1 Introduction

The ongoing trend of miniaturization on the nanoscale has created many new thermal challenges for device engineers and scientists. In many solid state devices, increased power densities in combination with continued size reductions are giving rise to thermal processes that cannot be predicted by traditional macroscopic laws and models. For example, as transistor gate lengths are continuously decreasing in an effort to continue the trends projected by Moore’s law, power dissipation is becoming a growing concern. Moore’s law is commonly reported as the doubling of transistor density on an integrated circuit every 18 months. As device dimensions shrink and operating frequencies increase, ever-increasing amounts of thermal energy are being generated in smaller and smaller volumes. As devices shrink to length scales on the order of carrier mean free paths, thermal transport is no longer dictated by the thermal properties of the materials comprising the devices, but rather the transport of energy across the interfaces between adjacent materials in the devices. In this paper, current theories and experiments concerning phonon scattering processes driving thermal boundary conductance \( h_{BD} \) are reviewed. Experimental studies of thermal boundary conductance conducted with the transient thermoreflectance technique challenging specific assumptions about phonon scattering during thermal boundary conductance are presented. To examine the effects of atomic mixing at the interface on \( h_{BD} \), a series of Cr/Si samples was fabricated subject to different deposition conditions. The varying degrees of atomic mixing were measured with Auger electron spectroscopy. Phonon scattering phenomena in the presence of interfacial mixing were observed with the trends in the Cr/Si \( h_{BD} \). The experimental results are reviewed and a virtual crystal diffuse mismatch model is presented to add insight into the effect of interatomic mixing at the interface. The assumption that phonons can only transmit energy across the interface by scattering with a phonon of the same frequency—i.e., elastic scattering, can lead to underpredictions of \( h_{BD} \) by almost an order of magnitude. To examine the effects of inelastic scattering on \( h_{BD} \), a series of metal/dielectric interfaces with a wide range of vibrational similarity is studied at temperatures above and around materials’ Debye temperatures. Inelastic scattering is observed and new models are developed to predict \( h_{BD} \) and its relative dependency on elastic and inelastic scattering events.

**Keywords:** thermal boundary conductance, pump probe transient thermoreflectance technique, diffuse phonon scattering, material diffusion, Auger electron spectroscopy, elemental characterization, elastic scattering, inelastic scattering, nanoscale solid-solid interfaces
energy transport in these devices, since ultimately, heat is undesirable and must be removed from the active regions of these devices that are generating energetic carriers.

Although this nanoscale size effect poses a major problem for understanding energy transfer through materials in a device [3,4], as these materials become smaller, more critical to the thermal management of many nanoscale devices is understanding how energy is transferred across the interfaces of the many materials that make up a device. As device dimensions shrink, it is becoming more likely that an energy carrier will scatter at an interface between two adjacent materials, where the resistance to energy transfer at this interface is much higher than in the materials that form the interface [2]. This thermal boundary resistance, $R_{BD}$ (the inverse of thermal boundary conductance, $h_{BD}$), gives rise to a temperature drop, $\Delta T$, across the interface of materials where energy transport occurs.

Thermal boundary conductance, sometimes termed Kapitza conductance, was first observed by Kapitza in 1941 [5] between copper and liquid helium by observing that in the presence of a heat flux across the copper/liquid helium boundary, a temperature discontinuity existed. This phenomenon can be caused by, for example, the differing transport properties of the materials adjacent to the interface [6] or a disordered region of the materials resulting from device fabrication conditions [7]. The thermal boundary conductance, $h_{BD}$, relates the heat flux to the temperature drop $\Delta T$ across the interface.

$$q = h_{BD} \Delta T$$  

The consideration of $h_{BD}$ is vital in the design of nanostructures used in, for example, IC design, thermal interface materials [8–10], thermoelectric devices [11,12], thin-film high temperature superconductors [13,14], vertical cavity surface emitting lasers [15], optical data storage media [16], ultrashort pulse laser systems [17,18], and high power density field effect transistors [19,20].

In this paper, current theories and experiments concerning phonon scattering processes driving thermal boundary conductance ($h_{BD}$) are reviewed. Traditional models make assumptions about phonon scattering that limit their range of applicability. These models and assumptions are discussed in Sec. 2 along with the transient thermoreflectance (TTR) technique, a measurement technique common in measuring interfacial thermal conductance. The remainder of the paper will review experimental studies of thermal boundary conductance conducted with the TTR technique challenging specific assumptions about phonon scattering during interfacial heat transfer. The experimental results are summarized and several new models, developed as a result of these experiments, are reviewed.

2 Phonon Interfacial Transport: Theory and Measurements

Although much work has been done in the area of interfacial thermal transport, most of the work has been done at low temperatures ($<10$ K) and for liquid-solid interfaces. While there have been a few proposed theories for room temperature application, most of which are adaptations of the low temperature models, there is no model that reliably captures the variability in measured interfacial thermal conductance. An understanding of the basic transport mechanisms involved in interfacial transport is critical to the design and engineering of nanostructured material systems used in a wide range of technologies, from state-of-the-art nanoelectronics, to thermoelectric modules, to thermal barrier coatings used in turbine engines.

Thermal energy is transported in metallic materials nearly completely by the electron system, whereas in nonmetals, the energy is stored and transported by phonons. Phonon scattering, the main transport mechanism across a wide range of device interfaces, has been successfully predicted by various models in limiting cases. These models are based on the specular or diffuse nature of phonon scattering at the interface. When a phonon undergoes specular scattering, the angle of the incident phonon equals the reflected angle and the angle of the transmitted phonons can be determined by Snell’s law. When a phonon undergoes diffuse scattering, the scattering event is completely independent of any information about the particle before the scattering event, such as the angle of incidence. The particle scatters with equal probability in all directions. The specularity parameter, $p$, estimates the probability that phonons are specularly scattered [21]:

$$p = \exp \left[ -\frac{16\pi^2 \delta^2}{\lambda^2} \right]$$  

where $\delta$ is the roughness parameter and $\lambda$ is the phonon wavelength. In the case of interfaces, the roughness parameter, $\delta$, is the mean square deviation of the height of the surface from the reference plane [22]. A representative wavelength of the phonon system approaching the interface can be estimated by the thermal coherence length, $\ell_{th}$, which assuming a thermal spread of $k_BT$, can be calculated by [22]

$$\ell_{th} = \frac{2\pi \nu}{k_BT}$$  

Here $k_B$ is Boltzmann’s constant, $\hbar$ is Planck’s constant, and $\nu$ is the phonon group velocity. At low temperatures, $\ell_{th}$ is large and $p$ approaches 1 (completely specular scattering). As temperature increases, $\ell_{th}$ decreases, which decreases the probability of specular scattering (increases the probability of diffuse scattering).

Specular scattering is most likely experienced by long wavelength phonons (which represent the majority of phonons that are excited at low temperatures) at perfectly smooth interfaces. For example, consider an acoustically hard material, such as diamond, at 5 K. The diamond phonons approach an interface with only one monolayer of roughness (the lattice constant of diamond is $\approx 3.57$ Å). Given an average phonon velocity of $v_{diamond} = 14,367$ m s$^{-1}$ [23], a specularity parameter of $p = 0.997$ is calculated for the diamond phonon scattering. However, as temperature is increased up to 300 K, the specularity parameter drops down to $p = 0$, indicating that all phonons will undergo diffuse scattering events.

To predict $h_{BD}$ in the event of purely specular scattering, Little proposed the acoustic mismatch model (AMM) [24,25]. In the AMM the transmissivity, that is, the percentage of the incident phonons that will be transmitted across the interface, is calculated based on the ratio of acoustic impedances of the materials on either side of the interface. The AMM has proven successful at predicting $h_{BD}$ at low temperatures ($T<7$ K) and at ideal interfaces [7]. However, this ideal case only represents a very limited population of interfaces in modern devices, which often operate at higher temperatures and have disordered regions near the interface that would induce diffuse scattering. To account for this type of phonon scattering, Swartz and Pohl [26] developed the diffuse mismatch model (DMM) to predict $h_{BD}$ at more realistic interfaces.

To apply the DMM in its simplest form, the following assumptions must be made: (1) phonons are elastically scattered—i.e., a phonon from side 1 with frequency $\omega$ can only emit a phonon into side 2 with the same frequency $\omega$ after the scattering event (for discussions, side 1 will refer to the softer material with lower phonon velocities and side 2 will refer to the stiffer material with higher phonon velocities); (2) phonon scattering is completely diffuse—i.e., a scattered phonon has no memory of the mode (longitudinal or transverse) or direction of the incident phonon; and (3) the materials on both sides of the interface are elastically isotropic—i.e., the longitudinal and transverse acoustic velocities are constant in all crystallographic directions. The DMM is mathematically stated as
where the transmissivity from side $i$ to side $3-i$, $\xi^{3-i}$, has no angular or phonon mode dependence because of the nature of diffuse scattering. $D(\omega)$ is the density of states, $\omega$ is the phonon frequency, and $v$ is the phonon velocity. The generalized notation of superscript $3-i$ denotes the side opposite to side $i$, so that the side opposite to side 1 is 2 and the side opposite to side 2 is 1 [26]. The subscripts $i$ and $j$ refer to the side and the phonon mode (longitudinal or transverse), respectively, and the superscript 0 on $\rho^0$ refers to an equilibrium distribution. Diffuse scattering will rethermalize the phonon system (thermalizing black boundaries) [4] so the phonon system can be described by the equilibrium Bose–Einstein distribution ($\rho^0(\omega, T)$) and can therefore be characterized by a temperature at the interface, $T$. The cutoff frequency, $\omega_c$, of each phonon mode $j$ can be calculated for the separate phonon modes assuming an isotropic Debye solid, $\omega_c^j = v_j(6\pi^2N)^{1/3}$, where $N$ is the total number of phonons per unit volume [27]. Assuming a Debye density of states, the transmission probability is calculated by [26]

$$
\xi^{3-i}(\omega) = \sum_{j} \frac{\omega_c^j}{\omega_c^j + \omega} = \sum_{j} \frac{1}{\omega_c^j + \omega} = \frac{1}{v_{3-i,L}} + \frac{2}{v_{3-i,T}}
$$

which is a result of applying the principle of detailed balance [28] to the phonon fluxes from sides $i$ and $3-i$ approaching a perfect interface and assuming single phonon elastic scattering.

This model has been shown to predict conductance across higher temperature interfaces ($T > 15$ K) relatively well [7,26]. However, at much higher temperatures (such as the operating temperatures of high frequency microelectronic devices), the DMM has been shown to either underpredict or overpredict experimental data, depending on the material systems [6]. Neither the AMM and DMM accurately predict $h_{BD}$ in most practical material systems at conditions of technological interest.

Another model for $h_{BD}$, the phonon radiation limit (PRL), estimates the maximum conductance for interfacial transport from elastic scattering [29]. Development of the PRL is very similar to that of the DMM. However, the PRL assumes that all of the phonons in side $3-i$ up to the cutoff frequency in side $i$ (assuming $\omega_{c}^i < \omega_{c}^{3-i}$) contribute to thermal transport though elastic collisions ($\xi^{3-i}=1$). With these assumptions, the PRL is given as

$$
h_{BD}^{PRL} = \frac{1}{4} \sum_{j} \int_{0}^{\omega_{c}^{j}} v_{3-i,L} \beta a D_{3-i,j}(\omega) \frac{\partial \rho^0(\omega, T)}{\partial T} d\omega
$$

which represents the maximum conductance due to elastic scattering. Since the PRL represents the upper limit of the elastic contribution to thermal transport, it will always predict a higher $h_{BD}$ than the DMM. The DMM and PRL predict a constant $h_{BD}$ at temperatures approaching the Debye temperature, $\theta_D$, of the lower Debye temperature material (acoustically “softer” material or the material with the lower phonon velocity). This has to do with the change in the phonon population of the metal film as a function of temperature, and the fundamental assumption of elastic scattering employed in the DMM and PRL.

### 3 Experimental Measurement of $h_{BD}$ Using the Transient Thermoreflectance Technique

There are many different techniques that have been used to measure thermal boundary conductance. An in-depth review of these techniques put into historical context is given by Swartz and Pohl [26]. This paper reviews studies by several groups who have used the TTR technique to measure $h_{BD}$ for a wide range of material interfaces. The TTR technique employs a “pump” light pulse that is focused to a small spot on the surface of a metallic film that, upon absorption of the incident photons by the electrons in the metal, creates a temperature rise in the electron system. This change in temperature of the film produces a proportional change in the reflectivity. The change in the reflectivity as the film cools by conduction into the underlying structures is measured with a time-delayed “probe” light pulse, which is focused onto the center of the heated region of the film.

The experimental results presented here were obtained using the TTR experimental setup shown schematically in Fig. 1. The primary laser output emanates from a Coherent RegA 9000 am- plexer seeded with a Coherent MIRA 900 oscillator operating at a 250 kHz repetition rate with about 4 $\mu$J pulse and a 150 fs pulse width at 800 nm (1.55 eV), which is split at a 9:1 pump to probe ratio. The pump beam, which is modulated at 125 kHz by an acousto-optic modulator (AOM), provides a modulated sequence of excitation events on the sample surface. The probe beam passes through a half-wave plate, rotating the polarization by 90 deg relative to the pump, which enables improved noise filtering. The length of the probe path is set by precise control of a dovetail prism mounted on a variable delay stage, with a total maximum delay between the pump and probe pulses of 1500 ps. The probe is directed through a polarizing filter, oriented such that only the probe light is passed and not the pump, which is positioned before a silicon photodiode, which monitors the reflection of the probe beam off the sample. A lock-in amplifier triggered at the modulation frequency of the pump monitors the photodiode response to the modulation in intensity of the probe beam. The radii of the pump and probe beams are measured with a sweeping knife edge technique [30]. Although the low repetition rate of the RegA system and the “one shot on–one shot off” modulation rate of the pump beam ensure minimal residual heating between pump pulses, the phase of the signal must still be taken into account for electronic noise. Phase correction is performed by the procedures for signal phase adjustment outlined by Stevens et al. [30]. The thermal boundary conductance is determined by fitting the TTR data to a lumped capacitance thermal model with $h_{BD}$ as the free parameter, as outlined in Refs. [31,32].

### 4 Inability of the DMM to Accurately Predict $h_{BD}$

The TTR method has been used to determine $h_{BD}$ on a wide variety of interfaces and experimental measurements show a wide range of agreement with the DMM. This is easily seen in Fig. 2, which shows the ratio of measured $h_{BD}$ with the TTR technique to predict $h_{BD}$ with the DMM calculated via Eqs. (4) and (5) as a function of the ratio of the materials’ Debye temperatures. The ratio of the two materials’ Debye temperatures gives a quantitative value to compare the degree of differing vibrational states between two materials. If the ratio is close to unity, then the materials have very similar cutoff frequencies, and are considered acoustically matched. If the ratio is much smaller or greater than unity, then the samples are considered acoustically mismatched.

Figure 2 clearly demonstrates the inability of the DMM to accurately predict $h_{BD}$. It is seen that in acoustically well-matched material systems with a Debye temperature ratio close to 1, the DMM overpredicts the boundary conductance while for mismatched systems the DMM underpredicts the conductance by as much as an order of magnitude. It should be noted, however, that the interfaces of these samples were not abrupt junctions, and the influence of the possible formation of a finite-size mixing or two-phase region at the interface could not be determined. This work investigates the underprediction and overprediction of the DMM by systematically investigating two effects, interatomic mixing and inelastic scattering. These investigations seek to further explore the validity of the single phonon elastic scattering assumption.
Fig. 2 Ratio of measured $h_{BD}$, $h_{BD}^{\text{meas}}$, to $h_{BD}$ predicted from the DMM, $h_{BD}^{\text{DMM}}$, versus the ratios of the Debye temperatures of the metal film to the dielectric substrate. The data presented in this figure are selected results from Stevens et al. [6], Lyeo and Cahill [50], Stoner and Maris [41], and Hopkins et al. [31]. Some of the diamond substrates were subject to hydrogen termination before metal film deposition represented by the “H/diamond” after the metal film. The general trend shows that the DMM underpredicts measurements on acoustically mismatched samples and overpredicts measurements on acoustically matched samples.

Fig. 1 Schematic of the transient thermoreflectance setup at the University of Virginia’s Microscale Heat Transfer Laboratory.

Verdi V10
$\lambda = 532$ nm 10 W

Verdi V5
$\lambda = 532$ nm 5 W
A portion of the difference between the measured $h_{BD}$ and that calculated from the DMM in well-matched samples such as Cr/Si could result from varying degrees of mixing. The DMM does not take into account an interfacial mixing layer. Although the scattering-mediated acoustic mismatch model accounts for multiple scattering events that could result from interfacial disorder [39], it assumes specular phonon reflection, which clearly is not a valid assumption in this case since the interfacial region was observed to be significantly disordered.

At an ideal interface with no mixing, a phonon from the Cr film scatters at the Cr/Si interface, and is either transmitted into the Si or reflected back into the Cr. From Eq. (5) the phonon transmission probability for the Cr/Si interface is $P_{Cr/Si}=37\%$, meaning that at the ideal interface, 37\% of the phonons are transmitted from the Cr into the substrate. In the event of interfacial mixing, the phonons must propagate across a finite amount of space to conduct energy into the substrate. When these phonons scatter with Si at the beginning of the mixing layer, a certain percentage of the phonons are transmitted deeper into the mixing layer. As the thickness of the interfacial mixing layer increases, the probability that a phonon will scatter more than once increases thereby decreasing $h_{BD}$, which is expected with increased diffuse scattering in well-matched materials. Thus, the presence of an interfacial mixing region causing multiple elastic scattering events, which are not accounted for, may be the cause of the overestimation of the DMM in well-matched material systems with Debye temperature ratios close to 1.

Fig. 3 Thermal boundary conductance thickness measurements on various Cr/Si interfaces from Hopkins et al. [32] and corresponding VCDMM calculations from Beechem et al. [34]. Where the DMM predicts $h_{BD}$ that is almost eight times larger (0.86 GW m$^{-2}$ K$^{-1}$) than that measured on the samples with no dependence on mixing layer thickness or compositions, the VCDMM calculations are within 18\% of the measured values and show similar trends with mixing layer thickness when taking into account the change in Si composition in the mixing region.

6 Predicting the Interfacial Mixing Dependency of $h_{BD}$ With the VCDMM

Beechem et al. [34] presented a virtual crystal diffuse mismatch model (VCDMM) to predict the influence of mixing region thickness and composition on $h_{BD}$. This model introduces a simple correction to the DMM through use of a virtual crystal to account for the manner by which energy propagates through the interfacial region. In this manner multiple scattering events occurring at the interface can be quantified allowing for more accurate prediction of $h_{BD}$ as well as insight into the effect of interfacial quality on overall heat transfer.

To account for a finite interfacial thickness, the VCDMM replaces the interfacial region with a third material, the virtual crystal, which has properties that are a blend of the bulk materials on either side [42] and a thickness equal to the length of disorder. Incorporating the virtual crystal modifies the DMM to account for both the interaction between each of the bulk materials and interface as well as the finite thickness of the interface.

The interaction between the two materials and the disordered region is investigated by estimating the conductance between each of the bulk materials and the virtual crystal. This is accomplished by applying the DMM for each of the two interfaces with a modification of the transmission coefficient to account for the virtual crystal so that the transmission is calculated at the $i$/virtual crystal and 3–$i$/virtual crystal interfaces. Again, this calculation assumes all solids are Debye solids. It follows that $h_{BD}$ for the two-interface system is given by

$$h_{BD}^{\text{VCDMM}} = \left( \frac{1}{h_{BD}^{VC}} + \frac{1}{h_{BD}^{3-i-VC}} \right)^{-1}$$

(7)

The above relation accounts for only the efficiency by which energy transfers from the bulk to the interface but does not analyze the ease by which energy propagates through the interfacial region. To examine this effect, the results of Eq. (7) are scaled according to the depth factor, $\Xi$, which is a ratio of the interfacial thickness, $\delta$, to the mean free path of the virtual crystal, $\lambda_{VC} (\Xi = \delta / \lambda_{VC})$. The interfacial thickness, $\delta$, is also the roughness parameter used in Eq. (2). Using kinetic theory with the virtual crystal approximation for thermal conductivity [42] to estimate
the mean free path along with the measured thickness of the Cr/Si interface, the depth factor is calculated allowing for the estimation of $h_{BD}$ from the VCDMM by

$$h_{BD}^{VCDMM} = \left[ \frac{1}{h_{BD}^{VC}} + \frac{1}{h_{BD}^{i-VC}} \right]^{-1} = \frac{\Lambda_{VC}}{\delta} \left[ \frac{1}{h_{BD}^{VC}} + \frac{1}{h_{BD}^{i-VC}} \right]^{-1}. \tag{8}$$

Equation (8) describes the effect of interatomic mixing around the interface on phonon interfacial transport. However, in acoustically matched metal/dielectric material systems such as Cr/Si, another channel of energy transport associated with electron-phonon nonequilibrium could significantly affect interfacial energy transport [43]. In well-matched material systems, the thermal resistance associated with phonon-phonon interfacial transport, $R_{pp} = 1/h_{pp}$, is relatively small and on the same order as the resistance associated with an electron-phonon nonequilibrium in the film near the interface, $R_{ep} = 1/h_{ep}$, where this electron-phonon boundary conductance is given by [43]

$$h_{ep} = \sqrt{\frac{k_{ep}}{G}} \tag{9}$$

where $k_{ep}$ is the phonon thermal conductivity in the metal and $G$ is the electron-phonon coupling factor of the metal [44–47]. Therefore, in acoustically matched material systems, $R_{pp}$ must also be taken into account, which leads to

$$h_{BD}^{VCDMM} = \left[ \frac{1}{\sqrt{k_{ep}G}} + \frac{1}{h_{BD}^{VC}} + \frac{1}{h_{BD}^{i-VC}} \right]^{-1}. \tag{10}$$

Shown in Fig. 3 is a comparison of the virtual crystal model to the experimental data from Hopkins et al. [32]. The virtual crystal approach is within 18% of the measured values whereas the predicted $h_{BD}$ of the DMM, which does not account for any interfacial mixing, is about eight times these values. In both prediction and measurement, there is a distinct trend of decreasing $h_{BD}$ with increasing interfacial thickness. This results from the additional scattering, which occurs as the phonons must propagate through the disordered region.

### 7 Influence of Inelastic Phonon Scattering on Thermal Boundary Conductance

In an attempt to investigate the underpredictive trends of the DMM as seen in Fig. 2, several computational and experimental efforts have been undertaken. In 1993, Stoner and Maris [41] reported $h_{BD}$ at a range of acoustically mismatched interfaces from 50 K to 300 K. As expected from the DMM, the measured $h_{BD}$ decreased with an increase in sample mismatch and the change in $h_{BD}$ decreased with temperature. In the sample with the greatest mismatch, Pb/diamond, values of $h_{BD}$ were measured that exceeded the DMM prediction by two orders of magnitude. One possible explanation offered for the underestimate of $h_{BD}$ by the DMM was the occurrence of inelastic scattering—i.e., one or more phonons of frequency $\omega_0$ on side 1 were emitting one or more phonons of frequency $\omega_0$ on side 2—thereby offering additional channels for transport not accounted for in the DMM. At a Pb/diamond interface, a high frequency diamond phonon could scatter at the interface and emit low frequency phonons on the Pb side.

As the interface temperature increases above the Debye temperature of the softer material (i.e., in the classical limit), the DMM predicts that $h_{BD}$ is relatively constant. This is a result of the change in phonon population with temperature predicted by the Bose–Einstein distribution function. At temperatures close to a material’s Debye temperature, the change in phonon population with temperature becomes linear. The DMM is a function of the temperature derivative of the Bose–Einstein distribution, which results in the constant $h_{BD}$ predicted at higher temperatures ($T > T_D$) when elastic scattering is assumed. Assuming only elastic scattering and a Debye solid, the transmission coefficient is independent of temperature.

To check the temperature dependence of $h_{BD}$, Stevens et al. [37] performed molecular dynamics (MD) simulations at a range of temperatures. The simulations were conducted on both highly and lightly mismatched interfaces with Debye temperature ratios of 0.2 and 0.5. A strong linear relationship was observed in the $h_{BD}$ results for the temperature range considered, with $h_{BD}$ varying by nearly a factor of 4. This strong linear temperature dependence suggests a thermal transport mechanism that is dependent on temperature in the classical limit. The most likely explanation for this discrepancy is that while MD simulation accounts for both elastic and inelastic scattering at the interface, the DMM accounts only for elastic scattering. Chen et al. [48] used MD simulations to examine a Kr/Ar nanowire interface, showing a linear increase in $h_{BD}$ with an increase in temperature from 35 K to 55 K, which they ascribed to anharmonic processes. Kosevich [49] considered the role of inelastic scattering on the phonon transmission probability using a multiharmonic model to show that inelastic scattering makes a greater contribution to $h_{BD}$ than elastic scattering for interfaces with very different vibrational spectra.

Evidence of inelastic scattering has been observed experimentally by Lyo and Cahill [50] at low temperatures ($T \leq T_{room}$) and Hopkins et al. [31] at high temperatures ($T \geq T_{room}$). Lyo and Cahill [50] observed an approximately linear increase in $h_{BD}$ over a temperature range of 80–300 K on carefully prepared Pb and Bi thin films on diamond substrates. Hopkins et al. [31] observed a linear trend in $h_{BD}$ over temperatures from 300 K to 500 K on several different samples, including the heavily mismatched Pt/Al$_2$O$_3$ and Pt/AlN interfaces. The linear trends observed in these experimental works match the aforementioned simulation results, which suggested that multiple-phonon processes (inelastic scattering) can play a significant role in interface thermal conductance. However, these data do not agree with the trends predicted by the DMM. Selected data from Stoner and Maris [41], Lyo and Cahill [50], and Hopkins et al. [31] are shown in Fig. 4, which...
shows the ratio of measured $h_{BD}$ to that predicted from the DMM for six different samples over a 200 K temperature range. It is apparent that in these mismatched samples, the measured data show an increasing linear trend, which is much greater than the slightly increasing if not constant predictions from the DMM.

The presence of inelastic scattering events, which add an additional channel of interfacial energy transport, may be the cause of the underestimation of the DMM in mismatched material systems with distinctly different Debye temperatures. In well-matched material systems, such as Cr/Si as previously studied, the difference between the modes in the film and substrate is very small, so the joint vibrational modes near the interface are most likely present in both the film and substrate making elastic scattering highly probable.

8 Joint Frequency Diffuse Mismatch Model

An underlying assumption governing the DMM is that a phonon transmits energy across an interface by emitting a phonon with the same frequency, i.e., the phonons are elastically scattered. Therefore, as the interface temperature increases above the Debye temperature of the softer material, the DMM predicts that $h_{BD}$ is relatively constant. This implies that the DMM predicts a constant $h_{BD}$ above $\sim 100$ K for Pb/diamond since $\theta_D(Pb)=105$ K [27]. In fact, the DMM predicts a constant $h_{BD}$ above 100 K for any Pb interface regardless of the substrate. However, if inelastic phonon processes occur (i.e., a phonon with frequency $\omega$ diamond scatters into several phonons with frequencies below $\omega_{pd}$), then the change in $h_{BD}$ with temperature would be related to the change in the diamond phonon population in addition to the Pb population.

Hopkins and Norris [51] developed a simple correction to the DMM to account for the discrepancy between the DMM and the experimental data in the event of inelastic scattering. By blending the vibrational spectra of the film and substrate materials, an approximation for the contribution of the inelastic modes was developed with a diffuse scattering assumption, the joint frequency diffuse mismatch model (JFDMM). The JFDMM assumes the same form as the DMM but uses a modified phonon velocity that is calculated for each allowed frequency. The modified phonon velocity is a factor that is proportional to the ratio of measured $h_{BD}$ to $h_{BD}$ predicted from the DMM and is used to enhance the incident phonon flux to take into account the joint vibrations that are allowed after dampening effects. However, without computationally expensive computer simulations or a rigorous theoretical treatment, this weighting factor cannot be explicitly determined for every phonon mode, and therefore should be viewed as an estimation of the joint modes participating in $h_{BD}$. The JFDMM can be viewed as a starting point for estimating the maximum $h_{BD}$ due to inelastic scattering.

Consider atoms vibrating at joint modes around the interface with no dampening effects. These atoms can therefore vibrate at all allowable frequencies up to the maximum allowed frequency in the substrate. Atoms on sides 1 and 2 will be coupled in joint vibrational modes with frequencies up to the cutoff frequency of side 2. This is paralleled in the JFDMM through the weighted average of the two materials’ phonon states in the incident flux. The weighting factor, $\xi$, reflects the dampening of the substrate modes, and is used to enhance the incident phonon flux to take into account the joint vibrations that are allowed after dampening effects. However, without computationally expensive computer simulations or a rigorous theoretical treatment, this weighting factor cannot be explicitly determined for every phonon mode, and therefore should be viewed as an estimation of the joint modes participating in $h_{BD}$. The JFDMM can be viewed as a starting point for estimating the maximum $h_{BD}$ due to inelastic scattering.
\[ \alpha_{\text{mod},j}^i = \alpha_{i,j}^i \quad \text{and} \quad v_{\text{mod},j} = v_{2,i,j} \], respectively, and redefines Eq. (4) in terms of the flux transmitted from side 2 to side 1, given as [53]

\[ h_{\text{BD}}^{\text{meas}} = \frac{1}{4} \int_0^{\omega_2,j} v_{3,\omega,j} f_{\text{BD}}^3(T) \frac{\partial}{\partial T} f_{\text{BD}}(\omega, T) d\omega \]

From the nature of diffuse scattering, the inelastic transmission probability is \( \xi_2^{\text{inel}}(T) = 1 - \xi_2(T) \), which is different from the elastic transmission probability calculated with Eq. (5). Equation (15) allows higher frequency phonons that do not exist in the film to participate in \( h_{\text{BD}} \). Without knowledge of the explicit temperature dependence of \( \xi_2^{\text{inel}}(T) \), \( h_{\text{BD}} \) cannot be calculated. However, the use of Eq. (15) along with experimental data can give important insights into the role of inelastic phonon scattering in thermal boundary conductance.

Hopkins and Norris [53] used Eq. (15) to develop the inelastic phonon radiation limit (IPRL). Consider the case where all available substrate phonons are participating in \( h_{\text{BD}} \). In this case, the probability that a phonon on side 2 is inelastically transmitted (i.e., scatters into lower frequency phonons and is transmitted into side 1) is unity. By letting \( \xi_2^{\text{inel}}(T) = 1 \), Eq. (15) becomes an expression for the largest allowable thermal boundary conductance due to inelastic scattering, or the IPRL, expressed as

\[ h_{\text{BD}}^{\text{IPRL}} = \frac{1}{4} \int_0^{\omega_2,j} v_{2,\omega,j} f_{\text{BD}}^2(T) \frac{\partial}{\partial T} f_{\text{BD}}(\omega, T) d\omega \]

The IPRL assumes that all side 2 phonons are transmitted into the film, and does not explicitly take into account elastic or inelastic scattering processes. However, by allowing all frequencies of phonons in side 2 to transmit energy into side 1, which has the lower cutoff frequency, inelastic scattering is implied. Note that in this limit, similar to the JFDMM, which also takes into account some inelastic scattering, the assumption of equilibrium is relaxed and therefore the principle of detailed balance is not enforced.

From the trends in the IPRL as compared with the PRL and experimental data, the relative contributions of elastic and inelastic scattering can be examined [53]. Above the film’s Debye temperature, it is apparent that contributions from elastic scattering

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**Table 1** Pertinent thermophysical properties of materials in this work: from top to bottom: molar mass—\( M \) [23], molar density—\( n \) [23], longitudinal and transverse phonon velocities (which were calculated from the elastic lattice constants), \( v_L \) and \( v_T \) [23], Debye temperature—\( \theta_D \) [27], and mass density—\( \rho \) [23]

<table>
<thead>
<tr>
<th>Material</th>
<th>( M ) (kg mol(^{-1}))</th>
<th>( n ) (mol m(^{-3}))</th>
<th>( v_L ) (m s(^{-1}))</th>
<th>( v_T ) (m s(^{-1}))</th>
<th>( \theta_D ) (K)</th>
<th>( \rho ) (kg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(_2)O(_3)</td>
<td>101.2</td>
<td>0.0203</td>
<td>0.197</td>
<td>0.209</td>
<td>0.052</td>
<td>0.012</td>
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<tr>
<td>AlN</td>
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<td>97,990</td>
<td>46,794</td>
<td>138,269</td>
<td>290,008</td>
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<tr>
<td>Au</td>
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<td>11,120</td>
<td>3,390</td>
<td>1,543</td>
<td>6,980</td>
<td>17,500</td>
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<td>Bi</td>
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<td>6,267</td>
<td>1,290</td>
<td>1,107</td>
<td>4,100</td>
<td>12,800</td>
</tr>
<tr>
<td>Cr</td>
<td>3,970</td>
<td>3,255</td>
<td>19,300</td>
<td>9,780</td>
<td>7,190</td>
<td>3,512</td>
</tr>
<tr>
<td>Diamond</td>
<td>23</td>
<td>15</td>
<td>645</td>
<td>2,230</td>
<td>105</td>
<td>240</td>
</tr>
<tr>
<td>Pb</td>
<td>15</td>
<td>23</td>
<td>630</td>
<td>2,230</td>
<td>105</td>
<td>240</td>
</tr>
<tr>
<td>Pt</td>
<td>15</td>
<td>23</td>
<td>630</td>
<td>2,230</td>
<td>105</td>
<td>240</td>
</tr>
<tr>
<td>Si</td>
<td>3,970</td>
<td>3,255</td>
<td>19,300</td>
<td>9,780</td>
<td>7,190</td>
<td>3,512</td>
</tr>
</tbody>
</table>
The ongoing trend of miniaturization on the nanoscale has created many new thermal challenges for device engineers and scientists. An understanding of nanoscale energy transport is becoming increasingly important as standard device sizes continually decrease and classical heat transfer laws fail to predict energy transfer processes in a growing number of nanodevices. In nanodevices, it is more likely that energy carriers will scatter at an interface between two adjacent materials, where the resistance to energy transfer is much higher, than in the materials that form the interface. Traditionally used models do not adequately predict the rate of energy transfer across these interfaces, which is governed by the thermal boundary conductance, \( h_{BD} \). The most commonly used model of \( h_{BD} \) is the DMM, overpredicts \( h_{BD} \) in well-matched material systems with a Debye temperature ratio close to 1 and underpredicts \( h_{BD} \) for mismatched material systems by as much as an order of magnitude. The major limiting assumptions in the DMM are examined using experimental results obtained using the TTR technique, and several new models are presented.

A study of the interfacial transport in the presence of atomic mixing at the boundary between two materials lends insights into the effect of multiple-phonon scattering. The presence of an interfacial mixing region causing multiple elastic scattering events that are not accounted for may be the cause of the overestimation of the DMM in well-matched material systems with Debye temperature ratios close to 1. The VCDMM, which introduces a mixing region to the DMM, offers insight into the scattering processes that affect \( h_{BD} \) at these imperfect interfaces.

Experimental measurements of \( h_{BD} \) at elevated temperatures \((T \geq \theta_D)\) enable exploration of the influence of inelastic scattering mechanisms. A linear trend in \( h_{BD} \) has been observed in several samples, even when the temperature is driven above the Debye temperature of the softer film material. Since the DMM only accounts for elastic scattering, the \( h_{BD} \) calculations from the DMM predict a relatively constant temperature trend. The measured linear trend shows that inelastic scattering contributes to interfacial transport at temperatures around and above the Debye temperature of a material adjacent to a solid interface.

To further understand the role of inelastic and elastic scattering events in interfacial transport, the JFDMM was developed, which takes into account the contributions of inelastic scattering to \( h_{BD} \) by considering the phonon flux at the interface to consist of frequencies that exist in both solids. The JFDMM shows improved predictions from the DMM. From the basic assumptions of the JFDMM, an upper limit to \( h_{BD} \) was derived assuming all phonons are participating in energy transfer through inelastic scattering—the IPRL. To further understand inelastic scattering, experimental data on several interfaces were quantitatively compared, and the relative contributions of inelastic and elastic scattering to \( h_{BD} \) at these different interfaces were observed. The relative contribution of inelastic scattering to \( h_{BD} \) decreases as the materials adjacent to the interface become vibrationally similar.

Acknowledgment

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Nomenclature

- \( D \) = spectral phonon density of states per unit volume
- \( f \) = phonon statistical distribution of energy states
- \( G \) = electron-phonon coupling factor, \( \text{W m}^{-3} \text{K}^{-1} \)
- \( h \) = Planck’s constant divided by \( 2\pi, \text{s} \)
- \( h_{BD} \) = thermal boundary conductance, \( \text{W m}^{-2} \text{K}^{-1} \)
- \( k_B \) = Boltzmann’s constant, \( \text{J K}^{-1} \)
- \( L_B \) = thermal coherence length, \( \text{m} \)
- \( M \) = molar mass, \( \text{kg mol}^{-1} \)
- \( N \) = phonon number density, \( \text{m}^{-3} \)
- \( n \) = molar density, \( \text{mol m}^{-3} \)
- \( p \) = specularity parameter
- \( R_{BD} \) = thermal boundary resistance, \( \text{W}^{-1} \text{m}^{-2} \text{K}^{-1} \)
- \( T \) = temperature, \( \text{K} \)
- \( v \) = group velocity, \( \text{m s}^{-1} \)

Greek Symbols

- \( \delta \) = interfacial roughness (thickness), \( \text{m} \)
- \( \theta_D \) = Debye temperature, \( \text{K} \)
- \( \zeta \) = interfacial transmission probability
- \( \lambda \) = mean free path, \( \text{m} \)
- \( \lambda \) = wavelength, \( \text{m} \)
\[ \rho = \text{mass density, } \text{kg m}^{-3} \]
\[ \Xi = \text{interfacial depth factor} \]
\[ \omega = \text{angular frequency of vibration, } \text{s}^{-1} \]
\[ \xi = \text{weight factor for vibrational states} \]

**Subscripts**
- \( e_p \): due to electron-phonon scattering
- \( i \): side i
- \( j \): polarization (longitudinal or transverse)
- \( L \): longitudinal mode
- \( \text{mod} \): modified to account for joint vibrational states
- \( pp \): due to phonon-phonon scattering
- \( T \): transverse mode

**Superscripts**
- 0: equilibrium
- \( c \): cutoff
- DMM: calculated with the diffuse mismatch model
- el: accounting for elastic processes
- \( i \rightarrow 3-i \): from side j to side 3-i
- \( i \rightarrow VC \): from side j to the virtual crystal
- inel: accounting for inelastic processes
- IPRL: calculated with the inelastic phonon radiation limit
- meas: measured with the TTR technique
- PRL: calculated with the phonon radiation limit
- VCMDMM: calculated with the virtual crystal diffuse mismatch model

**References**


