QUASI-BALLISTIC HEAT TRANSFER FROM METAL NANOSTRUCTURES ON SAPPHIRE

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ABSTRACT

Quasi-ballistic phonon transport, where heat transfer does not obey Fourier’s law, occurs when length scales become comparable to the phonon mean free path (MFP). Understanding this regime of heat transport is of fundamental interest, as the manner in which the heat transport deviates from Fourier’s law reveals important information about the phonon mean free path distribution. While ultrafast techniques can provide the time resolution to observe heat transfer in this regime, the minimum size of the heated region is restricted by diffraction to approximately 1 µm, which is larger than phonon MFPs in many materials. To circumvent this limit, we study heat transfer from metallic dot arrays with sub-micron diameters on sapphire fabricated using electron beam lithography. We describe heat transfer models which allow us to determine how the heat transfer in sapphire deviates from Fourier’s law at these small length scales. Our results indicate that quasi-ballistic transport occurs in sapphire when length scales are on the order of hundreds of nanometers.

INTRODUCTION

Classical size effects in heat transfer, where the characteristic length scales of a system are comparable to the phonon mean free paths (MFPs), have long been of interest [1–4]. In this transport regime, thermal transport properties are modified from their bulk values, and heat transfer can become quasi-ballistic due to a lack of scattering. The ability to create nanostructured materials has led to many observations of size effects, and modified thermal conductivities have been demonstrated in nanoscale systems such as nanowires, superlattices, and nanocomposites [4,5]. Transient ballistic transport has also been studied using heat-pulse techniques at cryogenic temperatures in low defect materials such as single-crystal sapphire, where phonon MFPs are comparable to the dimensions of the sample itself [6]. More recently, the ballistic contribution to transport in GaAs was studied using a time-resolved x-ray diffraction and time-domain thermoreflectance technique [7]. A nonlocal theory of heat transport was proposed for the cases where ballistic modes are an important component of the heat transport [8].

Thermal conductivity modifications in systems like nanowires are due to internal size effects, where the characteristic length of the structure is comparable to the phonon MFPs. In contrast, a type of size effect external to a structure can occur in a semi-infinite material if phonons are emitted from a heated region that is smaller than the MFP. In this case, a lack of scattering causes phonons to be out of equilibrium, resulting in non-diffusive heat transport. The modified heat transfer due to this type of size effect has also been investigated. Numerical analysis of the heat transfer from a nanoparticle with diameter smaller than the MFP using the Boltzmann transport equation showed that Fourier’s law would significantly overpredict the heat flux [9].

This prediction was recently experimentally verified using a transient grating technique in sapphire [10]. In this experiment, the effects of quasi-ballistic transport were interpreted in terms of a net thermal resistance from a thin nickel line into the sapphire substrate. The net thermal resistance, which included contributions from the nickel-sapphire interface as well as from the sub-
strate, increased as the thickness of the line decreased, indicating a deviation from Fourier’s law.

In this paper, we examine how heat transfer specifically in the sapphire substrate deviates from Fourier’s law. While the transient grating technique requires the generation of soft x-ray light [10], we show we can observe quasi-ballistic transport simply by using transient thermoreflectance (TTR) to observe the heat transfer from metallic dot arrays on sapphire. The dots are fabricated using electron-beam lithography, and have diameters from 10 μm down to 300 nm.

The paper is organized as follows. First, we introduce the heat transfer model we use to describe the system. Next, we discuss the details of our experiment and the fabrication of the dot arrays. We then present the results, and finally conclude the paper and describe our future work.

HEAT TRANSFER MODEL
Introduction
If the heat transfer is diffusive, we can model the heat transfer using the heat equation, as has been done previously [11, 12]. Of course, in the quasi-ballistic regime, the heat transfer will not be diffusive, in which case the heat equation is no longer valid. However, we can still use the model to determine to what degree the transport is quasi-ballistic by the magnitude of the deviation from Fourier’s law.

The solution from the heat equation which accounts for radial heat transfer, Gaussian beams, and the high repetition rate of our laser is given in terms of the transfer function $Z$:

$$Z(t) = \sum_{m=-\infty}^{\infty} H(\omega_0 + m\omega_s) e^{im\omega_s t}$$  \hspace{1cm} (1)

The real and imaginary parts of $Z$ correspond to the in-phase and out-of-phase signal return by the lock-in amplifier, respectively [12]. Here $\omega_0$ is the angular modulation frequency, typically between 1 and 15 MHz; $\omega_s = 80$ MHz is the angular laser repetition frequency; $j = \sqrt{-1}$, and $H(\omega)$ is the solution of the heat equation.

The solution $H(\omega)$ can be written as the product of the transfer matrices for the layers [13]. The properties at the bottom of a layer can be related to the properties at the top of a layer using a transfer matrix given by:

$$\begin{bmatrix} \theta_b \\ f_b \end{bmatrix} = \begin{bmatrix} \cosh(qd) & \frac{-1}{\sigma_c q} \sinh(qd) \\ -\sigma_c q \sinh(qd) & \cosh(qd) \end{bmatrix} \begin{bmatrix} \theta_i \\ f_i \end{bmatrix}$$  \hspace{1cm} (2)

where $\theta$ is the temperature, $f$ is the heat flux, subscript $b$ and $t$ denote the bottom and top of the layer, respectively, $d$ is the layer thickness, $\sigma_c$ is the cross-plane thermal conductivity, and $q = j\omega / \alpha$, where $\alpha$ is the thermal diffusivity. Multiple layers can be conveniently treated simply by multiplying the matrices together:

$$\begin{bmatrix} \theta_b \\ f_b \end{bmatrix} = M_n M_{n-1} \ldots M_1 = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} \theta_i \\ f_i \end{bmatrix}$$  \hspace{1cm} (3)

$M_i$ is the transfer matrix for layer $i$. If the bottom layer is semi-infinite or adiabatic, which is usually the case, then the surface temperature at the top of the layers, $\theta_i$, is given in the terms of the heat flux boundary condition $f_i$ as:

$$\theta_i = -\frac{D}{C} f_i$$  \hspace{1cm} (4)

To account for radial conduction, a zero-order Hankel transfer is applied to the heat equation in cylindrical coordinates. It has been shown that the results above apply in this case with only a modification to the definition of $q$, which now becomes: [12]

$$q^2 = \frac{\sigma_r k^2 + C_r j\omega}{\sigma_z}$$  \hspace{1cm} (5)

where $\sigma_r$ is the in-plane thermal conductivity, $C_r$ is the volumetric specific heat, and $k$ is the Hankel transform variable. The heat transfer boundary condition $f_i$ is now a Gaussian function of the radial coordinate $r$, following the intensity distribution of the pump beam of radius $w_0$. Weighting this result with the Gaussian intensity distribution of the probe with radius $w_1$ gives the final solution to the heat equation $H(\omega)$: [12]

$$H(\omega) = \int_0^\infty k \left( -\frac{D}{C} \right) \exp \left( -\frac{k^2(w_0^2 + w_1^2)}{8} \right) dk$$  \hspace{1cm} (6)

Because the final solution is normalized to facilitate fitting with experimental data, the constants have been omitted from the above equation.

Single Dot Heat Transfer Model
The previous analysis models the heat transfer through continuous layers with a Gaussian heating and probing profile. This analysis must be modified to account for the discontinuous nature of the dot array, as illustrated in Fig. 1. We first assume that the heat transfer from a particular dot is independent from the other dots, making the modification is particularly simple. Since the dot radius $a$ is much smaller than the pump and probe radii, both the heating and probing profile can be well described by a radial step function of radius $a$. The zero-order Hankel transform of a step function is $J_1(ak) / k$ [14], where $J_1(z)$ is a first-order Bessel
A square array of circles is difficult to Fourier transform analyti-
cally, but a square array of squares, or a two-dimensional square
wave, can be represented exactly as a Fourier series. Therefore,
we model the heating profile as a two-dimensional square wave
with each square having a side length of \( w = 2a \) and a period \( L \).

It is now more appropriate to solve the heat equation in Carte-
sian rather than cylindrical coordinates, and so the definition of
\( q \) becomes:

\[
q^2 = \frac{\sigma_{xy}(k_x^2 + k_y^2) + C_r j \omega}{\sigma_z}
\]  

(8)

where \( \sigma_{xy} \) is the in-plane thermal conductivity, and \( k_x \) and \( k_y \) are
the spatial Fourier transform variables in \( x \) and \( y \), respectively.

To obtain \( H(\omega) \) we can perform the procedure as before;
namely, compute the transfer matrices for different values of \( k_x \)
and \( k_y \), compute the Fourier transform of the heating function \( f_t \),
and weight this by the probe function to get \( H(\omega) \). Since the square wave heating function is periodic, its
Fourier transform consists of discrete multiples of the fundamen-
tal spatial frequency \( \Omega_0 = 2\pi / L \):

\[
f_t(\Omega) = Q \sum_n \sum_m X_{nm} \delta(\Omega - n\Omega_0) \delta(\Omega - m\Omega_0)
\]  

(9)

where \( Q \) is the energy of the pump beam, \( \Omega \) is a continuous spa-
tial frequency variable, and \( X_{nm} \) are the Fourier components of
the square wave, given by:

\[
X_{nm} = \begin{cases} 
\frac{w^2}{L^2} & n = m = 0 \\
\frac{w}{2\pi L} (1 - \exp(-jm\Omega_0)) & n = 0, m \neq 0 \\
\frac{w}{2\pi L} (1 - \exp(-jm\Omega_0)) & n \neq 0, m = 0 \\
\frac{1}{4\pi^2 nm} & n \neq m \neq 0 
\end{cases}
\]  

(10)

Because \( f_t \) only contains discrete multiples of \( \Omega_0 \), \( \theta_t = -(D/C)f_t \) only contains these frequencies. It can be shown that
weighting \( \theta_t \) by the same probe profile results in the simple ex-
pression for \( H(\omega) \):

\[
H(\omega) = \sum_n \sum_m |X_{nm}|^2 \left( -\frac{D}{C} \right)_{n,m}
\]  

(11)

where the subscripts \( n \) and \( m \) correspond to evaluating the argument
at frequencies \( k_x = n\Omega_0 \) and \( k_y = m\Omega_0 \), respectively.
Note that this procedure has neglected the Gaussian intensity variation of the pump and probe beams. To account for this, it is necessary to modify the heating and probing profile by multiplying the square wave by a Gaussian. In the Fourier domain, the multiplication becomes convolution, and the result is essentially a Dirac comb of Gaussians at each discrete frequency point. The resulting Fourier transform is now a continuous function of frequency because the Gaussian is aperiodic, significantly complicating the analysis.

An approximation can be made if the squares are much smaller than the pump and probe radii. Intuitively, if the pump and probe radii \( w_0 \) and \( w_1 \) are much larger than the array period \( L \) then it is reasonable to approximate the pump and probe radii as infinitely large and with uniform intensity. In the frequency domain, this can be explained because of the mismatch in spatial frequencies. An array with a small period \( L \), relative to \( w_0 \) and \( w_1 \), will have a high spatial frequency \( \Omega_0 = 2\pi/L \). The frequency components in the Gaussian are distributed as \( \exp(-w_i^2 \Omega^2/8) \), where \( i=1 \) or \( 2 \) corresponds to the pump or probe radius. Thus if \( (w_i/L)^2 \gg 1 \), the frequency components of the Gaussian will be confined to a region in frequency space close to the discrete frequency of the square wave. In this case we can simply approximate the function as a delta function and recover the simpler result given in Eq. 11. Because the condition for this approximation to hold scales as \( (w_i/L)^2 \), the approximation is expected to be accurate even for periods approaching the probe radius \( w_1 \).

As described in the next section, the probe radius is around 5 \( \mu \text{m} \), and we are typically concerned with \( L < 2 \mu \text{m} \), and so the approximation is expected to be valid.

EXPERIMENTAL DETAILS

Description of pump and probe system

Our experimental system is a typical pump-probe setup which has been described elsewhere [12]. Briefly, a pulsed laser at 800 nm and 80 MHz repetition rate (Spectra-Physics) is split into pump and probe pulses. The pump pulse train is modulated at a frequency between 1-15 MHz using an electro-optic modulator to allow lock-in detection, then frequency doubled to 400 nm using a BIBO crystal. The probe pulse train is directed to a variable delay line which can provide up to 6.5 ns total time delay. Both pulses are then directed colinearly to the sample and focused using a 10X microscope objective. The pump and probe \( 1/e^2 \) radii are 27 \( \mu \text{m} \) and 5 \( \mu \text{m} \), respectively. The reflected probe light is directed to a photodiode, the output of which is fed to a lock-in amplifier. The lock-in amplifier returns the amplitude and phase of the probe beam relative to that of a reference wave.

Sample Fabrication

The metal nanostructures were fabricated using a standard metal lift-off process. A single crystaline c-plane sapphire wafer (University Wafer) was cleaved into approximately 2cm x 2cm pieces. The sapphire pieces were cleaned with acetone and isopropyl alcohol (IPA), then spin-coated with approximately 200nm of 495K PMMA resist. The resist was exposed using electron-beam lithography at 10 kV, permitting feature sizes down to 100 nm to be written. The pieces were developed with a 3:1 IPA:MIBK solution, then immediately coated with approximately 45 nm of Al using electron-beam deposition. The thickness of the metal layer was verified using profilometry. Finally, the remaining resist was removed using Microstrip at 80 C. The final result is shown in an SEM image in Fig. 2. The nanostructures consist of arrays of closely packed circles or squares of varying diameter. Because the dots are discontinuous and cannot exchange heat as they would in a metal film, each dot cools independently of the others. When the dot radius becomes comparable to the dominant phonon MFPs in sapphire, quasi-ballistic heat transfer will occur, with the heat transfer becoming less and less diffusive as the dot radius shrinks.

RESULTS

We created both circular and square individual dots with diameters from 1-10 \( \mu \text{m} \), along with dot arrays containing dots with diameters from 300 nm - 10 \( \mu \text{m} \). At the largest length scales of 10 \( \mu \text{m} \), the heat transport is expected to be diffusive and the model should return the bulk thermal conductivity of sapphire, which is approximately 35 W/mK along the c-axis at room temperature. Because of the large diameter and period of the dots, the heat transfer from a particular dot should not be affected by the presence of the other dots, an assumption we can test by mea-
FIGURE 3. AMPLITUDE SIGNAL FROM EXPERIMENTAL DATA (SYMBOLS) AND MODEL (LINES). HERE, AMPLITUDE IS THE PRIMARY FITTING VARIABLE. THE TOP AND BOTTOM LINES ARE 10% BOUNDS.

FIGURE 4. (A) IN-PHASE, (B) OUT-OF-PHASE, AND (C) PHASE SIGNAL FROM EXPERIMENTAL DATA (SYMBOLS) AND MODEL (LINES). THE TOP AND BOTTOM LINES ARE 10% BOUNDS.

FIGURE 5. MEASURED THERMAL CONDUCTIVITY OF SAPPHIRE VERSUS DOT DIAMETER.

suring both the dot arrays and the single dots. Figs. 3 and 4 show that the data and the model result for 6 µm dots are in excellent agreement for a thermal conductivity of \( k = 39 \) W/mK. Here, the in-phase signal \( X = \text{Re}(Z) \), out-of-phase signal \( Y = \text{Im}(Z) \), amplitude \( R = X^2 + Y^2 \), and phase \( \Phi = \tan^{-1}(Y/X) \), where \( Z \) is the transfer function. The individual dot and dot array models yield nearly the same result, indicating that the presence of other dots in the array can be neglected. Since one model assumed a square dot and the other a circular dot, and both are in agreement, we can conclude that the difference in shape does not play an important role.

The measured thermal conductivity for all the diameters is shown in Fig. 5. For all the cases shown here, both the individual dot and dot array heat transfer models gave similar values of thermal conductivity, indicating the dots are essentially independent of each other. As can be seen from the figure, deviations from Fourier’s law do not appear until the dot diameter is less than 1 µm, indicating that the dominant heat carrying phonons in sapphire have MFP < 1 µm. This is consistent with previously reported studies of sapphire [10]. For a 350 nm diameter dot, the measured thermal conductivity is much lower than the expected value, indicating that the heat transfer is significantly reduced from the Fourier law prediction due to quasi-ballistic transport. This suggests that a substantial fraction of phonons in sapphire have MFP on the order of hundreds of nanometers.

CONCLUSION AND FUTURE WORK

In this paper we have studied quasi-ballistic heat transfer from sub-micron diameter metal dots on sapphire using TTR. We described two models which can be used to calculate the heat transfer from individual dots and dot arrays. We find that quasi-ballistic transport does not occur until the dot diameters are smaller than 1 µm, indicating that most phonons in sapphire have MFP less than 1 µm. Our future work will focus on systematically varying the dot diameters at length scales below 1 µm so that we can more precisely map the thermal conductivity versus MFP. With the optimization of the fabrication process, we expect to be able to create dots with diameters as small as 20 nm, where the heat transfer will deviate strongly from Fourier’s law.

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REFERENCES


