TIME-DOMAIN THERMOREFLECTANCE PROBING OF TUNABLE THERMAL TRANSPORT IN SILICON METALATTICES

A Dissertation in
Materials Science and Engineering

by
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Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

December 2020
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ABSTRACT

In semiconductor materials, heat is predominantly carried by phonons which are characterized by two fundamental length scales, mean free path (10nm-1μm) and wavelength (1nm-10nm). On reducing the geometric length scale of material systems below the corresponding phonon mean free path, phonons no longer scatter amongst themselves and instead get scattered in the ballistic regime by the finite boundaries of the sample, thus providing geometrical control over thermal transport which has become essential for emerging technologies in the fields of thermal rectification, thermoelectric energy conversion, thermal insulation and efficient thermal management of high heat generating devices such as solid-state lasers and chips in integrated circuits. Various recent experimental and theoretical works have demonstrated the realization of such a tuning ability through the utilization of nanostructured material systems which can provide the required confinement in zero, one, two or three dimensions.

Amongst these, the system that inspired the present study is thermal transport behavior in a three-dimensional nanostructure composed of a semiconductor alloy matrix embedded with nanoparticles [36]. Thermal conductivity as low as 1W/m-K due to combined alloy and nanoparticle scattering was theoretically observed in this system [36]. In addition, a minimum in thermal conductivity was also calculated for an optimal nanoparticle size less than 100nm [36]. But a comprehensive experimental and theoretical implementation of such behavior for a three-dimensional periodic structure has been limited. This work demonstrates such a directional phonon flow through a three-
dimensional silicon nanostructure with a periodic distribution of pores composed of different materials and with periodicity ranging from 1-100nm.

Chapter 2 presents briefly a quantitative prediction of thermal transport through this three-dimensional periodic structure, referred to as silicon metalattice in this work, as a function of pore radius, pore volume fraction and pore material. In this chapter, ballistic transport of phonons, studied in collaboration with Dr. Ismaila Dabo’s group, is explored through these structures in addition to pore material dependent minimum in thermal conductivity as a function of pore diameter. This chapter also explains how these structures are synthesized experimentally, in collaboration with Dr. John Badding’s group, using high pressure infiltration of silicon into voids of templates constituted of closely packed silica spheres which are then later used for the experimental measurement of thermal transport.

Chapter 3 discusses the steps involved in setting up time-domain thermoreflectance setup which is then used for studying thermal transport of silicon metalattice structures. This chapter demonstrates how this technique can be used to characterize thermal properties of thin films accurately with nanometer depth resolution and with minimal sample fabrication. It elaborates on the issues that are encountered and corresponding solutions that are utilized to collect accurate data with high signal to noise ratio. It further explains the analytical model required for modeling the collected experimental data using MATLAB to extract thermal properties. It goes through the process of acquiring accurate values for different parameters that are to be used in the model used for experimental data fitting which is then used for calibrating the setup.
against standard samples. MATLAB code used for modeling the data is included in the Appendix B section. In addition, steps involved in building an air bearing delay stage used for providing an accurate delay to the probe beam is described in detail in Appendix A.

Chapter 4 explores experimental characterization of temperature dependent thermal properties for silicon metalattice structures using time-domain thermoreflectance setup. For each sample, it explains the process of data collection, evaluation of parameters and analyzing the collected data with TDTR model to extract the respective thermal properties. The chapter further compares the experimental data with the theoretical predictions, in collaboration with Dr. Ismaila Dabo’s group, to explain the nature of thermal transport through these structures.

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ACKNOWLEDGEMENTS

My journey as a PhD student at Penn State has been a very challenging yet an exciting one which helped me grow immensely on both personal and professional fronts. This was however made possible because of continual efforts and support given to me by a lot of people. Firstly, I would like to express my sincere gratitude to my PhD advisor, Dr. Venkatraman Gopalan. His commitment, knowledge, motivation and open-mindedness in various research discussions that we conducted in the course of my PhD helped me overcome different challenges that I faced while pursuing my research. I would also like to thank my co-advisor, late Dr. John Badding for his support and knowledge that further contributed to my research understanding and knowledge.

I would like to take this opportunity to extend my thanks to the rest of my committee members, Dr. Ismaila Dabo, Dr. Suzanne Mohney and Dr. Brian M. Foley for agreeing to serve on my committee. Their advice and useful insights guided my research in an appropriate direction and helped me shape this dissertation. I would also like to thank all my collaborators with whom I interacted to bring this research work together.

I spent numerous hours discussing interesting research and undertaking fun activities during my graduate life with my former and current lab group members. With that I would like to thank Dr. Vladimir Stoica, Dr. Shaun Mills, Dr. Arnab Sen Gupta, Dr. Ryan Haislmaier, Dr. Shiming Lei, Dr. Xiaoyu Ji, Dr. Yakun Yuan, Dr. Shashank Pandey, Dr. Yan Cheng, Dr. Yunzhi Liu, Dr. Shih-Ying Yu, Dr. Jennifer Russell, Dr. Shukai Yu, Dr. Weinan Chen, Dr. Alex Hendrickson, Dr. Yixuan Chen, Dr. Haw-Tyng Huang, Dr. Parivash Moradifar, Haricharan Padmanabhan, Huaiyu Wang, Rui Zu, Jingyang He, Lujin Min, Carly Mathewson, Pratibha Mahale, Nabila Nabi Nova, and Alex Grede.
But most importantly I would like to thank my mom and dad for constantly supporting and loving me which helped me endure the difficult times I faced during my PhD program. Talking to them made work here enjoyable and their advice constantly encouraged me to keep moving forward towards the future.

I’d like to finally thank National Science Foundation under MRSEC grant DMR-1420620 for providing me the funding required for conducting this research. The findings and conclusions in this work do not necessarily reflect the view of the funding agency.
Chapter 1

Introduction

1.1 Background and motivation

Achieving control over thermal transport is not only essential for emerging technologies in the fields of thermal rectification [1-4], thermoelectric energy conversion [5-6] and thermal insulation [7] but is also needed for efficient thermal management of high heat generating electrical, optical and optoelectronic devices such as solid-state lasers and chips in integrated circuits [8].

Figure 1-1: Numerical predictions of a) wavelength spectrum and b) mean free path spectrum at room temperature for silicon nanowires having a diameter of 100nm and bulk silicon. A shift in phonon spectrum for nanowires towards shorter wavelengths and shorter mean free paths as compared to bulk silicon is demonstrated. Adapted from Ref. 10.
Various recent experimental and theoretical works have demonstrated that the realization of such a tuning ability is possible through the utilization of nanostructured material systems.

In metals, heat is mostly carried by electrons. However, in semiconductor materials and insulators, heat is predominantly carried by phonons which are characterized by two fundamental length scales, mean free path (ℓ) and wavelength (λ). For a bulk semiconductor, mean free path and wavelength of phonons typically lie in the range of 10nm–several microns and 1-10nm respectively [9-11]. This is illustrated for bulk silicon in Figure 1-1.

Depending on the interaction between structural length scales and the two fundamental length scales of phonons, phonon mean free path ℓ and phonon wavelength λ, different regimes of phonon propagation can be defined as illustrated in Figure 1-2.

- **Diffusive regime**: In case of a bulk semiconductor, when the geometric dimensions are much greater than the respective length scales of phonons, local thermal equilibrium can be achieved through phonon-phonon scattering. Thus, Fourier’s law of heat conduction [12] can be used to describe thermal flow through them according to

\[
Q = -\Lambda \nabla T
\]

where \( Q \) is the local heat flux density flowing through a material with thermal conductivity \( \Lambda \) subjected to a temperature gradient \( \nabla T \).

- **Ballistic regime**: In nanoscale regime, when the geometrical confinement dimensions become smaller than the corresponding mean free path of the heat energy carriers, they no longer diffract amongst themselves and instead get scattered by the finite boundaries of the sample, due to which equilibrium is no longer attained in the system [13-17]. Fourier’s law therefore fails to explain thermal transport properties for such systems and sub-continuum effects come into play.
Various computational advances have been made towards evaluating thermal properties of such nanostructured material systems. One of the most commonly used approaches towards calculating thermal conductivity is solving linearized Boltzmann transport equation \[ \Lambda = \frac{1}{3V} \sum_{pq} C_{pq} v_{pq} \ell_{pq} \] under the relaxation time approximation as given by

\[ \Lambda = \frac{1}{3V N_q} \sum_{pq} C_{pq} v_{pq} \ell_{pq} \]  

Equation 1.2

where \( C, v \) and \( \ell \) define heat capacity, group velocity and effective mean free path respectively for phonons with wavevector \( q \) and polarization \( p \). \( V \) represents volume of unit cell and \( N \) is the number density of phonons. Although solving the full Boltzmann transport provides a much more accurate description of thermal transport, the approximation above has been used to a good measure for calculating thermal conductivity of bulk materials and nanostructured materials [19,20,21]. In order to solve Equation 1.2, it is essential to accurately determine phonon dispersion for a structure in addition to relaxation rates corresponding to different scattering mechanisms involved in it. Molecular dynamics and first principle calculations [21] have been shown as versatile methods to determine phonon dispersion curves which can be used to calculate heat capacity and group velocity required for solving Equation 1.2.
Matthiessen’s rule \([18,22]\) in Equation 1.3 has been used as a good approximation for calculating the effective relaxation time \(\tau\) (mean free path \(\ell\)/group velocity \(v\)) by adding contributions from different phonon scattering mechanisms.

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{Umklapp}}} + \frac{1}{\tau_{\text{boundary}}} + \frac{1}{\tau_{\text{alloy}}} + \frac{1}{\tau_{\text{GB}}} + \ldots
\]  

\text{Equation 1.3}

\begin{itemize}
  \item \textit{Inelastic scattering} is an intrinsic phonon-phonon scattering process which occurs in every solid due to anharmonicity present in its interatomic potential energy function. Four-phonon processes mostly exist at very high temperatures and have a much weaker contribution to scattering as compared to three phonon processes as estimated by Klemens \([23]\). Amongst the two types of three-phonon processes, normal (N) process conserves both energy and momentum. However, as shown by Callaway \([24]\) and Ziman \([22]\), it redistributes the energy to different frequency modes of phonons and hence indirectly offers a resistance to heat flow at intermediate temperatures through frequency dependent impurity scattering processes. Umklapp process, on the other hand, does not conserve momentum of phonons thus resulting in a finite thermal resistance of a solid at high temperatures. Klemens used perturbation theory \([23]\) to derive an expression for Umklapp scattering process given in Equation 1.4

\[
\frac{1}{\tau_{\text{Umklapp}}} = A\omega^2 T \exp \left( \frac{B}{T} \right)
\]  

\text{Equation 1.4}

where \(\omega\) is the phonon frequency, \(T\) is the temperature and \(A\) and \(B\) are empirical constants obtained through experimental data fitting.

\item \textit{Boundary scattering} is one of the dominant scattering mechanisms in nanostructures where phonons scatter against the boundaries when their intrinsic mean free path becomes much greater than the geometrical dimensions. This effect was first realized experimentally by de Hass and Biermasz in KCl and quartz crystals \([25]\) for which the measured thermal resistance started showing sample size dependence at temperatures below 10K. In 1938, Casimir \([26]\) studied heat conduction for such a system by assuming that phonons travelling through a crystal with minimal
internal and defect scattering is analogous to propagation of electromagnetic radiation in hollow space. It was further assumed that all phonons scattered diffusively at the sample surfaces. Using these conditions to solve Boltzmann transport equation, effective boundary scattering mean free path ($l_{b,\text{Casimir}}$) for a crystal has been calculated in the Casimir limit to be [18]

\[ l_{b,\text{Casimir}} = \frac{3}{4\pi S_c} \int \int |r-r_b| \cos^2 \theta d\Omega dS_c \]  

Equation 1.5

where integral is performed over solid angle $\Omega$ and cross-sectional area $S_c$. The phonon propagation direction $(r-r_b)$ with respect to boundary surface $r_b$ lies along $d\Omega$ and $\theta$ is the angle of $(r-r_b)$ with respect to temperature gradient $\nabla T$.

However, when surface roughness starts becoming comparable to dominant phonon wavelength, assumption of complete diffuse scattering no longer remains valid. Hence, improvements to the Casimir model were implemented by Ziman [22] in 1960 where he included the effect of specular reflection $p$ at the surface to evaluate the boundary scattering mean free path as

\[ l_{b,\text{Ziman}} = \frac{1+p}{1-p} l_{b,\text{Casimir}} \]  

Equation 1.6

Due to advancements in synthesis techniques, structures with confinement in zero, one, two and three dimensions are currently being fabricated which can be utilized to tune thermal transport through boundary scattering. One of the studies [10] is illustrated in Figure 1-1 which shows mean free path and wavelength spectrum for silicon nanowires 100nm in diameter and with different roughness levels. Boundaries of a silicon nanowire scatter the longer wavelength and longer mean free path phonons owing to boundary scattering effect thus showing a lower thermal conductivity as compared to bulk silicon. The corresponding shift in wavelength and mean free path spectra towards lower values as compared to bulk silicon can be observed in Figure 1-1. This shift being higher for higher boundary roughness further illustrates the effect of boundary scattering on reduction of thermal conductivity seen in nanowires.
Scattering due to imperfections: Adding imperfections in the form of point defects ($\tau_{\text{defect}}$), dislocations ($\tau_{D}$), grain boundaries ($\tau_{\text{GB}}$) and alloys ($\tau_{\text{alloy}}$), have also been shown as a measure used for tuning thermal transport properties as shown in Figure 1-3. Expressions for relaxation rates of phonons scattered due to them was derived by Klemens [23] in 1959 using perturbation theory.

Embedding nanoparticles in alloys for thermal conductivity reduction has been one of the systems that has been explored recently in a lot of studies. Mean free path of the phonons ($\ell_{\text{defect}}$) scattered due to such a spherical obstacle can be derived from kinetic theory [29] as

$$\ell_{\text{defect}} = \frac{1}{\sigma n}$$  \hspace{1cm} \text{Equation 1.7}$$

with $n$ and $\sigma$ representing the number density of the scattering centers and the net scattering cross section respectively.

Scattering of longitudinal acoustic waves travelling in an isotropic elastic solid medium by a spherical obstacle was first studied by Ying and Truell [30] and later generalized by Johnson and Truell [31]. They solved equation of motion for acoustic waves to obtain the expressions for
both scattered wave and wave generated inside the spherical obstacle. During this, the scattered wave was taken as a superposition of the unimpeded incident longitudinal wave and the spherical wave scattered by the obstacle. Continuity of displacement and stress across the obstacle surface were taken as the appropriate boundary conditions to solve for the respective coefficients.

Subsequently scattering cross section \( (\sigma_l) \) was obtained as a ratio of rate of total scattered energy to rate of incident energy per unit area of the plane perpendicular to propagation direction. Scattering cross section was later derived for transverse acoustic waves \( (\sigma_t) \) by Iwashimizu in 1975 \[32\].

Under Rayleigh approximation when the radius of the particles is much smaller than the corresponding phonon wavelength, this scattering cross section \[31\] was derived to be

\[
\sigma_{\text{Rayleigh}} = \left(\frac{4}{3}\right) g_e (q_1 R)^4 (\pi R^2)
\]

Equation 1.8

where \( R \) is the radius of the spherical obstacle and \( q_1 \) \((2\pi/\lambda)\) is the longitudinal wavevector. Coefficient \( g_e \) is a function of density and elastic properties of both matrix medium and spherical obstacle medium with its functional form dependent on the type of spherical obstacle. From Equation 1.8, it can be deduced that the scattering cross section in this regime varies as inverse of fourth power of wavelength of phonon.

However, in the geometric regime \[31,33\] in which the radius of the particle is much greater than the phonon wavelength, scattering cross section has been shown to be independent of frequency.

\[
\sigma_{\text{geometric}} = 2\pi R^2
\]

Equation 1.9
At Mie transition point between the two regimes [31], oscillatory behavior in the scattering cross section is observed. These regimes are illustrated in Figure 1-4 for spherical cavity embedded in different matrix materials and for Germanium sphere embedded in aluminum, taken from Ref. 31.

A simplified expression to explain the two regimes as formulated by Majumdar in Ref. 29 is shown in Equation 1.10

\[ \sigma = \pi R^2 \left( \frac{X^4}{X^4 + 1} \right) \]

Equation 1.10

Where X=qR is defined as the size parameter with X<<1 defining Rayleigh regime and X>>1 representing the geometric regime.

Considering the method in Ref. 31 to be computationally extensive, Kim et al. [34] developed approximate analytical models to calculate scattering cross section for the two extremes, namely, Rayleigh regime and geometric regime and then combined them as an inverse sum as shown in Equation 1.11. The former was modelled using an extension of perturbation theory that was earlier used by Klemens [23] for describing phonon scattering by point defects.
while the latter was developed using Van de Hulst theorem [35] which had been earlier used to describe scattering of electromagnetic radiation under near geometric approximation.

\[ \frac{1}{\sigma} = \frac{1}{\sigma_{\text{Rayleigh}}} + \frac{1}{\sigma_{\text{geometric}}} \]  

Equation 1.11

Kim et al. observed a decrease of almost 50% below the alloy limit in thermal conductivity of In\textsubscript{0.53}Ga\textsubscript{0.47}As alloy on epitaxial embedding of ErAs nanoparticles [27]. It was deduced that according to Rayleigh scattering shown in Equation 1.8, while atomic substitutions scattered short wavelength phonons, nanoparticles (1-5nm size regime) could additionally scatter mid and long wavelength phonons, thus causing the reported reduction. Later, Mingo et al. [36] performed calculations to understand the reduction of thermal conductivity caused due to addition of silicide nanoparticles to a SiGe alloy and could get a thermal conductivity value as low as 1W/m-K. In addition, the study also discovered a minimum in thermal conductivity as a function of nanoparticle size. The total relaxation time was evaluated using Equation 1.3, taking contributions from alloy scattering, phonon-phonon scattering and nanoparticle scattering.

Scattering time for nanoparticle was calculated using the stitching mechanism in Equation 1.11 and using the Rayleigh and geometric limits for scattering cross section given in Equations 1.8 and 1.9. As seen from Figure 1.5, minimum in this study was attributed to a transition between Rayleigh scattering and geometric scattering of phonons with the minimum itself labelled as a Mie scattering point.

Although stitching mechanism used by Kim et al. [34] provides an approximate evaluation of nanoparticle scattering in the two extreme regimes, utilizing the complete solution for the scattering cross section for both longitudinal and transverse waves [31,32] has been shown to be a more accurate way calculating thermal conductivity across the entire range of nanoparticle radii [37]. However, to our knowledge no experimental measurement has been performed yet which could demonstrate this transition in a three-dimensional solid.
Existence of one such minimum was theoretically predicted by Simkin and Mahan [38] for cross plane thermal transport in a superlattice system as a function of interface density. The study attributed this occurrence to a crossover between coherent and incoherent regimes of phonon transport. Using actual phonon modes for a superlattice structure, thermal transport was evaluated using [18,22]

\[
\kappa(T) = \sum_p \int \frac{d^3 q}{(2\pi)^3} \hbar \omega_p(q) |v_z(q)| \left| \frac{\partial n(\omega, T)}{\partial T} \right|
\]

Equation 1.12

It was postulated that in the incoherent regime, where the phonon mean free path was smaller than the thickness of the layers, phonons could be treated as particles. In this case, thermal transport trend could therefore be explained using particle transport/classical theory according to which increased interfacial density caused higher interfacial scattering thus resulting in a lower thermal conductivity. However, once the phonon mean free path exceeded the thickness, effect of wave interference of these phonons became a dominant factor in determining thermal transport through a superlattice. In this coherent regime, these phonon interference effects

Figure 1.5: Figure illustrating the theoretically calculated room thermal conductivity as a function of diameter of different silicide nanoparticles embedded at a volume fraction of 0.8% in SiGe alloy with a) metal silicides and b) semiconductor silicides. A clear minimum is observed at the transition between Rayleigh and geometric regime of phonon transport. Solid line shows thermal conductivity of SiGe alloy as a comparison, adapted from Ref. 36.
resulted in formation of mini-bands due to band folding [39,40] in the phonon band structure, thus causing reduction in average group velocity and thus in thermal conductivity. This was confirmed by the calculations performed for one, two and three-dimensional configurations by Simkin et al., which showed an increase in band folding effect with higher periodicity (smaller interface density) thus resulting in decreasing thermal conductivity as opposed to the predictions by particle transport theory.

![Figure 1-6: Calculations showing a) an increase in mini-band formation in phonon dispersion curves for superlattices with increasing periodicity N=2,4,8 and 16. Mass ratio of 2 is used for all cases, b) Thermal conductivity calculated for a one-dimensional chain of atoms as a function of superlattice periodicity for different phonon mean free paths l. It illustrates a minimum as it crosses over from particle transport to wave transport regime, adapted from Ref. 38.](image)

This minimum in superlattices was further illustrated by Yunfei Chen [41] who used nonequilibrium molecular dynamics to calculate thermal conductivity of superlattices as a function of period length. Although similar to previous study, this predicted the minimum to occur when phonon mean free path became comparable to period length, it imposed an additional criterion of a small lattice mismatch to exist between alternating layers for this minimum to exist.

Amongst many attempts made to study this crossover experimentally in superlattices, the first successful study was performed by Jayakanth et al. [42] by studying cross plane thermal
transport through superlattices of SrTiO$_3$/CaTiO$_3$ and SrTiO$_3$/BaTiO$_3$ fabricated on different substrates, details of which can be found in Ref. 42.

![Figure 1-7](image)

**Figure 1-7:** Figure illustrating the minimum obtained in experimentally measured thermal conductivity of SrTiO$_3$/CaTiO$_3$ superlattice on NGO, STO and LSAT substrates as a function of interface density. Theoretical data calculated using Modified Simkin Mahan model is plotted showing the divide between incoherent and coherent regime of phonon transport, adapted from Ref. 42.

Interface densities for each was varied by adjusting the respective individual layer thickness while maintaining the same total thickness for the overall structure. Thermal transport measurements conducted using time domain thermoreflectance method illustrated a clear minimum at the transition between particle and wave behavior of phonons. In addition, a shift in the minima towards lower interface densities was observed at lower temperatures, which was in agreement with the above theoretical arguments. Theoretical curves were generated for each system using a modified Simkin Mahan model which included corrections owing to interfacial disorder, volume fraction and size effects and as seen from Figure 1-7, these came out to be in reasonable agreement with the respective experimental data.

A lot of studies have focused on synthesizing two-dimensional nanoporous structures [17,43-48] for thermal transport studies. However, limited studies have been reported for thermal transport through three-dimensional semiconductor/metal nanostructures [28,49-51]. Diffusive
and quasi ballistic regimes [49] of thermal transport have been investigated for copper and nickel inverse opals fabricated through metal electrodeposition in polystyrene templates. Another study focused on understanding coherent scattering of phonons by grain boundaries through silicon inverse opal structures fabricated using chemical vapor deposition through silica sphere templates [28]. However, the size of spheres used as templates in these studies have been greater than 100nm. Much smaller sphere radii are required for an inverse opal structure to study the transition between Rayleigh and geometric regimes. This study therefore presents a comprehensive experimental and theoretical understanding of thermal conductivity through such a three-dimensional silicon nanostructure with a periodic distribution of pores constituted of different materials.

1.2 Organization of dissertation

This thesis discusses thermal transport through three-dimensional silicon nanostructures with a periodic distribution of pores, referred to as silicon metalattices in this work. Chapter 2 briefly describes the ballistic theory of phonon transport developed to provide a quantitative measure of thermal properties for different silicon metalattice structures: filled and empty metalattice. It focuses on the minimum in thermal conductivity observed as a function of pore radius for both the systems owing to the transition from Rayleigh scattering to Casimir scattering and how that minimum depends on pore volume fraction and pore material. This chapter further explains the experimental synthesis of these structures using high pressure infiltration of silicon into voids of templates constituted of closely packed silica spheres which are then later used for experimental thermal transport studies.

Chapter 3 focuses on the principle underlying time-domain thermoreflectance setup which is subsequently used for an accurate measurement of thermal properties through
metalattice films. It elaborates on the experimental steps and various issues encountered while setting up time-domain thermoreflectance setup and presents appropriate solutions to achieve accurate and high-quality data. It further explains the analytical model, as adapted from previous literatures, that is utilized to provide a theoretical fit to the collected experimental data using MATLAB for extraction of thermal properties. It explains the procedure required for collecting accurate values for different parameters required in the modelling process which is then tested along with the experimental setup by comparing the extracted thermal properties for standard samples such as silicon, fused silica and sapphire against literature values.

Chapter 4 utilizes time-domain thermoreflectance setup to experimentally derive temperature-dependent thermal properties for both filled and empty silicon metalattice structures as a function of pore radius. It summarizes the evaluation of parameters, experimental data collection and the analytical procedure used for evaluating these values for each sample. It further compares the generated experimental data against theoretical predictions to explain the fundamental nature of phonon transport through these structures and to elaborate on the reasons behind the discrepancy found between the two data.

Chapter 5 summarizes the work in this thesis and brings up potential future works that can be performed to explore the applications of silicon metalattices in fields of thermoelectricity and thermal rectification. It also discusses a potential idea of extending the existing TDTR setup to measure in-plane thermal properties of different materials with higher sensitivity.

Appendix A explains the procedure for setting up an air-bearing delay stage that is utilized to provide a repeatable and accurate delay to the probe beam in time-domain thermoreflectance setup. It discusses the different components involved in developing this assembly, hardware assembly process and software configuration settings to operate this stage.

Appendix B contains the MATLAB code used for modeling time-domain thermoreflectance data.
Chapter 2

Thermal transport in three-dimensional periodic silicon metalattices

Previous chapter introduced different regimes of phonon transport through semiconductors and how different scattering mechanisms in nanostructured semiconductors have been utilized as a measure for tuning thermal transport properties. One such study combined the effects of nanoparticle and alloy scattering for thermal conductivity reduction by embedding nanoparticles in semiconductor alloys and in the process discovered a minimum in thermal conductivity at an optimal nanoparticle size of less than 100nm. This chapter presents a quantitative prediction of such a minimum in thermal conductivity through a three-dimensional silicon nanostructure with a periodic distribution of pores as the pore diameter is varied from 1-100nm in Section 2.2. It further explores experimental synthesis of this structure, referred to as silicon metalattice in this study, using high pressure chemical vapor deposition method in Section 2.3, whose thermal transport properties will be discussed in Chapter 4.

2.1 Introduction to silicon metalattice

A silicon metalattice [52,53] is an artificial three-dimensional lattice with periodicities ranging from 1-100nm, as shown in Figure 2-1. Two types of metalattice structures will be studied in this work, namely, filled silicon metalattice and empty silicon metalattice.
A filled silicon metalattice is composed of a face centered cubic (fcc) arrangement of silica spheres with the corresponding tetrahedral and octahedral voids infiltrated with silicon. As indicated in Figure 2-1, the resultant structure can be interpreted as a lattice of meta atoms residing at interstitial sites of the fcc lattice connected with each other through narrow necks called as meta bonds. Replacing the silica spheres in a filled silicon metalattice with empty pores results in an empty silicon metalattice structure.

Such a phononic metalattice structure is characterized mainly by two length scales, namely, geometric confinement length \( L \) and pore radius \( r \) as labelled in Figure 2-2. Typically for bulk silicon, intrinsic mean free path of phonons roughly lies in the range of 50nm-several microns while wavelength lies in 0.5-10nm as was illustrated previously in Figure 1-1 [9-11]. Since for a metalattice structure, the neck size \( L \) is much lower than the intrinsic mean free path of phonons \( \ell \), thermal transport through these structures is expected to occur in the ballistic regime as defined in Figure 1-2. This ballistic regime can be further subdivided into Casimir and Rayleigh regimes based on how the pore radius \( r \) compares with wavelength of phonons \( \lambda \). In the Rayleigh limit [31,32], when \( r \ll \lambda \), thermal conductivity decreases with \( r \) according to
with $N$ being no. of atoms in unit cell, $V$ volume of unit cell and $\sigma$ scattering cross section of the pore.

However, in the Casimir limit $[17,26]$ when radius $r \gg \lambda$, thermal conductivity increases with $r$ as

$$\frac{\Lambda_{\text{bulk}}-\Lambda_{\text{ML}}}{\Lambda_{\text{bulk}}} \propto \frac{1}{L} \propto \frac{\ln N}{V} \propto \frac{r^3}{\lambda^4}$$

Equation 2.1

This qualitatively predicts an occurrence of a minimum in thermal conductivity as a function of pore radius for metalattice samples. In collaboration with Dr. Ismaila Dabo’s group, a quantitative ballistic model $[54,55]$ was developed for predicting thermal conductivity of the metalattice samples as a function of pore size, pore content and volume fraction of pore.

Figure 2-2: Schematic of different regimes of phonon transport through a periodic distribution of pores of radius $r$ in a silicon matrix, with $\lambda$, $L$ and $\ell$ defined as phonon wavelength, phonon ballistic length and phonon-phonon mean free path (star) respectively. 1) Rayleigh ballistic regime ($r<<\lambda$, $\ell >> L$), 2) Mie ballistic regime ($r \sim \lambda$, $\ell >> L$), 3) Casimir ballistic regime ($r >> \lambda$, $\ell >> L$) with circular points representing phonon boundary scattering, 4) Diffusive regime ($\ell << L$) with stars representing intrinsic phonon scattering. Adapted from Ref. $^{54,55}$. 
2.2 Ballistic model of phonon transport

In this model [54,55], a steady-state diffusion driven ballistic length scale was derived for a metalattice subjected to a small temperature gradient as a correction to self-driven ballistic lengths used for calculation of thermal conductivity in previous studies. Using ballistic theory derived by Casimir [26], current density at a certain position \( r_1 \) can be written as

\[
j(r_1) = \frac{1}{V \sqrt{N_q}} \sum_{pq} \int_{l_2} \hbar \omega_{pq} n_{pq}(r_2) v_{pq} \frac{d\Omega_2}{4\pi} \tag{2.3}
\]

where \( \omega, p, q \) and \( v \) correspond to frequency, polarization, wavevector and group velocity of phonons respectively. Statistical occupancy of phonons \( n \) with wavevector \( q \) and polarization \( p \) is given by Planck’s distribution function

\[
n = \frac{1}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \tag{2.4}
\]

The summation is done over \( N_q \) wave vectors in reciprocal space. Integral is performed over \( l_2 \) which defines the total ballistically accessible area from position \( r_1 \) and \( d\Omega_2 \) defines the corresponding solid angle. Expanding \( n \) for a small temperature gradient \( \nabla T \) and replacing in Equation 2.3

\[
j(r_1) = \frac{1}{V \sqrt{N_q}} \sum_{pq} \int_{l_2} c_{pq} \left| v_{pq}\right| \frac{d\Omega_2}{4\pi} \tag{2.5}
\]

where \( r_{12} \) is the vector distance between receiving point \( r_1 \) and emitting point \( r_2 \) (\( \hat{r}_{12} = \hat{v}_{pq} \)) and \( c \) is the phonon heat capacity given by \( \hbar \omega \partial n / \partial T \). Owing to a small temperature gradient, heat capacity and group velocity can be considered constant in area \( l_2 \) and can be taken out of the integral. On integrating Equation 2.5 over the receiving surface area \( A_1 \), the total heat flux can be derived as

\[
I_1 = \frac{1}{V \sqrt{N_q}} \sum_{pq} c_{pq} \left| v_{pq}\right| \int_{A_1} \int_{l_2} |\nabla T| \chi(r_{12} \cdot \hat{e}_||) \frac{d\Omega_2}{4\pi} \tag{2.6}
\]
with $\hat{e}_||(-\nabla T/|\nabla T|)$ being a unit vector in a direction anti-parallel to temperature gradient.

Comparing it to the Boltzmann equation under relaxation time approximation, ballistic mean free path can thus be defined as

$$L = \frac{3}{4\pi A_1} \int A_1 \int_{I_2} (r_{12} \cdot \hat{e}_||) \cos\theta_1 d\Omega_2 d\sigma_1 = \frac{1}{A_1} \int A_1 L(r_1) d\sigma_1 \quad \text{Equation 2.7}$$

This ballistic length is further corrected for the finite size of simulation domain, in this case a sphere of cutoff radius $R_c$, used for calculating it in Equation 2.8 \[54,55\]

$$L(r_1) = L_c(r_1) + \frac{R_m^2 - R_c^2}{8\pi^3} \frac{d\Omega}{d\Omega}(R_c) \quad \text{Equation 2.8}$$

where $R_m$ is the distance required for solid angle to reach $4\pi$ steradians. This ballistic length is rescaled by scattering efficiency factor $\gamma$, derived for both longitudinal \[31\] and transverse phonons \[32\] scattering against the spherical pore in silicon. This takes into effect the sub-wavelength enhancement of scattering cross section in the Rayleigh regime. Boltzmann transport equation is then utilized to evaluate thermal conductivity for metalattices. Effective mean free path \[54,55\] in BTE is calculated using Matthiessen’s rule taking contributions from phonon-phonon mean free path, ballistic mean free path and mean free path corresponding to phonon-isotope scattering.

The phonon-phonon mean free path and the phonon dispersion relations are derived using semi-local density functional theory \[54,55\]. Phonon-isotope scattering is calculated using perturbation theory given by Klemens \[23\] as described in Chapter 1. Phonon dispersion curves were found to be modified with respect to bulk silicon with presence of pores in a metalattice structure. Classical lattice dynamics simulations \[54,55\] were used to calculate the corresponding reduction in group velocity of phonons in metalattices occurring due to modified dispersion.
2.3 Theoretical results and discussion

Using the calculation above, thermal conductivity was calculated for both filled and empty metalattice structures as a function of pore radius as shown in Figure 2-3 [54,55]. A porosity of 74% was taken for both the systems. These predicted a minimum in thermal conductivity for both systems owing to the transition between Rayleigh and Casimir regimes of phonon transport. However, the radius at which minimum occurred shifted from 5nm for empty metalattices to 10nm for filled metalattice structures, thus indicating its dependence on the pore content. In addition, very low values of thermal conductivity were observed in comparison to previously studied two-dimensional nanoporous systems. This was attributed to a much higher scattering cross section offered to phonons in three dimensions.

Figure 2-3: Thermal conductivity calculation as a function of pore radius showing a minimum at 10nm for filled metalattice (green curve) and 5nm for empty metalattice (blue curve), thus illustrating dependence of minimum on pore content. Modified from Ref. 54,55.
Furthermore, thermal conductivity was also calculated as a function of temperature for both filled and empty metalattices as shown in Figure 2-4 [54,55]. At a porosity of 74%, thermal conductivity showed a trend characteristic of ballistic transport [13-17], where thermal conductivity increased with increasing temperature from 50K to 250K before reaching a saturation. However, as the porosity was reduced, the trend started shifting from ballistic to diffusive regime of phonon transport, a trend same as bulk silicon. This is illustrated in Figure 2-5, where thermal conductivity as a function of temperature is mapped for different porosities [54,55].
In order to further validate the different regimes contributing to thermal transport across the minimum, thermal conductivity was decomposed into respective wavelength spectrums for filled metalattice with radius of 0.5nm and 20nm [54,55]. This was compared with the wavelength spectrum for bulk silicon. As seen from Figure 2-5, for a radius of 0.5nm, since phonons are scattered according to Rayleigh criterion, contribution to thermal conduction is mostly due to long wavelength phonons. However, for bigger sphere size of 20nm, long wavelength phonons get scattered due to boundary scattering effect of Casimir regime. Thus, most of the thermal conduction is done by extremely short wavelength phonons (≤1nm). This theoretical study therefore shows that metalattices can be effectively used to tune thermal transport through variation in pore content, radius and volume fraction.

Figure 2-5: Comparing wavelength decomposed thermal conductivity for a filled metalattice at a pore radius of 20nm and 0.5nm with wavelength spectrum for bulk silicon. For pore radius of 20nm, thermal transport is seen to be dominated by shorter wavelength phonons owing to Casimir boundary scattering effect while for 5nm longer wavelength phonons contribute to thermal transport due to Rayleigh scattering effect. Modified from Ref. 54,55.
2.4 Experimental synthesis of a silicon metalattice

Synthesis of the silicon metalattice sample was accomplished in 3 steps:

- Silica template synthesis: As a first step, silica spheres were assembled as a close packed template on silicon substrate using vertical self-assembly process. This was performed in collaboration with Dr. Mallouk’s group at Penn State University [56]. Even though Stober’s method [57] is a conventional method for synthesizing silica nanoparticles having sizes larger than 200nm, it fails to achieve a good monodispersity for the smaller sphere sizes used in this study. Thus, the silica nanoparticles here were instead synthesized using the seeding and regrowth process described by Watanabe et al. [58] and Hartlen et al. [59] respectively. This was followed...
by forming a colloidal suspension by diluting the derived silica nanoparticles in nanopure water. Before utilizing silicon substrate for deposition process, it was immersed in Piranha solution for about 30 minutes for a clean and hydrophilic surface. This substrate was then placed tilted at approximately 30°C in a plastic vial containing the colloidal suspension prepared above. This vial was then placed in an oven where the solvent evaporated off the substrate under well-controlled temperature and humidity conditions for about two weeks, leaving behind a self-assembled template film of silica nanospheres [56,60]. This film was subsequently calcined at 600°C to remove all the remnant organic contamination. Depending on the deposition conditions and sphere size, template film achieved varied from 250nm to a 2μm in thickness as observed from their cross-sectional scanning electron microscopy (SEM) images.

Figure 2-7: Schematic illustrating high pressure confined chemical vapor deposition (HPcCVD) process used for infiltrating silicon into a fiber capillary with a) Showing reaction of silane (SiH₄) with hydrogen (H₂) in presence of Helium (He) as a carrier gas at high pressures of 35MPa to deposit a thin film of amorphous silicon inside the pore. Bottom diagram indicates the nucleation and growth of silicon particles in a conventional reactor at high pressures used thus preventing formation of a smooth film while top diagram indicates the significance of confinement in addition to high pressure which provides little time for silicon particles to nucleate and grow before they deposit on the pore walls, adapted from Ref. 63, b) Illustrating the reduction of mean free path from microns to around 1nm at high pressures used in the process thus facilitating higher diffusivity of gases and thus complete infiltration of silicon into the fiber capillary, adapted from Ref. 65.
Silicon infiltration: Interstitial voids in the assembled template were infiltrated with intrinsic silicon using high pressure confined chemical vapor deposition process in collaboration with Dr. John Badding’s group at Penn State University [52,61]. Unlike previous thermal transport studies of inverse opal structures, conventional chemical vapor deposition cannot be utilized to deposit silicon in this work due to inlet clogging caused prior to complete infiltration because of extremely slow rate of diffusion of reactants into the pores and out-diffusion of generated by-products at atmospheric or sub-atmospheric pressure used in the process [62-66]. Thus, high pressure chemical vapor deposition combined with confinement as explained below is utilized as an efficient measure to achieve void free infiltration of silicon in metalattice templates.

The deposition process utilized ultrahigh purity silane (99.999%) as a precursor mixed in concentrations of 2-10% in helium as a carrier gas. At a total gas pressure of 20-35MPa and temperature of 400°C, amorphous silicon derived as a product of decomposition of silane was infiltrated into the voids of these templates. High pressures [62-66] used in the process reduced the mean free path of the precursor molecules to around 1nm as opposed to microns in conventional CVD thus resulting in diffusivities high enough to infiltrate the tortuous voids of the nanosphere assembly. But in order to avoid homogenous nucleation of the molecules and the corresponding clogging of these voids before complete infiltration, rendered due to high pressures, spatial confinement using 25μm steel spacers between template pieces was done. This helped reduce the reactor size and thus the time required to reach the pore walls (reactor size²/diffusivity) and ensured heterogenous deposition of silicon as a uniform layer [62-66]. The deposition time, depending on the diameter of the silica spheres constituting the template assembly, was adjusted such that a Si overlayer was formed on top of the template. The overlayer was then etched off by deep reactive ion etch process using Plasma-Therm Versalock 700. The infiltrated amorphous metalattice was then subsequently crystallized by annealing it at 800°C for
30 minutes under inert atmosphere. A top view scanning electron microscopy image of the resultant silica filled silicon metalattice for a sphere radius of 15nm is shown in Figure 2-8.

Figure 2-8: a) Top view SEM image of a filled metalattice with a pore radius of 15nm, b) Top view SEM image of an empty metalattice with a pore radius of 15nm, adapted from Ref. 53.

- Empty metalattice synthesis: Silica filled metalattices synthesized above were subsequently etched with a vapor of 49% hydrofluoric acid to yield the respective empty metalattices. Top view SEM image for an empty pore metalattice for a pore radius of 15nm is shown in Figure 2-8.

Using the synthesis procedure described above, silica filled metalattices with sphere radii of 7nm, 10nm, 15nm and 30nm and empty metalattices with sphere radii of 7nm, 10nm and 15nm were fabricated for thermal measurements in this work. Thermal conductivity measurements on these samples was carried out using time-domain thermoreflectance setup whose details are described in Chapters 3 and 4.
Chapter 3

Time-domain Thermoreflectance: Experimental setup and Analysis

3.1 Introduction

Time domain thermoreflectance technique was first adapted by Paddock and Easley [67] for undertaking thermal transport measurements through metal thin films with thicknesses lying between 60-500nm. Various advances [68-83] and variations [84,85] have since then been made to this technique to develop it as a measure for characterizing both radial [79,86-88] and cross-plane thermal characteristics of materials ranging from bulk to ultra-thin films.

Figure 3-1: Schematic of the principle underlying time-domain thermoreflectance/optical pump-probe experiment. Left side shows the sample coated with metal transducer film heated due to pump pulse absorption and subsequently probed for its temperature change with a time delayed (τ) probe pulse. Right side shows the corresponding reflectivity change of probe beam as measured by the detector as a function of delay time.

The core principle for this is based on optical pump-probe technique as shown in Figure 3-1. In this, an optical pump beam with a pulse duration of few femtoseconds, deposits heat in a metal film coated on a substrate. The temperature change associated with this heating event modifies the complex dielectric function of the metal film. This shows up as a change in
reflectivity of the probe beam that arrives at the metal film surface after a certain time delay. Information on carrier dynamics and thermal dissipation can then be extracted by theoretically modelling this reflectivity change as a function of delay time.

Different transport mechanisms that occur over the delay time ranging from a few femtoseconds to several nanoseconds [83,89] are illustrated in Figure 3-2.

Figure 3-2: Dynamics of different carriers (electrons: red dots, phonons: grey atoms connected by springs) after a pump pulse is absorbed by a metal film deposited on the study material at different time scales ranging from a few femtoseconds to several nanoseconds.

TDTR setup is built and subsequently used in this study to characterize thermal properties of silicon metalattice films, described in detail in Chapter 4, due to following reasons:
a) It involves a non-contact and non-destructive optical heating and temperature sensing process, thus eliminating errors in thermal conductivity evaluation due to contact resistance effects, b) Being a transient technique, it reduces the effect of radiation and convection heat losses on accuracy of measured thermal conductivity in addition to reducing the longer wait times required
in steady state techniques, c) High temporal resolution (100s of fs to a few ps) available in this technique offers a nanometer scale depth resolution. This enables a more accurate measurement of thermal conductivity isolated from effects of interfacial thermal conductance or substrate properties. This provides an advantage over other transient measurement techniques such as 3ω method and d) Minimal sample fabrication and small spot sizes used in this technique enables measurement over multiple small areas of interest.

This chapter discusses the steps involved in setting up TDTR experimentally followed by the analytical model required for modelling the data extracted from these experiments.

**3.2 Experimental configuration**

**TDTR setup**

The experimental setup shown in Figure 3-3 and as adapted from previous setups [20,83] utilizes a train of pulses emitted from a Ti-sapphire laser at a repetition rate of 80MHz with each pulse having a duration of 100fs as measured by an autocorrelator. This beam centered at a wavelength of 800nm is passed through an optical isolator [90] in order to eliminate any back reflections from reaching the laser thus avoiding any destabilization in mode locking process of the laser.

This laser beam at an average power of 1W is then divided into a vertically polarized pump and a horizontally polarized probe beam using a polarizing beam splitter. A half-waveplate placed prior to the beam splitter is adjusted to tune the power distribution in the two beam paths.

A square wave modulation is then introduced on the pump beam with the corresponding frequencies ranging from 1-15MHz. This modulation is required to provide a reference frequency for lock-in amplifier (SR844) signal detection. In order to do so, the pump beam is passed
through an electro-optic modulator ‘model 350-210-2 KDP’ as designed by Conoptics, Inc. It is preferred over acousto-optic modulators (AOM) and other electro-optic modulators (EOM) due to (i) faster switching speeds and hence a higher frequency range of operation, (ii) lower noise contribution, (iii) better extinction ratio, and (iv) an optimal transmission thus reducing power loss. In order to achieve an efficient extinction ratio for an improved signal to noise ratio in the acquired data as shown in Fig 3-4, the beam is ensured to have a pure vertical polarization and an optimal beam diameter as indicated in the user manual [91] for the modulator operation.

Figure 3-3: Schematic illustrating various optical components involved in TDTR experimental setup, a) Isolator which prevents back reflected light reaching the laser, b) Delay stage which provides a maximum time delay of 6ns to probe beam, c) Beam expander which doubles probe beam size for minimal divergence over delay stage, d) Electro-optic modulator (EOM) providing a square wave modulation to pump beam, e) BIBO crystal generating 400nm from 800nm using SHG, f) Prism compressor which shortens the pulse duration for better SHG efficiency, g) Objective for focusing pump and probe beams on the sample at normal incidence, h) Camera for imaging laser spots and sample surface and i) Si detector, inductor and lock-in amplifier for data collection.

Sometimes a significant contribution from the pump beam can get added up to the signal due to its modulation frequency matching up with the signal thus giving erroneous results. Therefore, the system above is configured as a dual color pump-probe setup wherein 400nm
wavelength is used as pump beam. That helps eliminate any remnant pump beam reaching the detector by utilizing color filters in front of signal detector. This is achieved by focusing the pump beam using a 10cm convex lens through a 1mm BIBO (bismuth triborate) crystal to generate a corresponding 400nm second harmonic beam. But the efficiency of this process is low due to an increased laser pulse duration caused due to dispersion by the isolator and modulator. In order to compensate for this, pump beam is passed through a prism compressor system which helps reduce the pulse duration down to 120fs before being passed through BIBO crystal. This enables generating a maximum power of 120mW that can be used as a 400nm pump beam on the sample.

As the principle of pump-probe setup demands, a delay is applied on probe beam. This is achieved by passing the probe beam through a retroreflector mounted on an air bearing delay stage custom built in the lab whose detailed specifications and process are explained in the ‘delay stage’ section in Appendix A. The retroreflector is essential to reflect the light back in a direction parallel to the source so that there is minimal drift in the focused probe beam on the sample over the entire delay range, as confirmed by the drift measurement presented in the ‘knife edge measurement’ section.

Figure 3-4: Comparison of experimental data collected on sapphire at a modulation frequency of 5MHz with modulation provided by a) Acousto-optic modulator (AOM) and b) Electro-optic modulator (EOM). More than 10 times reduction in noise is observed in the experimental data collected when EOM is used for imposing modulation on the pump beam.
The delay stage, can travel a maximum distance of 500mm with 100nm resolution and a maximum speed of 1m/s. Therefore, a single pass of the stage could give a maximum delay of 3.3ns (1m). Thus, a double pass system is created using a combination of quarter waveplate, polarizing beam splitter and a normal incidence mirror as shown in the setup diagram to achieve a maximum delay of 6.7ns (2m).

But probe beam being a collimated Gaussian beam diverges as [92]

\[ w_i(z) = w_{io} \sqrt{1 + \left( \frac{z}{z_R} \right)^2} \]  

Equation 3.1

where \( w_i(z) \) is 1/e² beam radius at a distance \( z \), \( w_{io} \) is 1/e² beam radius at \( z=0 \), \( z_R \) is Rayleigh range given by \( \pi w_{io}^2 / \lambda \) with \( \lambda \) being the wavelength of light. Using initial probe beam diameter of 4mm and \( z=2m \), although Equation 3.1 predicted an increase of 0.8% change in beam radius, it propagated as 4-5% increase in focused beam size as measured experimentally. In order to minimize this divergence at long delay times, probe beam diameter is increased from 4mm to 8mm using a collimated beam expander as shown in Figure 3-3 above. This ensured the change in radius of the focused probe beam on the sample to be less than 1% over the delay range as measured in Figure 3-12 in ‘knife edge measurement’ section.

Both pump and probe beams are then focused coaxially through a 5X microscope objective onto the sample. Reflected probe beam from the sample is back reflected through objective and focused through a 300mm focal length lens onto a Si photodiode detector (Det10A) with a rise time<1ns [93] which is required to collect signals in the above stated modulation frequency range. A ring light is mounted on objective to shine white light onto the sample/razor blade. Scattered light is directed through a flip mirror onto a CMOS camera to create a dark-field image of sample/razor blade. Additionally, the focused pump and probe beam spots are also imaged on camera a) to ensure that they are spherical and b) to approximately overlap them.
The detector is subsequently connected to the lock-in amplifier through an inductor forming a resonant RLC circuit at the modulator reference frequency as shown in Figure 3-5. This enables removal of higher harmonic components introduced due to square wave modulation induced by electro-optic modulator and due to square wave mixing used by lock-in amplifier as a mechanism for signal processing.

Figure 3-5: Circuit diagram of a photodiode associated with a junction capacitance $C_J$ and shunt resistance $R_s$ connected in series with an inductor ($L$) and a total load resistance ($R_t$), forming a resonant RLC circuit. Diagram for detector circuit is adapted from Ref. 93.

In addition to it, at resonance frequency the signal is enhanced 10 times as compared to other frequencies thus improving overall signal to noise ratio in the data collected [78]. This ensures a better accuracy in experimental data collected which assists in achieving precise values of thermal parameters on theoretical data fitting. Figure 3-6 shows one such example in which experimental data is collected on sapphire substrate before and after applying an inductor circuit at a modulation frequency of 5MHz.
In reference to the manual from Thorlabs [93], DET10A is a Si based photodiode detector operated in a reverse bias mode to generate an output current \( I_{\text{out}} \) proportional to reflected probe beam intensity. Depletion region formed in the diode gives rise to a junction capacitance \( C_J \) which varies with the magnitude of reverse bias voltage applied and the diode volume. In addition to it, a zero biased junction resistance \( R_s \) and a series resistance \( R_{\text{series}} \) corresponding to Si diode and the various contacts utilized in the assembly is present in the system. It can be therefore be modelled as the circuit diagram shown in Fig 3-5 with diode acting as current source \( (I_{pd}) \) across \( C_J \) and \( R_s \) connected in parallel to it. Inductor \( L \) is connected in series to this detector which is connected to the lock in amplifier by using a 50Ω impedance BNC cable. This impedance is required for maximum signal transfer to the lock-in amplifier. Inductor is chosen such that its self-resonance frequency as listed in the specifications is much higher than the required resonance frequency. The 50Ω load resistance \( R_{\text{load}} \) at the lock-in amplifier thus generates a \( V_{\text{out}} \) corresponding to a periodic current signal \( I_{\text{out}} \) at frequency \( \omega \), generated from the sample. Solving it,

\[
V_{\text{out}} = I_{\text{out}} \left( \frac{R_t}{1 - \omega^2 L C_J + j\omega C_J R_s} \right)
\]

Equation 3.2
where $\omega$ is the modulation frequency and total resistance $R_t = R_{\text{load}} + R_{\text{series}} + R_L$, with $R_L$ being the resistance associated with the inductor utilized in the circuit. $R_{\text{shunt}}$ is typically $1\,\text{G}\Omega$ for this detector and therefore the current flowing through that branch is negligible and is therefore ignored while deriving Equation 3.2 above. Referring to the specifications of detector [93], inductor and the cables, $C_J$ is taken as $21.5\,\text{pF}$. As an example, for a given inductor of $47\,\mu\text{H}$ utilized in the circuit, Equation 2.2 was solved for $V_{\text{out}}$ as a function of frequency $\omega$, which shows a maximum at resonance frequency $\omega_0$, as plotted in Figure 3-7. With this inductor connected to the detector, magnitude of voltage signal was then measured experimentally from the lock-in amplifier in the frequency range around theoretically estimated resonance frequency and fitted with Equation 3.2. Similar calculations and experiments were performed for generating resonance at various other modulation frequencies used in this study by utilizing different inductors in the signal line between detector and lock-in amplifier.

Figure 3-7: Plot showing normalized magnitude of experimental signal from a sapphire substrate measured as a function of modulation frequency with an inductor $L=47\,\mu\text{H}$ connected between detector and lock-in amplifier, with maximum observed at resonant frequency of $5.1\,\text{MHz}$. Solid line represents the theoretical fit to experimental data generating total resistance $R_t=70\,\Omega$. Capacitance $C=21.5\,\text{pF}$ is taken while calculating theoretical magnitude as indicated in the plot.
In order to get an optimal signal to noise in the acquired data, besides increasing the signal as illustrated above, there are various sources of noise in the system that need to be eliminated.

One such contribution comes from external RF/EMI sources which gets picked up by signal carrying cables and power supply cords and gets registered as an unstable background offset to the signal. This background can be measured by blocking the pump beam and measuring the reflected probe beam as a function of delay time. Two measures are taken to stabilize and subsequently reduce this background signal which are explained below. After the background becomes much smaller than signal as shown in Fig 3-8, it is simply subtracted as a constant from the acquired data before processing.

![Figure 3-8: Comparison of experimental background data collected at a modulation frequency of 8.75MHz before and after using the measures: RF chokes and triple shielded BNC cables. A much stable and three times lower background signal observed after implementing these measures.](image)

a) Triple shielded BNC cables: BNC cables used as signal and reference cables to the lock-in amplifier are kept short and taut and are provided with a triple shielding. Conventionally, a single silver-plated copper braid used as a shielding layer has air gaps present in it due to its braided structure which increase with bending thus failing to provide a continuous coverage.
Adding a second and third shielding layer composed of an aluminum tape and a silver-plated copper braid respectively over the first layer and reducing the flexure in BNC cables aids in achieving a higher and more continuous coverage thus increasing the shielding efficiency. This helps minimize signal loss to the environment and simultaneously reduces external RF noise interference effects to the signal. Different length PE-P195 coaxial cables [94] from Pasternack company was utilized for this setup which aided in reducing the background noise level.

![Graph](image)

Figure 3-9: Figure showing a) inductive impedance (XL), resistance (R_s) and overall impedance (Z) as a function of frequency for a single turn around ferrite mix 31 core based RF choke, b) overall impedance as a function of no. of turns (N) in the same frequency range, indicating a minimum of 3 turns required to achieve an impedance greater than 500Ω. Adapted from Ref. 95.

b) RF chokes: RF/EMI pickup results in common mode noise travelling outside the coaxial cables which culminates as an unstable background. Palomar engineer company based MnZn ferrite core [95] mix 31 with permeability greater than 800μ is used for RF noise attenuation in this study. Wrapping the coaxial cables around the core results in a high impedance to this noise in the frequency ranging from 1-300MHz as shown in Fig 3-9. In order to achieve an optimal choking, this impedance should be at least 10 times larger than the BNC cable resistance which in this study is 50Ω. Calculating the required value in the frequency range of 10-100MHz
and comparing it to Fig 3-9, 3 to 4 turns of a cable is sufficient to eliminate the common mode noise and is henceforth implemented experimentally.

Other sources of noise [83] that need to be reduced to achieve an efficient signal to noise in experimental data are Johnson noise, shot noise and 1/f noise, amongst which contribution due to 1/f noise can be minimized either by utilizing high modulation frequency at which signal fluctuations are much lower than the signal voltage or by using a higher time constant for collecting data at lower modulation frequencies. This effect is illustrated in Figure 3-10 where experimental ratio is collected on a sapphire substrate at 0.8MHz and 5MHz at a time constant of 300ms.

![Figure 3-10](image)

Figure 3-10: Experimental ratio (-x/y) collected on a sapphire substrate coated with 103 nm Al at a modulation frequency of a) 0.8MHz and b) 5MHz, showing 20 times increase in signal to noise ratio in the latter. Data for both the cases is collected at lock-in amplifier time constant of 300ms.

**Knife edge technique: beam size and drift measurement**

Both pump and probe beam spot sizes used in TDTR measurement are extracted using knife-edge technique which is described below in Figure 3-11.
whose differential is then fitted to the Gaussian beam profile to extract the beam parameters. One such measurement is illustrated in Figure 3-12 for both pump and probe beam. The corresponding radius extracted came out to be 22μm for pump beam, 5.84μm for probe beam at start of delay range and 5.92μm for probe beam at end of delay range. The probe beam radius is taken as an average of radii at two delay positions, 6μm to be used in experimental analysis. As observed from the values the measured change in probe beam radius is <=1% across the entire delay line.

Figure 3-11: Schematic of knife edge setup for beam size measurement where a razor blade mounted on a x-y translation stage cuts through a focused laser beam whose intensity is recorded by a powermeter as a function of razor blade position.

The laser beam above has a TEM$_{00}$ Gaussian profile given by [92]

\[ I(x,y) = \frac{2P_0}{\pi w_0^2} \exp\left[-\frac{2(x^2+y^2)}{w_0^2}\right] \]

Equation 3.3

where $w_0$ is 1/e$^2$ beam size and $P_0$ is the total power in the beam.

To measure focal spot size, razor blade is brought into focus position of the probe beam using knife edge technique and is simultaneously focused on CMOS camera. This ensures that the sample focused on camera during data collection utilizes the beam spot sizes measured with razor blade. As shown in Figure 3-11, the blade placed on a translation stage is passed through the beam and the corresponding power is recorded using a photodiode. The intensity recorded is

\[ P = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I(x,y) \, dx \, dy = \frac{P_0}{2} \operatorname{erfc}\left(\frac{x}{w_0}\right) \]

Equation 3.4

whose differential is then fitted to the Gaussian beam profile to extract the beam parameters. One such measurement is illustrated in Figure 3-12 for both pump and probe beam. The corresponding radius extracted came out to be 22μm for pump beam, 5.84μm for probe beam at start of delay range and 5.92μm for probe beam at end of delay range. The probe beam radius is taken as an average of radii at two delay positions, 6μm to be used in experimental analysis. As observed from the values the measured change in probe beam radius is <=1% across the entire delay line.
Along with beam sizes, drift of the beam is also checked for by moving a focused razor blade across the beam till the power is reduced by half and measuring the change in power over entire delay range as shown in Figure 3-13.

Figure 3-12: Photodiode power plotted as a function of razor blade position for pump beam and probe beam at start and end of delay stage. Measured Gaussian profile fitted with a theoretical model to extract pump beam radius as 22μm and probe beam radius as 5.84μm and 5.92μm at start and end of delay range respectively. Less than 1% radius change observed for probe beam over the entire delay range.

Figure 3-13: Voltage output of a multimeter proportional to detector power at razor blade position cutting half of the focused beam plotted as a function of delay time. Full beam power corresponds to 0.78V. Drift of about 130nm can be calculated for the probe beam over entire delay range using this data.
This measured change in power is translated into a corresponding lateral shift of the focused probe beam using Equation 3.5 as derived by Schmidt in Ref. 83,

\[
\text{dx} = \frac{w_1^2 \sqrt{2\pi} \Delta A}{A_o}
\]

Equation 3.5

where \(\text{dx}\) is the lateral shift, \(\Delta A/A_o\) is the fractional change in DC multimeter voltage corresponding to power measured by the detector and \(w_1\) is \(1/e^2\) probe beam radius. Plugging in \(w_1\) as 5.8μm, \(A_o\) as 0.78V (19mW) and \(\Delta A\) as 0.014V (0.3mW) as measured from Figure 3-13 gives a shift of 130nm over the entire delay range which is considered acceptable based on literature.

Sample preparation

All the samples in this study are coated with an optimal thickness of Aluminum (Al) transducer layer using electron beam evaporation method. For the above experimental setup, Al proves to be the best transducer [96] compared to other metals due to a) it’s high absorptivity at 400nm which enables it to behave as an efficient heat source and b) its highest thermoreflectance at 800nm, thus providing an optimal signal to noise ratio in the experimental data. However, an appropriate thickness of Al film is required to capture accurate thermal conductivity of materials using this method as noted by Capinski and Maris [97] while evaluating thermal conductivity of bulk GaAs coated with different thickness Al films. This thickness was evaluated to approximately lie between 80-120nm which will be used for all the samples in this study. Thickness lower than this results in errors due to a probe beam reflectivity contribution arising from substrate in addition to reflectivity response owing to temperature change of Al film. On the other hand, a much larger thickness might create a temperature gradient in the metal film itself thus adding its contribution to the evaluated thermal response and rendering it inaccurate.
Thickness of Al layer is a critical parameter in signal analysis as shown in next section, hence its accurate characterization is done using acoustic echos observed in reflectivity data from a metal transducer surface.

According to the experimental study by Thomsen [98], an acoustic pulse is generated inside a film after pump beam absorption due to building up of an elastic stress in it. This acoustic oscillation, as it travels back and forth within the film, appears as echos in the reflectivity data as shown in Fig 3-14 for an aluminum film deposited on sapphire substrate. The time period between these echos,

$$t = \frac{2d}{v}$$  

Equation 3.6

as experimentally measured can then be used to derive thickness of the corresponding film (d) if velocity of sound in the material (v) is known. From Fig 3-14, this time period is measured as 23ps. Using literature value of v as 6240m/s [99] for Aluminum film, the corresponding thickness is then determined as 74nm for Al deposited on sapphire substrate which

Figure 3-14: In-phase component (x) of the reflectivity signal plotted as a function of delay time for a sapphire substrate coated with 74nm thick aluminum film, calculated from the measured time difference (tdiff) between the observed acoustic echos.
is used as a parameter in the signal analysis, as shown in next section, to derive thermal conductivity of sapphire substrate.

But unlike sapphire, some material systems are incapable of showing strong acoustic echos that could be effectively utilized to measure the corresponding metal thickness. In such situations, a sapphire substrate is placed right next to those samples during e-beam evaporation process such that thickness of Aluminum determined for sapphire using the method of acoustic echos could be used for those materials.

### 3.3 Analytical model for time-domain thermoreflectance

This section [78-79,81-83] explains the process of extracting unknown thermal properties of different material systems by utilizing least squares minimization principle to fit experimental data to a theoretically derived heat transfer model using MATLAB coding given in Appendix B.

**Phase correction**

Lock-in amplifier uses phase-sensitive detection by mixing a square wave at modulation frequency as a reference with the signal of interest to generate in-phase (x) and out of phase (y) components of the signal. But different electronics introduce some phase offset which is seen as a jump in out of phase signal at time t=0. Therefore, the experimentally derived signal needs to be phase corrected before it can be theoretically processed. The best way to perform phase correction is to make y component of signal constant across t=0 [78,83].

Numerically,

\[
\text{Instrument phase } \Delta \phi = \tan^{-1} \left( \frac{\Delta y}{\Delta x} \right)
\]

Equation 3.7

where \( \Delta y \) and \( \Delta x \) are changes in y and x observed respectively across time t=0
\[ x_{\text{corrected}} = x \cos(\Delta \phi) - y \sin(\Delta \phi) \quad \text{Equation 3.8} \]
\[ y_{\text{corrected}} = y \cos(\Delta \phi) + x \sin(\Delta \phi) \quad \text{Equation 3.9} \]

where \( x_{\text{corrected}} \) and \( y_{\text{corrected}} \) are the corrected components of the signal which can be used for analysis.

This phase correction process is illustrated below in Figure 3-15 for experimental data collected on a sapphire substrate coated with an aluminum metal transducer film.

![Figure 3-15: Plot showing experimental out-of-phase signal \( y_{\text{exp}} \) with a jump across zero-time delay owing to phase offset due to electronics and the phase corrected out-of-phase \( y_{\text{corrected}} \) signal with the phase correction indicated by constant signal across zero time delay.](image)

**Theoretical model derivation**

A brief review of theoretical model as reported by Schmidt [79,81,82,83] and Cahill [78], is now presented below to gain an understanding of the analysis procedure used for the measurements ahead. Essentially, the modelling process requires to derive a transfer function \( Z(\omega) \) in terms of sample response that could relate output voltage of lock-in amplifier to
modulated pump input i.e. $Ae^{i(\omega_0 t + \theta)} = Z(\omega)e^{i\omega_0 t}$ where $A$ and $\theta$ are amplitude and phase of the voltage signal observed on lock-in amplifier.

Some underlying considerations taken during the analysis are a) Laser pulses are taken to be delta functions as pulse duration is much smaller than pulse repetition period $(2\pi/\omega_s)$ and time scale of study, b) The laser powers and spot sizes used are optimized to avoid large temperature excursions on sample surface. Under these conditions, the thermo-physical properties can be assumed to be constant and the sample response to laser input can be assumed to be linear and time invariant, c) Since generally all the sample systems take a much longer time to equilibrate than the repetition period between pulses (12.5ns), heat accumulation effect is expected to contribute to the signal received by the detector and is therefore included in the modelling.

The process of modulated surface heating by the pump beam and the resultant temperature detection process by the probe beam is illustrated in Figure 3-16 [79]. The square wave modulation applied on the pump beam by the electro-optic modulator, can be broken down into sine waves at fundamental modulation frequency $\omega_0$ and its higher harmonics. Considering linear nature of the response, overall sample response can then be calculated as a summation of responses to each component. However, lock-in detection and inductor circuit in signal path eliminates all the higher harmonic components, hence the response below has been derived only for the fundamental component of modulation.

Pump beam pulses at a repetition rate of $\omega_s$ and modulated with a sinusoidal wave at a frequency of $\omega_0$ create a periodic heating event $q(t)$ on sample surface given as [82]

$$q(t) = Q_o e^{i\omega_0 t} \sum_{k=-\infty}^{\infty} \delta(t - \frac{2nk}{\omega_s})$$  \hspace{1cm} Equation 3.10

where $Q_o$ is energy absorbed by the sample from pump pulse.
In order to solve it in frequency domain, Fourier transform of Eq 3.1 is taken

\[ \tilde{q}(\omega) = Q_o \omega_o \sum_{k=\omega_o}^{\infty} \delta(\omega-k\omega_o-\omega_o) \]  

Equation 3.11

Oscillating temperature response induced by the pump beam heating on sample surface can then be expressed as [82]

\[ \tilde{\theta}(\omega) = \tilde{h}(\omega) \tilde{q}(\omega) \]  

Equation 3.12

where \( \tilde{h}(\omega) \) is the frequency response of the sample.

Probe beam pulses at a repetition rate \( \omega_o \) and with pulse energy \( Q_i \) are then incident at the sample surface at a delay time \( \tau \) with respect to pump beam which can be represented as [82]

\[ q_i(t) = Q_i \sum_{m=-\infty}^{\infty} \delta(t-\frac{2\pi}{\omega_o}m) \]  

Equation 3.13

Figure 3-16: Illustrates the modulated surface heating and temperature detection process in TDTR setup, a) Surface heating caused by sine-wave modulated pump beam pulses incident on the sample surface, b) Temperature response of the sample surface to the pump beam input, c) Probe beam pulses incident on sample surface after a delay time \( \tau \) with respect to pump beam pulses and subsequently reflected to the detector with an intensity proportional to surface temperature and d) Comparison of reference sine wave with the measured probe beam response at modulation frequency, generating the amplitude and phase of the voltage collected by lock-in amplifier. Adapted from Ref. 79.
which in frequency domain can be derived as
\[ \tilde{q}_i(\omega) = Q_i \omega_s \sum_{m=-\infty}^{\infty} \delta(\omega - m\omega_s) e^{jm\omega_s \tau} \]  
Equation 3.14

Reflected probe beam signal reaching the detector is taken to be directly proportional to the surface temperature response and thus in frequency domain can then be expressed as a convolution of temperature response and incident probe beam as shown in Equation 3.15 [82]
\[ \tilde{q}_r(\omega) = (\tilde{\theta}(\omega) * \tilde{q}_i(\omega))(\beta/2\pi) \]  
Equation 3.15

where \( \beta \) is thermoreflectance coefficient of the metal transducer at probe beam wavelength.

This signal from the detector is recorded by lock-in amplifier using phase sensitive detection to generate the in-phase (\( x(\tau) \)) and out-of-phase components (\( y(\tau) \)) of the signal at delay time \( \tau \) in Equation 3.16 [82]
\[ z(\tau) = x(\tau) + jy(\tau) = \frac{\beta Q_o \omega_s^2}{4\pi^2} \sum_{k=\infty}^{\infty} e^{jk\omega_s \tau} \tilde{h}(k\omega_s + \omega_o) \]  
Equation 3.16

To evaluate \( z(\tau) \), a critical component is \( \tilde{h}(\omega) \) corresponding to sample response which needs to be calculated. This sample response is however governed by nature of conduction through it which is decided by two factors, thermal penetration depth [81,100] and spot size.

\[ \text{Thermal penetration depth: } d = \sqrt{\frac{2\Lambda}{C\omega_o}} \]  
Equation 3.17

where \( \Lambda \) is thermal conductivity of the sample and \( C \) is volumetric heat capacity of the sample. Depending on sample parameter values if modulation frequency is chosen in a way such that thermal penetration depth is much smaller than spot size then heat transfer becomes predominantly one-dimensional in cross-plane direction. Otherwise radial conduction becomes dominant and in-plane thermal properties start playing a role specifically in anisotropic solids [79,83].
Single frequency response of a sample to a Gaussian pump beam as shown below is for the general case of radial conduction through a multilayer structure as derived by Schmidt [81] and Cahill [78].

Heat generated in Al layer by a cylindrical pump beam conducts through underlying sample as [81]

\[
\frac{\Lambda_r}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial \tilde{\theta}(r,z)}{\partial r} \right] + \frac{\Lambda_z}{z} \frac{\partial^2 \tilde{\theta}(r,z)}{\partial z^2} = C \frac{\partial \tilde{\theta}(r,z)}{\partial t}
\]

Equation 3.18

where \(r\) and \(z\) correspond to in-plane and cross-plane directions respectively with \(\Lambda_r\) and \(\Lambda_z\) defined as radial and cross plane thermal conductivity respectively, \(C\) as volumetric heat capacity and \(\tilde{\theta}\) as surface temperature. Taking Hankel transform to solve above equation in frequency domain(\(\omega\)) generates [81]
\[-\Lambda_{x}x^{2}\theta(z)+\Lambda_{z}\frac{\partial^{2}\theta(z)}{\partial z^{2}}=C\frac{\partial\theta(z)}{\partial t}\quad\text{Equation 3.19}\]

Assuming a solution, \(\theta(u(z)\exp[i(\omega t-\epsilon)]\) and putting in Equation 3.21 yields [81]

\[\frac{\partial^{2}\theta(\omega, z)}{\partial z^{2}}=q^{2}\theta(\omega, z)\quad\text{Equation 3.20}\]

where \(q\) is defined as \(\sqrt{\frac{\Lambda_{x}s^{2}+\alpha_{0}}{\Lambda_{z}}}\) at pump beam modulation frequency \(\omega=\omega_{0}\)

On solving Equation 3.20, a transfer matrix \(M_{i}\) can be derived relating temperature \((\theta_{\text{top}})\) and heat flux \((F_{\text{top}})\) at the top of ith layer of thickness \(d\) to the respective temperature \((\theta_{\text{bottom}})\) and heat flux \((F_{\text{bottom}})\) at the bottom of the layer as [81]

\[
\begin{bmatrix}
\theta_{\text{bottom}} \\
F_{\text{bottom}}
\end{bmatrix} = M_{i}
\begin{bmatrix}
\theta_{\text{top}} \\
F_{\text{top}}
\end{bmatrix}
\]

where \(M_{i}=\begin{bmatrix}
\cosh(q_{i}d_{i}) & -\sinh(q_{i}d_{i})/(\Lambda_{z}q_{i}) \\
-(\Lambda_{z}q_{i})\sinh(q_{i}d_{i}) & \cosh(q_{i}d_{i})
\end{bmatrix}\]

Heat flux across an interface imposed with a temperature gradient can be defined as [81]

\[F_{\text{top}}=F_{\text{bottom}}=G_{i}(\theta_{\text{top}}-\theta_{\text{bottom}})\quad\text{Equation 3.21}\]

where \(G_{i}\) represents interfacial thermal conductance of ith interfacial layer.

This can be written as Equation with \(M_{i}=\begin{bmatrix} 1 & -1/G_{i} \\ 0 & 1 \end{bmatrix}\)

Thus, for a multilayer system, heat flux \((F_{\text{top}})\) and temperature at top surface \((\theta_{\text{top}})\) can be related to the corresponding heat flux \((F_{\text{bottom}})\) and temperature \((\theta_{\text{bottom}})\) at bottomside of it as [81]

\[
\begin{bmatrix}
\theta_{\text{bottom}} \\
F_{\text{bottom}}
\end{bmatrix} = M_{\text{total}}
\begin{bmatrix}
\theta_{\text{top}} \\
F_{\text{top}}
\end{bmatrix}
\quad\text{Equation 3.22}
\]

where \(M_{\text{total}}=\begin{bmatrix} A & B \\ C & D \end{bmatrix}=M_{n}M_{n-1}…….M_{1}\) with \(M_{i}\) defining the property matrix for each layer in sequence.

Taking substrate (bottommost layer) to be semi-infinite with respect to thermal penetration, \(F_{\text{bottom}}\) can be taken as 0. Thus, temperature at the top surface can be calculated with respect to heat flux \(F_{\text{top}}\) applied by pump beam at the surface as [81]:
\[ \theta_{\text{top}} = \frac{D}{C} F_{\text{top}}, \quad \text{Equation 3.23} \]

In the experimental setup, pump beam is a Gaussian cylindrical beam of \(1/e^2\) radius \(w_o\).

Power absorbed by the sample surface from this beam is taken to be \(AQ_{\text{pump}}\). Thus, heat flux at the top surface can be derived in the frequency domain by taking Fourier transform of the Gaussian profile to give

\[ F_{\text{top}} = I_{\text{pump}}(s) = \frac{AQ_{\text{pump}}}{2\pi} \exp\left(-\frac{s^2 w_o^2}{8}\right) \quad \text{Equation 3.24} \]

In a similar fashion, intensity distribution of probe beam with \(1/e^2\) radius \(w_1\) in frequency domain can be written as

\[ I_{\text{probe}}(s) = \frac{Q_{\text{probe}}}{2\pi} \exp\left(-\frac{s^2 w_1^2}{8}\right) \quad \text{Equation 3.25} \]

where \(Q_{\text{probe}}\) is the power of incident probe beam.

From equations 3.23 and 3.24, the temperature response to pump input at the surface is generated. This temperature response is detected as change in reflected probe intensity which can be derived by multiplying it with the thermoreflectance coefficient \(\beta\) at probe beam wavelength and then weighing it over intensity distribution of probe beam in equation 3.25. Taking inverse transform of the resultant expression defines this response in real space as \([81]\)

\[ H(\omega) = \beta \frac{Q_{\text{p}} Q_{\text{i}}}{2\pi} \int_{-\infty}^{\infty} s \left( \frac{-D}{C} \right) \exp \left[ \frac{-s^2 (w_o^2 + w_1^2)}{8} \right] ds \quad \text{Equation 3.26} \]

which when used with equation 3.16 can generate the lock-in response to be fitted with experimental data.

Fitting the experimental ratio \((-x/y)\) to theory is an optimum way for thermal parameters extraction. As can be seen from theoretical equations above, \(x\) and \(y\) both depend on various experimental conditions such as pump and probe beam powers and thermoreflectance coefficient which can get cancelled out while using ratio, thus eliminating any uncertainty in parameter estimation due to these variables \([78, 83, 101]\). Secondly errors due to laser power fluctuations and
beam defects also get removed in the ratio data thus ensuring enhanced signal to noise ratio in data being fitted.

**Steady state temperature rise measurement**

As stated in theoretical calculations, steady state temperature rise in the sample should not be too large, otherwise assumption of linearity used above would no longer remain valid and the physical properties would not remain constant in the said regime. Thus, steady state temperature rise calculation in the metal transducer film and the sample will be performed for the fluences used for different samples measured in this study to ensure validity of theoretical calculations.

Temperature rise in the metal film can be estimated [83] as

$$\Delta T = \frac{AQ}{\rho C_p d}$$ \hspace{1cm} \text{Equation 3.27}

where AQ is absorbed energy per unit cross section from pump pulse, $\rho C_p$ is volumetric heat capacity of Al and d is optical absorption depth in Al at 400nm. Using approximate values for max pump power used in the experiments as 50mW, spot size as 21µm, reflectivity of aluminum R as 98% and d as 10nm, this temperature rise comes approximately 0.37K which is small enough to assume constant physical properties and linear behavior.

Secondly, steady state temperature rise in the sample due to incident pump and probe beams on the sample can be estimated [78,83,102] as

$$\Delta T = \frac{(1-R)\dot{Q}}{\lambda \sqrt{2w_o^2 + 2w_1^2}}$$ \hspace{1cm} \text{Equation 3.28}

where R is reflectivity of Al, $\dot{Q}$ is total power of the laser incident on sample, $\lambda$ is thermal conductivity of the substrate and $w_o$ and $w_1$ are pump and probe beam radius respectively.
Sensitivity Analysis

Sensitivity analysis is performed as a measure of understanding the effect of various experimental parameters on the measured ratio data as a function of delay time. For a given parameter \( p \), it can be quantified as \([81,101,103]\)

\[ S_p = \frac{\partial \ln(-x/y)}{\partial \ln p} \]  

Equation 3.29

where \( x \) and \( y \) represent the in-phase and out-of-phase component of the signal respectively and \( p \) represents the parameter with respect to which sensitivity is calculated. Different sensitivities of the ratio for various parameters aids in segregating their influence involved in a given time range thus enabling the fitting procedure to be implemented in a much easier fashion. This is demonstrated in the next section for standard samples and will be utilized to process data for the samples studied in this thesis.

Experimental setup calibration

In order to test the accuracy of the experimental setup and the analysis used for the same, the system is utilized to measure thermal properties of three standard substrates namely, fused silica, sapphire and silicon, each coated with an aluminum transducer layer with thickness ranging from 70-120nm, determined using the procedure mentioned in sample preparation section. Experimentally, ratio (-\( x/y \)) of in-phase (\( x \)) to out-of-phase component (\( y \)) is collected for all three samples at different modulation frequencies ranging from 1-10MHz. Experimental parameters utilized for the data collection process for all three samples are listed out in Table 3.1.
Taking the parameter values and assuming literature values for thermal conductivity for all three substrates, steady state temperature rise is then derived using Equation 3.28 as 13-15K for fused silica, 0.5-0.7K for sapphire and 0.2-0.3K for Si substrate which are small enough for linearity and thus the corresponding signal analysis derived above to hold.

Thermal penetration depth is calculated using Equation 3.17 for the three samples at their respective experimentally used modulation frequency as given in Table 3-1. For the calculation, their respective bulk thermal conductivity and heat capacity values are taken as literature reported values as listed in Table 3-2. Penetration depth is worked out to be approximately 200nm for fused silica, 700nm for sapphire and 2μm for silicon. Since it is much smaller than the corresponding spot sizes utilized experimentally for all three samples, radial conduction can be ignored in the theoretical model and their respective cross plane thermal conductivity values can be extracted during fitting. This is further confirmed from the sensitivity analysis below in Figure 3-18 where ratio is observed to be insensitive to spot size utilized in experiments.

**Table 3-1:** Experimental parameters utilized for calibrating TDTR setup with standard substrates

<table>
<thead>
<tr>
<th>Material</th>
<th>Modulation Frequency (MHz)</th>
<th>Pump beam (μm)</th>
<th>Probe beam (μm)</th>
<th>Aluminum thickness (d_{Al}) (nm)</th>
<th>Total incident power (Q) (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused silica</td>
<td>8.55MHz</td>
<td>22</td>
<td>8</td>
<td>100</td>
<td>40-60</td>
</tr>
<tr>
<td>Sapphire</td>
<td>8.75MHz</td>
<td>21</td>
<td>6</td>
<td>74</td>
<td>50-70</td>
</tr>
<tr>
<td>Silicon</td>
<td>4.96MHz</td>
<td>20</td>
<td>10</td>
<td>159</td>
<td>60-80</td>
</tr>
</tbody>
</table>
Figure 3-18: Sensitivity analysis for fused silica, sapphire and silicon substrates respectively with respect to the following parameters: thermal conductivity and heat capacity of the respective substrate represented by $\Lambda_s$ and $C_s$ respectively, thickness and heat capacity of Aluminum film represented by $d_{Al}$ and $C_{Al}$ respectively, interfacial thermal conductance between substrate and Aluminum metal film represented by $G_{Al-s}$ and pump beam spot size represented by $w_o$. Calculations are performed while assuming best fit and literature values for the physical properties in Table 3-2 and experimental parameters from Table 3-1.
The experimental data and the respective theoretical fits are shown in Figure 3-19 for all three samples.

Figure 3-19: Figure shows the experimentally measured ratio ($-x/y$) with their respective theoretical fits for three standard samples: Silicon, sapphire and fused silica with the experimentally utilized modulation frequencies labelled on each curve.

Deriving a theoretical model for a two-layer system from the analysis procedure above indicated five unknown parameters, namely, thermal conductivity of the substrate ($\Lambda_s$), heat capacity of the substrate ($C_s$), thermal conductivity of aluminum ($\Lambda_{Al}$), heat capacity of aluminum ($C_{Al}$) and interfacial thermal conductance between aluminum and substrate ($G_{Al,s}$), to be evaluated before it could be used to fit the experimental data. Thus, before proceeding with the theoretical analysis, sensitivity calculation is performed for all three samples as shown in Figure 3-18. These calculations are performed using the experimental parameters listed in Table 3-1 and assuming the best fit values for the three physical properties of thermal conductivity, interfacial conductance and heat capacity as shown in Table 3-2.

Some observations made from this figure are: a) for high thermal conductivity materials, silicon and sapphire, for instance, the ratio has high sensitivity to effusivity of the substrate in the
intermediate time range (100-500ps) but that sensitivity becomes negligible in the longer time scale (2-6ns). In this regime, it becomes more sensitive to interfacial thermal conductance as that becomes the limiting thermal resistance to heat flow at longer times, b) for low thermal conductivity material like fused silica, however, it is relatively insensitive to interfacial thermal conductance over the entire delay range due to the inherent high resistance provided by the substrate to thermal flow, c) sensitivity to thickness and heat capacity of Aluminum film is high in all cases and thus need to be determined accurately to provide minimum uncertainty in thermal conductivity evaluation, d) since the spot sizes used in all three cases are much larger than their respective thermal penetration depth estimates, ratio is insensitive to spot size.

From these observations, effusivity of the substrate and thermal interfacial conductance can be extracted simultaneously from theoretical fit to experimental ratio since their sensitivities are different in different time delay range. But in order to extract thermal conductivity at the labelled frequencies, heat capacity must be known as the sensitivity is similar for both the parameters and hence cannot be determined simultaneously.

Thus, heat capacity of Aluminum and substrates (silicon, sapphire and fused silica) and thermal conductivity of Aluminum are taken from literature with the values listed down in Table 3-2. The theoretical model is then fitted to the experimental data using thermal conductivity of the substrate (Λ) and interfacial thermal conductance (G_{Al-s}) as fitting parameters as shown in Figure 3-19. The derived values of thermal conductivity and interfacial conductance as tabulated in Table 3-2 show a reasonable agreement with the literature reported values thus validating the setup and the analysis procedure used.
Error analysis

Uncertainty analysis on thermal conductivity data derived from TDTR experiments is performed using Equation 3.30 [103,108]

\[
(\frac{\delta p}{p})^2 = (R \frac{\delta \phi}{\phi})^2 + \sum \left( \frac{S_{ip} \delta ip}{S_p} \right)^2
\]

Equation 3.30

where \(\delta p\) is the total error in the experimentally measured parameter \(p\) such as thermal conductivity, heat capacity etc. The first term on the right corresponds to uncertainty that propagates from the error \(\delta \phi\) in determining the phase \(\phi\) utilized for the phase correction process. The second contribution comes from error in the input parameters that are utilized in the analytical model fitting process for parameter estimation. This is shown as the second term in Equation 3.30 where \(\delta ip\) is the uncertainty in input parameter \(ip\) and \(S_{ip}\) and \(S_p\) are the sensitivities of experimental ratio signal \(R\) to an input parameter and experimentally derived parameter respectively.

Table 3-2: Experimentally derived vs literature reported values of physical properties for aluminum and three standard calibrated samples: fused silica, sapphire and silicon.

<table>
<thead>
<tr>
<th>Material</th>
<th>Literature [104-107]</th>
<th>Experimentally derived</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thermal Conductivity (W/m-K)</td>
<td>Heat Capacity (J/cm³-K)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>200</td>
<td>2.44</td>
</tr>
<tr>
<td>Fused silica</td>
<td>1.3-1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>Sapphire</td>
<td>30-50</td>
<td>3.02</td>
</tr>
<tr>
<td>Silicon</td>
<td>130-160</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Chapter 4

**Thermal transport measurement of silicon metalattices using TDTR**

Chapter 2 presented the quantitative prediction of thermal transport through silicon metalattice structures which were defined to be three-dimensional silicon nanostructures with a periodic distribution of pores. This chapter presents an experimental study of thermal transport using TDTR through these structures, the synthesis process of which was described in detail in Chapter 2.

### 4.1 Room temperature TDTR on Si metalattices

**Experimental and Material parameters**

TDTR setup is utilized to evaluate thermal conductivity for both filled and empty silicon metalattice structures fabricated above. The samples were coated with 70nm-120nm thick aluminum film as determined by acoustic echos generated either from the corresponding metalattice film or from the sapphire substrate deposited right next to it. Experimental data was collected at 4-5 different spots on each sample at a modulation frequency of 8.75MHz. Experimental ratio (-x/y) was evaluated for each sample after applying phase correction to the respective in-phase (x) and out-of-phase component (y) of the signal collected from the lock-in amplifier. Experimental parameters utilized for the data collection process for all the samples are listed out in Table 4.1.
Using the experimental parameter values in Table 4-1 and assuming literature value for thermal conductivity of silicon substrate, steady state temperature rise at room temperature was estimated using Equation 3.28 to be 0.1K-0.2K for all the samples studied in this work which was small enough to ensure the validity of the theoretical model derived in Chapter 3.

In order to employ the theoretical model for a three-layer system for fitting the above extracted experimental ratio, eight unknown parameters, namely, thermal conductivity of the metalattice film ($\Lambda_{ML}$), volumetric heat capacity of the film ($C_{ML}$), thermal conductivity of silicon substrate ($\Lambda_{Si}$), volumetric heat capacity of silicon substrate ($C_{Si}$), thermal conductivity of aluminum ($\Lambda_{Al}$), volumetric heat capacity of aluminum ($C_{Al}$), interfacial thermal conductance between aluminum and metalattice film ($G_{Al-ML}$) and interfacial thermal conductance between metalattice film and silicon substrate ($G_{ML-Si}$), need to be determined. Amongst these, literature reported values as presented in Table 3-2 are taken for thermal conductivity [104] and volumetric heat capacity [106] of aluminum and silicon respectively. Volumetric heat capacity for the metalattice film is calculated using rule of mixtures as given in Equation 4.1

$$C_{ML}=V_{pore}C_{pore}+(1-V_{pore})C_{Si}$$  \quad \text{Equation 4.1}
where $V_{\text{pore}}$ and $C_{\text{pore}}$ represent volume fraction and volumetric heat capacity of pore material respectively. Thus, for a silicon metalattice with silica spheres in, $C_{\text{pore}}$ is taken as the literature reported value for heat capacity of silica [107] while for an inverse opal with silica spheres etched out, first term is neglected due to negligible heat capacity of air with respect to silicon.

Using a reasonable estimate for thermal conductivity and heat capacity at a particular temperature and taking the experimentally used modulation frequency of 8.75MHz, thermal penetration depth is calculated for each sample in the given temperature range using Equation 3-17. The derived values are listed in Table 4-2 with the temperature range indicated right next to it. Since for each sample and for the given temperature range, this depth turned out to be much smaller than the corresponding spot sizes utilized experimentally, corresponding radial conduction was ignored in the theoretical model while fitting the experimental data. This was further confirmed from the sensitivity analysis where the ratio ($x/y$) was observed to be insensitive to spot size for all the metalattice samples studied in this work.

Table 4-2: Material parameters including Aluminum film thickness and Metalattice film thickness. Film thickness compared against the respective thermal penetration depth calculated for a modulation frequency of 8.75MHz and with the temperature range indicated in brackets indicated next to it.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Penetration Depth(d) (nm)</th>
<th>Film thickness(d$_{ML}$) (nm)</th>
<th>Aluminum thickness(d$_{Al}$) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7nm filled metalattice</td>
<td>120-240 (30K-300K)</td>
<td>1500+19</td>
<td>109</td>
</tr>
<tr>
<td>10nm filled metalattice</td>
<td>100-180 (30K-300K)</td>
<td>480+33</td>
<td>109</td>
</tr>
<tr>
<td>15nm filled metalattice</td>
<td>90-250 (30K-300K)</td>
<td>1650+34</td>
<td>109</td>
</tr>
<tr>
<td>30nm filled metalattice</td>
<td>200-250 (140K-300K)</td>
<td>410+10</td>
<td>96</td>
</tr>
<tr>
<td>7nm empty metalattice</td>
<td>100-125 (300K)</td>
<td>1400+29</td>
<td>99.5</td>
</tr>
<tr>
<td>10nm empty metalattice</td>
<td>125-150 (300K)</td>
<td>1200+31</td>
<td>119</td>
</tr>
<tr>
<td>15nm empty metalattice</td>
<td>120-250 (30K-300K)</td>
<td>910+39</td>
<td>106</td>
</tr>
</tbody>
</table>
**Sensitivity analysis**

Sensitivity of ratio (-x/y) at room temperature calculated using Equation 3.29 for all four filled silicon metalattice samples is shown in Figure 4-1 and for the three empty silicon metalattice samples is shown in Figure 4-2. For each sample, these calculations are performed assuming reasonable values for their corresponding physical parameters, namely, thermal conductivity of the metalattice film ($\Lambda_{ML}$), interfacial thermal conductance between metalattice film and aluminum film ($G_{Al,ML}$) and interfacial thermal conductance between metalattice film and substrate ($G_{ML-Si}$). Literature reported values are taken for thermal conductivity and heat capacity of aluminum [104,106] while metalattice heat capacity is calculated from Equation 4.1.

Since film thicknesses of all the metalattice samples are much greater than their respective thermal penetration depth estimates, the ratio has almost negligible sensitivity to interfacial thermal conductance between the film and substrate ($G_{ML-Si}$) and to silicon substrate properties for all the samples as observed from Figures 4-1 and 4-2. Secondly, for all the cases, sensitivity to volumetric heat capacity and thermal conductivity of metalattice lie very close to each other and therefore cannot be extracted simultaneously from the theoretical fit to the experimental data. Therefore, volumetric heat capacity ($C_{ML}$) theoretically calculated from Equation 4.1 is used as a fixed parameter in the model before experimental data fitting. Experimental data can now be fitted to the analytical model using thermal conductivity of the metalattice film ($\Lambda_{ML}$) and interfacial thermal conductance between aluminum and metalattice film ($G_{Al,ML}$) as free parameters. This fitting is illustrated in Figure 4-3 for filled metalattice samples for all four sphere sizes.
However, for empty metalattices, due to a much lower value for thermal conductivity of the film, sensitivity of ratio to $G_{\text{Al-ML}}$ is negligible as compared to sensitivity to $\Lambda_{\text{ML}}$ and hence the fit results obtained for interfacial thermal conductance seemed unreliable. Hence the fitting was performed with thermal conductivity of the film as the only free parameter as shown in Figure 4-3.
Figure 4-2: Sensitivity analysis for empty silicon metalattice samples with sphere radius of 7nm, 10nm and 15nm respectively with respect to the following parameters: thermal conductivity and heat capacity of the metalattice represented by $\Lambda_{\text{ML}}$ and $C_{\text{ML}}$ respectively, thickness and heat capacity of Aluminum film represented by $d_{\text{Al}}$ and $C_{\text{Al}}$ respectively, interfacial thermal conductance between metalattice film and Aluminum metal film represented by $G_{\text{Al-ML}}$, interfacial thermal conductance between metalattice film and silicon substrate represented by $G_{\text{ML-Si}}$ and metalattice film thickness represented by $d_{\text{ML}}$. For the calculations, literature reported values are taken for silicon substrate and aluminum while assuming reasonable values for $\Lambda_{\text{ML}}, C_{\text{ML}}, G_{\text{ML-Si}}$ and $G_{\text{Al-ML}}$.

Results and discussion

Table 4-3: Experimentally extracted room temperature thermal conductivity values for both filled and empty metalattice samples with their respective error bars.

<table>
<thead>
<tr>
<th>Sphere radius</th>
<th>Metalattice type</th>
<th>Filled metalattice (W/m-K)</th>
<th>Empty metalattice (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7nm</td>
<td></td>
<td>1.33±0.09</td>
<td>0.16±0.05</td>
</tr>
<tr>
<td>10nm</td>
<td></td>
<td>0.94±0.06</td>
<td>0.24±0.04</td>
</tr>
<tr>
<td>15nm</td>
<td></td>
<td>1.68±0.11</td>
<td>0.26±0.07</td>
</tr>
<tr>
<td>30nm</td>
<td></td>
<td>2.08±0.12</td>
<td></td>
</tr>
</tbody>
</table>
Room temperature thermal conductivity values extracted from the above fitting are tabulated in Table 4-3 for both filled and empty silicon metalattice samples. The error bar associated with each sample is calculated by combining a) standard deviation associated with different sample spots measured experimentally and, b) standard deviation contribution generating as a result of uncertainty associated with different thermophysical properties used in the theoretical fitting model. Equation 3.30 is utilized for calculating the latter for each sample by using the respective sensitivity calculation and uncertainty in different properties. Amongst these, maximum contribution comes from uncertainty in aluminum thickness taken as 3% and heat capacity taken as 2%, as seen from the sensitivity curves. Apart from these, contributions from uncertainty in spot size and metalattice film thickness are also included in the error calculation.

![Filled metalattice data @300K](filled_data.png) ![Empty metalattice data @300K](empty_data.png)

Figure 4-3: Figure shows the experimentally measured data at room temperature with the respective theoretical fit for a) filled metalattices with sphere radius of 7nm, 10nm, 15nm and 30nm and b) empty metalattices with sphere radius of 7nm, 10nm and 15nm. All the datasets are collected at a modulation frequency of 8.75MHz.

Thermal conductivity is plotted as a function of sphere radius for both filled and empty silicon metalattice samples as shown in Figure 4.4 and compared against the theoretical data derived in Chapter 2 [54,55].
A minimum in thermal conductivity was observed at a sphere radius of 10nm for filled silicon metalattice samples. However, no such minimum could be seen in the thermal conductivity curve of empty metalattice samples. Thermal conductivity increase with increasing sphere size was instead noticed for empty silicon metalattice samples, a trend similar to that for filled silicon metalattice system above 10nm sphere radius. Secondly, extremely low thermal conductivity value of 0.16W/m-K was measured for empty silicon metalattice with 7nm sphere radius.

The observed experimental trend agreed with the theoretical prediction from Chapter 2 [54,55] which attributed the occurrence of this minimum in filled metalattices to a cross-over from Rayleigh regime to Casimir regime of phonon transport in these structures. According to theory, since a much smaller sphere radius of 5nm is required for observing the minimum in empty metalattices, trend characteristic of Casimir regime of transport is observed experimentally in accordance with theory. In addition, experimental values are found to be in quantitative

Figure 4-4: Experimental values for thermal conductivity plotted as a function of sphere radius for both filled and empty metalattice systems. Minimum observed at a sphere radius of 10nm for filled metalattices but no minimum seen for empty metalattice samples. Theoretical curves modified from Ref. 54,55 are plotted as solid lines for both the systems as a comparison to experimental data.
agreement with the data predicted using ballistic model, suggesting that ballistic transport [13-17] of phonons occurring through these structures is indeed responsible for the ultra-low values of thermal conductivity observed in them.

**4.2 Temperature dependent TDTR on Si metalattices**

**Experimental setup and procedure**

In order to further confirm the ballistic nature of phonon transport through these structures, low temperature thermal conductivity measurement was performed for both filled and empty silicon metalattice samples.

For the low temperature measurement, samples were mounted inside a liquid Helium continuous flow optical cryostat with a temperature stability of <1K. Experimental conditions except for the total incident power were kept identical to room temperature study. Total incident power on the filled metalattice samples was reduced from 65mW at room temperature to 6mW at 30K. However, for empty metalattice samples the power was instead reduced from 40-50mW at room temperature to 4-5mW at 30K. This allowed the temperature rise of Aluminum film due to pump beam heating to stay below 0.5K and steady state heating to stay within 0.1K-0.2K in the entire temperature range of 30K-300K.

**Sensitivity analysis**
At low temperatures, it is observed that sensitivity of ratio to different parameters of interest closely resemble ones at 300K for filled silicon metalattice samples. This is illustrated in Figure 4-5, which compares the sensitivity plots for 15nm filled metalattice at four different temperatures. For all the samples, heat capacity at each temperature was calculated using temperature dependent heat capacity values of silicon and pore material in Equation 4.1. Thermal conductivity ($\Lambda_{ML}$) and interfacial thermal conductance between film and Aluminum ($G_{Al-ML}$) at each temperature was therefore extracted simultaneously from the respective theoretical fit to
experimental data without getting influenced by interfacial conductance between metalattice film and substrate and substrate properties.

For empty metalattices, even though the sensitivity trends at all other temperatures closely match those at 300K, at 30K due to a much lower value for interfacial conductance $G_{Al-ML}$, sensitivity of ratio to this parameter becomes higher as shown in Figure 4-6. Hence, unlike other temperatures theoretical fit to experimental data at 30K is achieved by using both $\Lambda_{ML}$ and $G_{Al-ML}$ as free parameters. This experimental data fitting to theory is shown for 15nm
sphere radius filled and empty metalattice samples at three different temperatures in Figure 4-7: lowest temperature 30K, one temperature in the increasing region (90K for empty metalattice and 140K for filled metalattice) and 230K: temperature in the saturation region for both the systems.

Results and discussion

![Graph showing thermal conductivity vs temperature for filled and empty metalattices at different temperatures](image)

Figure 4-7: Figure shows the experimentally measured data with the respective theoretical fits at three different temperatures: a) 15nm sphere radius filled metalattice at 30K, 140K and 230K and b) 15nm sphere radius empty metalattices at 30K, 90K and 230K. All the datasets are collected at a modulation frequency of 8.75MHz. Low signal to noise ratio observed at 30K due to very low probe and pump beam powers used to ensure small temperature rise in Aluminum.

Extracted thermal conductivity is plotted for both 15nm filled metalattice and 15nm empty metalattice as a function of temperature in Figure 4-8. Error bars are calculated using Equation 3.30 by combining the uncertainties associated with spot size, Aluminum thickness, Aluminum heat capacity and metalattice film thickness measurement.
As seen from Figure 4-8, thermal conductivity for both filled and empty metalattice sample increases initially with temperature before reaching saturation, a trend characteristic of ballistic phonon transport mechanism \([13-17]\) and thus resembling the prediction made using ballistic model previously in Chapter 2. This is further illustrated in Figure 4-9(a) in which thermal conductivity for filled metalattice samples is plotted as a function of temperature for three different sphere radii, 7nm, 10nm and 15nm respectively, across the minimum. All three curves show the saturation effect in the temperature range 140K-300K, characteristic of ballistic transport. In addition, the minimum in thermal conductivity is preserved at 10nm sphere radius throughout the entire temperature range as shown in Figure 4-9(b) where thermal conductivity for the four filled metalattice samples is plotted as a function of sphere radius at three different temperatures, namely 140K, 200K and 300K.

Figure 4-8: Experimental and theoretical thermal conductivity as a function of temperature for both filled and empty metalattice at a sphere radius of 15nm, illustrating ballistic nature of thermal transport. Theoretical curves modified from Ref.\(^5\)\(^4\)\(^5\) are plotted as solid lines for both the systems as a comparison to experimental data.
These experimental measurements illustrate that phonon transport in metalattices occurs through ballistic mode with a cross-over occurring between Rayleigh ballistic region and Casimir ballistic region depending on pore content and pore radius. This is in accordance with the theoretical predictions described in Chapter 2.

It is noted that theoretical calculations were performed on single crystalline silicon metalattice structures with perfect order and pore size distribution. However, with decreasing size of silica nanospheres used in template assembly process, an increase in particle roughness and dispersity was observed and particles tended to deviate from ideal spherical shape. Secondly, the template was infiltrated with polycrystalline silicon. Considering the effect of these defects and grain boundaries in the theoretical model might assist in providing a much better agreement with the experimental data.

It is further observed that although ballistic model could provide a reasonable agreement to the experimentally measured temperature dependent thermal conductivity data for 15nm sphere.

**Figure 4-9:** a) Thermal conductivity plotted as a function of temperature ranging from 140K-300K for filled metalattice samples with three different sphere radii: 7nm, 10nm and 15nm respectively. All three curves show saturation behavior characteristic of ballistic mode of phonon transport while preserving the minimum at 10nm sphere radius, b) Thermal conductivity for filled metalattice samples plotted as a function of sphere radius at three different temperatures: 140K, 200K and 300K showing that the minimum stays preserved at 10nm sphere radius for all three temperatures. Theoretical curves modified from Ref. 54,55 are plotted as solid lines for all three temperatures as a comparison to experimental data.
radius filled metalattice in Figure 4-8, a larger discrepancy is observed between theory and experiment for 15nm sphere empty metalattice sample, especially higher at low temperatures. This might be due to specular scattering effect described by Ziman [22] which is higher for longer wavelength phonons, dominant wavelengths at lower temperatures and thus can result in a larger ballistic mean free path as compared to the above theory.
Chapter 5

Summary and Future work

Amongst various methods of nanostructuring utilized for tuning thermal transport, one such study combined the effects of nanoparticle and alloy scattering for thermal conductivity reduction by embedding nanoparticles in semiconductor alloys and in the process discovered a theoretical minimum in thermal conductivity at an optimal nanoparticle size of less than 100nm. One such minimum in thermal conductivity as a function of pore radius is presented in this work while conducting thermal transport study on a silicon metalattice structure, a three-dimensional silicon nanostructure with a periodic distribution of pores. Quantitative predictions based on ballistic phonon transport through these structures is briefly discussed for two different silicon metalattice systems: one with empty pores and one with silica pores. Dependence of this minimum on pore volume fraction and pore material is further studied in this work. Procedure for experimental synthesis of both filled and empty metalattices using high pressure confined chemical vapor deposition is then briefly discussed. This work also discusses the method of time-domain thermoreflectance, the principle underlying this method and its advantages in accurate determination of thermal conductivity of thin films with nanoscale spatial resolution. It describes the experimental procedure required for establishing this setup, a corresponding analytical model utilized for extracting thermal parameters from experimental data and the calibration performed to validate this setup. This method subsequently used to experimentally measure thermal conductivity as a function of pore radius for both filled and empty silicon metalattice systems is then studied and theoretically predicted minimum is identified in the experimental results in addition to a reasonable agreement between theory and experiment. Temperature dependent thermal conductivity measurements performed to further validate the ballistic transport of phonons through these structures is then presented for both filled and empty metalattice systems.
and compared to theoretically calculated values. Transition from Rayleigh ballistic regime to Casimir ballistic regime is identified as the basis for observation of this minimum and its dependence on pore material and pore volume fraction while ballistic phonon transport as the cause for the extremely low values of thermal conductivity observed in these structures. The studies presented above inspired certain future directions of study that can be performed which are briefly described below.

5.1 Si metalattices as potential thermoelectrics

Thermoelectric efficiency for a material can be defined by figure of merit $ZT$ [5] given by Equation 5.1

$$ZT = \frac{S^2 \sigma T}{\Lambda}$$  \hspace{1cm} \text{Equation 5.1}

where $S$, $\sigma$, $\Lambda$ and $T$ represent Seebeck coefficient, electrical conductivity, thermal conductivity and temperature respectively. As seen from this Equation, this efficiency can be enhanced if thermal conductivity can be reduced with simultaneous increase in Seebeck coefficient and electrical conductivity which is currently being explored in a lot of nanostructured semiconductor material systems [5-6].

In this work, extremely low thermal conductivity values have been demonstrated for undoped polycrystalline silicon metalattices with different sphere radii owing to ballistic transport of phonons in these structures and thus can be explored as a potential measure to enhance thermoelectric efficiency. An advantage of a metalattice structure lies in its three-dimensional connectivity which is expected to maintain high electrical conductivity through uninterrupted flow of electrons in addition to observed low thermal conductivity. However, electrical transport measurements performed on heavily doped polycrystalline silicon metalattices with sphere radii of 7nm, 15nm and 50nm showed resistivity values approximately two orders of magnitude larger
than the corresponding bulk polycrystalline silicon with the same grain size and doping concentration as determined by secondary ion-mass spectroscopy (SIMS). This low value of electrical conductivity observed could be attributed to a combined effect of grain boundaries, defects and lower metabond (neck) size.

Thus, one of the ways that can be utilized to increase electrical conductivity is by increasing the metabond size which can facilitate improved electrical conduction through them. This can be accomplished by re-infiltration of silicon in empty silicon metalattice system as illustrated by Badding group in Figure 5-1.

Figure 5-1: Schematic illustrating the process of re-infiltrating silicon in an empty metalattice with a porosity of 74% to derive a metalattice with a reduced porosity of 37%, showing an increase in the size of metabonds (neck) required for better electrical conduction but becoming responsible for a simultaneous increase in thermal conduction. Second sequence illustrates the process of Phosphorus (P) doping in a porosity tuned metalattice which can enhance electrical conduction but reduce thermal conductivity due to scattering on dopant atoms and the corresponding free and bound electrons and holes.

For a heavily doped silicon metalattice with lower porosity, two factors will determine their thermal conductivity. Increasing the neck size will increase the thermal conductivity value due to reduced effect of interfacial scattering on phonons as shown in Figure 5-2.
However, increasing doping has shown to reduce thermal conductivity in polysilicon due to scattering of phonons on dopant atoms which carry a different mass than silicon and on free and bound electrons and holes introduced in the system due to dopants. The doping effects on thermal conductivity are illustrated by McConnell et al. for Phosphorus (P) and Boron doping (P) in a layer of polysilicon, showing a decrease in thermal conductivity with an increase in doping concentration. Adapted from Ref. 109.

Thus, performing thermal and electrical transport studies on metalattices with an optimal control of porosity, doping material and doping concentration can pave a way towards some interesting thermoelectric research in future.
5.2 Thermal Rectification in Graded Si Metalattice

Thermal rectification in a material system is defined as a phenomenon where heat flow through a material depends on the polarity of temperature gradient applied across it. Its efficiency is defined by figure of merit $\gamma$ [1] given by

$$\gamma = \frac{|Q_{\text{forward}}| - |Q_{\text{reverse}}|}{|Q_{\text{reverse}}|}$$

where $Q_{\text{forward}}$ and $Q_{\text{reverse}}$ represent heat flow in forward and reverse directions. Heat flow is related to the temperature gradient by a transfer function which is required to be asymmetric and non-linear for this rectification to occur. One of the ways this is achieved is either by combining two bulk materials showing different thermal conductivity trends as a function of temperature or introducing a spatial gradient in a single material such that different temperature dependent thermal conductivity is observed locally in different regions of the material [1-4].

This can be accomplished using silicon metalattice systems by exploiting their capability to tune thermal conductivity with pore size, content and volume fraction. Two such possible systems are illustrated in Figure 5-3 where a graded metalattice system is created with respect to sphere size in Figure 5-3(a) and with respect to porosity in Figure 5-3(b). For the first case, a graded template of silica spheres can be formed with sphere radius gradually decreasing from left to right and infiltrated with silicon. Under this condition, left side being a silicon metalattice at Mie point shows a low value of thermal conductivity in addition to weak temperature dependence owing to ballistic transport of phonons. However, on moving towards the right silicon metalattice system enters Rayleigh regime with the rightmost radius showing thermal conductivity trend characteristic of bulk silicon. While in the second case, sphere radius can be kept fixed while the porosity is varied across the film such that thermal conductivity trend changes from ballistic to bulk silicon behavior with porosity reducing from 74% to 20%. For both cases, since the left side shows a saturation with respect to temperature, thermal conductivity comparable to fused silica
will persist on this side at both higher and lower temperatures. However, the right side when kept at a lower temperature will show a higher thermal conductivity thus creating a low resistance channel and vice-versa, thus introducing rectification in the system.

In this work, thermal conductivity has been experimentally extracted for both filled and empty metalattice systems with pore radius larger than 7nm. However, for achieving thermal rectification using Figure 5-3(a), a radius much lower than 7nm is required according to theoretical predictions. However, due to a much higher particle dispersity and roughness, it is experimentally less feasible to create ordered templates with lower sphere radii.

But on adjusting the pressure and confinement conditions while re-infiltrating silicon using high pressure infiltration process, porosity can be controlled in different regions and a
graded porosity metalattice structure can be obtained. Thus, utilizing steady state thermal measurement techniques, heat flux can be measured with different polarities of temperature gradient to observe potential thermal rectification in these structures.

5.3 Ring-spot method: Measure of in-plane thermal transport

Recently, a lot of research has been carried out in building systems that could be utilized to accurately characterize anisotropic thermal properties of different material systems ranging from bulk samples to thin films due to its requirement in applications such as thermoelectric energy conversion, thermal insulation and efficient heat dissipation in various optical, electrical and optoelectronic devices. Amongst various techniques, different variations have been developed around time-domain (TDTR) and frequency-domain thermoreflectance (FDTR) methods such as variable spot size approach [110], beam-offset approach [86,87] and elliptical beam approach [88]. However, high thermal conductivity of metal transducer layers utilized in these methods causes lateral heat spreading resulting in reduction of sensitivity to the corresponding in-plane thermal properties of a material. In response to this issue, techniques such as transient grating approach [111,112], combined TDTR/FDTR [113] and FDTR combined with beam-offset approach [114] have also been developed which could measure in-plane thermal properties of different materials without depositing metal transducer layer with a much higher sensitivity and accuracy.

Ring-spot thermoreflectance method can be defined as an extension of beam-offset approach which can prove as a much more simplified procedure as opposed to transient grating method, can provide more sensitivity as compared to beam-offset approach and be a generalized method for probing materials with low-high in-plane thermal conductivity values. The geometry utilized to implement this has been illustrated before by Feser et al. [86] as shown in Figure 5-4.
It can either be executed with a Gaussian pump beam heating up the metal surface which is sensed by a concentric ring-shaped probe beam or vice-versa. Theoretically expected TDTR signal has been calculated for this geometry by Feser et al. [86], however experimental implementation has been limited to laser spots offset in one direction (x/y) at a time.

Utilizing an axicon lens to convert pump/probe Gaussian beam into a corresponding ring-shaped Bessel beam is one way to execute this measurement experimentally. This lens can be inserted in either pump/probe beam path of TDTR/FDTR setup just before focusing both these beams through the objective onto the sample. The back-reflected probe beam signal can then be detected by lock-in amplifier which can subsequently be fitted with the theoretical model to study lateral transport.

Figure 5-4: Sample surface heated by a Gaussian pump beam with the heat conducting in lateral directions owing to the in-plane thermal properties of the sample. The temperature achieved is detected with a ring-shaped probe beam which lies concentric to the pump beam and whose reflectivity can be utilized to study lateral thermal transport.
Appendix A

Delay Stage Configuration

A.1 Hardware configuration

Introduction

A high-performance linear air bearing delay stage designed for pump-probe study is discussed in detail in this section with the general layout shown in Figure A-1.

Figure A-1: Schematic diagram showing different components involved in operation of delay stage: a) Stage is driven by Aerotech company based BLMUC linear motor travelling between magnetic tracks, b) Motor is driven by Aerotech company based BL linear amplifier, c) Position feedback is provided by Renishaw company based TONIC linear encoder, d) Labview programming is utilized to configure the parameters of NI-7350 controller for controlling motion on delay stage axis, e) Delay stage axis is wired up to amplifier and encoder through UMI7764 interface which provides a user platform for delay stage operation.

This stage allows a maximum travel range of 500mm with a resolution of 100nm and a maximum speed of 1m/s. Along with providing a high positioning accuracy and reproducibility, this stage has an added advantage over the conventional mechanical stages in terms of complete isolation from mechanical vibrations owing to the air bearing mechanism utilized for its
operation. Various components involved in construction of the delay stage can be subdivided into a) mechanical assembly, b) electrical assembly and c) software configuration.

**Mechanical assembly**

Five homemade aluminum plates combined with an air bearing system is utilized for the entire delay stage assembly. The aluminum plates were machined in a workshop according to their respective engineering diagrams shown below and subsequently anodized.

- **Bottom Plate** - It used as a base for mounting the entire delay stage assembly. As shown in the Figure A-2, it is equipped with screw holes for fixing the end clamps for air bearing assembly, magnetic track used in motor assembly and encoder plate respectively.

![Figure A-2: Bottom plate for the entire delay line assembly, all measurements are in inches.](image)

- **Air Bearing arrangement** - Air bearing mechanism is utilized over conventional contact roller bearings for this system to eliminate the various disadvantages associated with the latter
such as high friction, wear and oil lubrication handling. It makes use of a thin film of pressurized air flow introduced through orifices present on the bearing surface into a restricted gap present between the bearing surfaces to act as a drive mechanism for the stage. Controlling the air pressure, orifice geometry and placement and gap restriction in an optimal manner provides the necessary stiffness for moving the stage in a non-contact configuration. This enables to achieve straighter motion of the stage with higher speed and acceleration, better resolution and repeatability in addition to a smoother, cleaner and more durable operation of the stage.

Air bushing products from New Way Air Bearings is used for providing the air bearing mechanism in this delay stage. Referring to the user manual [115], four bushings are used to accomplish optimal linear sliding of the stage with two bushings on each side. Each bushing with O-rings seated securely in their grooves is inserted into a pillow block as shown in Figure A-3. Inner surface of the pillow block should be checked for any rough edges and wetted with alcohol before this insertion.

Figure A-3: Schematic of air bearing assembly process with a) Showing the insertion of an air bushing into a pillow block which is provided with air inlet holes through which compressed air of 40-100psi is passed and b) Showing insertion of shaft into this pillow block with the air pressure on such that a thin film of pressurized air forms between shaft and this block which subsequently supports the top plate of the delay stage. Adapted from Ref. 115.

Compressed air at a pressure of 40-100psi [115] is passed through the air inlet provided on the pillow blocks. On both sides, a 28inch long shaft cleaned with alcohol is then inserted
through the two bushings while supported with the help of end mounts fixed on the bottom plate as shown in Figure A-4. Gauge blocks are placed between the shafts and the position of shafts and end blocks are adjusted till parallelism between the shafts is achieved. Thin film of pressurized air between the shaft and air bushings on the two sides of the stage enables the four bushings to support and subsequently move the top plate of the stage.

Figure A-4: Schematic showing the complete arrangement of the air bearing system with respect to bottom plate. End mounts fixed on the bottom plate support the shafts on the two ends of the stage. Shafts are passed through air bushings with a thin layer of pressurized air between the two supporting the top plate mounted on the four air bushings. Adapted from Ref. 115.

- Encoder plate- Encoder plate in Figure A-5 is bolted to the bottom plate. RGSZ20 scale used in encoder assembly is affixed to this plate using the adhesive present on back of it. The detailed process for the same is consulted from the corresponding user manual [116].
• Motor spacer- Linear motor [117] used for providing motion to this stage is bolted to this motor spacer (Figure A-6) which is fixed to the top plate at the position indicated in Figure A-8. This spacer provides the optimized flatness tolerance to the forcer with respect to magnetic track.

![Diagram](image)

Figure A-5: Encoder plate for fixing the scale, all dimensions are in inches.

• Encoder spacer- Encoder is fixed to the top plate via this spacer in Figure A-7, which is essential to provide the optimal clearance between encoder and the scale over which it travels.
Top plate - After inserting the motor forcer in an off state from one end of the magnetic track, it is freely moved through it to guide the top plate (Fig A-8) attached to it over to the pillow blocks. The top plate is subsequently bolted down to these blocks after some careful alignment. This also places the encoder attached to the top plate at an optimal clearance from the scale.

Figure A-7: Encoder spacer to attach the encoder to top plate, all dimensions are in inches.

Figure A-8: Top plate with all the dimensions in inches. Positions for attaching the air bearing pillow blocks, motor spacer and encoder spacer to the top plate are indicated in the figure.
Alignment process of the encoder spacer, motor spacer and top plate are iterated till the required straightness and flatness clearance values referred from the respective manuals [116,117] are achieved for the motor and encoder.

**Electrical assembly**

This includes motor, linear amplifier, encoder, motion controller and an interface between controller and amplifier.

- **Linear Motor assembly** - It is composed of a non-ferrous forcer ‘BLMUC 79’ that can travel sandwiched between magnets lying on the facing rows of a U-channel magnetic track ‘MTUC’ as shown in Figure A-9 [117,118]. Sinusoidal commutation provides each of the motor windings with sinusoidal varying currents phase shifted by 120° with respect to each other. These currents generate magnetic field which interact with the magnets on the track to produce a force creating linear motion of the forcer. This helps eliminate backlash, windup and wear associated with most of the mechanically operated motors.

Two magnetic tracks, 416mm and 288mm in length respectively, are stacked end to end on the bottom plate in order to provide a total travel distance of 500mm for the motor. The motor itself is connected to the top plate via motor spacer such that the required straightness and flatness tolerances as mentioned in the user manual [117] are met. Resolution of this motor is limited by the linear encoder that is utilized for providing position feedback to it and will be discussed in detail later. From Figure A-9, 3 wire coil design is used for this assembly, the connections for which are described in the amplifier section next.
BL Linear Amplifier:

BL 10-40 Linear Amplifier from Aerotech is utilized to drive the servo brushless motor presented above. The functional diagram for this amplifier as taken from the manual [119] is shown in Figure A-10.
In Figure A-10, control supply is used to maintain the communication on the amplifier even if the motor power is removed in case of emergency. Motor/main supply provides power for motor operation. Both the power connections are shown in Figure A-11 below.

Figure A-10: Diagram depicting functioning of BL linear amplifier. Motor supply provides power to amplifier, control supply maintains communication on amplifier even under conditions of power failure. TB101 motor output connects with the three phases of motor and J101 control connection receives current command inputs from controller and delivers it to the amplifier in addition to providing power to the UMI7764 interface. Adapted from Ref. 119.

Figure A-11: Schematic depicting connection between power cable and motor supply terminals which provides power to the amplifier and between motor and control supply terminals which maintains communication on the amplifier under conditions of power failure.
Motor output TB101 provides the terminals for connecting the three phases of motor wiring as shown in Fig A-12. Return terminal connection is not utilized in this study.

![Linear motor BLMUC](image)

**Figure A-12:** TB101 Motor output terminal connections to the 3 phases of BLMUC-79 motor windings illustrated in Figure A-9. Modified from Ref. 119.

Control interface J101 provides terminals for receiving input from the controller and delivering output to the amplifier.

![Control interface diagram](image)

**Figure A-13:** Wiring diagram of control interface under dual phase configuration used for this delay stage. Labels in the diagram indicate the signal function corresponding to pin numbers located next to them with arrows pointing in representing inputs and arrows pointing out representing output, details of which are explained in Ref. 119.

Amplifier is operated in a dual phase command configuration in which sinusoidal commutation is provided by the controller. Sinusoidal current command inputs for phase A and B are supplied from controller to the control interface terminals ICMDA and ICMDB respectively.
with current command C, ICMDC generated internally by the amplifier. Output currents proportional to these are passed on to drive the servo motor. In order to operate in this mode, jumpers 9 and 13 on the control board are set to 3-4 following the manual [119]. This ensures application of current command input instead of going through differential input, pre-amplifier and commutation circuit.

BLMUC motor driven by this amplifier can sustain a maximum value of 3.1A for peak continuous current under ‘no forced cooling’ condition [117]. For an input voltage of 10V, this amplifier generates an output continuous current of 5A [119]. Thus, in order to ensure safe operation of the motor, input voltage range should be limited to -3.1V to +3.1V. This is accordingly configured in the torque limit settings on the motion controller as shown later in the software settings section.

- Encoder:

  Encoder is an electromechanical transducer in which an optical readhead reads a coded pattern present on a linear scale while moving and converts it into a corresponding electrical output which is subsequently decoded to generate position and velocity of the motion. This is used as a feedback system for the motor to generate an accurate positioning of the delay stage.

  Renishaw’s TONIC incremental encoder system comprising of a RGSZ20 linear scale, a Ti0200 optical readhead and a TONIC interface is used for this stage. It can travel up to a speed of 1m/s while providing a resolution of 100nm. The scale is a thin and flexible gold-plated steel strip that is provided with incremental (alternating dark and light lines) marks at a pitch of 20μm and IN-TRAC reference marks separated by 50mm [116].
It’s basic working principle [116] as described on the website is illustrated in Figure A-14 where a collimated LED light source is used to shine light onto the patterned scale through readhead optical window. Light from the scale is passed through an index grating integrated with reference mark lens and subsequently recorded by a photodiode array. Based on the relative position of grating with respect to opaque and transparent regions on the scale, light intensity reaching the detector is sinusoidally modulated which is processed digitally using an interpolator to generate a pulse train, labelled as phase A in Figure A-15. A second channel output is produced in a similar fashion in form of pulse train B from a grating and sensor phase shifted by 90° with respect to channel A. This quadrature encoder output is required to detect direction along with position, with A leading B indicating forward motion and vice versa. Differential RS422A signal mode is used such that negative conductor cable carries pulse trains $\bar{A}$ and $\bar{B}$ phase shifted by 180° with respect to A and B respectively which are present on the respective positive conductor. This helps eliminate all the common mode noise and provides a much more stable differential signal for both the phases A and B.
These quadrature signals are then converted into up/down counter values using motion controller which are summed up together for the number of pulses generated to calculate the corresponding position of the stage. There are four transition states corresponding to each edge of the two phases A and B in one cycle which causes the counter to increase or decrease as determined by the leading phase. The total number of quadrature counts per revolution (cpr) for this encoder is evaluated from Equation A.1

$$\text{cpr} = \frac{1}{\text{res}} \times (2 \times \text{pp})$$

Equation A.1

where res corresponds to encoder resolution (100nm) and pp corresponds to magnetic pole pitch (16mm) on the linear motor.

But the position determined in this incremental encoder is relative and thus requires a reference with respect to which an absolute position can be calculated. Such reference marks are integrated on the scale and can be automatically electronically phased into the third channel output Z and its respective phase shifted component $\bar{Z}$. This is a single pulse per revolution and is indicated as an index output in Figure A-15 [116]. A cable carrying information on these three channel outputs and encode power input extends from readhead and ends up in the form of a small connector which is plugged into the socket in the TONIC Interface [116] shown in Figure
A-16. This interface is then connected to the motion controller via UMI interface, details of which are discussed in later sections.

Figure A-16: Wiring diagram of a Renishaw interface connector where labels indicate the signal functions corresponding to pin numbers listed next to them with arrows pointing in representing inputs and arrows pointing out representing output, details of which are described in Ref. 116.

- **UMI interface:**

  UMI interface 7764 [120], as indicated in Figure A-17, is used for providing a simplified integration of motion controller (NI-7350) with motor driver/amplifier, encoder feedback system and motion limit and inhibit switches. Each of these functionalities are accessible on four different axes which can be either be used simultaneously for one motion control or individually for 4 different axes motion. A National Instruments designed SH68-C68-S cable connected between the controller and interface enables transfer of input and output signals used for delay stage operation.

  Different regions of the interface are shown in the terminal block diagram in Figure A-17. Terminal blocks and the corresponding wiring used in this delay stage are explained in detail below [120].
a) Power Input Terminal Block: The 2 terminals, +5V and GND, provided on this block are used to power up the interface [120]. This power is distributed to +5V terminal present on each axis of motion I/O terminal block which is used to power up the encoder, limit switches and inhibit output switches. The two terminals are respectively connected to 5V power output and signal common provided for an encoder on J101 control interface of linear amplifier as can be seen from Figure A-13 and Figure A-18.

b) Motion I/O terminal block: Each axis on the interface has a motion I/O terminal block [120] associated with it which is further divided into four subsections: amplifier terminal block, encoder terminal block, limit switch and inhibit input terminals block and distributed power terminal block.
Amplifier Terminal block [120] provides five terminals per axis for connecting the controller to amplifier as shown in Fig A-18 through this interface. Since the amplifier here is utilized to drive a servo motor, two terminals amongst them, namely, Step and Dir terminals, are not used. Analog Output (AOUT) and Analog Output Ground (AOGND) terminals are used to provide the required current command output and signal ground to the amplifier respectively. Since amplifier needs two current command inputs for the 2 phases, one of the analog output terminals from a second axis is used for the connection. Inhibit output terminal, if active, disables the drive for the corresponding axis. This occurs when any one of the conditions is met, a) Host bus monitor power interlock detects insufficient power supply from the controller due to PC/controller shutdown or some error in connection of controller with the interface, b) any one of the switches amongst inhibit input, inhibit all or per axis controller inhibit output is activated. In this state, an active high inhibit output (active-low INHOUT) connected to the shutdown terminal of amplifier removes all the power off the motor and halts the operation of the stage. This is indicated by a turned off LED corresponding to enable function (ENB) on the amplifier.

![Figure A-18](image)

Figure A-18: Wiring of control interface of the amplifier to amplifier terminal and power terminal blocks on UMI 7764 interface.

Encoder Terminal Block and distributed power terminal block [120] enables operation of encoder through controller by providing connections for encoder interface. Distributed power block is wired up to power input terminals, +5V and GND, of the encoder interface to provide
operational power to the encoder. Encoder terminal block consists of six terminals for working of TONIC incremental encoder system used for this stage, the wiring diagram for which is presented in Figure A-19.

![Wiring Diagram](image)

Figure A-19: Wiring of Renishaw encoder interface to encoder terminal and distributed power terminal blocks on UMI-7764 interface.

- **Motion Controller:**

  Hardware Configuration: PXI 7350 [121] is a controller system that uses high speed communication with a computer to offer real time control of motion of a motor. It provides independent and coordinated motion control over eight different axes through motion I/O, home and limit switch, position feedback and various other functional configurations.

  This is accomplished by installing this card in a PXI-1033 chassis [122] and connecting it to UMI interface using a NI SH68-C68-S cable. MXI express chassis controller connector present at the back of the chassis is connected via x1 MXI-express cable to a PCI express card installed on a computer. This allows fully programmable control of servo motor motion used for this stage. Power and Link LEDs on the chassis are checked for power and link activity status respectively after installation/powering up process, details of which can be found in the user manual [122].
A.2 Software configuration

National Instruments Measurement and Automation Explorer combined with Labview programming is utilized to configure the parameters of NI-7350 [121] for controlling motion on the axis wired up in UMI7764 interface and to provide a user platform for delay stage operation. For this study, these settings accessible on Axis 1 under PXI-7350 (2) device listed in NI-MAX are explained in detail below.

In case of the stage not initializing properly, encoder and motor might not be wired up in the right orientation. Positive and negative movement direction of a servo motor can be determined based on the relative phasing of the three motor leads A, B and C. Before initializing, it needs to be verified if the encoder shows incremental counts when the motor is moved in positive direction and vice versa in order to establish a stable motion.

NI 7350 Motion Controller Software Settings:

These settings are accessible under PXI-7350 (2) device listed under NI motion devices in NI-MAX as explained in Figure A-20 below.
Figure A-20: Settings tab under ‘Devices and Interfaces’ section on NI-MAX software through which axis initialization settings are configured.
Axis 1 as wired up in UMI 7764 interface is configured for this system as shown in Figure A-21.

➢ Axis Configuration- It allows to specify the type of motor, in this case servo brushless motor and the type of feedback system, namely encoder, employed for the closed loop delay stage operation.

In this system, onboard sinusoidal commutation is provided by the controller connected to the drive via UMI 7764. It commutes two of the phases of the motor with the third phase determined by the servo drive. These are sent through two DAC outputs of the controller which are connected to their respective current command input signals on servo drive.

Figure A-21: Axis configuration settings under Axis 1 tab indicating the type of motor and encoder feedback used for this stage.

After enabling the axis used for motion, it needs to be initialized every time the controller is powered off or reset for the controller to determine the initial commutation phase angle of the
brushless servo motor. This assists the controller to calculate the overall commutation accurately. Amongst the various methods for initialization supported by NI-7350, shake and wake method is used for this stage as shown in Figure A-22. An optimal settling time of 0.6sec is required before the motor completely initializes in a stable manner. In case of an unstable initialization this duration can be increased in the program.

Electrical counts per cycle is then calculated to be 320000 counts/cycle using [121]

\[
\text{Counts per electrical cycle} = \frac{\text{encoder counts per revolution} \times 2}{\text{no of poles}}
\]

Equation A.2

Figure A-22: Settings for sinusoidal commutation provided by controller to the linear amplifier.

This is required by the controller to calculate commutation phase over the entire range of travel based on which the output voltage to the amplifier can be updated and servo motor operated in a continual manner.
Motion I/O settings - These allow to configure various hardware and software limit settings which are mainly utilized in the find reference configuration tab for recording reference position of the stage. These are shown in Figure A-23.

Trajectory settings - These settings shown in Figure A-24 are applied on trajectory generator function to provide the necessary threshold values and move constraints for an axis motion.

Move constraints for velocity, acceleration and deceleration are set to their default maximum values under trajectory settings as shown in Figure A-24.

Find Reference settings - Reference settings in Figure A-25 are used to find the index pulse from the encoder to provide the system with a reference position with respect to which
other positions are evaluated. Therefore, index tab on find reference settings is configured while keeping default settings for others.

➢ Gearing settings: Since encoder position feedback is used for closed loop operation of the motor, electronic gearing is disabled for this stage operation as shown in Figure A-26.
Figure A-24: Upper window shows motion status and velocity filter settings to configure motion trajectory while the lower window configures move constraints imposed on a S curve trajectory used for this motion.
Figure A-25: Find Reference settings with respect to home, index, forward limit, reverse limit and center of axis 1 motion. Default settings are kept for all the tabs except for index tab in which settings are configured to locate index pulse from the encoder to be used as a reference position.
Control Loop settings- Control loop settings are optimized to provide stability to the motion system. It helps the stage to arrive at a commanded position and stay steadily there without oscillations until next move is commanded.

Figure A-26: Gearing settings for Axis 1 of the stage. For this stage, gearing is disabled since encoder is utilized for providing position feedback in this system.
Figure A-27: Control loop parameters: proportional gain $K_p$, differential gain $K_d$ and integral gain $K_i$ are tuned to achieve a stable motor response.
In order to do so, three gain parameters, a) proportional gain ($K_p$) providing stiffness, b) differential gain ($K_d$) providing damping, and c) integral gain ($K_i$) providing static torque load under the control loop settings in Fig A-27, are adjusted to get a stable step response function shown in Figure A-28.

Figure A-28: Step response function for the gain tuning parameters required in control loop settings which are adjusted in servo tune menu present under calibration section of the settings.

Filter settings are disabled in Figure A-27 since no static friction compensation is required for a stable motion for this stage. A range of torque settings for the two DAC outputs is provided as well under the control loop settings which match up with the maximum current command inputs indicated in the drive amplifier section.
Figure A-29: Torque settings corresponding to the voltage that can be used by the linear amplifier to drive maximum current through the servo motor as calculated in the linear amplifier section.

Control loop 1 and control loop 2 are configured with their respective default settings.
Figure A-30: Control loop and filter settings corresponding to control loop 1.
➢ **Compare and Capture settings** - Synchronous triggering of data measurement device at specified positions through position breakpoint configuration is not utilized as a mechanism for data collection in this study. Thus, both position breakpoint and high-speed capture are set with their respective default conditions in active low state.

Figure A-31: Control loop 2 settings set to their default values.
Figure A-32. Position breakpoint and position capture settings, not being used for data collection, are set to active low.

- Digital I/O settings - Digital I/O settings are not utilized in this system and are therefore set to their default values as shown in Figure A-16. Similar default settings are used on all the four ports shown under Digital I/O header.
ADC settings- Four analog input channels in the range of -10V to +10V enabled on this axis are accessible on analog input terminal block on UMI-7764 interface and can be utilized for any general-purpose motion I/O functionalities.
Encoder settings: Differential encoder signals connected to UMI interface for both phase A and B are converted to single ended output signals to the controller. Filter frequency for this system is set to 25.6MHz which is slightly higher than the clocked output frequency (20MHz) from Renishaw encoder [116]. This ensures minimal noise generation in encoder counts collected and hence provides higher accuracy in position feedback calculation. Index reference criteria corresponds to an index pulse generation when both phases A and B are in their active high state. Find reference setting uses this criterion to determine the reference position as mentioned before. Since encoder1 is used as feedback in this system, it is enabled by default for encoder1 as shown in Figure A-35. Settings for all other encoders are set as default settings since they are not utilized for this motion.
After software configuration is complete and axis is initialized, 1-D interactive window is utilized to ensure that a stable straight-line motion towards a commanded position is achieved. Reset position option is pressed every time the axis is initialized in order to zero the reference position with respect to which subsequent positions are determined.

Figure A-35: Settings for encoder 1 used for position feedback for this stage with the reference criteria adapted from user manual for tonic encoder in Ref. 116.

After software configuration is complete and axis is initialized, 1-D interactive window is utilized to ensure that a stable straight-line motion towards a commanded position is achieved. Reset position option is pressed every time the axis is initialized in order to zero the reference position with respect to which subsequent positions are determined.
Maximum values for velocity, acceleration and deceleration as indicated in the move constraints section are used for stability check. Target position is specified in counts/sec with 1 count corresponding to 100nm, the resolution of the encoder. Axis status for a stable completed motion is checked on main and advanced tabs as shown in Figure A-36 and Figure A-37 respectively. An unstable motion will be reflected either as a red indicator on following error option or fluctuations greater than 10 counts showing up on position and velocity data under current trajectory. This should be corrected with either improving the control loop settings or checking out the motor-encoder connections. This motion can be checked graphically in Misc Plots tab under 1-D interactive section as shown in Figure A-38 for the delay stage moving linearly towards a commanded position of 500mm.
Figure A-37: Advanced axis and following error status on advanced tab of 1D interactive section.

Figure A-38: Plot showing a straight-line motion towards the maximum target position of 500mm on the stage.
Appendix B

MATLAB codes for TDTR analysis

The scripts are called in a sequence as shown below:

a) Phasecorrectionmod.m
b) Functionmineval.m
c) Leastquarecal.m
d) Trilayergeom.m
e) Senscal.m

Content of each script is described below:

Phasecorrectionmod.m

This script is used to generate an updated in-phase and out-of-phase component of the signals after performing the procedure of phase correction. Two data files are used in this code: signal collected from the sample and background signal collected after blocking the pump beam.

```matlab
%input data files
sumrexpback=dlmread('file1.txt'); %file1 contains background data
h=size(sumrexpback,1); % h is size of file1
sumrexpbackx=sumrexpback(:,1); % in-phase component of background
sumrexpbacky=sumrexpback(:,2); % out-of-phase component of background
%mean of both components of background
sumrexpbackavgx=mean(sumrexpbackx);
sumrexpbackavgy=mean(sumrexpbacky);

sumrexpsignal=dlmread('file2.txt'); % file2 contains signal data
k=size(sumrexpsignal,1);
sumrexpsignalx=sumrexpsignal(:,1); % in-phase component of signal
sumrexpsignaly=sumrexpsignal(:,2); % out-of-phase component of signal

%background corrected in-phase and out-of-phase components
expsigfinx=sumrexpsignalx-sumrexpbackavgx;
expsigfiny=sumrexpsignaly-sumrexpbackavgy;

%determining time 0
sumrexpsignal = sumrexpsignal(:,3); % experimental time delay

% background corrected in-phase component vs delay time
plot(sumrexpsignal, sumrexpsigfinx, '-r', 'MarkerSize', 3);

% user selects time0 on the rising edge of in-phase vs time delay
plot
[time0, xtime0] = ginput(1);

% corrected time delay sumrexpsigfint with respect to time0
mt = 1:1:k;
sumrexpsigfint (mt) = (sumrexpsignal (mt) - time0);
sumrexpsigfint1 = sumrexpsigfint;

% position of zero time delay
n = find(sumrexpsignal > time0 & sumrexpsignal <= time0 + 1)

[x, h] = size(sumrexpsigfint); % h denotes no. of elements in corrected time delay

% time delay from where elements are entered in final file
tminus = find(sumrexpsigfint > 200 & sumrexpsigfint < 205)

% loop calculating the phase corrected components (x and y) across zero delay time and minimizing the jump of out-of-phase component (y) across time0
flag = 0;
l = n - 20;
diffy = zeros(l, h - 1);
xnew = zeros(1, h);
ynew = zeros(1, h);
for i = 1:1:1
  for j = 1:1:1:1
    ix = i;
    iy = j;
    delx = expsigfinx(i) - expsigfinx(j); % change in x
    dely = expsigfiny(i) - expsigfiny(j); % change in y
    delp = atan(dely/delx); % change in phase
    
    % calculating corrected x and y for each iteration
    for k = 1:1:h
      xnew(k) = (expsigfinx(k) * cos(delp)) - (expsigfiny(k) * sin(delp));
      ynew(k) = (expsigfinx(k) * sin(delp)) + (expsigfiny(k) * cos(delp));
    end
    
    % evaluating difference in y across t=0
    diffy(ix, iy) = abs((ynew(n-10) - ynew(n+5)));
  end
end
delp;
%minimum jump across t=0 and its position evaluated
[mindiff,in]=min(diffy(:));
[in_row,in_col]=ind2sub(size(diffy),in);
coeff1=in_row;
coeff2=in_col+1;

%new and corrected x and y calculated for indices producing
minimum jump in y across t=0 in above iteration
delx=expsigfinx(in_row)-expsigfinx(in_col+1);
dely=expsigfiny(in_row)-expsigfiny(in_col+1);
delp=atan(dely./delx)
for km=1:1:h
    xnew(km)=(expsigfinx(km)*cos(delp))-(expsigfiny(km)*sin(delp));
    ynew(km)=(expsigfinx(km)*sin(delp))+(expsigfiny(km)*cos(delp));
end
rnew=-xnew/ynew; %phase corrected ratio(-x/y)
magnew=sqrt((xnew^2)+(ynew^2)); %phase corrected signal magnitude
phasenew=(atan(ynew/xnew))*(180/3.14); %corrected phase

%corrected ratio and delay time written in ‘finalfile’ from time
delay of 200ps denoted by tminus
rnewmod=zeros(1,h-tminus);
sumrexptmod=zeros(1,h-tminus);
for kmod=tminus:1:h
    rnewmod(kmod-tminus+1)=rnew(kmod);
    sumrexptmod(kmod-tminus+1)=sumrexpsigfint(kmod);
end
Ma=[sumrexptmod;rnewmod];
fid=fopen('C:\studies\phd acads\research work\tdtr analysis codes\finalfile.txt', 'w');
fid;
fprintf(fid,'%6.2f %12.8f
',Ma);
fclose(fid);

%Phase corrected y, x, magnitude and ratio plotted in 4 subplots
subplot(2,2,1)
plot(sumrexpsigfint1,ynew,'-r','MarkerSize',3)
hold
plot(sumrexpsigfint1,xnew,'-b','MarkerSize',3)
title('y comp')
xlabel('time(ps)')
ylabel('Y(V)')
subplot(2,2,2)
plot(sumrexpsigfint1,xnew,'-b','MarkerSize',3)
title('x comp')
xlabel('time(ps)')
ylabel('X(V)')
subplot(2,2,3)
Functionmineval.m

Parameters, thermal conductivity (tc) and interfacial thermal conductance (G), with respect to which fitting needs to be performed are introduced as a vector z0 in this code. It searches for a minimum in experimental data phase corrected before (‘finalfile’) and theory with respect to these parameters, returns the value in vector z1 and plots the experimental data and respective theoretical fit corresponding to these values.

%z0: array of thermal conductivity (tc3=thermal conductivity film/substrate) and interfacial thermal conductance (G2=G_{Al-substrate/thinfilm})
z0=[tc3,G2];

%options set in the process of fminsearch looking for minimum
options=optimset('MaxFunEvals',100000,'TolFun',1e-7,'TolX',1e-7);
%options = optimset('Display','iter','PlotFcns',@optimplotfval);

%fminsearch calls next script ‘leastsquarecal’ with respect to z0
[z1,prm,exitflag,output]=fminsearch(@leastsquarecal,z0,options);

%A and G corresponding to minimum returned to array z1
disp('located at')
disp(z1(1)) %fitted thermal conductivity
disp(z1(2)) %fitted interfacial thermal conductance
%disp(z1(3))
disp(exitflag)
output %displays iterations required while searching for minimum

calling function ‘trilayergeom’ with z1 vector as argument, returning theoretically calculated ratio(sumratioth) for z1 and experimental time delay(sumrexpmt) and ratio(sumrexpmr) stored in phasecorrected file ‘finalfile’.
[sumratioth,sumrexpmt,sumrexpmr]=trilayergeom(z1);

%plotting experimental data and theoretical fit
plot(sumrexpmt,sumratioth,'-b','LineWidth',3)
hold on
plot(sumrexpmt,sumrexpmr,'ok','MarkerSize',8)
xlabel('time(ps)')
ylabel('ratio')
ax=gca;
ax.FontSize=15;

Leastsquarecal.m

This script is called by the previous code ‘functionmineval’ and evaluates the least squares between experimental data and theoretical values calculated for $z_0$ passed as an argument to this script by ‘functionmineval’. Theoretical values of ratio are calculated by calling function ‘trilayergeom’ and passing $z_0$ as an argument to it.

% function leastsquarecal defined
function lsf=leastsquarecal(z)

% function trilayergeom called with argument $z_0$, returned arguments: theoretical ratio calculated(sumratiotheory), experimental ratio(sumrexpmr) and delay time(sumrexpmt)
[sumratiotheory,sumrexpmt,sumrexpmr]=trilayergeom(z);

h=size(sumrexpmt,1); %no. of elements under delay time
me=1:1:h;

% least square between theoretical and experimental ratio calculated with the value returned to variable ‘lsf’
lsfvec=(sumratiotheory(me)-sumrexpmr(me))^2;
lsfsum=sum(lsfvec);
lsf=(lsfsum);
end

Trilayergeom.m

In this script, all the parameters required for calculating theoretical ratio are defined. For experimental data fitting, thermal conductivity and interfacial thermal conductance to be extracted are passed as an argument to this code. Theoretical ratio is evaluated with this code which is then used by the previous two scripts to calculate least squares minimum with respect to experimental data and subsequently extract the required parameters. The code below is written for
a trilayer geometry for a generalized case which includes the effect of radial conduction with
layer 1 as Aluminum film, layer 3 as metalattice film and layer 5 as silicon substrate. Under one-
dimensional conduction approximation, radial term is removed terms no longer remain a function
of transform variable k as shown in comments.

%function trilayergeom defined
function [sumratiotheory2,sumrexpmt,sumrexpmt]=trilayergeom(z)
tc3=z(1); %cross-plane thermal conductivity of third layer
(1st element of argument array z)
tcr3=tcr3; %radial thermal conductivity of third layer
(1st element of argument array z)
C3=1.6e6; %Volumetric heat capacity of third layer
G2=z(2); %Layer2: Interfacial thermal conductance between layer 1
and layer 3(2nd element of argument array z)
G4=200e6; %Layer 4: Interfacial thermal conductance between layer
3 and layer 5

k=sym('k','real');
w0=20.5e-6;
%input('enter pump beam spot size');
w1=6.32e-6;
%input('enter probe beam spot size');
tc1=240;
%input('enter cross-plane thermal conductivity of first layer');
tcr1=tcr1;
%input('enter radial thermal conductivity of first layer');
C1=2.44e6;
%input('enter volumetric heat capacity of first layer');
d1=106e-9;
%input('enter thickness of first layer');
tc5=140;
%input('enter cross-plane thermal conductivity of fifth layer');
tcr5=tcr5;
%input('enter radial thermal conductivity of fifth layer');
C5=1.6e6;
%input('enter volumetric heat capacity of fifth layer');
d3=910e-9;
%input('enter thickness of third layer');
d5=1e-3;
%input('enter thickness of fifth layer');
Qpump=16e-3;
%input('enter pump beam power');
Qprobe=8e-3;
%input('enter probe beam power');
ws=502400000;
%input('repetition rate of laser');
wo=2*3.14*8.75e6;
%input('modulation frequency of pump');
g=1;
%input('gain of electronics');
RT=2e-4;
%input('input thermoreflectance coefficient of metal');

%calculating frequency-domain thermal response of surface
temperature change
Hwnet=zeros(1,10001);
j=-5000:1:5000;
wm=j+5001;
wm2=(j*(ws))+(wo);

%under one-dimensional approximation:
%Ygam=@(tc,C)sqrt((1i.*(C.*(wm2).*tc)));
Ygam=@(tc,tcr,k,C)sqrt((tc*tcr*k^2)+(1i*(C*(wm2)*tc)));
Y1=@(k)Ygam(tc1,tcr1,k,C1);
Y3=@(k)Ygam(tc3,tcr3,k,C3);
Y5=@(k)Ygam(tc5,tcr5,k,C5);

%under one-dimensional approximation:
%theqd=@(d,tc,C)tanh(d.*sqrt((1i.*((C.*(wm2))./tc))));
theqd=@(d,k,tc,tcr,C)tanh(d*sqrt(((tcr*k^2)/tc)+(1i*((C*wm2)/tc))));
m=@(k)theqd(d1,k,tc1,tcr1,C1);
n=@(k)theqd(d3,k,tc3,tcr3,C3);

Ccoeff=@(k)Y5(k)+(n(k)*(((Y3(k)*Y5(k)))/(G4)+Y3(k)))+((m(k)*Y1(k))*((Y5(k)/G2)+(n(k)*(((Y3(k)*Y5(k)))/(G2*G4))+(Y3(k)/G2)+(Y5(k)/Y3(k))))+((Y5(k)/G4)+1));
Dcoeff=@(k)(m(k)*((Y5(k)/Y1(k))+(n(k)*(((Y3(k)*Y5(k)))/(G2*G4))+(Y3(k)/G2)+(Y5(k)/Y3(k))))+(Y5(k)/G4)+1);
Coeffr=@(k)(Dcoeff(k)/Ccoeff(k));
Funcfin=@(k)k*Coeffr(k)*(exp(-((k^2*(w0^2+w1^2))/8)));
Hwnet(wm)=integral(@(k)Funcfin(k),0,10/sqrt(w0^2+w1^2),'ArrayValued',true);

%experimental ratio and time delay data read from file
sumrexpm=dlmread('finalfile.txt');
h=size(sumrexpm,1);

sumrexpmt=sumrexpm(:,1);
sumrexpmr=sumrexpm(:,2);

%evaluating the theoretical ratio of x and y components
sumr1=zeros(1,h);
Hwnet1=zeros(h,10001);
tcoeff=1:1:h;
Hwnet1=Hwnet(wm)*exp(1i*j*ws*sumrexpmt*1e-12);
sumr1(tcoeff)=sum(Hwnet1,2);
sumreal=(abs(real(sumr1)));
%theoretical value of in-phase comp
sumimg=(abs(imag(sumr1)));
%theoretical value of outofphase comp
sumratio=transpose(sumreal/sumimg);
%theoretical value of ratio
sumratiotheory2=sumratio;
end

Senscal.m

This script in combination with trilayergeom is utilized to generate sensitivity curves and evaluate
the total uncertainty in extracted thermal conductivity due to errors in different parameters
utilized for performing experiment and calculations as explained more in Chapter 3.

%thc: reasonable estimate for film thermal conductivity
thc=2.2; thcs=thc*1.01;
%hc: reasonable estimate for film volumetric heat capacity
hc=1.6e6; hcs=hc*1.01;
%itc: reasonable estimate for interfacial conductance G2
itc=8e7; itcs=itc*1.01;
%itc2: reasonable estimate for interfacial conductance G4
itc2=50e6; itc2s=itc2*1.01;
%hAl: Aluminum film thickness
hAl=96e-9; hAls=hAl*1.01;
%df: film thickness
df=412e-9; dfs=df*1.01;
%sp: pump spot size
sp=20.6e-6; sps=sp*1.01;
%CAl: Volumetric heat capacity of Aluminum film
CAl=2440000; CAls=CAl*1.01;

%z(i):Arguments passed to function ‘trilayergeom’ for evaluating
theoretical ratio.
z1=[thc,hc,itc,itc2,hAl,df,sp,CAl];
z2=[thcs,hc,itc,itc2,hAl,df,sp,CAl];
z3=[thc,hcs,itc,itc2,hAl,df,sp,CAl];
z4=[thc,hc,itcs,itc2,hAl,df,sp,CAl];
z5=[thc,hc,itc,itc2s,hAl,df,sp,CAl];
z6=[thc,hc,itc,itc2,hAls,df,sp,CAl];
z7=[thc,hc,itc,itc2,hAl,dfs,sp,CAl];
z8=[thc, hc, itc, itc2, hAl, df, sps, CA1];
z9=[thc, hc, itc, itc2, hAl, df, sp, CA1s];

% read from experimental data file
sumrexpmt=dlmread('finalfile.txt');
sumrexpmt=sumrexpmt(:,1);
h=size(sumrexpmt,1);

% calling function ‘trilayergeom’ function with arguments z(i)
summratiothor=trilayergeom(z1);
summratiothnewtc=trilayergeom(z2);
summratiothnewC=trilayergeom(z3);
summratiothnewG2=trilayergeom(z4);
summratiothnewG4=trilayergeom(z5);
summratiothnewAlt=trilayergeom(z6);
summratiothnewft=trilayergeom(z7);
summratiothnewssize=trilayergeom(z8);
summratiothnewCA1=trilayergeom(z9);

% evaluating sensitivity with respect to different parameters
senstc=(log(summratiothnewtc)-log(summratiothor))/(log(thcs)-log(thc));
sensC=(log(summratiothnewC)-log(summratiothor))/(log(hcs)-log(hc));
sensG2=(log(summratiothnewG2)-log(summratiothor))/(log(itcs)-log(itc));
sensG4=(log(summratiothnewG4)-log(summratiothor))/(log(itc2s)-log(itc2));
sensdAl=(log(summratiothnewAlt)-log(summratiothor))/(log(hAls)-log(hAl));
sensdf=(log(summratiothnewft)-log(summratiothor))/(log(dfs)-log(df));
sensssize=(log(summratiothnewssize)-log(summratiothor))/(log(sps)-log(sp));
sensCA1=(log(summratiothnewCA1)-log(summratiothor))/(log(CA1s)-log(CA1));

% plotting sensitivity of ratio to different parameters as a function of delay time
plot(sumrexpmt,senstc,'-.r')
hold on
plot(sumrexpmt,sensC,'-.b')
hold on
plot(sumrexpmt,sensG2,'-.g')
hold on
plot(sumrexpmt,sensG4,'-.k')
hold on
plot(sumrexpmt,sensdAl,'-.m')
hold on
plot(sumrexpmt,sensdf,'-.c')
hold on
plot(sumrexpmt,senssspsize,'-y')
hold on
plot(sumrexpmt,sensCAI,'-b')

%errorcalculation
%fractional error in Aluminum film thickness
ddAl=0.028;
%fractional error in spot size
dsp=0.015;
%fractional error in Aluminum film volumetric heat capacity
dhAl=0.02;
%fractional error in thin film thickness
ddf=0.021;
%fractional error in phase correction procedure
dphi=5e-3;
%fitted value of thermal conductivity of the film extracted
tc=2.2

%evaluating fractional error in thermal conductivity using evaluated sensitivity, theoretical ratio and fractional errors in parameters.
v=(((senstc)^2)*((sumratiothor)^2));
alpha=sum(v);
v1=(senstc*sensdAl*)((sumratiothor)^2));
beta1=sum(v1);
v2=(senstc*senssspsize*)((sumratiothor)^2));
beta2=sum(v2);
v3=(senstc*sensCAI*)((sumratiothor)^2));
beta3=sum(v3);
v4=(senstc*sensdf*)((sumratiothor)^2));
beta4=sum(v4);
v5=(senstc*)((sumratiothor)^3));
beta5=sum(v5);
netb=((beta1^2)*(ddAl^2))+((beta2^2)*(dsp^2))+((beta3^2)*(dhAl^2)
+((beta4^2)*(ddf^2))+((beta5^2)*(dphi^2));
vark=netb/(alpha^2);
sterrk=sqrt(vark);

%uncertainty in thermal conductivity
unctc=sterrk*tc
Bibliography


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