energies and mean free paths to the thermal transport in solids. However, as material systems decrease to length scales less than the phonon mean free paths, thermal transport can become much more impacted by scattering and transmission across interfaces between two materials than the intrinsic relaxation in the homogeneous solid. To elucidate the fundamental interactions driving this thermally-limiting interfacial phonon scattering process, we analytically derive and experimentally measure a thermal boundary conductance accumulation function. We develop a semi-classical theory to calculate the thermal boundary conductance accumulation function across interfaces using the diffuse mismatch model (DMM), and validate this derivation by measuring the interface conductance between nine different metals on native oxide/silicon substrates and five different metals on sapphire substrates. Measurements were performed at room temperature using time-domain thermoreflectance and represent the first-reported values for interface conductance across several metal/native oxide/silicon and metal/sapphire interfaces. The various metal films provide a variable bandwidth of phonons incident on the metal/substrate interface. This method of varying phonons cutoff frequency in the film while keeping the same substrate allows us to mimic the accumulation of thermal boundary conductance and thus provides a direct method to experimentally validate our theory. We show that the accumulation function can be written as the product of an average interfacial phonon transmission function and the accumulation of the temperature derivative of the phonon flux incident on the interface; this provides the framework to extract an average, spectrally dependent phonon transmissivity from a series of thermal boundary conductance measurements. Based on the assumptions made in this work and the measurement results on different metals on native oxide/silicon and sapphire substrates, we demonstrate that thermal transport across solid interfaces may not necessarily be dictated by phonon mismatch of materials and interfacial transmission, but is rather directly correlated to the temperature derivative of phonon flux incident on the interface.
I. INTRODUCTION

Solid-solid interfaces can dominate the thermal processes of devices and material systems when the interface spacing becomes less than the carrier mean free path. This has pronounced effects on thermal transport in nanosystems, as the rate of energy transmission across the interface between two solids is often less than the intrinsic rate of conduction in the solids. In fact, even the near-interface regions in a solid can lead to additional thermal resistance due to growth bi-products, atomic imperfections, chemical impurities, and other “non-idealities”. Although only a few studies have presented experimental measurements of the thermal boundary conductance across atomically smooth, chemically abrupt interfaces, even these works have shown that heat transport across these seemingly “perfect” interfaces can still generate a significant source of thermal resistance.

Even with this thermal boundary conductance (or Kapitza conductance), being immensely important to nanoscale thermal engineering of solids, a void exists in the current knowledge of how phonons interact at interfaces and spectrally contribute to . For example, measurements of thermal boundary conductance are typically compared to semi-classical models, such as the acoustic or diffuse mismatch models (AMM or DMM, respectively) to analyze how phonons are contributing to interfacial transport. However, due to the many assumptions inherent in these models, agreement between the model predictions and experimental data can often be argued as coincidence. This being said, several previous works, including our own, have developed refinements to the AMM and DMM to garner further insight into how phonon energies are transmitted across solid interfaces. Limitations imposed by the fundamental kinetic theory assumptions in which the AMM and DMM are rooted can still raise questions when simply comparing to experimental data. More rigorous classical molecular dynamics simulations have addressed several unanswered questions regarding phonon scattering and subsequent energy transfer across interfaces, however, these simulations can not account for quantum mechanical phonon populations below a material’s Debye temperature. As a result, the current understanding of how phonons couple and transmit energy across interfaces at moderate temperatures is limited by the mismatch theories or their variants.

Due to these theoretical limitations, knowledge of the physics driving phonon thermal boundary conductance across solid interfaces has lagged considerably compared to the comprehension of phonon scattering processes in homogeneous media. Recent theoretical and computational...
and experimental works have established the basis of an “accumulation function” for thermal conductivity in homogeneous solids, which has resulted in substantial advances in understanding how phonons scatter and transport energy in solids. This accumulation function provides a direct relationship between carrier mean free path and thermal energy transferred by a solid. The ability to define the accumulation function gives direct insight into how phonons couple energy to other carriers in a solid.

Clearly, a “thermal boundary conductance accumulation function” would substantially advance the field of phonon transport across interfaces, in nanosystems, and through composite media. Although this accumulation function can be easily calculated from the semi-classical mismatch theories, as shown below, an experimental measurement of this accumulation function will provide direct insight into phonon transmission across interfaces. Furthermore, an experimental measurement of this thermal boundary conductance accumulation would provide direct validation of the fundamental assumptions in theories for $h_{1K}$ while providing a measure of how phonons are spectrally transmitting across solid interfaces.

In this work, we report on a series of theoretical advancements and experimental measurements that provide evidence into how phonons transmit energy across solid interfaces at room temperature. In doing so, we directly assess the validity of the assumptions of phonon transmission calculations in the DMM. First, we analytically define the thermal boundary conductance accumulation function, and derive this accumulation function assuming diffusive scattering, one of the fundamental assumptions of the DMM. To validate this theory, we measure the thermal boundary conductance across interfaces of nine different metal films and silicon substrates with a native oxide layer. Our experiments show that for native oxide/silicon interfaces, the assumptions of the DMM are acceptable for describing interfacial phonon transmission. Additionally, we further support this assertion through a similar series of measurements on five different metal/sapphire interfaces.

This work provides experimental measurements that give insight into the spectral nature of phonon transport across interfaces. Several previous works have computationally and experimentally shown that $h_{1K}$ across solid/solid interfaces increases with an increase in phonon spectral overlap. However, this does not differentiate between the changing phonon energy flux and transmission probability as the phonon spectra is modified. In this current work, our experimental approach is to keep the substrate constant while changing the metal film deposited on the substrate surface.
We show that with a carefully designed experimental approach, a series of metal/substrate interfaces with different metals can be used as a measure of the spectral accumulation of phonon transmission into the substrate and accumulation of phonon thermal boundary conductance. Furthermore, the data we report provides benchmark values for various transition metal/native oxide/silicon thermal boundary conductances that currently do not exist in the literature. Our choice of various transition metals ensures that the metal/native oxide/silicon interface is well bonded so our results are not affected by weak interfacial adhesion. In doing so, we also report on the effects of a Ti adhesion layer between Au and native oxide/Si substrates and show that Ti layers as thin as 2 nm still exhibit thermal boundary conductances that are more in line with a “thick” Ti/Si interface. As a final result of our work, we show that regardless of the metal transducer, we are able to consistently measure the thermal conductivity of a single crystalline silicon substrate in agreement with bulk literature values within the experimental uncertainty. This further validates time-domain thermoreflectance (TDTR) as an effective measurement tool for measuring the thermal conductivity of bulk materials.

II. ACCUMULATION OF THERMAL BOUNDARY CONDUCTANCE

A simplistic mathematical description of phonon thermal boundary conductance from side 1 to side 2 is given by:

\[ h_K = \sum_j \int_{\omega_{\text{min},j}}^{\omega_{\text{max},j}} \frac{\partial q_{1,j}(\omega)}{\partial T} \zeta_{1\rightarrow2}(\omega) \, d\omega \]  

(1)

where \( \omega \) is the phonon angular frequency in rad s\(^{-1}\), \( T \) is the temperature, \( \zeta_{1\rightarrow2} \) is the phonon transmission coefficient from side 1 to side 2, \( \omega_{\text{min},j} \) and \( \omega_{\text{max},j} \) are the minimum and maximum frequencies in branch \( j \), respectively, and \( q_{1,j} \) is the spectral phonon flux in side 1 of phonon polarization \( j \), where the temperature derivative of this phonon flux is defined as:

\[ \frac{\partial q_{1,j}(\omega)}{\partial T} = \frac{1}{4} \hbar \omega D_{1,j}(\omega) v_{1,j}(\omega) \frac{\partial f(\omega)}{\partial T} \]  

(2)

where \( \hbar \) is Plank’s constant divided by \( 2\pi \), \( f \) is the Bose-Einstein distribution at equilibrium, and \( D_{1,j} \) and \( v_{1,j} \) are the density of states and phonon group velocity in side 1, respectively. We can absorb the branch dependence into the integral by rewriting the equation as:

\[ h_K = \int_{\omega_{\text{min}}}^{\omega_{\text{max}}} \frac{\partial q_1(\omega)}{\partial T} \zeta_{1\rightarrow2}(\omega) \, d\omega \]  

(3)
where $\omega_{\text{max}} = \max(\omega_{\text{max},j})$, $\omega_{\text{min}} = \min(\omega_{\text{min},j}) = 0$ and $\partial q_1 (\omega) / \partial T$ is given by:

$$\frac{\partial q_1 (\omega)}{\partial T} = \sum_j \frac{\partial q_{1,j} (\omega)}{\partial T} \begin{cases} \omega > \omega_{\text{max},j} \\ \omega < \omega_{\text{min},j} \end{cases} \frac{\partial q_{1,j} (\omega)}{\partial T} \bigg|_{\omega > \omega_{\text{max},j}} = 0$$  \hspace{1cm} (4)

Equation 5 expresses $h_K$ as a product of two functions. In parallel to previous theoretical works on thermal conductivity accumulation\cite{50,51}, we can now define a thermal boundary conductance accumulation, $\alpha_K$, as:

$$\alpha_{K,1\rightarrow2} (\omega_\alpha) = \frac{1}{h_K} \int_0^{\omega_\alpha} \frac{\partial q_1 (\omega)}{\partial T} \zeta_{1\rightarrow2} (\omega) d\omega = \int_0^{\omega_\alpha} h_K (\omega) d\omega$$  \hspace{1cm} (5)

which represents the fraction of the total thermal boundary conductance due to carriers in the metal (side 1) with phonon frequencies less than $\omega_\alpha$ transmitting energy to side 2. The equation on the far right of Eq. 5 recasts the integrand into a spectral thermal boundary conductance, $h_K$. Ultimately, this accumulation function is dictated by the product of $\partial q_1 / \partial T$ and $\zeta_{1\rightarrow2}$, both of which are dependent on frequency and therefore difficult to explicitly separate from this integral to compare with experimental data. However, we can separate these quantities using the Generalized Mean Value Theorem for definite integrals\cite{72} which states that there exists a frequency $x \in [0, \omega_\alpha]$ such that:

$$\alpha_{K,1\rightarrow2} (\omega_\alpha) = \left( \frac{1}{h_K} \right) \zeta_{1\rightarrow2} (x (\omega_\alpha)) \int_0^{\omega_\alpha} \frac{\partial q_1 (\omega)}{\partial T} d\omega$$  \hspace{1cm} (6)

where $\zeta_{1\rightarrow2} (x (\omega_\alpha))$ is the average of interfacial transmission from side 1 to side 2 over the frequency interval $[0, \omega_\alpha]$ weighted by $\partial q_1 / \partial T$. Since $\omega_\alpha$ is the independent variable in our formulation, and $x$ is a function of $\omega_\alpha$ we can write $\zeta_{1\rightarrow2}$ solely as a function of $\omega_\alpha$ so that Eq. 6 becomes

$$\alpha_{K,1\rightarrow2} (\omega_\alpha) = \left( 1 / h_K \right) Q_T (\omega_\alpha) \zeta_{1\rightarrow2} (\omega_\alpha)$$  \hspace{1cm} (7)

where $Q_T (\omega_\alpha) = \int_0^{\omega_\alpha} \partial q_1 / \partial T d\omega$ is the un-normalized accumulation of $\partial q_1 / \partial T$. We note that this approach provides the separation of flux and average transmission (which is related to the fundamental mechanisms of phonon scattering at interfaces) in the formulation of thermal boundary conductance. We show example calculations of Eq. 5 in Fig. 1 for Al/Si and Au/Si interfaces using DMM assumptions. This assumption of diffusive phonon scattering directly impacts calculations of the phonon transmissivity but not the calculations of the metal phonon flux. These assumptions and our specific procedure for the DMM are outlined in detail in our previous works, and are not repeated here.\cite{24,25} For these calculations, we ignore the contribution from optical modes and assume a 4th order polynomial fit to the one-dimensional phonon dispersion in the $\Gamma \rightarrow X$ direction.
FIG. 1. (a) Un-normalized accumulation of thermal boundary conductance for Al/Si and Au/Si interfaces calculated with Eq. [5] without normalizing by $h_{1K}$. The features in curves are related to the cutoff frequencies of the phonon branches. (b) and (c) Normalized accumulation of thermal boundary conductance (Eq. [5], $\alpha_{K,1\rightarrow2}$) and normalized accumulation of the temperature derivative of the phonon flux ($\alpha_{\omega T}$) plotted as a function of $\omega_\alpha$ for Au/Si and Al/Si, respectively. The various modeling calculations shown in these plots and the MATLAB code used to generate these accumulation models are given in the supplementary materials. 

in Au (Ref. [76]), Al (Ref. [77]), and Si (Ref. [78]), and an isotropic Brillouin zone, which is an acceptable approximation for cubic structures [79]. Finally, we assume two-phonon elastic scattering as the mechanism for phonon transmission across interfaces [20,21] and therefore we only conduct these calculations up to the maximum phonon frequencies in the metal which corresponds to the cutoff frequency of the longitudinal acoustic branch (e.g., frequencies above $\sim$30 Trad s$^{-1}$ in Au are assumed to not contribute to $h_{1K}$). The dispersion curves used for this calculation are shown in Fig. 2(a) for aluminum on silicon denoted by "Real Dispersion". The shaded area in the figure represents the $k - \omega$ space over which the integration is carried when $\omega_\alpha = 40$ Trad s$^{-1}$, where $k$ is the wavevector. In this case, the integration is carried over a subset of the Brillouin zone in the metal. Points $A'$ and $B'$ on the shaded region will coincide with $A$ and $B$ on the solid rectangle when $\omega_\alpha = \omega_{\text{max}}$. Note that the integration limits correspond to the angular frequency vector de-
scribing the longitudinal acoustic (LA) branch in the metal as the cutoff frequency of this branch is higher than that in the transverse acoustic (TA). The un-normalized accumulation of thermal boundary conductance for Al/Si and Au/Si interfaces calculated with Eq. 5 without normalizing by $h_K$ is plotted in Fig. 1a. The figure shows that Kapitza conductance is 250.1 MWm$^{-2}$K$^{-1}$ and 102.9 MWm$^{-2}$K$^{-1}$ across Al/Si and Au/Si interfaces, respectively. The value for Au/Si agrees to within 83% with the DMM calculations by Dechaumphai et al. using a three-dimensional real dispersion. This agreement suggests that the use of a one-dimensional realistic dispersion along the $\Gamma \rightarrow X$ direction is an acceptable approximation. Up to the cutoff frequency of the Au, the accumulations of $h_K$ for Au/Si and Al/Si are nearly identical. The features in curves are related to the Van Hove singularities and our assumptions in the DMM calculations. The similarity between these two curves implies that the frequency trends in accumulation of phonon thermal boundary conductance at a metal/Si interface is a direct function of the silicon properties. The differing values for thermal boundary conductance are a function of the metal film flux and maximum phonon frequency in the metal, which drives the total phonon energy incident on the interface.

More insight into these trends is gleaned by considering the calculations of Eq. 7. We plot $\alpha_{K,1\rightarrow 2}$ and the normalized accumulation of $\partial q_1/\partial T$ here denoted by $\alpha_{qT}$ for Au/Si and Al/Si in Figs. 1b and c, respectively. The accumulation of both flux and interface conductance predictions for Au/Si and Al/Si have very similar shapes - note, discontinuities in slope occur at the frequencies corresponding to the Brillouin Zone edge of either the metal or silicon (note, for Al/Si accumulation in Fig. 1c, there is a very slight second kink in the trend of $\alpha_{K,1\rightarrow 2}$). The fact that these DMM predicted accumulation functions overlap have implications on the interpretation of experimental thermal boundary conductance. While $q_1$ (and therefore $\partial q_1/\partial T$) is an intrinsic property of the material and can be relatively well predicted from accurate phonon dispersion relations without any assumptions of the interfacial scattering mechanisms, $\zeta_{1\rightarrow 2}$ relies heavily on the nature of phonon scattering and energy transfer across interfaces. For example, in the discussion above, we implemented the assumptions of the DMM in our calculations, which directly impacted our calculation of $\zeta_{1\rightarrow 2}$. However, this is simply an assumption, and we will now turn to experimental measurements to gain more insight into the nature of phonon scattering and energy transmission across solid interfaces.
FIG. 2. (a) The dispersion curves used in the calculation of $\alpha_{K, 1 \rightarrow 2}$ in Eqs. 5 & 7 for Al/Si and plotted in Fig[1]. The shaded area represents the $k - \omega$ space over which the integration is carried when $\omega_\alpha = 40$ Trad $s^{-1}$. Points $A'$ and $B'$ on the shaded region will coincide with $A$ and $B$ on the solid rectangle when $\omega_\alpha = \omega_{max}$ where both points will move along the longitudinal acoustic branch (LA) in aluminum and silicon, respectively. (b) The dispersion curves used in the calculation of $h_K (v_1 (\omega_{max}))$ given by Eq. 9 for metal/Si and plotted in Fig. 4. The shaded area represents the $k - \omega$ space over which the integration is carried when $\omega_{max} = 20$ Trad $s^{-1}$ and $v_1 (\omega_{max})$ is given by the dispersion curves contained within the shaded region. Points $A'$ and $B'$ will coincide with $A$ and $B$ and the dispersion curves in the shaded region will coincide with the dispersion curves in the solid rectangle when $\omega_{max} = 70$ Trad $s^{-1}$ with point $B'$ moving along the LA branch in silicon and point $A'$ moving vertically along the left side of the solid rectangle. The blue arrows denote the movement direction of the vertices of the shaded region as the angular frequency increases.

III. TDTR MEASUREMENTS OF THERMAL BOUNDARY CONDUCTANCE

Experimental measurements of the phonon transmission coefficient driving thermal boundary conductance at non-cryogenic temperatures do not exist, and insight into the fundamental assumptions and processes of $\zeta_{1 \rightarrow 2}$ at elevated temperatures would greatly advance phonon interfacial physics and heat transfer. In the work that follows, we use the analyses and results presented in Fig. 1 to extract the thermal boundary conductance accumulation and phonon transmissivity from experimental measurements of $h_K$ across metal/native oxide/silicon and metal/sapphire interfaces. By varying the metal while keeping the substrate otherwise identical, we change the “phonon flux” term, which changes the maximum frequency in the metal and the accessible modes in the
substrate that couple to the metal phonons. With relation to Fig. 1, by changing the metal film, we incrementally increase the phonon frequency on the accumulation curve (i.e., the metal film systematically changes the maximum value of $\omega_\alpha$ in Eq. 5). This approach yields direct insight into the mechanisms of phonon transmissivity into the substrate, as we describe in the remainder of this work.

We design a series of experiments to investigate $\zeta_{1\rightarrow2}(\omega_\alpha)$ via measurements related to the thermal boundary conductance accumulation function ($\alpha_{K,1\rightarrow2}$, Eq. 7). Without having to make any assumptions about how the phonons scatter at the interface, $h_K$ is directly related to both the phonon transmission coefficient and the temperature derivative of the heat flux in side 1. To a first approximation (i.e., no extreme temperature gradients), in a homogeneous material, $\partial q_1(\omega)/\partial T$ is easily calculated from knowledge of the phonon dispersion relations. With this, a consistent set of measurements can probe $\zeta_{1\rightarrow2}(\omega_\alpha)$, the interplay between phonon flux and transmission contributions to thermal boundary conductance, and the accumulation of phonon thermal boundary conductance.

Our experimental approach is based around measurements of $h_K$ on a series of metal films on (001)-oriented silicon substrates with a native oxide layer; in this case, $q_1$ is well defined by the phonon dispersion and well known lattice heat capacities in the metal, while $\zeta_{1\rightarrow2}(\omega_\alpha)$ is contained in our measurements by comparing to calculations of $\partial q_1(\omega)/\partial T$. We use consistent cleaning procedures on our substrates (alcohol and oxygen plasma clean) to ensure similar surface conditions upon metal evaporation. Various metal films were sputtered or evaporated at both Sandia National Laboratories and the University of Virginia, where several of each type were repeated at each institution to ensure consistency in our reported data. Several previous works have measured $h_K$ across a select few metal/native oxide/silicon interfaces. We report on measurements with nearly identical silicon surfaces to avoid effects due to contamination and surface roughness.

We measured the thermal boundary conductance using time domain thermoreflectance (TDTR), which is well suited to measure $h_K$. In our experiments, we use a modulation frequency of 8.81 MHz and a pump and probe $1/e^2$ radii of 35 and 12 $\mu$m, respectively. To minimize uncertainty, we measure the metal film thickness with a combination of profilometry, white light interferometry, atomic force microscopy, and when possible, picosecond acoustics. We fit widely used thermal models derived for TDTR to our experimental data using both $h_K$ and the substrate thermal conductivity as free parameters. As a calibration of our measurements, we report the best fit silicon thermal conductivity as a function of the metal film Debye temperature in Fig. 3.
Regardless of metal film, we measure the thermal conductivity of silicon within the uncertainty of the range of literature values for bulk silicon. This not only gives further confidence to our reported values, but also shows that TDTR is a suitable experimental technique to measure the thermal conductivity of bulk Si. We caution that we used large pump and probe spot sizes to avoid radial spreading effects, and in spite of operating at a relatively high modulation frequency for TDTR, we were able to accurately measure the thermal conductivity of the silicon substrates. Relatively large spot sizes must be employed if attempting to accurately measure the thermal conductivity of a bulk substrate, especially substrates with relatively high thermal effusivities, as pointed out in a recent work by Wilson and Cahill.

The thermal boundary conductances across the metal/native oxide/Si interfaces as a function of metal Debye temperature are shown in Fig. 3b. For the most part, our data and trends with metal
Debye temperatures agree well with the previously reported values (open symbols). We will examine this in terms of phonon accumulation and transport physics in the next section, however, we note that these data provide first-reported values for $h_K$ across several transition metal/native oxide/Si interfaces, which are important for an array of applications due to the wide spread use of silicon and metallized silicon contacts.

As another aside, it is interesting to note that the inclusion of Ti adhesion layers between Au and native oxide/Si increases the thermal boundary conductance substantially, as we have reported recently. We tested 3 different Au/Ti/native oxide/Si samples with different Ti thicknesses (2, 15, and 40 nm). Within experimental uncertainty, we measure the same thermal boundary conductance for each sample. The very similar agreement among the 2, 15 and 40 nm Ti cases suggests that the phonons in Ti play a role in $h_K$ at thicknesses as small as 2 nm.

IV. ANALYSES OF EXPERIMENTAL DATA AND PHONON TRANSMISSION COEFFICIENT ACROSS METAL/NATIVE OXIDE/SILICON AND METAL/SAPPHIRE INTERFACES

We can now analyze the data in Fig. 3 to quantify various aspects of thermal boundary conductance accumulation. The different metal films’ cutoff frequencies vary between 13.5 and 60 Trad s$^{-1}$. This provides a varying “bandwidth” of phonons that are incident on the metal/native oxide/silicon interface where each metal has a corresponding dispersion curve defined over the entire metal Brillouin zone and of maximum cutoff frequency less than or equal to 60 Trad s$^{-1}$.

However, the formulation in Section II derives the accumulation of Kapitza conductance assuming a single dispersion in the metal side. As a result, we can not directly compare the measurement results on Kapitza conductance to the accumulation function defined earlier. Instead, we reformulate the accumulation function to account for the varying dispersion relation by making $h_K$ a function of the phonon group velocity in side 1. In the most general case Eq. 1 is rewritten:

$$h_K(\omega_{\text{min},j}, \omega_{\text{max},j}, \nu_{1,j}(\omega, \omega_{\text{min},j}, \omega_{\text{max},j})) = \sum_j \int_{\omega_{\text{min},j}}^{\omega_{\text{max},j}} \frac{\partial q_{1,j}(\nu_{1,j}(\omega, \omega_{\text{min},j}, \omega_{\text{max},j}))}{\partial T} \zeta_{1\rightarrow 2}(\nu_{1,j}(\omega, \omega_{\text{min},j}, \omega_{\text{max},j})) d\omega$$

(8)

where the dependence of $\nu_{1,j}$ on $\omega_{\text{min},j}$ and $\omega_{\text{max},j}$ is to emphasize that while $\nu_{1,j}$ is dependent on $\omega$, the variable of integration, its domain of definition, $[\omega_{\text{min},j}, \omega_{\text{max},j}]$, is also variable. Using the same approach as in Section II we can also separate a weighted average of the transmission...
coefficient and simplify the above equation to:

\[ h_K(v_1(\omega_{\text{max}})) = Q_T(v_1(\omega_{\text{max}})) \frac{\zeta_{1\rightarrow2}(v_1(\omega_{\text{max}}))}{v_1(\omega_{\text{max}})} \]  

(9)

where

\[ Q_T(v_1(\omega_{\text{max}})) = \int_0^{\omega_{\text{max}}} \frac{\partial q_1(v_1(\omega_{\text{max}}))}{\partial T} d\omega \]  

(10)

and we dropped the dependence on \( \omega \) and the different cutoff frequencies and set the lower integration limit to zero for simplicity. Defining a generic expression for \( v_1 \) and varying the cutoff frequency in the metal allows us to compare \( h_K(v_1(\omega_{\text{max}})) \) to the experimental measurements on different metals. In this case, \( h_K(v_1(\omega_{\text{max}})) \) is thought of as the un-normalized Kapitza conductance accumulation across metal/Si interface.

In Eq. 9, \( h_K(v_1(\omega_{\text{max}})) \) and \( Q_T(v_1(\omega_{\text{max}})) \) are calculated assuming a sine-type dispersion for the metal phonons and using the polynomial fitted dispersion for silicon. Assuming a sine-type dispersion in the metal allows us to continuously vary the approximated phonon spectrum in the metal film by simply changing the cutoff frequency in the dispersion calculations, yielding a model input for the metal phonon flux in Eq. 9. The dispersion curves used in this calculation are shown in Fig. 2(b). For these calculations, we assume a ratio of longitudinal to transverse cutoff frequencies in the metal based on the ratio of cutoff frequencies in Al and assume the lattice constant to be that of Al. The solid line in Fig. 4 shows the computed values of \( h_K(v_1(\omega_{\text{max}})) \) along with the data from Fig. 3b. It is important to understand that the model plotted in Fig. 4 is not the mathematically known accumulation function and is thus different from the model plotted in Fig. 1. However, to a first approximation, the data and model in Fig. 4 “mimic” the accumulated phonon thermal boundary conductance across metal/Si interfaces. In this case, the different metal films change the accumulated frequency, so metal films with higher \( \omega_{\text{max}} \) simply increase the frequencies of phonons in silicon that contribute to \( h_K \). The difference between the formulation in this section and that in Section II can be further understood from the difference between the dispersion curves and the \( \omega - k \) space over which the integration is carried out shown in Fig. 2.

While we used a single dispersion curve for the calculation of \( \alpha_K(\omega_{\alpha}) \) in Section II, for each point of abscissa \( \omega_{\text{max}} \) on the solid line plotted in Fig. 4, there corresponds a sine-type dispersion curve defined over \( [0, \omega_{\text{max}}] \) and over the entire Brillouin zone in the metal side. In Fig. 2(b), the shaded area represents the \( k - \omega \) space over which the integration is carried when \( \omega_{\text{max}} = 40 \text{ Trad s}^{-1} \) and \( v_1(\omega_{\text{max}}) \) is given by the dispersion curve contained within the shaded region. Points \( A' \) and
$B'$ will coincide with $A$ and $B$ and the dispersion curves in the shaded region will coincide with that in the solid rectangle when $\omega_{\text{max}} = 70 \text{ Trad s}^{-1}$. Our model prediction for the thermal boundary conductance accumulation shown in Fig. 4 agrees well with our experimental data, especially considering the simplicity of our approach and phonon dispersion assumptions that we used in this procedure. We note that no fitting parameters are used in this model.

The isotropic solid assumption used in the calculation of the DMM is acceptable for cubic structures, however, bulk Ti and Ru have hcp crystal structure. Furthermore, thin Ti films can exhibit fcc, hcp, or a mix of hcp and fcc structures as has been shown in Al/Ti bilayers depending on the film thickness. With the lack of literature on the crystal structure of thin Au/Ti bilayers, it is hard to assess the applicability of the isotropic solid assumption to the Au/Ti/Si samples characterized. However, the agreement between Kapitza conductance measurement on Au/Ti/Si and Ru/Si with the other metals with cubic structures over the range of cutoff frequencies may justify this assumption. We also note that while a Sine-type dispersion is valid for simple cubic structures, all the metals measured had fcc, bcc, or hcp structures. To check this approximation, we compare the Kapitza conductance across Al/Si and Au/Si interfaces using Sine and real type dispersions. The result shows that the ratio of Sine to real dispersion Kapitza conductances is 0.96 for Al/Si and 1.04 for Au/Si. Noting the excellent agreement between Sine and real dispersion and the fact that Al and Au have fcc structures, suggest that the use of a Sine dispersion is an acceptable approximation.

The inset of Fig. 4 shows normalized $h_K(v_1(\omega_{\text{max}}))$, denoted by $\alpha_K(v_1(\omega_{\text{max}}))$, and the normalized model calculations for $Q_T(v_1(\omega_{\text{max}}))$, denoted by $\alpha_{qT}(v_1(\omega_{\text{max}}))$, normalized to the values of $h_K(v_1(\omega_{\text{max}}))$ and $Q_T(v_1(\omega_{\text{max}}))$ at the maximum cutoff frequency (60 Trad s$^{-1}$), respectively. The accumulated temperature derivative of the phonon flux increases monotonically with phonon cutoff frequency, $\omega_{\text{max}}$, as seen in the inset of Fig. 4. Even though this is a prediction from our model, this result is not surprising since to a first approximation, the cutoff frequency of metals with one atomic basis will directly scale with sound velocity and is related to the phonon density of states. At room temperature, the metals considered in this work can be considered in or near the classical limit (even for higher Debye temperature metals, such as Al and Cr, as their heat capacities are relatively flat around room temperature, justifying this assumption). In this case, the Bose-Einstein distribution can be estimated by: $f = k_B T / \hbar \omega$. Using the isotropic solid expression for the density of states given by $D_{1,j}(\omega) = \omega^2 / (2\pi^2 v_{1,j}^3(\omega))$ and invoking the Debye approximation for this analytical example, the phonon flux in the metal can be estimated
FIG. 4. Measured thermal boundary conductance as a function of metal cutoff frequency (phonon frequencies are taken from phonon dispersion curves in the literature). Our model for thermal boundary conductance as a function of $\omega_{\text{max}}$ agrees well with the data discussed in this work. The nature of the increasing trend in $h_K$ with $\omega_{\text{max}}$ is apparent by considering calculations of $\alpha_{qT}(\nu_1(\omega_{\text{max}}))$ in the inset. The linear change in $\alpha_{qT}$ with $\omega_{\text{max}}$, which is consistent with basic phonon physics arguments, implies that the nonlinear features in the measurements can be attributed to the phonon transmissivity across the metal/native oxide/Si interfaces. We provide the MATLAB code used to generate this accumulation model in the supplementary materials.

by: $q_{1,j} = k_B \omega^2 T / (8a^2 \omega_{\text{max},j}^2)$ where $a$ is the lattice constant in the metal. Carrying out the integration $Q_T$ can be estimated by:

$$Q_T \approx \frac{k_B}{24a^2} (\omega_{\text{max},\text{LA}} + 2\omega_{\text{max},\text{TA}}) = \frac{k_B}{24a^2} (1 + 2p)\omega_{\text{max}}$$  \hspace{1cm} (11)

where $p = \omega_{\text{max},\text{TA}} / \omega_{\text{max},\text{LA}}$ is the ratio of the transverse to longitudinal acoustic cutoff frequencies in aluminum used for the calculation shown in Fig. 4 and $\omega_{\text{max},\text{LA}} = \omega_{\text{max}}$. This approximation explains the origin of the linear behavior in $\alpha_{qT}$ in the inset of Fig. 4.
FIG. 5. Measured thermal boundary conductance across various metal/native oxide/Si and metal/sapphire interfaces as a function of metal cutoff frequency. The measured data show that the magnitude of the thermal boundary conductance across solid interfaces are not necessarily solely driven by the “phonon spectral mismatch”, but also are related to the phonon energies and velocities incident on the interface.

This brings to light one of the first conclusions that we find from our accumulation analysis: the magnitudes of thermal boundary conductances across solid interfaces are not necessarily dictated by the “phonon mismatch” of the materials, but are directly correlated to the temperature derivative of the phonon flux impinging on the interface. Accordingly, thermal boundary conductance across interfaces comprised of materials that have a larger phonon mismatch (for example, based on Debye temperature ratio) will not necessarily be smaller than $h_K$ across interfaces that have a smaller mismatch. The actual value of $h_K$ will depend on the phonon flux (energies and velocities).

This conclusion is further strengthened by considering the measured value of thermal boundary conductance across metal/sapphire interfaces compared to metal/native oxide/silicon interfaces, shown in Fig. 5. As an aside, the experimental procedures for fabricating and testing these various metal/sapphire interfaces were identical to that discussed in Section III, and each pair of substrates shown in Fig. 5 were coated in the same deposition chamber. It is evident that these metal/sapphire thermal boundary conductance data can be larger than the metal/Si data, even though the “phonon mismatch” is greater by a Debye temperature argument (note, for example, the Al and Cr data). This result reinforces the findings from our previous molecular dynamics work.

Referring back to our discussion regarding $\alpha_{\alpha T}$ in the inset in Fig. 4, the linear increase in the accumulation of this quantity will not change for different substrates. Therefore, the difference
between the metal/Si and metal/sapphire data can be attributed to the substrate modes and the average phonon transmission across the interface in the frequency range of the metal phonon spectra, \( \overline{\zeta_{1 \rightarrow 2}} (v_1 (\omega_{\text{max}})) \). We can rearrange Eq. 9 to find that \( \overline{\zeta_{1 \rightarrow 2}} (v_1 (\omega_{\text{max}})) \) is simply a function of \( h_K \) and \( Q_T \), represented as

\[
\overline{\zeta_{1 \rightarrow 2}} (v_1 (\omega_{\text{max}})) = \frac{h_K}{Q_T}.
\]

As demonstrated, the thermal boundary conductance measurements on the various samples construct the thermal boundary conductance accumulation function (i.e., the measured data are the quantity \( h_K \)). Since if we can accurately predict \( \partial q_1 / \partial T \) (and hence \( Q_T \)), we can determine the average of phonon transmission in the phonon spectrum of the metal by using the measured TDTR data in Eq. 12. Values for \( \overline{\zeta_{1 \rightarrow 2}} \) for the metal/native oxide/silicon and metal/sapphire are shown in Fig. 6. Note that these values did not require any information about phonon distributions in the substrate. Nevertheless, the quantity shown in Fig. 6a and b, gives direct insight into how phonons couple energy across solid interfaces comprised of silicon with a native oxide layer and sapphire, respectively. For example, our data indicate that the phonon transmission coefficients across metal/native oxide/Si and metal/sapphire interfaces are relatively constant for phonon frequencies greater than \( \sim 30 \) Trad s\(^{-1}\) and \( \sim 45 \) Trad s\(^{-1}\), respectively. This implies that the increase in thermal boundary conductance that is observed when the maximum phonon frequency in the metal goes beyond these two frequencies is due to an increase in phonon flux from high frequency modes and velocities in the metal, and not due to an increase in phonon transmission or better “matching” of the phonon modes near the interface. Thus the change in the metal phonon flux is what dominates interface conductance for high frequency phonons. The fact that \( \overline{\zeta_{1 \rightarrow 2}} (v_1 (\omega_{\text{max}})) \) flattens at 2 different frequencies for Si and sapphire is directly attributed to the substrate modes and phonon coupling between the metal film and the substrate.

Figure 6a also shows the calculations of \( \overline{\zeta_{1 \rightarrow 2}} (v_1 (\omega_{\text{max}})) \) for metal/silicon interfaces using the assumptions of the DMM. We show acceptable agreement between the DMM calculations and our experimentally derived data of \( \overline{\zeta_{1 \rightarrow 2}} (v_1 (\omega_{\text{max}})) \), which provides an additional platform for us to validate the DMM assumptions of phonon transmissivity beyond simply comparing DMM calculations of \( h_K \) to measured data. The model and data agreement in Fig. 6(a) support our assertions in the DMM calculations, namely that phonons scatter diffusively and elastically at metal/native oxide/silicon interfaces. We do not attempt to model \( \overline{\zeta_{1 \rightarrow 2}} (v_1 (\omega_{\text{max}})) \) for the sapphire data using the DMM due to the non-cubic crystal structure and additional assumptions that we must apply. Looking ahead, this approach provides a convenient method to determine average phonon trans-
FIG. 6. Average phonon transmission across various (a) metal/native oxide/Si and (b) metal/sapphire interfaces as a function of metal cutoff frequency. The experimental data are derived from the measurements of thermal boundary conductance using Eq. 12. The two low frequency silicon data are derived from measurements reported in Ref. [88] where all other data are derived from measurements in this current work. The solid line in (a) is $\zeta_{1 \rightarrow 2} (\nu_1 (\omega_{\text{max}}))$ modeled with the DMM. The acceptable agreement between the model and data suggest DMM-like average transmission of phonons across metal/native oxide/silicon interfaces at room temperature.

385 missivity across solid interfaces while testing assumptions of phonon scattering at interfaces.

V. SUMMARY AND OUTLOOK

386 In summary, we have developed the analytical theory to calculate the accumulation of phonon thermal boundary conductance as a function of phonon frequency across solid/solid interfaces. Based on the Generalized Mean Value Theorem for integrals, we show that this analytical formal-
ism can be related to the average interfacial phonon transmission across interfaces by considering the accumulation of the temperature derivative of the phonon flux incident on the interface. We test our theory with a series of thermal boundary conductance measurements across metal/native oxide/silicon and metal/sapphire interfaces. We use the measured values of thermal boundary conductance and calculations of the temperature derivative of the phonon flux to back out the average interfacial phonon transmission across the interfaces. Across the metal/native oxide/Si interfaces, we show good agreement with calculations of average spectral phonon transmission predicted from the DMM. This approach represents a relatively straightforward method to analyze thermal boundary conductance data across a series of carefully prepared interfaces and to quantify the spectral phonon transmission component to thermal boundary conductance, a quantity that has not been previously measured above superconducting temperatures.

In addition to the advancement in experimental analysis of thermal boundary conductance data and the development of a formalism for frequency accumulation of phonon thermal boundary conductance across interfaces, we also report several experimentally supported conclusions that advance the field of phonon interactions at interfaces. As a broad conclusion, we show that the magnitudes of thermal boundary conductances across solid interfaces are not necessarily dictated by the “phonon mismatch” of the materials, but are directly correlated to temperature derivative of the phonon flux impinging on the interface. This interplay between transmission due to phonon mismatch and phonon flux on the magnitude of phonon thermal boundary conductance changes spectrally, and for metal/native oxide/silicon and metal/sapphire interfaces, the phonon transmissivity is flat for high frequency phonons in the substrate, indicating that the changing metal phonon flux dominates the phonon thermal boundary conductance for high frequency phonons. In performing this analysis, we also validate the assumptions of the DMM for metal/native oxide/silicon interfaces based on comparison of the spectrally averaged phonon transmission. In our experimental measurements, we also provide measurements of thermal boundary conductance across metal/native oxide/silicon and metal/sapphire interfaces that have not previously been reported. In doing so, we show that for the Au/Ti/Si interface, the influence of phonons in the Ti adhesion layer can affect the thermal boundary conductance for layers as thin as 2 nm. Finally, we demonstrate the utility of TDTR for measuring the thermal conductivity of bulk Si substrates, which gives further demonstrates the capability of TDTR to measure the thermal conductivity of bulk, homogeneous materials with high thermal effusivity.

The utility of this approach lies in the generality in which it was developed. A similar approach
can be used with TDTR measurements of thermal boundary conductance across any interface in which this quantity is measurable (i.e., relatively high conductivity substrates). This could be very useful for understanding phonon transmission and interactions across interfaces comprised of a wide array of single crystals, dilute alloys, and some superlattices. When the thermal conductivity of the materials comprising the interface becomes too low, it is difficult to resolve the thermal boundary conductance, so advances in basic metrology must be achieved to extend this approach to low thermal conductivity materials, such as some complex oxides, soft materials (e.g., polymers), amorphous materials, and liquids.

Finally, this study sets the stage for robust theoretical and computational advances in phonon scattering and transmission across interfaces. A more computationally rigorous calculation of phonon flux accounting for the deviation from equilibrium can enhance the accuracy of our model. Including contributions due to inelastic scattering processes and using a more realistic dispersion could also account for additional deviations between our model and experimental measurements, especially when using this approach with more complicated interfaces not comprised of a simple metal in which the phonon flux can be relatively well predicted. In addition, it should be possible to study the accumulation of thermal boundary conductance and the average interfacial transmission with molecular dynamics, which could then be used to relate these trends to pure spectral transmission (i.e., not bandwidth averaged). This could provide a systematic computational approach to understand more complex phonon scattering processes such as inelastic scattering or transmission across disordered interfaces, which, when coupled with this experimental approach, will provide great advances in the understanding of phonon transport and thermal conductance in nanosystems.

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