THERMAL TRANSPORT IN NANOSTRUCTURED POLYMERS

by

Jun Liu

B.S., Huazhong University of Science and Technology, 2008

M.S., University of Colorado at Boulder, 2010

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Professor Ronggui Yang, Chair

Professor Yung-Cheng Lee

Date_____

The final copy of this thesis has been examined by the signatories, and we Find that both the content and the form meet acceptable presentation standards Of scholarly work in the above mentioned discipline.

ABSTRACT

Liu, Jun (Ph.D., Department of Mechanical Engineering)

Thermal Transport in Nanostructured Polymers

Thesis directed by Associate Professor Ronggui Yang

In recent years, with the discovery of low-dimensional materials and the advance of fabrications, nano-structuring has opened new possibilities for a variety of novel applications with either increased or reduced thermal conductivity. Nanostructured organic materials or polymer-based materials have received much less attention compared to inorganic materials although there are significant application advantages, such as being easy to process, light-weight, and flexible. Extreme thermal conductivity and fundamental new physics of phonon dynamics and thermal transport might exist in nanostructured polymers, either polymers with aligned chains or hybrid organic-inorganic materials. The objective of this thesis is to investigate the thermal transport in nanostructured polymers by simulation and characterization.

First, the effect of the chain parameters of polymers, such as chain orientation, backbone flexibility, monomer type, and molecular weight, on the thermal transport in polymers is investigated through molecular dynamics simulations. Thermal conductivity of amorphous polymers is related with the orientational order parameter (a quantitatively indicator of the chain conformations and alignments) through an exponential relation. Moreover, the thermal conductivity of single extended polymer chain of various polymers, which can be 1-2 orders of magnitude higher than their bulk counterparts, is a strong function of their monomer types and molecular chain lengths.

The ultrafast pump-and-probe characterization system is then extended for measuring thermal properties of nanostructured materials, including in-plane and cross-plane thermal conductivity, heat capacity, and interfacial thermal conductance between materials. The measurement of the thermal properties of hybrid organic-inorganic materials enabled by the atomic/molecular layer deposition confirms that the backbone flexibility plays a critical role in the structural morphology and thermal conductivity in these films. These results also suggest that dramatic material difference between organic and inorganic materials may provide a route for producing materials with ultralow thermal conductivity. The effective thermal conductivity of the polystyrene thin films is measured to be increased with decreasing sample thickness compared to the radius of gyration of bulk polystyrene, which indicates a strong polymer chain confinement effect in ultrathin polymer films. The findings in this thesis could be useful for further understanding of nanostructured polymer materials for thermal management and energy conversion.

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Table of contents

Contents	
CHAPTER I INTRODUCTION	1
I.1 Research advances in nanoscale thermal transport	1
I.2 Interesting physics in nanostructured polymers	2
I.3 Objective of the thesis	5
I.4 Organization of the thesis	3
CHAPTER II THERMAL CONDUCTIVITY ENHANCEMENT OF POLYMERS WITH MECHANICAL STRAINS	Э
II.1 Introduction	Э
II.2 Modeling and simulation method10)
II.3 Thermal conductivity enhancement	5
II.4 Chain alignment improvement	3
II.5 Thermal conductivity-orientational order parameter relationship22	1
II.6 Summary of this chapter2	5
CHAPTER III LENGTH-DEPENDENT THERMAL CONDUCTIVITY OF SINGLE EXTENDED POLYMER CHAINS	5
III.1 Introduction	5
III.2 Material model of single extended polymer chains	Э
III.3 NEMD simulation for thermal conductivity	2
III.4 The effect of polymer types on the thermal conductivity	5
III.5 The average phonon relaxation time in single extended chains	Э
III.6 Length-dependent thermal conductivity4	3
III.7 Summary of this chapter	7
CHAPTER IV IMPROVEMENT ON THE PUMP-AND-PROBE CHARACTERIZATION SYSTEM .48	3
IV.1. Ultrafast pump-and-probe characterization system49	Э
IV.2 Simultaneous measurement of heat capacity and thermal conductivity of bulk and thin film materials	4
IV.3 Measurement of in-plane thermal conductivity of bulk and thin film materials	5
IV.4 Measurement using backside-pumping arrangement	Э

IV.5 Summary of this chapter	.96
CHAPTER V THERMAL CONDUCTIVITY OF HYBRID ORGANIC-INORGANIC THIN FILMS AND POLYMER THIN FILMS	.98
V.1 Ultralow thermal conductivity of atomic/molecular layer deposition enabled hybrid organic- inorganic zincone thin films	.98
V.2 Size effect of effective thermal conductivity of ultrathin polystyrene films1	111
V.3 Summary of this chapter1	122
CHAPTER VI FUTURE WORK1	124
BIBLIOGRAPHY 1	126
APPENDIX1	148
Appendix I. Frequency-domain Response of the Surface Temperature Change1	148
Appendix II. Sample fabrication and characterization of zincone thin films	153

TABLES

Table V.1. Three sets of type-A, type-B, and type-C zincone thin films with various thicknesses were fabricated with different MLD and ALD:MLD cycles and cycle numbers. The average growth rate is estimated by dividing the thickness of each film with the cycle number......103

Table V.2. The mass density, the average growth rate, the idealized linear growth rate, and the
estimated reactive site density of the 43 nm-thick type-A MLD zincone film, 136 nm-thick type-
B MLD zincone film, and 139 nm-thick type-C ALD:MLD zincone film106
Table V.3. The molecular weight and radius of gyration of the three sets of polystyrene films.113
Table V.4. Thermal conductivity and volumetric heat capacity of three polystyrene films with
thickness larger than 100 nm118
Table V.5. Thermal conductivity and interfacial thermal conductance of three polystyrene films
with the thickness around 60 nm119
Table A.II.1. Areal size estimation of the atom-thick ZnO flakes using Scherrer's formula156
Table A.II.2. The ratio of mass gain during deposition of EG (HQ) to that of DEZ when
fabricating the 43 nm-thick type-A MLD zincone film (136 nm-thick type-B MLD zincone film),
which is measured at 150 °C by the QCM in the linear growth region. The reactive site density
during one MLD cycle of the EG (HQ) and DEZ can be estimated by the measured ratio of mass
gain divided by the idealized ratio of mass gain159
Table A.II.3. The mass density, the average growth rate, the idealized linear growth rate, and the
mass gain of the 43 nm-thick type-A MLD zincone film, 136 nm-thick type-B MLD zincone film,

and 139 nm-thick type-C ALD:MLD zincone film......159

FIGURES

Figure III. 2. The thermal conductivity of single extended polymer chains of various polymers as a function of the number of segments: (a) effect of aromatic backbone; (b) effect of double bonds and bond-strength disorder compared to polyethylene; (c) effect of bond-strength disorder/mass

Figure IV.2.2. Demonstration of simultaneous measurement of thermal conductivity and volumetric heat capacity of bulk Si using frequency-dependent TDTR measurements. (a) The

Figure IV.2.3. Demonstration of simultaneous measurement of thermal conductivity and volumetric heat capacity of SiO₂ thin films using frequency-dependent TDTR measurements. (a) The experiment data and best-fit results of $-V_{in}/V_{out}$ for 110 nm thick SiO₂ film under modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz. (b) The κ -C diagram for 110 nm thick SiO₂ film. The crossing point of κ -C for those three modulation frequencies is the measured value of the sample. (c) The experiment data and best-fit results of $-V_{in}/V_{out}$ for 860 nm thick SiO₂ film under modulation frequencies of 0.5 MHz, 2.08 MHz, 2.08 MHz, and 11.26 MHz. (d) The κ -C diagram for 860 nm thick SiO₂ film. (e) The sensitivity of $-V_{in}/V_{out}$ signal to the thermal conductivity κ_{z3} (solid line) and the heat capacity C_3 (dash line) of 310 nm thick SiO₂ film and the interfacial thermal conductance G₄ (dash dot line) from 0.98 MHz to 6.8 MHz at a 0.5 ns delay time. (f) The experiment data and best-fit results of $-V_{in}/V_{out}$ for 310 nm thick SiO₂ film under modulation frequencies of 0.98 MHz, 2.08 MHz, 3.4 MHz, and 6.8 MHz. (g) The κ -C diagram of 310 nm thick SiO₂ film at 2.08 MHz, 3.4 MHz, and 6.8 MHz. (h) The measured

Figure IV.3.5. (a) The TDTR measurement data and the best-fit result of -X/Y at a modulation frequency of 11.26 MHz using the average beam spot size 15.8 µm, for measuring cross-plane thermal property. (b) The TDTR measurement data and the best-fit result of -X/Y using varied spot sizes at 7.07-14.86 µm at a modulation frequency of 0.98 MHz and at a delay time of 0.5 ns Figure IV.4.1. The schematics of the sample configuration for (a) frontside-pumping and Figure IV.4.2. The TDTR signals and their best-fits both in the frontside-pumping and backsidepumping arrangements of Al-coated glass measured at a modulation frequency of 2.08 MHz and Figure IV.4.3. The sensitivity of thermal conductivity κ and heat capacity C of the glass, and the interfacial thermal conductance G between the Al film and the glass at different experimental Figure IV.4.4. The experimental data and the best-fit for thermal properties of (a) PMMA and (b) SiO₂ thin films at modulation frequencies of 2.08 MHz, 3.4 MHz, and 6.8 MHz.....94 Figure IV.4.5. The results on the temperature-dependent heat capacity and thermal conductivity of VWR[®] glass, and interfacial thermal conductance between Al and glass at a temperature range Figure V.1.1. (a) Schematic drawing of MLD cycles for type-A MLD zincone film using diethyl zinc (DEZ) and ethylene glycol (EG). (b) Schematic drawing of MLD cycles for type-B MLD

Figure V.2.1. The sensitivity analysis and measurement procedure for the thermal properties of polystyrene thin films. (a) the TTR measurement signal of the set-1 18.5 nm-thick polystyrene film at 2.08 MHz. (b) the TTR measurement signal of the set-1 191 nm-thick polystyrene film at 0.98 MHz, 2.08 MHz, and 6.8 MHz. (c) The sensitivity analysis of measuring the set-1 191 nm-thick polystyrene film under modulation frequencies of 2.08 MHz and 6.8 MHz. (d) The κ -C diagram that used to extract the thermal conductivity analysis of measuring the set-1 60 nm-thick polystyrene film under modulation frequencies of 2.08 MHz and 6.8 MHz. (f) The TTR measurement signal of the set-1 60 nm-thick polystyrene film under modulation frequencies of 2.08 MHz and 6.8 MHz. (f) The TTR measurement signal of the set-1 60 nm-thick polystyrene film at 2.08 MHz, 3.4 MHz, and 6.8 MHz.

CHAPTER I INTRODUCTION

I.1 Research advances in nanoscale thermal transport

Thermal transport at nanoscale may differ significantly from that in macro- and microscales.[1, 2] With device or structure characteristic length scales becoming comparable to the mean free path and wavelength of heat carriers (electrons, photons, phonons, and molecules), the classical laws are no longer valid and new approaches must be taken to study thermal transport at nanoscale.[3, 4] One well-known example is the failure of Fourier law to predict the thermal conductivity of nanostructures such as nanowires and superlattices.[5, 6] There are typically two types of problems in nanoscale thermal transport. One is the management of heat generated in nanoscale devices to maintain the functionality and reliability of these devices, such as integrated circuits[7, 8] and semiconductor lasers.[9] The other is to utilize nanostructures to manipulate the heat flow and energy conversion. Understanding nanoscale thermal transport will help thermal management of electronic, optical, and optoelectronic devices, and design new materials with different thermal transport properties for energy conversion and utilization.

In recent years, with the discovery of low-dimensional materials and the advance of fabrications, nano-structuring has opened new possibilities for a variety of novel applications. Ultrahigh thermal conductivity has been demonstrated in carbon nanotube[10-19] and graphene,[20-23] which are low-dimensional forms of carbon material. At room temperature, the thermal conductivity of carbon nanotube and graphene is on the order of 3000 W/mK,[12, 20] which is much higher than that of the common materials such as copper and silicon. These carbon nanostructures could be potential solutions to the ever-increasing thermal management

challenges of electronic chips.[24, 25] In the meantime, the thermal conductivity in superlattices,[26-30] nanowires,[31-33] thin films,[34-43] and nanocomposites[36-43] can be much smaller compared to their bulk counterparts, due to the scattering of energy carriers at various surfaces or boundaries. For instance, the thermal conductivity of a 37nm-long Si nanowire is only 1/10 of that of bulk Si at room temperature.[31-33] Nanostructured materials with ultra-low thermal conductivity can greatly benefit thermoelectric energy conversion,[44-47] thermo-photovoltaic power generation,[44, 48] and data storage.[49, 50]

However, almost all the previous investigations focus on inorganic materials. Organic materials or polymer-based materials have received much less attention although there are significant application advantages, such as being easy to process and fabricate, light-weight, inexpensive, and flexible. The fundamental research on nanoscale heat transfer in organic materials will render new generation of thermal management and energy conversion materials.

I.2 Interesting physics in nanostructured polymers

Polymers have been widely used in many conventional fields as functional or structural materials.[51, 52] There are also significant and new applications of polymers in macroelectronics, such as large-scale flexible organic display panels,[53] solar panels,[54] and batteries.[55] The thermal conductivity of polymers is of great importance for many of these applications because it governs the temperature-rise magnitude and temporal thermal behavior of polymer-based products.[56] However, polymers typically have very low thermal conductivity of 0.1-1 W/mK at room temperature[57] which is 2-3 orders of magnitude lower than inorganic semiconductors and metals and thus greatly limiting the heat spreading capability of polymers. Engineering the thermal conductivity of polymer based-materials, including thermal interface materials, shape memory polymers, and conductive polymers for electronics, is of great technical importance but remains a big challenge although some progress have been made.

Experimental and theoretical analyses have been employed in the past to study the heat conducting mechanisms in polymers. It has been shown that the thermal conductivity of polymers can exhibit significant anisotropy when the polymer chains are partially aligned with each other. This behavior is observed for all kinds of polymer materials: crystalline, semicrystalline, and amorphous.[56] The anisotropy found in polymers can be related to a statistically averaged orientation of the molecular chains with respect to a reference direction. Hennig[58] proposed a model that an un-oriented polymer is a random aggregate of small fully-oriented units. The unit can be either a molecular chain segment called a monomer or a local volumetric unit consisting of aligned molecular chains. They found out that the random orientation of the polymer chains and the weak couplings between the chains are the two main reasons accounted for the experimentally observed low thermal conductivity of polymers. Random orientation of the polymer chains in amorphous polymers can shorten the mean free path of the phonons, which are the major energy carriers in polymers, thus causing the low thermal conductivity value of polymers. This is then further confirmed with the experiments, which shows that the thermal conductivity can be increased when the polymer sample is stretched.[56]

On the other hand, a single polymer chain can potentially have much higher thermal conductivity than its bulk counterpart since it is an intrinsically low-dimensional material system.[59] Theoretical studies of various one-dimensional lattice models suggest that low-dimensional materials can have a very large or even infinite thermal conductivity.[60] Two excellent examples of low-dimensional system are carbon nanotubes and graphene sheets, which

have room temperature thermal conductivity of 3000 W/mK and 5000 W/mK,[20] respectively. Freeman *et al.*[61] performed early molecular dynamics (MD) simulations of thermal conductivity in a fairly realistic polymer chain. They found that the thermal conductivity of individual chains is higher than the corresponding bulk polymer material. Recently, the simulations by Henry *et al.* show that the thermal conductivity of a single polyethylene chain can exceed 100 W/mK if the chain is longer than 40 nm.[62, 63] Their analysis shows that the single polyethylene chain can have many times higher thermal conductivity than the bulk polyethylene material. Recent simulation results also predict the axial thermal conductivity of a polyethylene crystal with fully aligned chains to be as high as 310±190 W/mK.[64]

If polymer chains could be aligned, one would expect anisotropy and high thermal conductivity of polymers in the aligned directions. Technically, it would be much more favorable to increase thermal conductivity of polymers by aligning polymer chains than adding high thermal conductivity metallic or ceramic fillers for some applications such as polymer electronics. Several mechanisms could be explored to practically align polymer chains, including mechanical stretching as mentioned above, and recently developed molecular layer deposition (MLD) techniques[65] which can fabricate hybrid organic-inorganic thin films with aligned chains. A value of 37.5 W/mK[66] has been measured for polyethylene in the stretching direction. When stretching a polymer sample, the draw ratio is defined as the ratio of the final length after stretching to the original length. As draw ratio increases, the thermal conductivity in the stretching direction increases rapidly and a value of 70 W/mK is extrapolated from experiments for polyethylene with fully aligned chain.[67] An even higher value has been measured on the polyethylene nanofibers.[68] When a polyethylene gel is drawn to 400 times of its original length to obtain polyethylene nanofibers with diameters of 50-500nm, the thermal

conductivity is increased to about 104 W/mK (~300 times that of bulk polyethylene). Another recent discovery is that an individual micrometer-size spider silk fiber has an exceptionally high thermal conductivity up to 416 W/mK due to the highly oriented polymer chains in silk fibers.[69]

Compared to high thermal conductivity polymers, ultralow thermal conductivity might be readily achievable in nanostructured polymers, such as metal-polymer alloy, hybrid organicinorganic superlattices or thin films. The heterogeneous inter-atomic/molecular bonding and interface between organic molecules and inorganic atoms can significantly scatter the phonons and reduce the thermal conductivity to be much lower than its inorganic counterparts.

In short, extreme thermal conductivity and fundamental new physics of phonon dynamics and thermal transport might exist in nanostructured polymers, either pristine polymers with aligned chains or organic-inorganic alloy or superlattices. However, there have been no systematic studies on the thermal transport in this new class of materials while the applications are ubiquitous.

I.3 Objective of the thesis

The objective of this thesis is to investigate the thermal transport in nanostructured polymers by simulation and characterization. Nanostructured polymers include polymers with aligned chains or improved chain orientation and hybrid organic-inorganic materials. The simulation work is to find out the polymer chain parameters that affect the thermal transport in polymers. Computational simulations are aimed to understand the properties of assemblies of molecules in terms of their structures and microscopic interactions between them. This serves as

a complement to conventional experiments, enabling us to study the effects of individual parameters. Molecular Dynamics (MD) simulation is a powerful technique to study the equilibrium and transport properties of polymers, in which the motion of the molecules is treated classically, an approximation that is reasonable for many important problems in polymer materials.[70-72] Though a few experiments and simulations have been done to show the great promise of increasing or decreasing the thermal conductivity of polymers, systematic research is still needed to study the fundamental mechanisms of how the structure and thermal conductivity of polymers can be tuned. We also explore the dependence of thermal conductivity of single extended polymer chains on monomer type and chain length. To eliminate other factors that strongly affect the thermal transport in polymer chains, such as random orientation of chains in amorphous state and inter-chain interactions in the fully chain-extended crystals, and to identify particularly the effect of chain monomer type and chain length, we have thus chosen single extended chains that are free from random orientations and inter-chain interactions.

To systematically study the thermal transport in nanostructured polymers, we also need the characterization tools for thermal properties of nanostructured polymers. To measure thermal transport properties and study fundamental heat transfer physics, a range of experimental methods and apparatus has been optimized and developed, including 3ω method,[73] micro-fabricated platform,[74] scanning thermal microscopy,[75] bi-material cantilever,[68] optical methods.[76] Using optical methods, it is usually difficult to perform absolute thermal conductivity measurements because optical heat input to the sample is hard to measure accurately. Time variations of the optical heating are often used to obtain thermal diffusivity or effusivity of the target bulk or thin film sample. In periodic heating methods, temperature rise at the surface causes either reflectance change,[77] emittance change,[78] absorptance

change, [79] photoacoustic signal change, [80] thermal expansion on the sample surface or in the surrounding media.[81] Either the amplitude or phase signals can be used to extract thermal properties of thin films and interfaces. Among those methods, ultrafast-laser based transient thermoreflectance (TTR) method is increasing popular and suitable for nanostructured polymer materials since this method has high spatial resolution with nanometer range and high temporal resolution with picosecond to nanosecond range. The thermal properties of nanostructured polymer thin films can be measured by applying this method. Moreover, the interfacial thermal conductance between different materials can also be measured. This TTR technique is accomplished by heating the surface of a material using a train of laser pulses and by monitoring the resulting temperature change through the reflectivity of the surface sampled using a timedelayed sensing system. The TTR method has been applied to measure the properties of a wide range of thin films, multilayers, bulk materials, and their interfaces.[6, 82] However, the TTR characterization system is further developed to enable the measurement of nanostructured polymer thin films. We demonstrate a technique for simultaneous measurement of thermal conductivity and volumetric heat capacity of bulk and thin film materials using a frequencydependent time-domain TTR method. Then, we measure the thermal properties of atomic/molecular layer deposition enabled thin films using this method. We experimentally investigate the effects of atomic configuration on the thermal conductivity of these films. The characterization system is also extended for measurement of anisotropic thermal conductivity of nanostructured materials and materials that needs protection during metal transducer deposition.

Combined with the simulation results and measurement data, we can understand the thermal transport mechanisms in the nanostructured polymer thin films and hybrid organic-inorganic materials. We will test the hypothesis proposed by the theoretical/simulation studies. For

instance, whether the aligned polymer chains would have much higher thermal conductivity than their bulk counterparts still needs to be tested for a broad range of polymer monomer types and thickness of samples. Also, we will try to provide design guidance on thin films with tunable thermal properties.

I.4 Organization of the thesis

In chapter I, the motivation and objective of this thesis for the thermal transport in nanostructured polymers are introduced. In chapter II, we demonstrate the tuning of thermal conductivity of polymers using mechanical strains and reveal the structure-property relationship between the thermal conductivity and the chain orientation. In chapter III, we investigate the effect of polymer monomer type and chain length on the thermal conductivity of single extended polymer chains. After we show how the chain parameters affect the thermal transport in polymers, we turn to experimental characterization of nanostructured polymers. In chapter IV, we improve the pump-and-probe measurement system to extend its capability for the measurement of polymer thin films, including measuring both cross-plane and in-plane thermal conductivity, heat capacity, and interfacial thermal conductance between materials. In chapter V, we then measure the thermal properties of atomic/molecular layer deposition enabled thin films and ultrathin polymer thin films. In chapter VI, future work is proposed based on the discussions in the thesis.

CHAPTER II THERMAL CONDUCTIVITY ENHANCEMENT OF POLYMERS WITH MECHANICAL STRAINS

The simulation work is aimed at finding the chain parameters that affect the thermal transport in polymers. Based on the main reason of the low thermal conductivity of bulk polymer, the first parameter we target is the chain orientation. In this chapter, we systematically study the fundamental mechanisms on how mechanical strains can be used to tune the structure and thermal conductivity of polymers. This study can be used to guide the future development of advanced reconfigurable and tunable thermal management technologies.

II.1 Introduction

The low thermal conductivity of polymers limits their heat spreading capability, which is one of the major technical barriers for polymer-based products, especially electronics, such as organic light emitting diodes. As stated in Chapter I, the thermal conductivity of polymers is not intrinsically low. A single polymer chain, which is a low-dimensional material, has a rather high thermal conductivity. The measured low thermal conductivity of bulk polymers could be attributed to the random orientation and entanglement of polymer chains. If polymer chains could be aligned, one would expect anisotropy and high thermal conductivity of polymers in the aligned directions. Technically, it would be much more favorable to increase thermal conductivity of polymers by aligning polymer chains than adding high thermal conductivity metallic or ceramic fillers for some applications such as polymer electronics. Several mechanisms could be explored to practically align polymer chains, including mechanical stretching mentioned above, and recently developed MLD techniques[65] which can fabricate polymer thin films with aligned chains.

Though a few experiments and simulations have been done to show the great promise in enhancing the thermal conductivity of polymers, a systematic research is still needed to study the fundamental mechanisms on how mechanical strains can be used to tune the structure and thermal conductivity of polymers. Such studies could play significant roles in the development of polymer electronics and polymer thermal interface materials. In this chapter, an all-atom molecular dynamic simulation is applied to conduct stretching deformation and thermal conductivity simulations to study the tuning mechanisms of thermal conductivity under mechanical strains. The thermal conductivity change is correlated with the change of chain conformation under mechanical strains. This study can be used to guide the future development of advanced reconfigurable and tunable thermal management technologies.

In section II.2, the modeling and simulation method is introduced. In section II.3, the thermal conductivity enhancement with the strain is shown. In section II.4, the orientational order parameter is calculated and shown increase with the strain. In section II.5, we correlate the thermal conductivity enhancement with the increase of the orientational order parameter and demonstrate the structure-property relationship. In section II.6, this chapter is summarized.

II.2 Modeling and simulation method

In this work, molecular dynamic simulation is used to study the effect of mechanical strains on the thermal conductivity of polymers. MD simulation is a powerful technique for studying the equilibrium and transport properties of polymers, in which the motion of the molecules is treated classically, an approximation that is reasonable for many important problems in polymer materials.[70-72] Various studies have been carried out on the mechanical properties of polymers under mechanical strains, [83, 84] the chain orientation change due to strains, [85, 86] and the thermal properties of polymers (without strain).[64, 87-89] However, there are very few existing work studying how and why the strain could affect the thermal conductivity of polymers. The most relevant study is a simulation by Enrico *et al.*,[90] which calculated the thermal conductivities of stretched polymer samples in parallel and perpendicular to the stretching directions, which confirms the measured thermal conductivity anisotropy of polymers under mechanical strain. However, two fundamental questions remain if one would explore mechanical strains to tune the thermal conductivity for advanced thermal management technologies: how the chain conformation changes under mechanical strains, and could the thermal conductivity change be correlated to the conformation change? This work is to shed some lights on fundamentals on answering these questions.

Polyethylene is chosen as our model material system to study the strain effects on the thermal conductivity of polymers due to its simplicity.[91-93] Polyethylene is a polymer consisting of long chains of ethylene monomers. The all-atom model[94] which takes into account all the carbon and hydrogen atoms is adopted in this study and is expected to reveal the atomic details under mechanical strains.²² We note that both Freeman *et al.* and Enrico *et al.* used united-atom model for their studies, which lumps all the hydrogen atoms into the carbon atoms.

Our simulation is conducted in a simulation domain that contains 10 randomly coiling polyethylene chains with each chain containing N=200 carbon atoms, corresponding to a

molecular weight (molar mass) M = 2802 g/mol. Small N gives a poor representation of bulk behavior. As N becomes larger, we would expect an increasingly better approximation to a dense amorphous system at a significant increase of computational cost. Lavine *et al.*[85] calculated the influences of chain length on the polyethylene deformation and their results show that N=200 is large enough to represent bulk deformation behavior. We also build a polyethylene sample containing 5 randomly coiling chains with N=400 carbon atoms in each chain with a molecular weight M = 5602 g/mol to observe whether there is molecular weight dependence. We used COMPASS force field[95] for our simulation, which is a general all-atom force field for atomistic simulation of common organic molecules, small inorganic molecules and polymers. The COMPASS force field is one of the Class II force field, which closely predicts the conformational energies and vibration frequencies, both closely relevant to thermal properties of polymers. The details of the COMPASS force field functional form and associated parameters can be found in literature.



Figure II.1. Numerical simulation procedure for building structure-property relationships of polymers when they are under mechanical strains, which involves three major steps: sample preparation, deformation and thermal conductivity calculation simulations. After amorphous polymer sample is prepared, the deformation process generates a series of strained samples at different strains, then the thermal conductivity of these strained samples are calculated.

The MD simulations were performed using LAMMPS simulation package.[96] All the simulations used 1 femtosecond (fs) timestep and the force cutoff distance was chosen to be 10 Angstroms (Å). Verlet algorithm was used for the integration of Newton's equations of atomic motion. The neighbor list was checked in every timestep. Periodic boundary conditions were applied in all three directions and thus allowing the representation for bulk material. Figure II.1 shows the simulation procedure which consists of three modules: sample preparation, deformation (mechanical stretching) and thermal conductivity simulation. To generate representative glassy polymer sample at low temperature, which would be a much easier way to form aligned chain during mechanical straining, we generated polymer melts at 500K and then cooled down the polymer melts from 500K to 200K, which is below the glass transition temperature of polyethylene. Following the procedure in reference [97], initial structures of the polymer melts at 500K were generated using a modified Markov process, based on rotational isomeric state theory and incorporating long-range interactions. Energy minimization was used to relax the samples for 1ns at 500K at an applied isotropic pressure of 1 atm. Samples at 200K were then obtained by stepwise cooling at a rate of 0.1K/ps to a desired temperature under isotropic controlled pressure conditions followed by subsequent relaxation of 1ns. 0.1 K/ps cooling rate is chosen based on the simulation results from Lyulin *et al.* [98], who showed that 0.1K/ps is slow enough for annealing simulations. In order to eliminate the possible differences brought by initial density, we tested five different initial densities, and they all led to the same equilibrium density 0.68 g/cm³, which is reasonable compared to the experimental density value 0.73 g/cm³ at 1 atm[99] because real polyethylene is very difficult to prepare in a completely amorphous state.[100]



(b)

Figure II.2. (a) A schematic representation of the simulation cell used to compute the thermal conductivity, (b) typical temperature profile and linear fitting of nonequilibrium molecular dynamic simulation for thermal conduction.

After the sample preparation process, deformation simulations were performed under constant strain rate condition at 200K. The constant strain at each timestep was applied uniaxially along the x-axis of the periodic simulation cell, which is in the same direction as the temperature gradient is applied in later thermal conductivity simulations. Pressure was kept

constant at 1 atm for all other boundaries during deformation, which uses constant-NPT (number of particles, pressure and temperature) ensemble to adjust the atom positions. Both strain rates of 10^9 s^{-1} and 10^8 s^{-1} were simulated. We periodically stopped the stretching during the deformation process to generate a series of samples under different mechanical strains. Before calculating the thermal conductivity, these strained polymer samples were relaxed until the structures are stable employing constant-NVT (constant number of particles, volume and temperature) ensemble, which typically takes 0.5ns for the relaxation. The thermal conductivity was then calculated using the nonequilibrium molecular dynamics simulation[101-103]. This approach relies on imposing a temperature difference across a simulation cell and calculating the resulting heat flux[35] or imposing a heat flux and calculating the resulting temperature gradient[104, 105]. The thermal conductivity can then be calculated using the Fourier's law of heat conduction, shown in Eq. (II.1)

$$\mathbf{J} = -\kappa \nabla T \tag{II.1},$$

where **J** is the local heat flux, κ is the thermal conductivity and ∇T is the temperature gradient. A schematic representation of the simulation cell used to compute the thermal conductivity κ is shown in Fig. II.2(a). The simulation cell that is stretched to a length L is divided into twenty slabs, each with thickness δ . To create a heat flux along the x-axis direction of the simulation cell, which is the same direction of the applied strains, a small amount of heat ΔE is added into a thin slab of thickness δ centered at x=0 (hot region) at each time step and the same amount of heat is removed from two half-slabs of thickness 0.5 δ centered at x= L/2 and x= -L/2(cold regions). Such heat addition and removal is done through velocity rescaling. For consistency, we have checked the dependence of the computed thermal conductivity on the cross-sectional area, heat source/sink width, and the magnitude of the input heat flux and found the dependence on computational variables to be quite weak[106]. When the system reached steady state, typically after 1.7ns, the heat flux can be calculated as $J_z = \Delta E/2A\Delta t$, where A is the cross-sectional area of the simulation domain and Δt is the timestep, respectively. To calculate the temperature gradient, the temperature of each slab is averaged over the last 1ns of the simulations. Figure II.2(b) shows a typical temperature profile. We fit only the linear temperature region which is not close to the hot and cold region, as shown in Fig. II.2 (b), to calculate the thermal conductivity using the Fourier heat conduction equation.

II.3 Thermal conductivity enhancement

Figure II.3 shows the thermal conductivity of polyethylene samples stretched at different strains (0 to 2.0) under different strain rates of 10^8 s^{-1} and 10^9 s^{-1} . The thermal conductivity in the stretching direction of the polymer sample is enhanced with increasing strain for both strain rates. Thermal conductivity perpendicular to the stretching direction decreases with the increasing strain. When the polymer sample is stretched three times of the original length, the thermal conductivity in the stretching direction is enhanced for more than five times. Stretching deformation forces the polymer chains to orient in the stretching direction which induces the chain alignment. Therefore, in a stretched sample, there are more backbone bonds oriented in the stretching direction than perpendicular to the stretching direction. Thermal energy transports more efficiently along the polymer chain, which consists of the strong carbon-carbon covalent bonds, than perpendicular to the polymer chain. Similar thermal conductivity enhancement in the stretching direction has been found experimentally.[66, 107-110] High density or ultra-high molecular weight polyethylene are often used in such stretching experiments. We also found that

the enhancement of thermal conductivity in the stretching direction is dependent on the strain rate that the polymer samples are stretched with. The slower the sample is stretched, the higher the thermal conductivity enhancement. Figure II.4 shows the dependence of the thermal conductivity enhancement on molecular weight. The larger the molecular weight, the higher the thermal conductivity when the polymer is stretched at the same strain rate of $10^9 \, \text{s}^{-1}$ to the same strain.



Figure II.3. The change of the thermal conductivity of polymers in the stretching direction and perpendicular to the stretching direction as a function of tensile strains. It also shows that the slower the strain rate, the higher the enhancement of the thermal conductivity in the stretching direction.



Figure. II.4. The dependence of the thermal conductivity enhancement on molecular weight. The larger the molecular weight, the higher the thermal conductivity when the polymer is stretched at the same strain rate of 10^9 s^{-1} to the same strain.

II.4 Chain alignment improvement

In order to understand the strain effects on the polymer chain structures and to develop the thermal conductivity-chain orientation relationship, we investigated the chain alignment due to the stretching deformation. Figure II.5 shows the chain alignment visualization figures, plotted using VMD software[111] and Material Studio software package. In these figures, ten different colors (including the white color) represent ten different polymer chains in a simulation domain. Figure II.5(a) shows the 3-D unit cell of the polymer sample before mechanical tuning
(stretching deformation). The initial chains are in random coil conformations. To see it more clearly, Fig. II.5 (b), (c) and (d) are the XY plane projection of the 3D snapshots of the sample before deformation, stretched at ε =1 and stretched at ε =2 respectively, under the strain rate of 10⁹ s⁻¹. Clearly the chains gradually align themselves to the stretching direction.



Figure II.5. (a) 3D unit cell of the polymer sample under zero strain, (b) projection to XY plane of the samples before deformation, (c) when stretched at $\varepsilon = 1$ with a strain rate of 10^9 s^{-1} and (d) when stretched at $\varepsilon = 2$ with a strain rate 10^9 s^{-1} .

To quantify the polymer chain alignment, we calculated the orientational order parameter,[83-85, 112, 113] which is a useful indicator for chain alignment. The local chain direction at each atom is characterized by the unit vector, which is computed from the chord vectors connected to the atom: $\mathbf{e}_i = (\mathbf{r}_{i+1} - \mathbf{r}_{i-1})/|\mathbf{r}_{i+1} - \mathbf{r}_{i-1}|$. A chord is defined as a line segment connecting two second nearest neighbors on the same chain[85]. Alignment of chain chord vectors with the applied strain direction, or orientational order parameter P_2 , is then computed as

$$P_2 = 1.5 \left\langle \left(\mathbf{e}_i \bullet \mathbf{e}_x \right)^2 \right\rangle - 0.5 \tag{II.2},$$

where \mathbf{e}_x is the unit vector in the direction of applied strain. The orientational order parameter is sometimes called the Herman's orientation function[114]. The orientational order parameter for the polymer system is simply the average of the values of each single chain.

We calculated the orientational order parameters of the polymer samples during relaxation after the samples are deformed at different strains. As the relaxation proceeds, the orientational order parameter values decay slightly. Figure II.6 plots the averaged orientation order parameters for the last 400ps during the 0.5 ns relaxation process. The orientational order parameter increases due to the stretching, which means the structure will be more aligned, as visualized in Fig. II.5. Moreover, the orientational order parameter increases mostly at small strains and slows down the increasing rate at relatively larger strains. This is reasonable because the chainunfolding process largely increases the chain alignment while the chain stretching through monomer rotation improves the chain alignment relatively slowly. When the polymer sample is stretched at a slower rate, there is much more time (ten times more in our case) for the chains to uncoil themselves and for the monomers in the chains to rotate and adjust the positions to reach better alignment. Thus we observed the phenomena that the enhancement of the orientational order parameter is larger when the sample is stretched at slower strain rate. This strain rate dependence of chain orientation gives us another controlling parameter to tune the thermal conductivity with mechanical strain, agreeing with the observations of the strain-rate dependent thermal conductivity in Fig. II.3.



Figure II.6. The change of orientational order parameter P_2 as a function of the mechanical strain after relaxation. The orientation will increase mostly at small strains while slow down the increasing rate at relatively larger strains.

II.5 Thermal conductivity-orientational order parameter relationship

Figures II.3 and II.6 in the previous sections show that the thermal conductivity and the orientational order parameter have similar enhancement trends with the applied mechanical strains. The reason is that mechanical strain induces the chain conformation change in order to align polymer chains to the stretching direction. Heat transport is more efficient along aligned chain structures than through randomly coiled structures. Additionally, the enhancement of both the thermal conductivity and the orientational order parameter is larger when the sample is stretched at slower strain rate.

There should be direct relationship between the thermal conductivity and the orientational order parameter. In figure II.7, we plotted the thermal conductivity versus the orientational order parameter for two strain rates and two molecular weights and found the exponential curve $\kappa = \kappa_0 \exp(aP_2)$ fits the relationship very well. The fitting parameters are shown in Table II.1. Hennig[58] predicts a linear relation between the thermal resistivity and P_2 using the series thermal resistance model, which assumes that the total thermal resistance of the material is given by the series of the thermal resistances of the individual units. Their analytical approach gives lower bound of the thermal conductivity and does not reflect the detailed molecular nature of polymers. Our molecular dynamic simulation reflects the structural evolution of polymer material polyethylene when under applied strain. P_2 is then calculated based on structure details in the molecular level. We have thus predicted an exponential dependence of thermal conductivity with P_2 , different from Hennig's analytical model. The reason for the exponential dependence is explained as follows. When P_2 is small, which means some of the chains are still folded or coiled, heat transport is limited by the folded or even entangled regions. However, as the P_2 improves, the chains gradually unfold themselves and stretch out along the stretching direction. Then heat transport through aligned structure is preferred and a little improvement in chain alignment will result in relatively larger improvement in heat transport.



Figure II.7. The relationship between the logarithm of the enhanced thermal conductivity and the orientational order parameter P_2 using linear fit.

It is interesting to take a closer look to the two parameters in the fitting formula, which are helpful to predict the material property. K_0 represents thermal conductivity of isotropic polymer material, which can be also seen from the formula when P_2 is zero. We obtained $K_0 = 0.275$ W/mK for $P_2=0$ which is comparable to the literature value 0.20~0.25 W/mK for isotropic low density amorphous polyethylene[57, 115]. The parameter *a* represents how fast the thermal conductivity increases with the orientational order parameter. If we extrapolate the thermal conductivity in our simulation for $P_2=1$, we obtained a value of 4.64 W/mK for perfect polymer with molar mass of 2800 g/mol. Ni et al⁹ performed a molecular dynamics simulation on perfect aligned polymers and predicted a thermal conductivity of 11.7 W/mK.[64] Considering the possible differences that could be from the different force fields used for simulations and the defects (voids) might be involved in our bulk material simulation, we believe our results are consistent with Ni et al. Moreover, the close value of the exponential fitting parameters for both

strain rates suggests that the thermal conductivity is only determined by the orientational order parameter. Strain rate differences could result in thermal conductivity difference, but are captured by the orientational order parameter.

	κ_0	а
Strain rate 10 ⁹ s ⁻¹ , M=2802g/mol	0.27547	2.82401
Strain rate 10 ⁸ s ⁻¹ , M=2802g/mol	0.27968	2.83779
Strain rate 10 ⁹ s ⁻¹ , M=5602g/mol	0.25655	2.94617

Table II.1. The fitting parameters for $K-P_2$ relationship

It is worthwhile to discuss the dependence of thermal conductivity on molecular weight. In our simulation, we find that the dependence of the thermal conductivity on molecular weight of polyethylene at the same strain rate and constant P_2 is different. Figure II.4 shows that higher thermal conductivity is obtained for polymers with higher molecular weight when stretched at the same strain rate 10^9 s^{-1} to the same strain. Figure II.7 shows that smaller thermal conductivity is obtained for polymers with larger molecular weight at constant P_2 within our calculation range. By calculating the thermal conductivity of crystalline polyethylene with perfectly aligned chains $(P_2 = 1)$ along the polymer chains for different molar mass (molecular weight), Ni *et al.*[64] found that the calculated thermal conductivity increase monotonically as the molecular weight of the polymer increases. Both Ni *et al.*[64] and Henry *et al.*[63, 68] explained the dependence on molecular weight by viewing the polymer chain ends as chain defects, which prevent the effective heat transport in the perfectly aligned chain polymer. Apparently, we find a different trend for the dependence of thermal conductivity on molecular weight for amorphous polymers than the work by Ni *et al* and Henry *et al* in perfectly aligned polymers due to the chain entanglements in the polymers.

II.6 Summary of this chapter

The low thermal conductivity of polymers limits their heat spreading capability, which is one of the major technical barriers for polymer-based products, especially electronics, such as organic light emitting diodes. Mechanical stretching could align the polymer chains and enhance their thermal conductivity. All-atom model molecular dynamic simulation has been conducted to study the tuning of polymer thermal conductivity using mechanical strains. The simulation results show that both the thermal conductivity of polymers and the orientational order parameter, which is a quantitatively indicator of the chain conformations and alignments, increases with the increasing strain. Strain rate is another controlling parameter to tune the thermal conductivity with mechanical strain. The enhancements of the thermal conductivity and the orientational order parameter are larger under the same strain when the polymer is stretched slower. Molecular weight also influences the thermal conductivity of strained polymers. Finally, we relate the thermal conductivity with the orientational order parameter through an exponential relation. This structure-property relationship can guide us on tuning the thermal conductivity of polymers with the mechanical strains.

CHAPTER III LENGTH-DEPENDENT THERMAL CONDUCTIVITY OF SINGLE EXTENDED POLYMER CHAINS

In Chapter II, we show that mechanical stretching could align the polymer chains and enhance the thermal conductivity. The thermal conductivity correlates with the orientational order parameter through an exponential relation. The orientation of chains is one of the most important factors affecting the thermal transport in polymers. Other than the orientation, we are interested in investigating what other parameters could significantly affect the thermal transport and thermal conductivity of polymers. In this chapter, we investigate the thermal conductivity of single extended polymer chains, where the orientational order parameter is almost 1. In these perfected extended chains, we demonstrate the two important parameters that affect the thermal conductivity of polymers: chain length and monomer type. This study could provide guidance for the development of advanced polymer products with high thermal conductivity.

III.1 Introduction

One of the main reasons for the low thermal conductivity of bulk polymers is that the polymer chains are randomly coiled in bulk polymers, as shown in Fig. III.1(a), which effectively shortens the mean free path of heat-carrying phonons.[115] The low thermal conductivity of polymers will be one of the major roadblocks for polymer-based microelectronics and macroelectronics such as organic displays[53] and organic solar cells[54] due to the limited heat spreading capability. Although the thermal conductivity of bulk polymers

is usually low, a single extended polymer chain that has a well-aligned polymer segment, as illustrated in Fig. III.1(b), could have a very high thermal conductivity.



(c)

Figure. III.1. (a) Schematic drawing of a randomly coiled polyethylene chain. The random orientation of the chain segments is one of the main reasons for the low thermal conductivity of bulk polymers. (b) Schematic drawing of a single extended polyethylene chain. A single extended polymer chain with well-aligned polymer segments might have high thermal conductivity. (c) Upper panel: a typical NEMD simulation system for the thermal conductivity of a single extended polymer chain. The simulation system was divided into several slabs (twenty to fifty slabs, depending on the total length), each with a thickness δ . At each end, the atoms in one slab were fixed to act as a heat-insulating wall. A small amount of heat ΔE (~10 J/mol) was added into the slab adjacent to the fixed slab (hot region) at each timestep; the same amount of heat was removed from the slab adjacent to the fixed slab at the other end (cold region). Lower panel: a typical temperature profile in the simulation domain. The linear temperature region was fitted using the least-square method to obtain the temperature gradient dT / dx for the calculation of the effective thermal conductivity using the Fourier's law of heat conduction.

Both the chain length and monomer type of polymer chains could affect the thermal conductivity. For instance, reports show that the thermal conductivity of a single extended *polyethylene* chain is 50 times that of a single extended *polydimethylsiloxane* chain and thermal conductivity of both chains increases with increasing chain lengths.[63, 116] With the development of the various techniques to practically obtain samples with more aligned polymer chains, such as mechanical stretching[56] and the recently developed molecular layer deposition technique[117], general design guidance for tuning the thermal properties of these novel materials with extended polymer chains is in critical need. In this work, we study the dependence on the monomer type and the chain length of the thermal conductivity and phonon transport

mechanism of single extended polymer chains using molecular dynamics simulations. This study could provide guidance for the development of advanced polymer products with high thermal conductivity.

The objective for this work is to explore the dependence of thermal conductivity of single extended polymer chains on monomer type and chain length, instead of precisely calculating the thermal conductivity of polymers either in their amorphous or crystalline states. To eliminate other factors that strongly affect the thermal transport in polymer chains, such as random orientation of chains in amorphous state and inter-chain interactions in the fully chain-extended crystals, and to identify the effect of chain monomer type and chain length, we have thus chosen single extended chains that are free from random orientations and inter-chain interactions in this work.

In section III.2, the modeling of single extended polymer chains is introduced. In section III.3, the method for thermal conductivity is shown in detail. In section III.4, the effect of polymer types on thermal conductivity is shown. In section III.5, we discuss the phonon transport mechanism in these chains. In section III.6, the length-dependent thermal conductivity is analyzed. Finally, we summarize this chapter in section III.7.

III.2 Material model of single extended polymer chains

We investigated single extended polymer chains of eight different polymer monomers as shown in Table III. I to study the effect of the monomer types on the phonon transport. *Poly(p-phenylene)* and *polybenzimid* are the two representative polymer chains with aromatic backbone.

In aromatic backbone structures, the monomer usually contains planar cyclic rings or ring-like structures. Compared to *polyethylene*, *polyacetylene* has double bonds in the aliphatic chains. We also studied the effect of chain disorder on phonon transport in single extended polymer chains, which includes bond-strength disorder, mass disorder, and orientation disorder. We note that these "chain disorders" termed in this work are only for the convenient comparisons among polymer chains of different monomer types and are not the same as the disorders (e.g. weak disorder such as defects and dislocations, and strong disorder such as in liquid, amorphous solids, and composites) commonly defined in solid state physics. Alternating single carboncarbon bonds and double carbon-carbon bonds exist in *polybutadiene*. When the covalent bonds with different strengths are mixed together in a chain, we term it as bond-strength disorder in this work. The mass disorder termed here is generated by the incorporation of other elements or functional groups with different masses into an otherwise aliphatic or aromatic pristine chain. For example, *poly(oxymethylene)* and *poly(ethylene oxide)* can be viewed as incorporating oxygen atoms into a *polyethylene* chain. Similarly, incorporating oxygen atoms into a *poly(p*phenylene) chain leads to a poly(phenylene ether) chain. Orientation disorder, which can be observed in *poly(p-phenylene)* and *poly(phenylene ether)*, is the misalignment of the orientation of aromatic rings compared to the well-aligned aromatic rings in the chain.

In our polymer model, each atom is treated as a single site and assigned a corresponding mass. The interactions between atoms are described by the polymer consistent force field (PCFF)[118]. The force cutoff distance was 10 Angstroms (Å). The software package Material Studio^{®[119]} is used to build the initial configuration of the single extended polymer chains by connecting together multiple segments of the polymer monomers. For instance, after energy optimization of the *ethylene* monomer (-CH₂-CH₂-) by adjusting the atomic coordinates

iteratively to reach the minimum energy, a single *polyethylene* chain is obtained by replicating the monomer in the chain backbone direction, as shown in Fig. 1(b). The repeating units of polymer chains are called segments in this work.

Table III.1 Eight different types of polymers are investigated in this work. The effective crosssectional area A of a single extended polymer chain is calculated by dividing the effective volume V_s of a polymer chain with its length L. Here we assume the effective volume of a single extended polymer chain V_s equals to the volume of a polymer chain in the amorphous state with fully relaxed and coiled chain orientation V_a . The exponent β is the index when the lengthdependent diverging thermal conductivity κ is fitted with the chain length L using $\kappa \sim L^{\beta}$, as discussed in Section III.5.

		Effective	Effective	
Name	Chemical structure	density	cross-sectional	β
		(g/cm^3)	area A ($Å^2$)	
Polyethylene	-[CH ₂ -CH ₂] _n -	0.74	24.66	0.438 ± 0.009
Polyacetylene	-[CH=CH] _n -	0.88	19.53	0.689 ± 0.019
Deleterte d'ana	-[CH ₂ -CH=CH-	0.79	10.24	0.417 . 0.007
Polybutadiene	CH ₂] _n -	0.78	19.34	0.417 ± 0.007
Polybenzimid		1 27	25.28	0.881 ± 0.046
roryconziniu		1.27	25.20	0.001 ± 0.040

Poly(p- phenylene)		1.17	26.65	N/A
Poly(phenylene ether)		1.10	30.55	N/A
Poly(methylene oxide)	-[CH ₂ -O] _n -	1.20	17.37	0.564 ±0.067
Poly(ethylene oxide)	-[CH ₂ -CH ₂ -O] _n -	1.02	28.08	0.287 ±0.023

III.3 NEMD simulation for thermal conductivity

The thermal conductivity of single extended polymer chains was calculated using the NEMD simulation of the LAMMPS simulation package.[96] [101-103] A schematic representation of the simulation system used to compute the thermal conductivity is shown in the upper panel of Fig. III.1(c). The simulation system was divided into several slabs (twenty to fifty slabs, depending on the total length), each with a thickness δ . To keep the extended-chain state, which is an entropically unfavorable state, the atoms in one slab at each end were fixed to act as a heat-insulating wall. The force at the chain ends eventually evolves into the tensile stress on the polymer chains. The tensile stress in the single extended polymer chains might have some effects on the thermal conductivity values, which is discussed in Section III.3. To choose a proper timestep for the simulations, we have tested the timesteps of 1 femtosecond (fs) and 0.5 fs in our

simulations. Using both timesteps, the temperature and energy of the system is stable and the difference of the calculated values of thermal conductivity is within 5%. The results presented in this work are calculated using 1 fs as the timestep.

Before calculating the thermal conductivity, all the samples were relaxed to release the thermal stress by employing a constant-*NVT* (constant number of particles, volume, and temperature) ensemble at a prescribed temperature (300K) and then a constant-*NVE* (constant number of particles, volume, and energy) ensemble. The thermostat for the constant-*NVT* and constant-*NVE* ensemble is Nose-Hoover.[120] Typically, it takes about 1-2.5ns to relax the system so that stable values of temperature, pressure, and energy of the system can be reached. To obtain thermal conductivity, a small amount of heat ΔE (~10 J/mol) was added into the slab adjacent to the fixed slab (hot region) at each timestep to create a heat flux along the *x*-direction (the chain backbone direction) of the simulation system. The same amount of heat was removed from the slab adjacent to the fixed slab at the other end (cold region). The heat flux *J* along the *x*-direction is then calculated as $J = \Delta E / A \Delta t$, where *A* is the effective cross-sectional area and Δt is the timestep.

The effective cross-sectional area A of a single extended polymer chain is calculated by dividing the effective volume V_s of a polymer chain with its length L. Here we assume the effective volume of a single extended polymer chain V_s equals to the volume of a polymer chain in the amorphous state with fully relaxed and coiled chain orientation V_a .[116] We have calculated the effective cross sectional area of the polymers using the densities of fully amorphous state rather than taking the cross-sectional area of perfect crystals based on the following reasons: (1) not all the crystallography data for the perfect crystals of the polymers we studied can be found in literature. To make a reasonable comparison among eight types of

polymers studied, a computationally consistent way is needed. (2) Physically, we are not computing the thermal conductivity of perfect polymer crystals. There are strong inter-chain interactions in perfect polymer crystals, which significantly affect the thermal transport in the crystal. We tend to believe that the cross-sectional area of a single chain should be closer to that in their amorphous state, where the chains have much weaker interactions. This methodology is similar to the calculation of carbon nanotubes, where a cross-sectional area corresponding to annular shell of width of 3.4 Å is used, the distance between the graphene planes in graphite.[12] We define the cross-sectional area using the volume of the amorphous polymers. Overall, the difference in these two definitions would be only a few percent, not significant enough to overshadow the conclusion of this work. Table I lists the effective density and the cross sectional area for all the polymers studied. For instance, the simulation domain with ten 50 Å-long amorphous *polyethylene* chains at 300 K and 1 *atm* has a density of 0.76 g/cm³. The simulated density is lower than the measured density (0.9 g/cm³) of semi-crystalline *polyethylene* samples because pure amorphous polymer materials are difficult to prepare in experiment, [100, 121] but very close to the density 0.79 g/cm³ obtained from quenching the polymer melt samples.[100] Such a density 0.76 g/cm³ yields an effective cross sectional area of 24.66 $Å^2$ for a single polyethylene chain. As a result, the effective cross sectional area is larger than that of a polyethylene crystal, where much stronger inter-chain interaction exists.

After the system reaches steady state, which typically takes 0.5-1 ns, the effective temperature of each slab was averaged over the following 2ns. The lower panel of Fig. 1(c) shows a typical temperature profile. We then fit the linear temperature region using the least-square method to obtain the temperature gradient dT/dx so that the thermal conductivity κ can be calculated by $\kappa = J/(dT/dx)$, according to the Fourier's law of heat conduction. To reduce

the statistical errors in the calculated thermal conductivity, the effective temperature of each slab was separately averaged over four consecutive 0.5 ns simulation time. Moreover, the thermal conductivity values were averaged over at least three simulations with different heat fluxes. The error bars shown in Fig. 2, around 5%, represent the percentage deviation of the averaged thermal conductivity from the thermal conductivities calculated from different simulation times and heat fluxes. The error bars are not plotted explicitly when they are small compared to the plot scales.

III.4 The effect of polymer types on the thermal conductivity

Figure III.2 shows the thermal conductivity of single extended polymer chains of various polymers as a function of the number of segments, i.e., the length of polymer chains. In general, the thermal conductivity of single extended polymer chains is 1-2 orders of magnitude higher than that of their bulk counterparts[121], 0.1-1 W/mK. The thermal conductivity of all types of simulated polymer chains increases when the number of segments (or chain length) increases. We note here that thermal conductivity of polymer chains with different monomer types is compared under the same number of segments.

Figure III. 2(a) shows that the thermal conductivity of the chains with aromatic-backbone structures is higher than that of aliphatic-backbone structures by comparing the thermal conductivity of *poly(p-phenylene)* and *polybenzimid* with that of *polyethylene* when the number of segments is larger than 20. The thermal conductivity of *polybenzimid* can be 4 times higher than that of *polyethylene* when the number of segments is 200. In the aromatic-backbone

structure, carbon atoms form a planar ring by the conjugated π bonds. The sp^2 hybridization in aromatic-backbone structure is similar as that in CNT and graphene, which makes this structure very stiff. Thermal conductivity usually increases with the increasing stiffness of the backbone as discussed in Ref. [[116]]. Figure III.2(b) shows that the thermal conductivity of *polyacetylene* is higher than that of *polyethylene* due to the stronger double bonds in *polyacetylene*. The bond strength of a double carbon-carbon bond is 1.82 times stronger than that of a single carboncarbon bond.[118] The thermal conductivity of single extended polymer chains with double carbon-carbon bonds is up to 2.6 times that of a *polyethylene* chain. Interestingly, the thermal conductivity of *polybutadiene* is much lower than that of *polyacetylene* and *polyethylene* due to the bond-strength disorder, where there are mixing single and double carbon-carbon bonds in polybutadiene. Figure III.2(c) shows that the thermal conductivity of poly(methylene oxide) is lower than that of *polyethylene* due to the mass disorder in the chain, where the oxygen atoms are incorporated in *poly(methylene oxide)* compared to *polyethylene*. The thermal conductivity of poly(ethylene oxide) is much lower than that of both polyethylene and poly(methylene oxide) due to both the bond-strength disorder and mass disorder presented in the chain compared to *polyethylene*. For instance, the thermal conductivity of *poly(ethylene oxide)* is only 1/25 as that of polyethylene when the number of segments is 600 or larger. Similarly, the thermal conductivity of *poly(phenylene ether)* is lower than that of *poly(p-phenylene)* due to the mass disorder in the chain compared to *poly(p-phenylene)*. All the atoms or functional groups incorporated into the aliphatic/aromatic pristine chains can be viewed as mass disorder. Generally, these mass disorders in the chain create localized vibrational modes, which impede the energy transport with delocalized, long-wavelength phonon modes and significantly reduce the thermal conductivity as that in alloys.[59] Similarly, Figure III. 2(d) shows the dependence

of the thermal conductivity of single extended polymer chains of the five polymers as a function of chain length. Similar trends are seen as those observed in Fig. III.2(c).



(b)







(d)

Figure III. 2. The thermal conductivity of single extended polymer chains of various polymers as a function of the number of segments: (a) effect of aromatic backbone; (b) effect of double bonds and bond-strength disorder compared to polyethylene; (c) effect of bond-strength disorder/mass disorder by incorporation of oxygen atoms in polyethylene; (d) the thermal conductivity of single extended polymer chains of five polymers as a function of chain length.

Indeed, a force must be applied at both ends of the chain to keep the chain in the extended configurations. All the motions of the monomers, including vibrational, translational, and torsional movement, are still allowed in the simulations. However, the motions of the monomers might become restricted depending on the force applied. The force applied at the chain ends eventually evolves into the tensile stress on the polymer chains. The tensile stress in the single extended polymer chains might have some effects on the thermal conductivity values compared to that in the coiled state of the polymer chains in bulk counterpart, as we showed in our previous chapter.[122] We have calculated how large of an effect that the tensile stress might have on the thermal conductivity in single extended polymer chains. Deformation simulation was performed on all the extended polymer chains studied. We found that the *poly(p-phenylene)* chain is the stiffest amongst all the polymer chains. When the *polyethylene* chain is stretched to have the same tensile stress as in the *poly(p-phenylene)* chain with the same number of segments, the increase of the thermal conductivity of *polyethylene* chain is less than 18%. The effect of the tensile stress on the thermal conductivity of polymer chains is a small factor compared to the effects of the monomer type and the chain length, thus the stress effect of extended polymer chains does not change the conclusions in this work.

III.5 The average phonon relaxation time in single extended chains

In this section, we calculate the averaged phonon relaxation time and analyze the dominant phonon scattering mechanisms in single extended polymer chains of different chain lengths. The averaged phonon relaxation time $\bar{\tau}$ can be calculated using the kinetic theory $\bar{\tau} = 3\kappa/C\bar{v}^2$, where κ is the thermal conductivity of an extended polymer chain, *C* is the volumetric heat capacity, and \bar{v} is the averaged phonon group velocity.[2] We calculated the volumetric heat capacity *C* of different extended polymer chains using equilibrium molecular dynamics simulation. The *NVT* ensemble was applied for 2 ns to calculate the fluctuations in energy and temperature. The heat capacity is calculated by $C = (\langle E^2 \rangle - \langle E \rangle^2)/Vk_B < T >^2$, where k_B is the Boltzmann constant, *E*, *V* and *T* are the total energy, volume, and temperature of the simulated system, and <> represents the ensemble average.[123] The averaged phonon group velocity \bar{v} is calculated from the phonon dispersion curves of the single extended polymer chains, which is obtained by the standard lattice dynamics calculations using the GULP software package.[124] The phonon group velocity $v(\omega, p)$ at vibrational frequency ω and branch *p* is calculated as $v(\omega, p) = (\partial \omega / \partial q)_p$, where *q* is the averaged phonon dispersion curve obtained. The averaged phonon group velocity \bar{v} is the arithmetic average over all the phonon dispersion branches and vibrational frequencies.

Using the Mathiessen rule, the averaged phonon relaxation time $\bar{\tau}$ can be written as,

$$\frac{1}{\overline{\tau}} = \frac{1}{\tau_1} + \frac{1}{\tau_2}, \qquad (\text{III.1})$$

where τ_1 and τ_2 are the relaxation time of phonon-boundary scattering and intrinsic phonon relaxation time, respectively. By assuming τ_1 is L/\bar{v} , where L is the length between the two thermal reservoirs (hot region and cold region), τ_2 can then be calculated from Eq.(III.1).



Figure III. 3. The averaged phonon boundary relaxation time τ_1 and the averaged intrinsic phonon relaxation time τ_2 of polyethylene, poly(p-phenylene), and polybutadiene chains as a function of the number of segments.

Figure III. 3 shows the relaxation time τ_1 of phonon-boundary scattering and intrinsic phonon relaxation time τ_2 of *polyethylene*, *poly(p-phenylene*), and *polybutadiene* chains as a function of the number of segments. First, we analyze the dominant phonon transport mechanism in the single extended chains of different chain lengths. Phonon-boundary scattering dominates the phonon scattering mechanisms in a short *polyethylene* chain (number of segments N < 60). For example, the phonon boundary relaxation time τ_1 is 3.13 ps whereas the intrinsic phonon relaxation time τ_2 is 5.69 ps in a 20-segment *polyethylene* chain. The thermal

conductivity of short *polyethylene* chains are limited by the phonon-boundary scattering due to the limited length of the chain. Intrinsic phonon scattering dominates in a long polyethylene chain (N>200). For example, the phonon boundary relaxation time τ_1 is 36.25 ps while the intrinsic phonon relaxation time τ_2 is 10.54 ps in a 240-segment *polyethylene* chain. The dominant phonon transport mechanism in the *poly(p-phenylene*) chain is similar as that in the polyethylene chain. Phonon boundary scattering dominates the phonon scattering mechanisms in a short chain (N < 100) while intrinsic phonon scattering dominates in a long polymer chain (N>200). If the polymer chain has any kind of "disorder", such as bond-strength disorder in polybutadiene compared to polyethylene, the intrinsic phonon scattering has a dominant effect in phonon transport, as we can see that τ_2 is always shorter than τ_1 . Then, we compare the phonon boundary relaxation time τ_1 among polyethylene, poly(p-phenylene), and polybutadiene chains. The phonon boundary relaxation time τ_1 of both poly(p-phenylene) and polybutadiene is larger than that of *polyethylene*. This result is due to the fact that the averaged phonon group velocity of *poly(p-phenylene)* is about half that of *polyethylene* due to the aromatic backbone. Similarly, the averaged phonon group velocity of *polybutadiene* is about 60% that of *polyethylene* due to the bond-strength disorder in *polybutadiene* compared to *polyethylene*. Last, we compare the intrinsic phonon relaxation time τ_2 among polyethylene, poly(p-phenylene), and polybutadiene chains. The intrinsic phonon relaxation time τ_2 of *poly(p-phenylene)* is much longer than that of *polyethylene* due to the aromatic backbone. The intrinsic phonon relaxation time τ_2 of polybutadiene is shorter than that of polyethylene due to the bond-strength disorder.

III.6 Length-dependent thermal conductivity



Figure III.4. Schematic drawing shows the normal vector of planar aromatic rings \mathbf{n}_1 and \mathbf{n}_2 and the backbone vector \mathbf{e}_1 and \mathbf{e}_2 in the aromatic backbone structure.

Figure III. 2 (c) shows a very different length-dependent thermal conductivity of poly(p-phenylene) and $poly(phenylene \ ether)$ than that of others, which converges when the number of segments increases. Such a convergent thermal conductivity indicates that the intrinsic phonon relaxation time decreases rapidly with increasing chain length, as can be seen in Fig. III. 3 for the poly(p-phenylene) chain. This occurs because the planar aromatic rings in the single extended chains of poly(p-phenylene) and $poly(phenylene \ ether)$ can rotate around an imaginary axis formed by the two atoms connecting the adjacent functional groups. To understand how these rotations lead to orientation disorder in a chain and the differences between aliphatic chains and aromatic chains, we define the orientational parameter P_{2b} due to the backbone alignment as $P_{2b} = 1.5 < (e_1 \cdot e_2)^2 > -0.5$, where e_1 and e_2 are the backbone vector and < > represents the

ensemble average, which is similar to the commonly used definition in an aliphatic chain.[122] Similarly, we define the orientational parameter P_{2rot} due to the planar aromatic ring rotation in the chain as $P_{2rot} = 1.5 < (\mathbf{n_1} \cdot \mathbf{n_2})^2 > -0.5$, where n_1 and n_2 are the normal vectors of the planar aromatic rings. A schematic example is shown in Fig. III. 4 for the definition of the normal vector of planar aromatic rings n_1 and n_2 and the backbone vector e_1 and e_2 in the aromatic backbone structure. Table III.2 shows the orientational parameters P_{2b} and P_{2rot} in poly(pphenylene) and poly(phenylene ether) with two different chain lengths. The orientational parameters due to the backbone alignment, P_{2b} , for 16-segment and 400-segment poly(p*phenylene*) are close to 1, which shows that the chain is still in the extended state during the simulation, the same as in the case of aliphatic chain. However, the orientational parameters due to the planar aromatic ring rotation P_{2rot} are 0.61 and 0.27 for 16-segment and 400-segment chains, respectively, which shows that the rotation misaligns the planar aromatic rings, creating the orientation disorders in the chain for phonon transport. P_{2rot} in a 16-segment chain is larger than that in a 400-segment chain, which indicates that more orientation disorders are generated in a relatively longer chain. The situation is similar in *poly(phenylene ether)*, where the rotation of aromatic rings in the chain induces changes in chain orientation. Such increase of orientation disorders with the increasing chain length of planar aromatic rings explains well the converging length-dependent thermal conductivity in the single extended chains of *poly(p-phenylene)* and poly(phenylene ether).

Table III.2. The orientational parameters due to the backbone alignment, P_{2b} , and the orientational parameters due to the planar aromatic ring rotation in the chain, P_{2rot} , in poly(p-phenylene) and poly(phenylene ether) chains with two different chain lengths.

	poly(p-phenylene)		poly(phenylene ether)		
	16 segments	400 segments	16 segments	400 segments	
P_{2b}	0.98	0.97	0.49	0.45	
P _{2rot}	0.61	0.27	0.16	0.09	

Other than *poly(p-phenylene)* and *poly(phenylene ether)*, most of the single extended polymer chains studied in Table III.1 have a diverging length-dependent thermal conductivity. Similar diverging thermal conductivity behavior has been discussed in a number of low dimensional materials such as the harmonic lattice model,[125] 1-D nonlinear lattice model,[126] Si nanowire,[33] CNT,[127] and more recently a single *polyethylene* chain.[63] Similar to *Li et al.*,[128] we can fit the diverging thermal conductivity κ with the chain length *L* using $\kappa \sim L^{\beta}$ for these six types of polymer chains in Fig. III. 2. There are two regimes of phonon transport mechanisms in single extended polymer chains[116]: (1) phonon propagates ballistically across the polymer chain before reaching the reservoir if the intrinsic phonon relaxation time is much larger than the relaxation time of phonon-boundary scattering; Such phonon-boundary scattering dominated transport is often called ballistic transport. (2) Phonon

experiences numerous scattering events if the intrinsic phonon relaxation time is short, which is often called diffusive transport. [129] According to Li et al., [128] β indicates the competition between diffusive and ballistic phonon transport, where diffusive phonon transport leads to $\beta = 0$ and ballistic phonon transport leads to $\beta = 1$. The weaker the phonon scattering, the closer is the β value to 1. Table III.1 compares the exponent β for polymer chains with different monomer types. *Polyacetylene* has a higher β value than *polyethylene* due to the much weaker intrinsic phonon scattering mechanism in polyacetylene than that in polyethylene. Polybutadiene and *poly(ethylene oxide)* have a lower β value than *polyethylene*, and *poly(phenylene ether)* has a lower β value than *poly*(*p*-*phenylene*), which is due to the increased intrinsic phonon scattering in a chain with bond-strength/mass disorder compared to that in an otherwise aliphatic/aromatic pristine chain. However, *poly(methylene oxide)* chain does not seem to obey this rule. The β value of *poly(methylene oxide)* is even higher than that of *polyethylene*. Very likely, even though the mass disorder in *poly(methylene oxide)* creates localized vibrational modes, the anharmonic forces in *poly(methylene oxide)* (which corresponds to the third-order or even higher-order terms in the force field expression) induces frequent energy exchanges between the localized modes and leads to an increase in β value.[130] The fitting of thermal conductivity κ with chain length L using the formula $\kappa \sim L^{\beta}$ is merely used to compare the diffusive phonon transport and ballistic phonon transport in polymer chains. The β value indicates the relatively dominant phonon transport mechanism. The β value does decrease from a short chain to a longer chain. However, this formula is by no way rigorously quantitative and not suitable for extrapolating to chains with infinite length. Figure III. 2(d) shows that the fitting value of β is 0.411 from 5nm to 1000nm and the value is 0.438 from 5nm to 230nm. Likely, the β value would decrease gradually with even

longer chain length (much larger than the phonon mean free path) due to more intrinsic phonon scattering.

III.7 Summary of this chapter

Atomistic simulation studies were conducted for analyzing phonon transport mechanisms in single extended polymer chains of various polymers as a function of polymer chain length. It is found that the thermal conductivity of single extended polymer chains can be 1-2 orders of magnitude higher than their bulk counterparts. Moreover, the thermal conductivity of single extended polymer chains is a strong function of monomer type. For example, the thermal conductivity of the extended polymer chain with an aromatic backbone can be up to 5 times as high as that of a *polyethylene* chain while the thermal conductivity of the extended polymer chains with bond-strength or mass disorder can be only 1/25 as that of a *polyethylene* chain. Phonon-boundary scattering dominates the phonon scattering mechanisms in a short polymer chain (e.g. number of segments N < 50 in the *polyethylene* chain) whereas intrinsic phonon scattering dominates in a long polymer chain (e.g. number of segments N>200 in the polyethylene chain). Intrinsic phonon scattering has a dominant effect in phonon transport if the polymer chain has "disorder" compared to the aliphatic/aromatic pristine chain. Moreover, the competition between ballistic phonon transport and diffusive phonon transport in the chain leads to a diverging length-dependent thermal conductivity of a single extended polymer chain.

CHAPTER IV IMPROVEMENT ON THE PUMP-AND-PROBE CHARACTERIZATION SYSTEM

In chapter II and III, we apply modeling and simulation techniques to investigate the effects of chain orientation, monomer type, and chain length on the thermal transport in polymers and polymer chains. In this chapter, we improve the ultrafast pump-and-probe characterization system used to measure the thermal properties of nanostructured organic or hybrid organicinorganic materials, for better understanding of the thermal transport mechanisms in nanostructured polymers. In section IV.1, the basic principle of the ultrafast pump-and-probe characterization system built in the CU-Boulder NEXT lab is discussed. This characterization system is widely used to measure the thermal properties of nanostructures and interfaces in recent years. However, the capability of this system has to be improved for nanostructured polymer materials. In section IV.2, the simultaneous measurement of heat capacity and thermal conductivity of bulk and thin film materials using frequency-dependent pump-and-probe method is discussed. This development enables us to measure the new nanostructured polymer materials with obtaining both the thermal conductivity and heat capacity. In section IV.3, we show the development in the measurement of the in-plane thermal conductivity of thin film materials. In section IV.4, the development on the measurement of the special materials that needs protection using the 'pumping-from-the-backside' approach is discussed.



IV.1. Ultrafast pump-and-probe characterization system

Figure IV.1.1. The pump-and-probe characterization system in the NEXT lab in University of Colorado at Boulder. (a)The sample configuration usually employed in the measurement of thin film. (b) The photo of the characterization system in the lab.

To systematically study the thermal transport in nanostructured polymers, we generally need the characterization tools for thermal properties of nanostructures, such as thin films. Thermal properties of nanostructures may deviate significantly from their bulk counterparts due to the size effects of electron and phonon transport.[1, 2, 6, 34, 35, 82] There has been great interest in the thermal properties of thin films, which leads to the development of various transient measurement techniques.[131-137] The most widely used techniques can be roughly grouped into $3-\omega$ method[138-142] and transient thermoreflectance (TTR) methods including frequency-domain thermoreflectance (FDTR) method,[143-145] and time-domain thermoreflectance (TDTR) method.[131, 146] In the TDTR method, repeated laser pulses are

divided into pump and probe beams. The pump beam excites a sample and the probe beam measures the changes in the reflectivity or diffraction, which is temperature-dependent. The probe beam arrives at the sample surface at a different time intervals after the pump beam through a mechanical delay stage. The pump beam is modulated so that the signals can be measured by the lock-in amplifier. The temporal decay of the measured signals is used to deduce thermal conductivity κ and interfacial thermal conductance *G* with a heat transfer model through a multi-parameter fitting process. Figure IV.1.1 shows the basic measurement principle, the sample configuration, and the pump-and-probe characterization system in the NEXT lab in University of Colorado at Boulder.

Figure IV.1.2 shows the schematic diagram of the optical paths of our ultrafast pump-andprobe thermoreflectance system. The Spectra-Physics Tsunami femtosecond Ti-sapphire laser, pumped by a 10W diode laser, emits a train of 150 fs pulses at a repetition rate of 80 MHz. The central wavelength is 800 nm and the power per pulse is roughly 19 nJ. The laser pulse is split into pump and probe beams. The pump beam passes through an electro-optic modulator (EOM) that modulates the beam at a frequency between 0.1 and 20 MHz. The modulation frequency serves as the reference for a lock-in amplifier which extracts the thermoreflectance signal from the background. The second-harmonic generator (SHG) is used to double the frequency of the probe pulses, which produces a light train with a central wavelength of 400 nm and are timedelayed relative to the pump pulses with the mechanical stage. Such a near infrared (NIR)-blue two-color system has significant advantages over a single-color one since it is easier to isolate the scattered pump light from the detector by using dielectric mirrors and color filters which could have a transmission of 10⁻⁹ at the wavelength around 800 nm, much more efficient than a polarization arrangement. This also allows us to use a simple coaxial geometry where pump and probe beams are focused by the same objective lens, simplifying the overlap of pump and probe pulses and producing less deformation of the laser profile. In the TDTR measurement, an inductor is placed between the output of the photodiode and the lock-in amplifier to maximize the response at the modulation frequency and remove the higher harmonic components in the measured signal.[147] In the measurement, the signal needs a phase correction by adjusting the phase of the lock-in until the out-of-phase component of the signal is constant as the stage moves across the zero delay time.[143, 147]



Figure IV.1.2. Schematic diagram of the optical paths of our ultrafast pump-and-probe thermoreflectance system in the NEXT lab.

Even though this characterization system has become a standard system for measuring cross-plane thermal properties of nanostructures in recent years, there are further developments in this thesis to enlarge its capability. The first improvement is to enable the simultaneous measurement of the heat capacity and thermal conductivity of bulk and thin film materials. In the TTR methods, the heat capacity is often used as an input to obtain the thermal conductivity of the measured materials.[145, 148] As such, the accuracy of the thermal conductivity measurement depends strongly on the heat capacity input. Measuring the heat capacity of nanostructures such as thin films and nanowires are very challenging, which often requires time-consuming and costly micro/nano-fabrication steps.[149] A common practice is adapting bulk values for the heat capacity of nanostructures, where the bulk values can be easily measured, such as using the differential scanning calorimeter.[150] This is usually a reasonable assumption for most of the well-studied dense materials, such as aluminum (Al), silicon (Si), and silicon dioxide (SiO₂), since nanostructuring does not significantly change the heat capacity.[133, 151] However, for many new materials, it is either questionable to assume bulk heat capacity for thin films or difficult to obtain the bulk form of these new materials for a conventional heat capacity measurement. The material development/discovery cycle could be significantly shortened if thermal conductivity and heat capacity of materials can be measured simultaneously or even just using the same equipment. Schmidt et al. [143] showed that simultaneous measurement of thermal conductivity and heat capacity of bulk Si and sapphire samples using FDTR is possible if the difference between the sensitivities of these two properties is larger than 0.05. The simultaneous measurement of heat capacity and thermal conductivity of bulk and thin film materials is discussed in section IV.2.

Thermal conductivity of most crystalline and thin film materials is anisotropic, which is generally caused by the intrinsic atomic/molecular structure, or due to the size effects associated with boundary or interface scattering of heat carriers.[152-154] Many techniques have been

developed for thermal conductivity measurement with some suitable for anisotropic thermal conductivity measurement. For example, both the cross-plane (i.e. perpendicular to the sample surface) and in-plane (*i.e.* parallel to the sample surface) thermal conductivity of thin film can be measured using the 3- ω method by varying the width of the thin film metal lines, which serves as both heaters and temperature sensors.[155, 156] The AC laser calorimetry method, where a modulated laser beam heats the sample surface and the temperature change is detected at another location on the sample surface, has often been used for anisotropic thermal conductivity of thin films.[157, 158] However, these established methods usually can only measure anisotropic thermal conductivity of thin films with thicknesses on the order of microns or larger. On the other hand, tremendous progress has been made over the past few years in measuring the crossplane thermal conductivity of ultra-thin films, with thickness on the orders of 1-100 nm, using the ultrafast-laser based TTR method. [76, 82] In typical experimental conditions used in TTR method (e.g. a modulation frequency of 10 MHz and a beam spot radius of 15-25 µm), usually only cross-plane thermal properties are measured since the beam spot sizes (on the order of 10 μ m) are usually much larger than the thermal diffusion length (~50 nm - 1 μ m) in the material. [133]

To measure the in-plane thermal conductivity of thin film materials using the TTR method, the experimental conditions need to be chosen where the in-plane thermal diffusion length is comparable to the beam spot size. Schmidt *et al.*[159] extended the TTR modeling to include multilayers with anisotropic thermal conductivity and demonstrated the ability of TTR to measure the anisotropic thermal conductivity of bulk materials and transducer film by scanning a large range of modulation frequencies (0.025-20 MHz).[143, 160] The in-plane thermal diffusion length in the measured material is comparable to the beam spot size when the sample is heated

by the pump beam at a relatively low modulation frequency. Feser *et al.*[161] demonstrated the measurement of anisotropic thermal conductivity of bulk materials and transducer film through a series of offset laser spots enabled by a two-axis goniometer. The pump beam scans through the sample while the probe beam is kept stationary, then the thermal diffusion in the radial or inplane direction can be captured in the measured signal. In this thesis, we demonstrate an alternative approach for measuring the anisotropic thermal conductivity of bulk and thin film materials using varied beam spot sizes based on the TTR method, which is discussed in section IV.3.

Another important improvement on the TTR experiment system is to enable the measurement of special materials that requires protection during the sample preparation. For instance, certain soft materials or biomaterials cannot sustain at high fabrication temperatures (~100 $^{\circ}$ C), such as the protein or DNA, which will decompose when exposed at the chamber for depositing Al thin film. Pumping from the backside enables the measurement of those materials, which is discussed in section IV.4.

IV.2 Simultaneous measurement of heat capacity and thermal conductivity of bulk and thin film materials

In this section, we demonstrate the realization of simultaneous measurement of thermal conductivity κ and volumetric heat capacity *C* for both bulk and thin film materials using a frequency-dependent TDTR method. This section is organized as following. In Section IV.2.1, the heat transfer model for frequency-dependent TDTR measurement is analyzed to find how
different combinations of κ and *C* determine TDTR signals at different frequency ranges. Simultaneous measurement of thermal conductivity and volumetric heat capacity of bulk Si and SiO₂ thin film samples are demonstrated in Section IV.2.2.A and IV.2.2.B, respectively.

IV.2.1 Heat transfer analysis

To analyze the possibility for simultaneous measurement of thermal conductivity and heat capacity of bulk and thin film materials, we start with the heat transfer model in typical sample configurations of TTR measurements. Figure IV.2. 1(a) shows the simplified working principle of a typical ultrafast laser-based TDTR measurement.[82, 144, 162, 163] The details of experiment setup and the data reduction scheme have been presented in literature.[144, 146, 162]

Figures IV.2.1(b) and IV.2.1(c) show the schematics of the typical bi-layer (for bulk materials) and tri-layer (for thin films) sample configurations used in TTR techniques, respectively. The bi-layer structure consists of a metallic thin film and a substrate with unknown thermal properties. Similarly, the tri-layer structure consists of a metallic thin film, a thin film with unknown thermal properties, and a substrate with known thermal properties. The metallic thin film with a thickness of ~100 nm is usually deposited on the samples, which serves both as an energy absorber for the laser beams and as the temperature transducer for the probe beam. The heat of the pump beam is absorbed by the surface of the metallic layer, and then conducted through the layers and interfaces in the sample. In Section IV.2.2.A, the heat transfer model based on the transform matrix method for heat transfer through layers and interfaces[133, 144, 146, 162] and the lock-in signal are presented. More details are placed in the Appendix I to ease the reading.



Figure IV.2.1. (a) The working principle of a typical ultrafast laser-based TDTR measurement. (b) A bi-layer sample configuration with a metallic thin film (layer 1) on a bulk substrate (layer 3) with unknown thermal properties. The interfacial thermal conductance between layer 1 and layer 3 is noted as G_2 . (c) A tri-layer sample configuration that consists of a metallic thin film (layer 1), a thin film with unknown thermal properties (layer 3), and a substrate (layer 5). The interfacial thermal conductance between layer 1 and layer 3 is noted as G_2 . The interfacial thermal conductance between layer 3 and layer 5 is noted as G_4 .

IV.2.1.A. Heat transfer model and lock-in signal

Considering a cylindrical heating spot on the metallic transducer that absorbs pulsed laser heating, *e.g.* Figs. IV.2.1(b) and 1(c), the transient heat conduction equation for each layer can be written as the following,

$$\frac{\kappa_r}{r}\frac{\partial}{\partial r}\left[r\frac{\partial\widetilde{\theta}(r,z)}{\partial r}\right] + \kappa_z \frac{\partial^2\widetilde{\theta}(r,z)}{\partial z^2} = C\frac{\partial\widetilde{\theta}(r,z)}{\partial t}, \qquad (IV.2.1a)$$

where *r* is the radial coordinate, *z* is the cross-plane coordinate (in the depth direction), *t* is time, $\tilde{\theta}$ is the temperature, *C* is the volumetric heat capacity, and κ_r and κ_z are the in-plane and cross-plane thermal conductivity, respectively. To solve the equation with radial symmetry, the zeroth-order Hankel transform is performed to simplify Eq. (IV.2.1a), which yields[162]

$$-\kappa_r x^2 \theta(z) + \kappa_z \frac{\partial^2 \theta(z)}{\partial z^2} = C \frac{\partial \theta(z)}{\partial t}, \qquad (\text{IV.2.1b})$$

where *x* is the Hankel transform variable, and θ is the temperature in the Hankel transform. Due to the periodic laser heating at the modulation frequency ω , the solution for the temperature field in Eq. (IV.2.1b) should depend on the modulation frequency. Applying the Fourier transform, Eq. (IV.2.1b) becomes

$$\frac{\partial^2 \theta(\omega, z)}{\partial z^2} = q_j^2 \theta(\omega, z), \qquad (IV.2.2)$$

where $\theta(\omega, z)$ is the temperature at any arbitrary point z in the depth direction at the modulation frequency ω , and the thermal wave vector q_i of the j^{th} layer is

$$q_{j} = \sqrt{\frac{\kappa_{rj}x^{2} + iC_{j}\omega}{\kappa_{zj}}} = \sqrt{\frac{\kappa_{rj}}{\kappa_{zj}}x^{2} + \frac{i\omega}{D_{zj}}} \quad , \tag{IV.2.3}$$

where κ_{rj} and κ_{zj} are the in-plane and cross-plane thermal conductivity of the j^{th} layer, respectively. C_j is the volumetric heat capacity of the j^{th} layer. D_{zj} is the cross-plane thermal diffusivity of the j^{th} layer, *i.e.* $D_{zj} = \kappa_{zj}/C_j$. The transform matrix method described by Carslaw and Jaegar[164] is adopted to solve the heat conduction equation in a multilayer structure. The temperature of the sample surface is given as

$$\theta_1 = -\frac{D^+}{C^+}F_1$$
, (IV.2.4)

where θ_I and F_I are the temperature and heat flux on the top side of the multilayer stack, C^+ and D^+ are the elements of the transform matrix, which is calculated in detail in Appendix.

The frequency-domain thermal response $H(\omega)$ of the surface temperature change in real space can then be found by taking the inverse Hankel transform of Eq. (IV.2.4) with the weighting using the probe intensity distribution which is taken as a Gaussian spot (see Appendix for details):

$$H(\omega) = v \frac{Q_{pump}Q_{probe}}{2\pi} \int_0^\infty x(-\frac{D^+}{C^+}) \exp\left(\frac{-x^2 R_{pp}}{8}\right) dx, \qquad (IV.2.5)$$

where ν is the thermoreflectance coefficient of the metal transducer; Q_{pump} and Q_{probe} are the power absorbed from pump and probe beams, respectively; the average beam spot radius

$$R = \sqrt{R_{pump}^2 + R_{probe}^2}, \qquad (IV.2.6a)$$

where R_{pump} and R_{probe} are the $1/e^2$ radius of pump and probe beam intensity distribution as a Gaussian spot, respectively. Similar to the analysis in Ref. [146], the upper limit x_{max} of the integral in Eq. (IV.2.5) can be set to

$$x_{\rm max} = \sqrt{32/R^2}$$
, (IV.2.6b)

without a significant loss of accuracy since $\left(-\frac{D^+}{C^+}\right)\exp\left(\frac{-x^2R^2}{8}\right)$ decreases rapidly when x gets larger.

A lock-in amplifier picks up the fundamental harmonic component of the probe signal $Z(\omega)$ at the modulation frequency ω and rejects all other components. In the case of pulsed pump and probe beams, $Z(\omega)$ is given as,[146]

$$Z(\omega) = \sum_{N=-\infty}^{\infty} H(\omega + N\omega_s) \exp(iN\omega_s \tau), \qquad (IV.2.7)$$

where N is an integer, ω_s is the probe pulsing frequency, τ is the delay time between the arrivals of the probe and pump pulses to the sample surface, and $H(\omega + N\omega_s)\exp(iN\omega_s\tau)$ is the weighted sampling frequency-domain response of the surface temperature change in real space. The largest contribution for the sum in Eq. (IV.2.7) is the response at the modulation frequency $H(\omega)$. Similar to Ref. [146], the ratio of the in-phase signal V_{in} and out-of-phase signal V_{out} ,

$$-V_{in}/V_{out} = -\operatorname{Re}(Z(\omega))/\operatorname{Im}(Z(\omega)), \qquad (IV.2.8)$$

is used in this work as the measurement signal for data analysis since the experimental errors due to the fluctuation in laser power are minimized and measuring the values of $v_{,}Q_{pump}$ and Q_{probe} can be avoided.

In Section IV.2.2.B and IV.2.2.C, we analyze how different combinations of κ and C determine the thermal response $H(\omega)$ in TDTR signals at different modulation frequency ranges for the bi-layer and tri-layer sample configurations, respectively.

IV.2.1.B. Bulk samples

For a bi-layer structure (bulk samples), the term $-D^+/C^+$ in the thermal response $H(\omega)$ is calculated by substituting the matrix elements for each layer or interface for the transform matrix, which is

$$-\frac{D^{+}}{C^{+}} = \frac{\frac{\gamma_{3}}{\gamma_{1}}m + \frac{\gamma_{3}}{G_{2}} + 1}{\gamma_{1}(\frac{\gamma_{3}}{\gamma_{1}} + \frac{\gamma_{3}}{G_{2}}m + m)},$$
 (IV.2.9)

where $m = \tanh(q_1d_1)$ with the thermal wave vector q_1 as defined in Eq. (IV.2.3) and the thickness d_1 of the metallic transducer film, G_2 is the interfacial thermal conductance between the metallic film and the bulk substrate, $\gamma_1 = q_1\kappa_{z1}$ with the cross-plane thermal conductivity of the metallic film κ_{z1} and $\gamma_3 = q_3\kappa_{z3}$ with the thermal wave vector q_3 as defined in Eq. (IV.2.3) and the cross-plane thermal conductivity κ_{z3} of the substrate.

From Eq. (IV.2.5) and (IV.2.9), the dominant thermal property in the thermal response $H(\omega)$ can be analyzed by considering the γ_3 term, which is the only variable related to the unknown thermal properties of the target bulk substrate to be measured. Generally, this analysis compares the averaged beam spot radius R with the radial thermal diffusion length L_r , to identify whether the heat transfer is more dominant in the radial direction or in the cross-plane direction. The radial thermal diffusion length L_r is defined as

$$L_r = \sqrt{2\kappa_{r3}/\omega C_3}, \qquad (IV.2.10)$$

where κ_{r3} and C_3 are the thermal conductivity in the radial direction and the volumetric heat capacity of the bulk substrate, respectively.

When the radial thermal diffusion length is much smaller than one fourth of the averaged beam spot radius,

$$L_r << \frac{1}{4}R$$
, (IV.2.11a)

radial heat transfer can be neglected. Considering that *R* is related to x_{max} by Eq. (IV.2.6b), Eq. (IV.2.11a) can be rewritten as

$$L_r^2 << \frac{2}{x_{\max}^2} \sim \frac{2}{x^2}$$
, (IV.2.11b)

The γ_3 term in Eq. (IV.2.9) then becomes

$$\gamma_{3} = \kappa_{z3}q_{3} = \kappa_{z3}\sqrt{\kappa_{r3}x^{2}/\kappa_{z3} + i\omega C_{3}/\kappa_{z3}} = \sqrt{\kappa_{r3}\kappa_{z3}x^{2} + i\omega\kappa_{z3}C_{3}}$$
$$= \sqrt{i\omega\kappa_{z3}C_{3}}\sqrt{1 - ix^{2}L_{r}^{2}/2} \approx \sqrt{i\omega\kappa_{z3}C_{3}}$$
(IV.2.11c)

This simplification tells that the thermal response is determined by the thermal effusivity $\sqrt{\kappa_{z3}C_3}$ at the high frequency limit when

$$\omega >> \frac{32\kappa_{r3}}{R_{pp}C_3}.$$
 (IV.2.11d)

Here, Eq. (IV.2.11d) is obtained by plugging Eq. (IV.2.10) into Eq. (IV.2.11a). Under this condition, the thermal effusivity $\sqrt{\kappa_{z3}C_3}$ determines the one-dimensional plane wave solution under the periodic planar heating condition, because the radial heat transfer can be neglected.[145, 146, 164]

When the radial thermal diffusion length is much larger than one fourth of the averaged beam spot radius,

$$L_r >> \frac{1}{4}R$$
, (IV.2.12a)

radial heat transfer dominates the transport. Eq. (IV.2.12a) can be rewritten as

$$L_r^2 >> \frac{2}{x_{\max}^2} \sim \frac{2}{x^2}$$
, (IV.2.12b)

The γ_3 term in Eq. (IV.2.9) then becomes

$$\gamma_3 = \sqrt{\kappa_{r_3}\kappa_{z_3}x^2 + i\omega\kappa_{z_3}C_3} = \sqrt{i\omega\kappa_{z_3}C_3}\sqrt{-ix^2L_r^2/2 + 1} \approx \sqrt{\kappa_{r_3}\kappa_{z_3}}x. \quad (IV.2.12c)$$

This simplification tells that the thermal response is determined by the averaged thermal conductivity $\sqrt{\kappa_{z3}\kappa_{r3}}$ at the low frequency limit when

$$\omega \ll \frac{32\kappa_{r_3}}{R^2 C_3}.$$
 (IV.2.12d)

Here, Eq. (IV.2.12d) is obtained by plugging Eq. (IV.2.10) into Eq. (IV.2.12a). Under this condition, the averaged thermal conductivity $\sqrt{\kappa_{z3}\kappa_{r3}}$ determines the three-dimensional spherical-wave quasi-steady state solution under a periodic point source heating condition, because radial heat transfer is dominant.[145]

When the radial thermal diffusion length is comparable to one fourth of the averaged beam spot radius, *i.e.* $L_r \sim \frac{1}{4}R$, both thermal conductivity $\sqrt{\kappa_{r3}\kappa_{z3}}$ and thermal effusivity $\sqrt{\kappa_{z3}C_3}$ play a role in the measured thermal response.

Table IV.2.1 summarizes the above analysis, *i.e.*, how different combinations of thermal conductivity and heat capacity determine the thermal response at different ranges of modulation frequency ω in a bi-layer sample configuration. It is challenging to simultaneously measure the thermal conductivities κ_{r3} and κ_{z3} in both radial (in-plane) and cross-plane directions and the heat capacity C_3 since the thermal responses are only determined by the two combinations of these three unknowns, which are thermal conductivity $\sqrt{\kappa_{r3}\kappa_{z3}}$ and thermal effusivity $\sqrt{\kappa_{z3}C_3}$. However, if the target material with unknown thermal properties is nearly isotropic ($\kappa_{r3} \approx \kappa_{z3}$)

or with a known anisotropy $(\kappa_{r_3}/\kappa_{z_3})$, it could be straightforward to extract the two unknown thermal properties κ_{z_3} and C_3 using the thermal response.

Table IV.2.1. Dominant thermal properties in the thermal response at different ranges of modulation frequency ω in a bi-layer sample configuration (bulk materials).

Thermal wave solution	Quasi-steady three-dimensional		One-dimensional
	spherical wave		plane wave
ω	$\omega << \frac{32\kappa_{r_3}}{R^2 C_3}$	$\omega \sim \frac{32\kappa_{r3}}{R^2 C_3}$	$\omega >> \frac{32\kappa_{r_3}}{R^2 C_3}$
L_r vs. R	$L_r >> \frac{1}{4}R$	$L_r \sim \frac{1}{4}R$	$L_r >> \frac{1}{4}R$
γ_3	$\sqrt{\kappa_{r3}\kappa_{z3}}x$	$\sqrt{\kappa_{r_3}\kappa_{z_3}x^2 + i\omega\kappa_{z_3}C_3}$	$\sqrt{i\omega\kappa_{z3}C_3}$
Thermal property	$\sqrt{\kappa_{z3}\kappa_{r3}}$	$\sqrt{\kappa_{z3}\kappa_{r3}}$, $\sqrt{\kappa_{z3}C_3}$	$\sqrt{\kappa_{z3}C_3}$

IIV.2.1.C. Thin film samples

For a tri-layer structure (thin film samples), the term $-D^+/C^+$ in the thermal response $H(\omega)$ is calculated by substituting the matrix elements for each layer or interface for the transform matrix, which is,

$$-\frac{D^{+}}{C^{+}} = \frac{m(\frac{\gamma_{5}}{\gamma_{1}} + \frac{\gamma_{3}}{\gamma_{1}}\frac{\gamma_{5}}{G_{4}}n + \frac{\gamma_{3}}{\gamma_{1}}n) + \frac{\gamma_{5}}{G_{2}} + \frac{\gamma_{3}\gamma_{5}}{G_{2}G_{4}}n + \frac{\gamma_{3}}{G_{2}}n + \frac{\gamma_{5}}{\gamma_{3}}n + \frac{\gamma_{5}}{G_{4}}n + \frac{\gamma_{5}}{G_{4}}n + \frac{\gamma_{5}}{G_{4}}n}{\gamma_{1}\left[\frac{\gamma_{5}}{\gamma_{1}} + \frac{\gamma_{3}}{\gamma_{1}}\frac{\gamma_{5}}{G_{4}}n + \frac{\gamma_{3}}{\gamma_{1}}n + m(\frac{\gamma_{5}}{G_{2}} + \frac{\gamma_{3}\gamma_{5}}{G_{2}G_{4}}n + \frac{\gamma_{3}}{G_{2}}n + \frac{\gamma_{5}}{\gamma_{3}}n + \frac{\gamma_{5}}{G_{4}}n + \frac{\gamma_{5}}{$$

where $m = \tanh(q_1d_1)$ with d_1 defined as the thickness of the metallic film, $n = \tanh(q_3d_3)$ with d_3 defined as the thickness of the thin film, $\gamma_1 = q_1\kappa_{z1}$ with κ_{z1} as the cross-plane thermal conductivity of the metallic film, $\gamma_3 = q_3\kappa_{z3}$ with κ_{z3} as the cross-plane thermal conductivity of the thin film, $\gamma_5 = q_5\kappa_{z5}$ with κ_{z5} as the cross-plane thermal conductivity of the substrate, G_2 is the interfacial thermal conductance between the metallic film and the thin film, and G_4 is the interfacial thermal conductance between the thin film and the substrate. Here q_j (j=1, 3, 5) is the thermal wave vector defined in Eq. (IV.2.3). Apparently the thermal properties of the target layer are reflected in the thermal response $H(\omega)$ through $\gamma_3 n$ and n/γ_3 terms in Eq. (IV.2.13).

When the in-plane thermal diffusion length in the target thin film layer is much smaller than one fourth of the averaged beam spot radius,

$$L_r \ll \frac{1}{4}R, \qquad (\text{IV.2.14a})$$

the cross-plane heat transfer dominates the heat transfer through the thin film layer. Similar to Eqs. (IV.2.11b) and (IV.2.11c), the γ_3 term in Eq. (IV.2.13) can then be simplified to

$$\gamma_{3} = \kappa_{z3}q_{3} = \kappa_{z3}\sqrt{\kappa_{r3}x^{2}/\kappa_{z3} + i\omega C_{3}/\kappa_{z3}} = \sqrt{\kappa_{r3}\kappa_{z3}x^{2} + i\omega \kappa_{z3}C_{3}}$$
$$= \sqrt{i\omega\kappa_{z3}C_{3}}\sqrt{1 - ix^{2}L_{r}^{2}/2} \approx \sqrt{i\omega\kappa_{z3}C_{3}}$$
(IV.2.14b)

Accordingly, under the condition of Eq. (IV.2.14a),

$$q_3 = \gamma_3 / \kappa_{z3} \approx \sqrt{i\omega\kappa_{z3}C_3} / \kappa_{z3} = \sqrt{i\omega/D_{z3}} . \qquad (\text{IV.2.14c})$$

Such simplifications can always be satisfied by choosing the pump and probe spot radius to ensure that $R >> 4L_r$. Assuming a typical heat capacity of 2 J/cm³K and the thermal conductivity of the thin film layer smaller than 10 W/mK, which is true for most of nanostructured materials[6] other than carbon nanotubes and graphene, Eqs. (IV.2.14a) -

(IV.2.14c) are valid for a wide range of modulation frequency 0.1-20 MHz if the radii of pump beam and probe beam are larger than 15 μ m and 5 μ m. This also confirms that most of thermal conductivity measurements in thin films are cross-plane for a wide range of modulation frequency.[133, 165]

The terms $\gamma_3 n$ and n/γ_3 in Eq. (IV.2.13) can then be analyzed by comparing the thickness d_3 of the target thin film layer to the thermal penetration depth L_z , to determine whether the thermal wave penetrates into a limited depth of the layer or throughout the layer. The thermal penetration depth L_z in the j^{th} layer, induced by the frequency modulation of the pump beam, is written as[133]

$$L_z = \sqrt{2D_{zj}/\omega} , \qquad (IV.2.15)$$

where D_{zj} is the cross-plane thermal diffusivity of the j^{th} layer. The term n/γ_3 can be simplified according to the two limit cases of the *tanh* function (when $|a| \le 1/3$, $tanh(a) \approx a$; when $|a| \ge 3$, $tanh(a) \approx 1$) as

$$\frac{n}{\gamma_{3}} = \frac{\tanh(q_{3}d_{3})}{\sqrt{i\omega\kappa_{z3}C_{3}}} = \frac{1}{\sqrt{i\omega\kappa_{z3}C_{3}}} \tanh(\sqrt{\frac{i\omega}{D_{z3}}}d_{3}) = \frac{1}{\sqrt{i\omega\kappa_{z3}C_{3}}} \tanh(\sqrt{2i}\frac{d_{3}}{L_{z}})$$

$$\approx \begin{cases} \frac{1}{\sqrt{i\omega\kappa_{z3}C_{3}}}, & \text{when } \left|\sqrt{\frac{i\omega}{D_{z3}}}d_{3}\right| \ge 3 \text{ or } \left|\sqrt{2i}\frac{d_{3}}{L_{z}}\right| \ge 3, \\ \frac{\tanh(d_{3}\sqrt{i\omega/D_{z3}})}{\sqrt{i\omega\kappa_{z3}C_{3}}}, & \text{when } \frac{1}{3} < \left|\sqrt{\frac{i\omega}{D_{z3}}}d_{3}\right| < 3 \text{ or } \frac{1}{3} < \left|\sqrt{2i}\frac{d_{3}}{L_{z}}\right| < 3, \end{cases}$$

$$(IV.2.16a)$$

$$\frac{d_{3}\sqrt{i\omega/D_{z3}}}{\sqrt{i\omega\kappa_{z3}C_{3}}} = \frac{d_{3}}{\kappa_{z3}}, \quad \text{when } \left|\sqrt{\frac{i\omega}{D_{z3}}}d_{3}\right| \le \frac{1}{3} \text{ or } \left|\sqrt{2i}\frac{d_{3}}{L_{z}}\right| \le \frac{1}{3}$$

Similarly, the term n/γ_3 can be simplified as

$$n\gamma_{3} = \tanh(q_{3}d_{3})\sqrt{i\omega\kappa_{z3}C_{3}} = \tanh(\sqrt{\frac{i\omega}{D_{z3}}}d_{3})\sqrt{i\omega\kappa_{z3}C_{3}} = \sqrt{i\omega\kappa_{z3}C_{3}} \tanh(\sqrt{2i}\frac{d_{3}}{L_{z}})$$

$$\begin{cases} \sqrt{i\omega\kappa_{z3}C_{3}}, & \text{when } \left|\sqrt{\frac{i\omega}{D_{z3}}}d_{3}\right| \ge 3 \text{ or } \left|\sqrt{2i}\frac{d_{3}}{L_{z}}\right| \ge 3, \\ \tanh(\sqrt{\frac{i\omega}{D_{z3}}}d_{3})\sqrt{i\omega\kappa_{z3}C_{3}}, & \text{when } \frac{1}{3} < \left|\sqrt{\frac{i\omega}{D_{z3}}}d_{3}\right| < 3 \text{ or } \frac{1}{3} < \left|\sqrt{2i}\frac{d_{3}}{L_{z}}\right| < 3, \end{cases}, \quad (IV.2.16b)$$

$$i\omega d_{3}C_{3}, & \text{when } \left|\sqrt{\frac{i\omega}{D_{z3}}}d_{3}\right| \le \frac{1}{3} \text{ or } \left|\sqrt{2i}\frac{d_{3}}{L_{z}}\right| \le \frac{1}{3}$$

With the condition $\left|\sqrt{2i} d_3/L_z\right| \ge 3$ in Eqs. (IV.2.16a) and (IV.2.16b), we found that when

$$L_z/d_3 \le 0.47$$
, (IV.2.17a)

the thin film layer can be viewed as semi-infinite, *i.e.* the thermal wave penetrates into a limited depth L_z of the target thin film layer. The terms n/γ_3 and $\gamma_3 n$ in Eq. (IV.2.13) can then be simplified to $1/\sqrt{i\omega\kappa_{z3}C_3}$ and $\sqrt{i\omega\kappa_{z3}C_3}$, respectively. This simplification tells that the thermal response is essentially determined by the thermal effusivity $\sqrt{\kappa_{z3}C_3}$ at the high frequency limit when

$$\omega > 9 \frac{\kappa_{z3}}{d_3^2 C_3}$$
 (IV.2.17b)

Here, Eq. (IV.2.17b) is obtained by plugging Eq. (IV.2.15) into Eq. (IV.2.17a). In such case, the data reduction for thin film measurement is similar to the bulk analysis (Section IV.2.2.B) since the thermal wave does not penetrate beyond the thin film layer.

With the condition $\left|\sqrt{2i} d_3/L_z\right| \le 1/3$ in Eqs. (IV.2.16a) and (IV.2.16b), we found that when

$$L_{z}/d_{3} \ge 4.24$$
, (IV.2.18a)

the thin film layer can be regarded as an interface layer since the heat diffuses deeply into the substrate. The terms n/γ_3 and $\gamma_3 n$ in Eq. (IV.2.13) can then be simplified to d_3/κ_{z3} and $i\omega d_3C_3$, respectively. This simplification shows that the thermal response is determined by the thermal resistance d_3/κ_{z3} and the heat capacity C_3 when the modulation frequencies ω satisfies this condition

$$\frac{32\kappa_{r_3}}{R_{pp}C_3} << \omega < 0.11 \frac{\kappa_{z_3}}{d_3^2 C_3}.$$
 (IV.2.18b)

Here, Eq. (IV.2.18b) is obtained by plugging Eq. (IV.2.15) into Eq. (IV.2.18a) and combining with Eq. (IV.2.12d).

When the modulation frequency is in between the ranges defined in Eq. (IV.2.17b) and (IV.2.18b), the terms n/γ_3 and $\gamma_3 n$ in Eq. (IV.2.13) cannot be simplified and both thermal diffusivity κ_{z3}/C_3 and thermal effusivity $\sqrt{\kappa_{z3}C_3}$ play a role in the thermal response.

Table IV.2.2 summarizes the above analysis, *i.e.*, how different combinations of thermal conductivity and heat capacity determine the thermal response at different ranges of modulation frequency ω in a tri-layer sample configuration.

Penetration depth of thermal waves	Penetrating throughout the layer		Penetrating into a limited depth of the layer
ω	$\frac{32\kappa_{r_3}}{R^2C_3} << \omega < 0.11 \frac{\kappa_{z_3}}{d_3^2C_3}$	$0.11 \frac{\kappa_{z3}}{d_3^2 C_3} < \omega < 9 \frac{\kappa_{z3}}{d_3^2 C_3}$	$\omega \ge 9 \frac{\kappa_{z_3}}{d_3^2 C_3}$
L_z vs. d_3	$L_{z}/d_{3} \ge 4.24$	$0.47 < L_z/d_3 < 4.24$	$L_{z}/d_{3} \le 0.47$
n	$q_3 d_3$	$tanh(q_3d_3)$	1
n/γ_3	$d_{\scriptscriptstyle 3}/\kappa_{\scriptscriptstyle z3}$	$\tanh(d_3\sqrt{i\omega\kappa_{z3}/C_3})/\sqrt{i\omega\kappa_{z3}C_3}$	$1/\sqrt{i\omega\kappa_{z3}C_3}$
$\gamma_3 n$	$i\omega d_3C_3$	$\tanh(d_3\sqrt{i\omega\kappa_{z3}/C_3})\sqrt{i\omega\kappa_{z3}C_3}$	$\sqrt{i\omega\kappa_{z3}C_3}$
Thermal property	$d_3 / \kappa_{z3}, C_3$	κ_{z3}/C_3 , $\sqrt{\kappa_{z3}C_3}$	$\sqrt{\kappa_{z3}C_3}$

Table IV.2.2. Dominant thermal properties in the thermal response at different ranges of modulation frequency ω in a tri-layer sample configuration (thin film materials).

IV.2.1.D. κ -C diagram for simultaneous measurement of κ and C

A conventional TDTR measurement is usually performed with a single modulation frequency for the measurement of thermal conductivity κ of materials and the interfacial thermal conductance *G* using heat capacity *C* as input. Cahill *et al.* showed that κ and *G* can be independently extracted at different delay times for both bulk and thin films.[166] Our previous FDTR measurements[144] on thin films showed that κ and *G* can be extracted at different modulation frequency ranges due to the different sensitivities of these two properties. Considering that the accurate extraction of the interfacial thermal conductance might affect the determination of k and C, in this work, we extract k and C either at a range of modulation frequencies where the measured signal is insensitive to the interfacial thermal conductance or at a range of delay times where the interfacial thermal conductance can be extracted first.

Based on the analysis in Sections IV.2.2.B and IV.2.2.C, we propose to conduct the TDTR measurement at different modulation frequencies for simultaneous measurement of κ and *C* for both bulk and thin film materials. At each modulation frequency, multiple pairs of κ and *C*, which satisfies the different combinations of the analysis in Section IV.2.2.B and IV.2.2.C, can fit the TDTR signals. Such pairs of κ -*C* for each modulation frequency are then presented together as a curve in the " κ -*C*" diagram where many curves are presented for the measurement at different modulation frequencies. Then the cross-point on the κ -*C* diagram for different modulation frequencies gives a unique set of κ and *C*, which represents the measured value of thermal conductivity and heat capacity of the material.

IV.2.2. Applying on bulk and thin film samples

In this section, the simultaneous measurement of thermal conductivity and heat capacity is demonstrated for both bulk Si and thin film SiO₂ samples.

IV.2.2.A. Bulk Si

A 350 μ m thick *n*-type (100)-orientated Si wafer was first cleaned with 5% HF solution to remove the native oxide and then coated with a 100 nm Al film by thermal evaporation. The thermal properties of Si at 300K were measured using frequency-dependent TDTR method. The radii of the pump and probe beams were chosen to be 15 μ m and 5 μ m, respectively.

We determined first the interfacial thermal conductance G_2 . Figure IV.2.2(a) shows the calculated sensitivity of $-V_{in}/V_{out}$ signal to the thermal properties of bulk Si at 6.8 MHz. Similar to Ref. [166], the sensitivity S_p of $-V_{in}/V_{out}$ signal to the thermal property p is defined as

$$S_{p} = \frac{d(-V_{in}/V_{out})/(-V_{in}/V_{out})}{dp/p},$$
 (IV.2.19)

where $d(-V_{in}/V_{out})/(-V_{in}/V_{out})$ is the fluctuation of $-V_{in}/V_{out}$ signal and p is the property that we are interested in measuring, which could thus be thermal conductivity, heat capacity, or interface thermal conductance in the multilayer structure presented in Fig. IV.2.1. Clearly, the $-V_{in}/V_{out}$ signal is very sensitive to the interfacial thermal conductance G_2 , but relatively insensitive to thermal conductivity κ_{z3} and heat capacity C_3 , at the delay time range of 4-7 ns. Using the measurement data for delay time at 4-7 ns, the interfacial thermal conductance is fitted to be 215 MW/m²K, which is in line with the literature values of 116-350 MW/m²K, depending on sample surface and deposition conditions.[143, 167, 168]

Figure IV.2.2(b) shows the TDTR experiment data and the best-fit results of $-V_{in}/V_{out}$ with modulation frequencies at 0.5 MHz, 0.98 MHz, and 6.8 MHz. Figure IV.2.2(c) shows the κ -*C* diagram with fitted κ_{z3} and C_3 under each frequency, where multiple pairs of κ_{z3} and C_3 satisfy the best-fit with the experiment data when only one single frequency measurement is conducted. For instance, the κ -*C* pairs of (1.4, 159), (1.59, 140), (1.8, 123.67) fit the experiment data collected at 6.8 MHz, represented as the black squares in Fig. 2(c). This clearly shows that the measurement accuracy for thermal conductivity using the conventional single frequency TDTR measurement depends strongly on the heat capacity input. A further calculation finds that the thermal effusivity $\sqrt{\kappa_{z3}C_3}$ for multiple pairs of κ_{z3} and C_3 is a constant at a frequency of 6.8 MHz. When the modulation frequency changes to 0.98 MHz and 0.5 MHz, the κ -*C* pairs deviate from the values at 6.8 MHz. The κ -*C* curves of the three modulation frequencies on the κ -*C* diagram cross at 140 W/mK and 1.59 J/cm³K for thermal conductivity and volumetric heat capacity for bulk Si at room temperature, which agree very well (within 5%) with the literature values,[82, 133, 143] as shown in Fig. IV.2.2(c).



Figure IV.2.2. Demonstration of simultaneous measurement of thermal conductivity and volumetric heat capacity of bulk Si using frequency-dependent TDTR measurements. (a) The sensitivity of $-V_{in}/V_{out}$ signal to the thermal conductivity κ_{z3} (solid line) and volumetric heat capacity C_3 (dash line) of bulk Si and the interfacial thermal conductance between Al and Si G_2 (dash dot line) at 6.8 MHz. (b) The experiment data and best-fit results of $-V_{in}/V_{out}$ under modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz. (c) The κ -C diagram of bulk Si showing that multiple pairs of thermal conductivity κ_{z3} and volumetric heat capacity C_3 can fit the measured signal under each modulation frequency. The crossing point of κ -C for those three modulation frequencies is the measured value of the Si sample. The measured data agrees very well (within 5%) with of the reported values (open diamond) of bulk Si.

IV.2.2.B. SiO₂ thin films

Three SiO₂ thin films samples with the thickness of 110 nm, 310 nm, and 860 nm were grown by thermal oxidization at 1100 °C on a 350 μ m thick Si wafer (same batch of wafers used in Section IV.2.3.A). Similarly, a 100 nm Al film was coated on the SiO₂ thin film samples by thermal evaporation to form the tri-layer configuration for thermal property measurements. The radii of the pump and probe beams were selected as 15 μ m and 5 μ m, respectively, which results in the cross-plane thermal conductivity measurement of the thin films as shown in Eq. (IV.2.14a) and (IV.2.14b).

For the 110 nm thick SiO_2 film sample, thermal resistance and heat capacity dominate the thermal response when the modulation frequency is lower than 1.18 MHz, calculated from Eq.

(IV.2.18b). At those frequencies below 1.18 MHz, the thermal waves penetrate throughout the SiO₂ layer, so this layer can be only treated as an interface for data reduction of TDTR measurement, where the interfacial thermal conductances G_2 and G_4 cannot be separated from the thermal resistance of the thin film layer. At modulation frequencies much higher than 1.18 MHz, the measured signal is insensitive to G_2 and G_4 compared to the low conductance of thin film layer. Figure IV.2.3(a) shows the measurement data and best-fit results of $-V_{in}/V_{out}$ for the 110 nm thick SiO₂ film with modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz. Figure IV.2.3(b) shows the κ -C diagram. At 0.5 MHz and 0.98 MHz, the best-fit value of κ_{z3} are independent of C_3 , which indicates the thermal resistance d_3/κ_{z3} dominates the measured signals. At a higher frequency such as 6.8 MHz, the fitted thermal conductivity κ_{z3} increases with the fitted volumetric heat capacity C_3 , which indicates that thermal diffusivity κ_{z3}/C_3 dominates in the signal. The κ -C curves of the three modulation frequencies on the κ -C diagram cross at 1.3 W/mK and 1.61 J/cm³K for the thermal conductivity and volumetric heat capacity, respectively, for the 110 nm thick SiO₂ thin film.

For the 860 nm thick SiO₂ film sample, the κ -*C* diagram can be constructed over 0.1-20 MHz, since we found that the measured signals are insensitive to the interfacial thermal conductances G_2 and G_4 at these frequencies. Thermal effusivity dominates the thermal response when the modulation frequency is higher than 1.58 MHz for the 860 nm thick SiO₂ film sample, calculated from Eq. (IV.2.17b), which is similar to the bulk Si measurement in Section IV.2.3.A. Figure IV.2.3(c) shows the measurement data and the best-fit results of $-V_{in}/V_{out}$ for the 860 nm thick SiO₂ film with modulation frequencies of 0.5 MHz, 2.08 MHz, 6.8 MHz, and 11.26 MHz. Figure IV.2.3(d) shows the κ -*C* diagram where the κ -*C* curves of the four

modulation frequencies on the κ -*C* diagram cross at 1.31 W/mK and 1.62 J/cm³K for the thermal conductivity and volumetric heat capacity, respectively for 860 nm thick SiO₂ thin film.

Figure IV.2.3(e) shows the sensitivity of $-V_{in}/V_{out}$ signal to the thermal properties of the 310 nm thick SiO₂ film from 0.98 MHz to 6.8 MHz at a delay time of 0.5 ns. The $-V_{in}/V_{out}$ signal is insensitive to the interfacial thermal conductance G_4 at 2.08 MHz and above, where the κ_{z3} and C_3 can be extracted. Both thermal effusivity and thermal diffusivity play a role in the thermal response when the modulation frequency range is 0.15-12.15 MHz for a 310 nm thick SiO₂ film sample, calculated from Eq. (IV.2.17b) and (IV.2.18b). Figure IV.2.3(f) shows the experiment data and best-fit results for of $-V_{in}/V_{out}$ for the 310 nm thick SiO₂ thin film at 0.98 MHz, 2.08 MHz, 3.4 MHz, and 6.8 MHz. Figure IV.2.3(g) shows the κ -*C* diagram of 2.08 MHz, 3.4 MHz, and 6.8 MHz. Figure IV.2.3(g) shows the κ -*C* diagram of 2.08 MHz, 3.4 MHz and 1.62 J/cm³K for the thermal conductivity and volumetric heat capacity, respectively for the 310 nm thick SiO₂ film are fitted at 0.98 MHz as 120 MW/m²K and 13 MW/m²K, respectively, which agree well with those reported values in Ref. [144].

Finally, Fig. IV.2.3(h) shows the measured values of thermal conductivity κ and volumetric heat capacity *C* for SiO₂ thin films of different thicknesses. Both κ and *C* do not change much with thickness, which indicates that the size effect of phonon transport is not important for SiO₂ at a thickness of 110nm and above. This result agrees very well with the literature values.[144, 165]



Figure IV.2.3. Demonstration of simultaneous measurement of thermal conductivity and volumetric heat capacity of SiO_2 thin films using frequency-dependent TDTR measurements. (a) The experiment data and best-fit results of $-V_{in}/V_{out}$ for 110 nm thick SiO₂ film under modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz. (b) The κ -C diagram for 110 nm thick SiO₂ film. The crossing point of κ -C for those three modulation frequencies is the measured value of the sample. (c) The experiment data and best-fit results of $-V_{in}/V_{out}$ for 860 nm thick SiO₂ film under modulation frequencies of 0.5 MHz, 2.08 MHz, 6.8 MHz, and 11.26 MHz. (d) The κ -C diagram for 860 nm thick SiO₂ film. (e) The sensitivity of $-V_{in}/V_{out}$ signal to the thermal conductivity κ_{z3} (solid line) and the heat capacity C_3 (dash line) of 310 nm thick SiO₂ film and the interfacial thermal conductance G_4 (dash dot line) from 0.98 MHz to 6.8 MHz at a 0.5 ns delay time. (f) The experiment data and best-fit results of $-V_{in}/V_{out}$ for 310 nm thick SiO₂ film under modulation frequencies of 0.98 MHz, 2.08 MHz, 3.4 MHz, and 6.8 MHz. (g) The κ -C diagram of 310 nm thick SiO₂ film at 2.08 MHz, 3.4 MHz, and 6.8 MHz. (h) The measured values of thermal conductivity κ_{z3} and volumetric heat capacity C_3 for SiO₂ thin films with different thicknesses, which agree well with the reported values in the literatures.

IV.3 Measurement of in-plane thermal conductivity of bulk and thin film materials

IV.3.1 Analysis and measurement procedure

This section shows how anisotropic thermal conductivity of bulk and thin film materials can be measured by using different combinations of TTR measurement conditions, such as modulation frequency and beam spot size. Based on the detailed heat transfer model analysis presented in the previous section IV.2.1, the measurement conditions for anisotropic thermal conductivity are identified analytically as in section IV.2.1.



Figure IV.3.1. (a) A summary of the two-step scheme used for measuring anisotropic thermal conductivity. (b) The beam spot sizes on the sample surface change correspondingly when the

sample stage moves with respect to the objective lens. (c) The beam spot sizes on the sample surface at different positions of the sample stage, which is measured by the knife-edge method.

To measure the anisotropic thermal conductivity of bulk materials (or thin film materials), a two-step scheme can be used where the modulation frequency and beam spot size are chosen according to the analysis above. When a relatively high modulation frequency f and a large beam spot size R are chosen to satisfy the conditions of Eqs. (IV.2.11a) or (IV.2.11c), the crossplane thermal conductivity κ_z and interfacial thermal conductance G_2 (or G_4) can be measured. When measuring cross-plane thermal properties, the heat capacity C of bulk material needs to be used as input, which can be either taken from literature or measured by the differential scanning calorimetry. The heat capacity of thin film material, if unknown, can be measured under the condition of Eqs. (IV.2.11a) or (IV.2.11c) using multiple modulation frequencies, as shown in the previous section. The thermal conductivity in the radial (or in-plane) direction κ_r is then extracted using a small beam spot size R at a relatively low modulation frequency f, where the condition of Eq. (IV.2.12a) or (IV.2.12d) is satisfied.

Figure IV.3.1 shows the details of the implementation of this measurement approach. Figure IV.3.1(a) shows a summary of the two-step scheme used for measuring anisotropic thermal conductivity. The time-domain thermoreflectance (TDTR) measurement is conducted first at a relatively higher modulation frequency f_1 and larger beam spot size R_1 that satisfy the conditions of Eq. (IV.2.11a), where the cross-plane thermal properties (*i.e.* cross-plane thermal conductivity and interfacial thermal conductance) can be measured, similarly as in the common practice. Then, the TTR measurement is conducted using varied small beam spot sizes $R_2,...,R_n$

 $(R_n < R_1)$ at a relatively low modulation frequency f_2 $(f_2 < f_1)$ and at a fixed time delay of the probe beam where the in-plane thermal conductivity plays a role in the thermal response and can be measured. Using a series of varied small beam spots improves the fitting accuracy compared with using only one small beam spot, where the fitting of in-plane thermal conductivity is very sensitive to the inaccuracy of beam spot size, beam spot misalignment, and eccentricity of the spot shape.[169] Figure IV.3.1(b) shows that the beam spot sizes on the sample surface change correspondingly when the sample stage moves with respect to the objective lens. Figure IV.3.1(c) shows the beam spot sizes on the sample surface at different positions when the sample stage moves, which is measured by the knife-edge method.[170] The beam spot sizes are also confirmed by additional TDTR measurements on bulk Si samples. Since the beam spot sizes of the pump beam impinging onto the objective are much larger than that of the probe beam, the changes of beam spot size of pump beam after objective is more sensitive with stage position than that of probe beam. The power of the pump and probe beams is carefully chosen so that the temperature rise of the sample surface is within 10 K when the beam spot sizes are varied. Similar to Ref. [146], the ratio of the in-phase signal X and out-of-phase signal Y, -X/Y, which is the same as $-V_{in}/V_{out}$, is used in this work as the measurement signal for data analysis.

IV.3.2 Sensitivity Analysis

To further estimate how the combinations of modulation frequency and beam spot size should be used for measuring anisotropic thermal conductivity with high accuracy and confirm the analysis in Section IV.3.1, the sensitivity of TTR signals as a function of thermophysical properties (*e.g.* thermal conductivity and interfacial thermal conductance) and experimental



conditions (e.g. beam spot size and modulation frequency) is analyzed.

Figure IV.3.2. The sensitivity S of the TTR signal on bulk samples to the thermal conductivity in the radial direction κ_r as a function of (a) modulation frequency, (b) average beam spot size, (c) cross-plane thermal conductivity κ_z .

Figure IV.3.2 shows the sensitivity S of the TTR signal to the thermal conductivity in the radial direction κ_r for bulk samples, calculated using the bi-layer configuration and plotted as a function of the thermophysical properties and experimental conditions. The interfacial thermal conductance between Al thin film and bulk sample G_2 is assumed to be 200 MW/m²K and the heat capacity of the bulk sample is assumed to be 2.0 J/cm³K, which are typical values for bulk materials. Figure IV.3.2(a) shows the sensitivity S of the TTR signal to κ_r as a function of modulation frequency f with the values of κ_r spanning four orders of magnitude. The spot sizes are assumed to be 5 μ m for both pump and probe beams with the average beam spot size as 7.07 µm. The cross-plane thermal conductivity is assumed to be 10 W/mK. The sensitivity of TTR signal to κ_r increases with decreasing modulation frequency and also increases with increasing κ_r . Figure IV.3.2(b) shows the sensitivity S of the TTR signal to κ_r as a function of the average beam spot size R with the same values of κ_r in Fig. 2(a). The modulation frequency is taken as 1 MHz. The sensitivity S increases with decreasing average beam spot size and increases with increasing κ_r . Figures IV.3.2(a) & 2(b) indicate that a relatively lower modulation frequency and smaller beam spot size are favorable for measuring κ_r , which is reasonable since the conditions of Eqs. (IV.2.12a) are more easily satisfied by using these experimental conditions. Figure IV.3.2(c) shows the sensitivity S of the TTR signal to κ_r as a function of the cross-plane thermal conductivity κ_z with the same values of κ_r in Fig. IV.3.2(a), where the average beam spot size is 7.07 µm and the modulation frequency is 1 MHz. The sensitivity S increases with increasing cross-plane thermal conductivity. As shown in Eq. (IV.2.12c), higher cross-plane thermal conductivity enhances the propagation of the three-dimensional spherical thermal waves in the bulk sample.



Figure IV.3.3. The sensitivity S of the TTR signal on thin film samples to the in-plane thermal conductivity κ_r as a function of (a) thermal conductivity of substrate, (b) interfacial thermal conductance between thin film and substrate G_4 , (c) cross-plane thermal conductivity of thin film,(d) the thickness of thin film.

Figure IV.3.3 shows the sensitivity S of the TTR signal to the thermal conductivity in the inplane direction κ_r for thin film samples, calculated using the tri-layer configuration and plotted as a function of the thermophysical properties and experimental conditions. The cross-plane thermal conductivity is assumed to be 10 W/mK, the thickness of the thin film is assumed to be 300 nm, the interfacial thermal conductance between Al thin film and thin film is assumed to be 100 MW/m²K, and the interfacial thermal conductance between thin film and the substrate is assumed to be 15 MW/m²K. From the analysis in Section IV.3.1, the selection of modulation frequency and beam spot size in measuring thin film samples is similar as in measuring bulk samples. Thus, the modulation frequency is 1 MHz and the average beam spot size is 7.07 µm. Figure IV.3.2(a) shows the sensitivity S of the TTR signal to κ_r as a function of thermal conductivity of substrate with the values of κ_r ranging from 0.2 to 50 W/mK. The sensitivity S increases with decreasing thermal conductivity of substrate and also increases with increasing κ_r . Figure IV.3.2 (b) shows that the sensitivity S of the TTR signal to κ_r increases with decreasing interfacial thermal conductance between thin film and substrate G_4 with the values of κ_r ranging from 10 to 50 W/mK. Figures IV.3.2 (a) & 3(b) indicate that the measurement signal is more sensitive to κ_r if using a substrate with lower thermal conductivity and lower interfacial thermal conductance between substrate and thin film. For example, the TTR signal is more sensitive to in-plane thermal conductivity when measuring a thin film fabricated on a glass substrate with a thermal-insulation layer compared to being fabricated on a Si substrate. The signal has stronger accumulation effect (*i.e.* the sample surface does not have enough time to cool down to the initial temperature before the next heating pulse) and the thermal waves propagate further in the inplane direction when a substrate with lower thermal conductivity is used. Figure IV.3.2 (c) shows

the sensitivity *S* of the TTR signal to κ_r as a function of cross-plane thermal conductivity with the values of κ_r ranging from 10 to 50 W/mK. The sensitivity *S* initially increases with increasing cross-plane thermal conductivity κ_z but reaches a plateau after κ_z reaches around 10 W/mK in this example. Similarly as in bulk samples, higher cross-plane thermal conductivity enhances the propagation of the three-dimensional spherical thermal waves in the thin film sample. However, this enhancement is limited or saturated when the thermal resistance of the thin film is much smaller compared to the interfacial resistance between thin film and substrate. Figure IV.3.2 (d) shows the sensitivity *S* of the TTR signal to κ_r as a function of film thickness *d* with the values of κ_r ranging from 10 to 50 W/mK. The sensitivity *S* increases with increasing film thickness first and reaches a plateau after the thickness reaches around 600 nm in this example. With larger thickness, the thin film can be viewed as a film (where the in-plane thermal conductivity could be sensitive) rather than a resistance (where the in-plane thermal conductivity is insensitive), since the thermal resistance of the film is comparable or much larger than the two interfacial resistances.

Through the sensitivity analysis, we identified the TTR measurement conditions that could make a more sensitive measurement of κ_r of bulk and thin film sample: (1) using a lower modulation frequency and smaller beam spot sizes; (2) for thin film sample, if possible, using a substrate with lower thermal conductivity and a lower interfacial thermal conductance between substrate and the thin film.

IV.3.3 Measuring anisotropic thermal conductivity of HOPG



Figure IV.3.4. Demonstration of measuring anisotropic thermal conductivity of bulk HOPG sample. (a) The TDTR measurement data and the best-fit result of -X/Y at a modulation frequency of 11.26 MHz using the average beam spot size 27.2 µm, for measuring cross-plane thermal properties. (b) The measurement data and the best-fit result of -X/Y using varied spot sizes at 13-21.3 µm at a modulation frequency of 2.08 MHz and at a delay time of 0.5 ns for measuring in-plane thermal conductivity. (c) The measurement results of anisotropic thermal conductivity of HOPG samples from 100 K to 450 K.

The bulk material measured as an example is the HOPG sample, which is composed of stacked graphene planes. The in-plane bonding forces are much stronger than cross-plane van der Waals forces, resulting in its highly anisotropic thermal conductivity. The HOPG samples were purchased from SPI supplies (Grade-2). The scotch tapes were used several times to clean the flakes on the sample and expose a fresh surface just before thermally evaporating the Al thin film onto the surface. The thickness of the Al thin film is confirmed to be 112 nm by the acoustic echoes in the signal. The in-plane thermal conductivity of Al thin film has been measured by additional measurements using the sample configuration of Al thin film on glass substrate and using the same approach described in Section II.B. The volumetric heat capacity value of HOPG is taken from literature.[171] Figure IV.3.4(a) shows the TDTR measurement data and the bestfit result of -X/Y at a modulation frequency of 11.26 MHz using the average beam spot size 27.2 μ m, which is the experimental condition satisfying Eq. (IV.2.11c). The TDTR signal is sensitive to the cross-plane thermal conductivity and the interfacial thermal conductance between Al thin film and HOPG. For instance, the theoretical solution obtained by varying κ_z by 20% is plotted to show the measurement is sensitive. Figure IV.3.4(b) shows the measurement data and the bestfit result of -X/Y using varied spot sizes at 13-21.3 µm at a modulation frequency of 2.08 MHz and at a delay time of 0.5 ns for measuring in-plane thermal conductivity of HOPG. The theoretical solution obtained by varying κ_r by 20% is also plotted to show the measurement is sensitive to in-plane thermal conductivity. The measurement results at room temperature show that the cross-plane thermal conductivity is 5.7 W/mK, the interfacial thermal conductance is 97 MW/m²K, and the in-plane thermal conductivity is 1893 W/mK. The measurement results agree with the literature values at room temperature where the cross-plane thermal conductivity ranges from 5.4-6.1 W/mK and in-plane thermal conductivity ranges from 1700-2100 W/mK.[159, 161,

171] Figure IV.3.4(c) shows the measurement results of anisotropic thermal conductivity of HOPG samples from 100 K to 450 K using the same procedure and experimental condition as in Figs. IV.3.4(a) and IV.3.4(b). Both the in-plane and cross-plane thermal conductivity of HOPG decrease with increasing temperature due to the increased phonon-phonon scattering with increasing temperature. The literature values measured by the guarded heat flow apparatus are also shown in the figure.[172] The cross-plane thermal conductivity measured by our approach agrees with the literature value. The in-plane thermal conductivity measured at temperature higher than 250K agrees with the literature value while the in-plane thermal conductivity measured at temperature lower than 250K shows a discrepancy compared to the literature values. This discrepancy could be due to the size effect of measured thermal conductivity using small beam spots, where the phonon mean free path at low temperatures is much larger than the beam spot sizes, similarly to the demonstration by Minnich *et al.*[167]

IV.3.4. Measuring anisotropic thermal conductivity of copper thin films

The 200 nm-thick copper film was coated on a 2 nm-thick Ti coated Si substrate. The Ti layer is used for the adhesion between Si substrate and copper film. Similarly, a ~100 nm Al film was coated on the copper thin film samples by thermal evaporation. Figure IV.3.5 (a) & 5(b) show the anisotropic thermal conductivity measurement of the copper thin film as an example.



Figure IV.3.5 (a) The TDTR measurement data and the best-fit result of -X/Y at a modulation frequency of 11.26 MHz using the average beam spot size 15.8 µm, for measuring the crossplane thermal property. (b) The TDTR measurement data and the best-fit result of -X/Y using varied spot sizes at 7.07-14.86 µm at a modulation frequency of 0.98 MHz and at a delay time of 0.5 ns for measuring the in-plane thermal conductivity.

Figure IV.3.5 (a) shows the TDTR measurement data and the best-fit result of -X/Y at a modulation frequency of 11.26 MHz using the average beam spot size 15.8 µm. The volumetric heat capacity of copper thin films is taken as the same with the bulk value, 3.45 J/cm³K.[173] Since the cross-plane thermal conductivity of copper thin film is on the order of 300-400 W/mK, the TDTR signal is only sensitive to the effective (or apparent) cross-plane thermal conductivity, which includes the two interfaces between the copper thin film and Al film or substrate, and the 'intrinsic' thermal conductivity of copper thin film. The best-fit effective cross-plane thermal conductivity is 11.55 W/mK. Figure IV.3.5 (b) shows the measurement data and the best-fit result of -X/Y using varied spot sizes at 7.07-14.86 µm at a modulation frequency of 0.98 MHz

and at a delay time of 0.5 ns for measuring in-plane thermal conductivity. The theoretical solution obtained by varying κ_r by 20% is also plotted to show the measurement is sensitive to in-plane thermal conductivity. The best-fit in-plane thermal conductivity is 327 W/mK. The thermal conductivity measurement results of the copper thin films is smaller compared to the that of single copper crystal, 401 W/mK,[173] which is due to the electron scattering at grain boundary and interfaces. Using the four-probe method, the in-plane electrical resistivity is measured to be 22.9 $n\Omega \bullet m$. The in-plane thermal conductivity due to electrons can be calculated using the Wiedemann-Franz law,

$$\frac{\kappa}{\sigma} = LT, \qquad (IV.3.1)$$

where κ is the thermal conductivity, σ is the electrical conductivity, *L* is the Lorenz number, 2.44×10⁻⁸ WΩK⁻², *T* is the measurement temperature. The in-plane thermal conductivity due to electrons is calculated as 316.3 W/mK at 300 K using the electrical conductivity measured by four-probe method, which agrees with our measurement result, 327 W/mK.

IV.4 Measurement using backside-pumping arrangement

Generally, in transient thermoreflectance method for thermal property characterization, a thin layer of metal transducer needs to be deposited on top of the target sample, as shown in Fig.IV.4.1 (a). For those materials, including grease/paste-like material, nanowire arrays, porous materials, and biomaterials, it is very challenging to deposit a metal transducer layer on top of them, so an alternate setup should be chosen instead for thermal property measurement. Figure IV.4.1 (b) shows the schematics of the sample configuration for backside-pumping arrangements.

The glass is first deposited with a 2 nm Ti adhesion layer and then an Al transducer layer. The target layer with unknown thermal properties is pasted /deposited on top of the Al thin film layer. The pump and probe laser beam impinge on the metal layer through the glass from the backside. The cooling of the metal film is used to deduce the thermal properties of the target layer.



Figure IV.4.1. The schematics of the sample configuration for (a) frontside-pumping and (b)backside-pumping.

The backside-pumping setup requires that the thermal properties of the Al-coated glass are well-known. The heat capacity of the VWR[®] glass we purchased was measured by the differential scanning calorimetry (DSC). We used time-domain thermoreflectance (TDTR) method to measure the thermal conductivity of the VWR[®] glass and the interfacial thermal conductance between Al thin film and glass. Figure IV.4.2 shows the TDTR signals and their best-fits both in the frontside-pumping (laser beams impinge on the metal transducer first and then glass) and backside-pumping (laser beams impinge on the glass first and then metal
transducer) measurements of Al-coated glass at a modulation frequency of 2.08 MHz and at room temperature. The measured heat capacity *C* of glass is $1.94 \text{ J/cm}^3\text{K}$. The thermal conductivity κ measured from the frontside is 0.88 W/mK and from the backside is 0.90 W/mK. The thermal conductivity values agree with the literature values from 0.76-1.16 W/mK depending on the types of glass.[162, 174] The interfacial thermal conductance between the Al film and glass is 178 MW/m²K.



Figure IV.4.2. The TDTR signals and their best-fits both in the frontside-pumping and backsidepumping arrangements of Al-coated glass measured at a modulation frequency of 2.08 MHz and at room temperature.











(d)







(e)

Figure IV.4.3. The sensitivity of thermal conductivity κ and heat capacity C of the glass, and the interfacial thermal conductance G between the Al film and the glass at different experimental conditions when measuring from the backside.

To select the optimal experimental conditions (e.g. modulation frequency) for thermal property measurement, we analyze the heat transfer model for the backside-pumping arrangement. Figure IV.4.3 shows the sensitivity of the experimental signal to the thermal conductivity κ and heat capacity C of the glass, and the interfacial thermal conductance G between the Al film and the glass at different experimental conditions when measuring from the backside. Figure IV.4.3(a) & (b) show the sensitivity of thermal properties (κ , C, and G) of the target layer at different modulation frequencies and delay times. The sensitivity of κ and C does not change much from delay time 1.08 ns to 5.08 ns. The signal is very sensitive (sensitivity>0.05) to κ and C at a modulation frequency range of around 1-2 MHz. The signal is not sensitive to G at those experimental conditions. Figure IV.4.3(c) (d) show the sensitivity of thermal properties of the target layer when the thermal conductivity of the layer changes. The sensitivity of κ peaks when thermal conductivity of the target layer is close to that of glass. The signal is very sensitive to κ and C of the target layer when the thermal conductivity κ of the target layer is roughly in the range of 0.2-3.0 W/mK. Figure 3(e) shows the sensitivity of thermal properties of the target layer when the layer thickness changes. The signal is sensitive to κ and C at the range we investigated (100nm-1100nm) while the signal is not sensitive to G.

We have measured PMMA and SiO_2 thin films at room temperature to verify the backsidepumping arrangement for thermal properties measurement. The 170 nm-thick PMMA thin film is spin-coated onto the Al thin film while the 338 nm-thick SiO_2 thin film is sputtered onto the Al thin film. Figure IV.4.4 shows the experimental data and the best-fit for thermal properties of PMMA and SiO₂ thin films at modulation frequencies of 2.08 MHz, 3.4 MHz, and 6.8 MHz. The heat capacity values for PMMA and SiO₂ are taken as 1.73 J/cm^3 K and 1.62 J/cm^3 K, respectively. The best-fit values for thermal conductivity of PMMA and SiO₂ thin films are 0.216 W/mK and 1.11 W/mK, respectively. Those values, measured with the backside-pumping arrangement, agree with the literature values.[174, 175]



*Figure IV.4.4. The experimental data and the best-fit for thermal properties of (a) PMMA and (b) SiO*₂ *thin films at modulation frequencies of 2.08 MHz, 3.4 MHz, and 6.8 MHz.*

To enable the measurement on the temperature-dependent thermal properties of the target layer, we are currently measuring the temperature-dependent properties of glass. Figure IV.4.5 shows our measurement results on the temperature-dependent heat capacity and thermal conductivity of VWR[®] glass and interfacial thermal conductance between Al and glass at a temperature range of 150K-400K.



Figure IV.4.5. The results on the temperature-dependent heat capacity and thermal conductivity of VWR[®] glass, and interfacial thermal conductance between Al and glass at a temperature range of 150K-400K.

We have measured a CNT-polymer composite grease sample from our collaborator, using this backside-pumping arrangement. The polymer used is liquid polymerized siloxane with organic side chains, similar to silicone oil. The CNT volume fraction is around 5%. The grease sample is pressed onto the Al thin film coated glass, as shown in Figure. IV.4.1. The thickness of the grease layer is larger than 1 mm. The volumetric heat capacity is 2.28 J/cm³K. We measured the sample at three different points and repeated the measurement three times. The measurement is conducted at three applied modulation frequencies of 2.08 MHz, 3.4 MHz, and 6.8 MHz. The measured thermal conductivity is 0.95 ± 0.05 W/mK, which agrees with the literature values.[176] The measured interfacial thermal conductance between the Al thin film and the grease is 173 ± 25 MW/m²K.

IV.5 Summary of this chapter

In this chapter, (1) we have described and validated a technique to simultaneously measure the thermal conductivity κ and volumetric heat capacity *C* of both bulk and thin film materials using the frequency-dependent TDTR method. The heat transfer model is analyzed first to figure out how different combinations of κ and *C* determine the frequency-dependent TDTR signals. A " κ -*C*" diagram is proposed to determine thermal conductivity and heat capacity of the measured material using frequency-dependent TDTR signals. This technique is validated by measuring the thermal properties of bulk Si and SiO₂ thin film samples. This method is applicable to a large variety of bulk and thin film materials for simultaneous measurement of thermal conductivity and volumetric heat capacity, which can significantly shorten the material discovery cycle. (2) We present the extension of the TTR method for the measurement of the anisotropic thermal conductivity of bulk and thin film materials. A two-step measurement scheme is adopted. The cross-plane thermal conductivity and the interfacial thermal conductance are measured first using a relatively high modulation frequency and larger beam spot size. The in-plane thermal conductivity is then extracted by varying beam spot sizes at a relatively low modulation frequency. Through the sensitivity analysis, we identified the measurement conditions that could make a more sensitive measurement of in-plane thermal conductivity of the thin film sample: (a) using a lower modulation frequency and smaller beam spot sizes; (b) if possible, using a substrate with lower thermal conductivity and a lower interfacial thermal conductance between substrate and the thin film. The anisotropic thermal conductivity of bulk highly ordered pyrolytic graphite and thin copper film samples is measured. Our results show that this method can be used to measure the anisotropic thermal conductivity of a wide variety of bulk and thin film materials. (3) Another important improvement on the experiment system is to enable the measurement of special materials that requires protection during the sample preparation by pumping from the backside using the Al/Ti/Glass platform. The thermal properties of the Al/Ti/glass platform are characterized and can be used as input for extracting the unknown materials.

CHAPTER V THERMAL CONDUCTIVITY OF HYBRID ORGANIC-INORGANIC THIN FILMS AND POLYMER THIN FILMS

With the improvement of the pump-and-probe system for thermal properties measurement in the last chapter, we are able to characterize the nanostructured polymers, including hybrid organic-inorganic thin films and polymer thin films. In this chapter, we show the thermal property measurement of polymer thin films and demonstrate the ultralow thermal conductivity of hybrid organic-inorganic zincone thin films and the size effect of the effective thermal conductivity of ultrathin polystyrene thin films.

V.1 Ultralow thermal conductivity of atomic/molecular layer deposition enabled hybrid organic-inorganic zincone thin films

Atomic layer deposition (ALD)[177] and molecular layer deposition (MLD)[178] have received great attention over the past two decades for the fabrication of ultra-thin functional materials with atomic level control for various applications such as low leakage dielectric films, diffusion barrier coatings, and transparent conducting coatings.[179] When alternated, ALD/MLD utilizing sequential and self-limiting surface reactions can enable a new class of hybrid organic-inorganic materials with enhanced electrical, optical, magnetic, and mechanical properties compared to conventional organic or inorganic materials.[180, 181] As an example, the hybrid zinc alkoxide (or zincone) thin films have recently been fabricated using alternate ALD/MLD process and demonstrated as a promising candidate for transparent conducting coatings.[182] The composition and thickness of each individual inorganic/organic layer in these zincone films can be controlled by the ALD/MLD cycles.[65, 178, 179, 183-188] The heterogeneous inter-atomic/molecular bonding and mass difference between organic molecules and inorganic atoms in these zincone thin films can significantly inhibit the phonon transport and reduce the thermal conductivity to be much lower than their inorganic and organic counterparts.[189-191] As a result, such ALD/MLD-enabled hybrid organic-inorganic materials could be promising thermal insulation materials or even high-efficiency thermoelectric materials due to the expected low thermal conductivity.[192-194] In this Letter, we study for the first time the thermal conductivity and volumetric heat capacity of such novel ALD/MLD-enabled hybrid organic-inorganic zincone thin films to investigate the effect of atomic configuration and structural morphology on the thermal properties of ALD/MLD-enabled hybrid organic-inorganic materials.

Three sets of hybrid organic-inorganic zincone thin films were prepared based on zinc precursors and organic diols on *p*-type (100) Si wafers.[184] A 1 nm alumina layer was deposited first by ALD at 150°C as the adhesion layer that promotes the initial ALD/MLD growth. Diethyl zinc (DEZ) can react with aliphatic organic diols such as ethylene glycol (EG) or aromatic organic diols such as hydroquinone (HQ), which forms type-A and type-B MLD zincone films, respectively.[179] Figures V.1.1(a) & V.1.1(b) show the schematic drawing of type-A and type-B MLD zincone films, which are fabricated with DEZ/EG (1:1) and DEZ/HQ (1:1) in sequence. ZnO can be deposited using ALD with DEZ and H₂O as the reactants. By alternating ZnO ALD and zincone MLD, the type-C ALD:MLD zincone film is fabricated with DEZ/H₂O (1:1) and DEZ/HQ (1:1) in sequence, as shown in Figure V.1.1(c). Details on the chemical reactions, the fabrication procedures, and fabrication conditions of zincone thin film

samples studied in this work can be found in literature [179, 182, 184] and in Section A.II.1 of the Supporting Information.



Figure V.1.1. (a) Schematic drawing of MLD cycles for type-A MLD zincone film using diethyl zinc (DEZ) and ethylene glycol (EG). (b) Schematic drawing of MLD cycles for type-B MLD zincone film using DEZ and hydroquinone (HQ). (c) Schematic drawing of type-C ALD:MLD zincone film deposited using DEZ/H₂O and DEZ/HQ in sequence.

By varying MLD or ALD:MLD cycle numbers, three sets of type-A, type-B and type-C zincone films with various thicknesses have been fabricated, as listed in Table V.1. The thickness of the zincone thin films was measured by the X-ray reflectometry (XRR) using a Bede D1 diffractometer and confirmed by scanning electron microscope (SEM) cross-sectional images after the sample was milled by focused ion beam (FIB) in a Nova 600i dual beam FIB instrument.

As an example, Figure V.1.2(a) shows the cross-sectional SEM image with a 52 °tilted view of a 436.8 nm-thick type-B MLD zincone film on a p-type (100) Si wafer after a trench was milled using FIB. The grazing incidence X-ray diffraction (GIXRD) data using the Bede D1 diffractometer was used to qualitatively analyze the atomic crystallographic order of these zincone films. Figure V.1.2(b) shows the GIXRD data of 43 nm-thick type-A MLD zincone film, 136 nm-thick type-B MLD zincone film, and 139 nm-thick type-C ALD:MLD zincone film. No obvious peaks are observed in the GIXRD data for the 43 nm-thick type-A and 136 nm-thick type-B MLD zincone films, which indicates that these films lack crystalline order. Six peaks appear in the GIXRD data for the 139 nm-thick type-C ALD:MLD zincone film, which matches with the characteristics of the (100), (002), (102), (110), (103), (112) crystal planes of ZnO crystal. Each crystal plane direction represents one orientation of the atomic flakes in the ALD ZnO layer. The 139 nm-thick type-C ALD:MLD film exhibits strong ZnO (100) preferred orientation parallel to the sample surface, which has the strongest signal in the GIXRD data. In these type-C ALD:MLD zincone thin films, the atom-thick ZnO flakes fabricated by ALD cycles are connected by the molecular layer-thick HQ enabled by the DEZ/HQ MLD process. Additionally, the areal size of these atom-thick ALD ZnO flakes can be estimated from the Scherrer's formula.[195] The areal size of the (100) oriented atomic flakes with the strongest GIXRD signal is estimated to be about 13 nm, while the size of other flakes are estimated to be about 6-9 nm. A detailed calculation of the areal size is presented in Section A.II.2 of the Supporting Information.



Figure V.1.2. (a) Cross-sectional scanning electron microscope (SEM) image with a 52° tilted view of a 436.8 nm-thick type-B MLD zincone film on a (100) Si wafer after a trench was milled using focused ion beam (FIB). (b)The grazing incidence X-ray diffraction (GIXRD) data of the 43 nm-thick type-A MLD zincone film, 136 nm-thick type-B MLD zincone film, and 139 nm-thick type-C ALD:MLD zincone film.

Table V.1. Three sets of type-A, type-B, and type-C zincone thin films with various thicknesses were fabricated with different MLD and ALD:MLD cycles and cycle numbers. The average growth rate is estimated by dividing the thickness of each film with the cycle number.

		Thickness		Average growth rate
Туре	One cycle	(nm)	Cycle Number	(nm/cycle)
А	DEZ/EG	43	500	0.086
А	DEZ/EG	56	1000	0.056
А	DEZ/EG	78	2000	0.039
В	DEZ/HQ	82	300	0.273
В	DEZ/HQ	136	500	0.272
В	DEZ/HQ	437	1600	0.273
С	DEZ/H ₂ O/DEZ/HQ	91	600	0.152
С	DEZ/H ₂ O/DEZ/HQ	139	900	0.154
С	DEZ/H ₂ O/DEZ/HQ	193	1300	0.148
С	DEZ/H ₂ O/DEZ/HQ	380	2500	0.152

The cross-plane (through film thickness direction) thermal conductivity and the volumetric heat capacity of zincone thin film samples were simultaneously measured using ultrafast laserbased time-domain thermoreflectance (TDTR) method.[146, 159, 196, 197] TDTR method has recently emerged as a high-accuracy thermal conductivity measurement techniques. Frequencydependent TDTR measurement has recently been explored by Liu *et al*[196] for simultaneous cross-plane thermal conductivity and volumetric heat capacity measurement. Figure V.1.3(a) shows the sample configuration for the TDTR measurement (left: zincone sample, right: reference sample). A ~100 nm-thick aluminum (Al) thin film is thermally evaporated on the top as the metal transducer and temperature sensor. The thickness of this metal transducer layer is determined by the acoustic echoes in the TDTR signal. Before thermal evaporation of Al transducer, an 8 nm-thick alumina capping layer is deposited using ALD on top of the zincone thin film, which prevents the zincone film from reacting with Al vapor when the Al layer is deposited. The thermal conductance of the alumina capping layers was extracted by measuring the reference samples (on the right) that consist of the Al thin film, 8 nm-thick (or 16 nm-thick) alumina layer, and the (100) Si substrate. The frequency-dependent TDTR measurements were carried out at modulation frequencies of 0.5 MHz, 0.98 MHz, and 6.8 MHz. The details of the experiment setup and the data reduction scheme have been presented in literature.[144, 196]

Figure V.1.3(b) shows the dependence on the sample thickness and chemical composition (film type) of the cross-plane thermal conductivity of zincone thin films at room temperature. The thermal conductivity of all the three types of zincone thin films increases only slightly with film thickness, which is attributed to the structural morphology, since a length-dependent thermal conductivity would have been observed if the MLD chains are vertically aligned.[63, 198]. The thermal conductivity of type-B MLD zincone films with DEZ/HQ sequence is higher than that of type-A MLD zincone films with DEZ/EG sequence. Thermal conductivity of the type-C ALD:MLD-enabled films with alternate DEZ/H₂O sequence and DEZ/HQ sequence is much lower, which is only around 1/3 that of type-B MLD zincone films.



Figure V.1.3. (a) Sample configuration for the TDTR measurement of zincone thin films (left: zincone thin film sample, right: reference sample). (b) The dependence on the sample thickness and chemical composition (film type) of the cross-plane thermal conductivity and volumetric heat capacity of zincone thin films.

Table V.2 shows the mass density, the average growth rate, idealized linear growth rate, and the estimated reactive site density during the growth of the 43 nm-thick type-A MLD zincone

film, 136 nm-thick type-B MLD zincone film, and 139 nm-thick type-C ALD:MLD zincone film, with the details in section A.II.3 of the Supporting Information. Apparently the measured average growth rate or deposition rate, which is the increase of the thin film thickness per deposition cycle, is much smaller than the idealized linear growth rate (molecular length per cycle). This indicates that the orientation of the backbone of molecular chain segments is randomly distributed rather than the hypothesized vertical alignment of MLD cycles. Such randomly-distributed orientation of MLD chains is likely the reason for the weakly dependence of thermal conductivity on the thickness as observed in Figure V.1.3(b).

Table V.2. The mass density, the average growth rate, the idealized linear growth rate, and the estimated reactive site density of the 43 nm-thick type-A MLD zincone film, 136 nm-thick type-B MLD zincone film, and 139 nm-thick type-C ALD:MLD zincone film.

	Density	Average growth	Idealized linear	Estimated
	(g/cm^3)	rate (nm/cycle)	growth rate	reactive site
	(greini)	rate (IIII/eyele)	(nm/cycle)	density
43 nm-thick type-A	1.9	0.086	~0.69	36.4%
136 nm-thick type-B	1.9	0.272	~0.84	98.1%
139 nm-thick type-C	5.0	0.154	~1.06	N/A



Figure V.1.4. Sketch of structural morphology of (a) type-A MLD zincone film, (b) type-B MLD zincone film, and (c) type-C ALD:MLD zincone film. In (a) and (b), the hybrid organic-inorganic molecular chains are tilt-oriented on the deposited surface rather than vertically-oriented on the deposited surface. The alternate layers of atom-thick ALD ZnO flakes and the MLD layer is formed in type-C ALD:MLD zincone films (c). The blue atom is Zn, the green atom is O, the orange atom is H, and the grey atom is C. The tetra-coordination formed by the interactions between Zn atoms and adjacent oxygen atoms in type-C ALD:MLD zincone films is also marked.

The key difference between type-A and type-B MLD zincone films is the organic component with aliphatic (EG) or aromatic (HQ) backbone, which has very different rotational

energy barrier or flexibility. It is easier for aliphatic backbone in type-A MLD zincone films to change its conformation by rotating to reach the minimum energy due to the lower rotational energy barrier than that of aromatic backbone in type-B MLD zincone films. This difference in rotational energy barriers would result in more 'double reactions' during the deposition process of type-A MLD zincone films using DEZ and EG than that of type-B MLD zincone films using DEZ and HQ, where both hydroxyl moieties (-OH) in the EG molecules react with adjacent surface sites to produce nonreactive Zn-ethylene oxide groups.[179]'[184] The double reactions in type-A MLD zincone films lead to a loss of reactive surface sites or the decrease of reactive site density and produce a less average growth rate during MLD compared to that in the growth of type-B MLD zincone films. For instance, the average growth rate for the 43 nm-thick type-A MLD zincone film is 0.086 nm/cycle, which is much less than the average growth rate 0.272 nm/cycle for the 136 nm-thick type-B MLD zincone film. The reactive site density in the linear growth region is 98.1% in the 136 nm-thick type-B MLD zincone film compared to 36.4% in 43 nm-thick type-A MLD zincone film. In addition, a decreasing average growth rate with increasing film thickness is found in type-A MLD zincone films while the average growth rates in type-B MLD zincone films and type-C ALD:MLD zincone films are rather constant, as shown in Table V.1. Due to the happening of a large number of double reactions, it is rather challenging to grow type-A MLD zincone films to exceed 100 nm-thick. Figures V.1.4(a) & 4(b) show the sketches of the structural morphology (atomic configuration and chain orientation) of type-A and type-B MLD zincone thin films inferred from the estimation of the growth rate, the reactive site density, and the GIXRD data. In both type-A and type-B MLD zincone films, the hybrid organicinorganic molecular chains are somewhat tilt-oriented rather than vertically-oriented on the deposited surface. However, the molecular chains in type-B MLD zincone films are tilted with a slightly larger angle with respect to the surface due to a more rigid aromatic structure using HQ precursor. The percentage of molecular chains in type-B MLD zincone films that lie down on the surface is also much less than that in type-A MLD zincone film. As a result, thermal conductivity of type-B MLD zincone films is larger than that of type-A MLD zincone films.

Even though the MLD cycles in the deposition of type-C ALD:MLD zincone films are the same as those in the deposition of type-B MLD zincone films, the introduction of alternate ALD cycles in the deposition process dramatically changes the atomic configuration of the type-C ALD:MLD zincone films. Besides forming the atom-thick ALD ZnO flake, HQ in the MLD cycle can react with both the DEZ in the ALD cycle and the MLD cycle in the growth of type-C ALD:MLD zincone film, which results in a much denser film compared to type-B MLD zincone film and a much lower average growth rate compared to the idealized linear growth rate, as shown in Table V.2. Figure V.1.4(c) shows the sketch of the atomic configurations of type-C ALD:MLD zincone films inferred from the estimation of the growth mechanism and the GIXRD data. In the type-C ALD:MLD zincone films, the alternate layers with atom-thick ALD ZnO flake and tilted MLD organic layer are formed, which is very different from the hybrid organicinorganic molecular chain structure in the type-A and type-B MLD zincone films as shown in Figures V.1.4(a) & 4(b). Such an alternate-layer structure with very different atomic configurations between atom-thick ZnO flakes and the molecule chains strongly scatters phonons and reduces the thermal conductivity of the type-C ALD:MLD zincone film compared to that of type-A and type-B MLD zincone films, which is a similar mechanism in the recent demonstrated hybrid organic-inorganic materials with ultralow thermal conductivity.[199, 200]

In an earlier work by Costescu *et al*,[192] the thermal conductivity of 40-70 nm-thick ALDenabled W/Al₂O₃ nanolaminates (electrically non-conductive) deposited by one of the co-authors of the present paper was measured to be 0.6-1.5 W/mK at room temperature. Here we showed that much lower thermal conductivity values, in the range of 0.13-0.38 W/mK, are obtained in ALD/MLD-enabled hybrid organic-inorganic zincone thin films, which promises to produce thermal super-insulators. In addition, the type-C ALD:MLD zincone thin films, which are electrically conductive,[182] could even be explored as thermoelectric materials.

Figure V.1.5 shows the temperature dependence of volumetric heat capacity and thermal conductivity for 78 nm-thick type-A MLD zincone film, 82 nm-thick type-B MLD zincone film, and 91 nm-thick type-C ALD:MLD zincone film. Figure V.1.5(a) shows that the volumetric heat capacity of all the three types of zincone thin films shows a very typical behavior of solids, which increases with temperature first and then reaches a plateau.[201] Higher frequency vibrational modes are excited at higher temperature, which leads to an increase in the heat capacity with temperature. However, the heat capacity reaches a plateau beyond the Debye temperature when all the vibration modes are excited. The heat capacities of type-B and type-C zincone films are larger than that of type-A zincone films, which is due to a much larger degree of freedom in the aromatic rings. Figure V.1.5(b) shows that the thermal conductivity increases with increasing temperature from 150 K to 400 K for type-A and type-B MLD zincone films, which is very similar to the temperature-dependent thermal conductivity of amorphous materials.[82, 175] However, a temperature-dependence trend similar to that of crystalline materials were observed in the thermal conductivity of the type-C ALD:MLD zincone thin films. Thermal conductivity increases from 150 K to 300 K due to the rapid increase of heat capacity, and then decreases with a temperature from 300 K to 400 K due to the increased phonon-phonon scattering with increasing temperature.[82] The temperature dependence observed in Figure V.1.5 further confirms the crystalline-nature structural morphology shown in Figure V.1.4.



Figure V.1.5. The temperature dependence of (a) volumetric heat capacity and (b) thermal conductivity of 78 nm-thick type-A MLD zincone film, 82 nm-thick type-B MLD zincone film, and 91 nm-thick type-C ALD zincone film.

V.2 Size effect of effective thermal conductivity of ultrathin polystyrene films

Polymers have recently been demonstrated to exhibit different chain dynamic behavior and thermal properties, as compared to the bulk counterpart, when confined to the geometry of ultrathin films. For instance, a Monte Carlo simulation shows that the chain confinement in ultrathin polymer film makes the polymer chains fold back into the volume it occupies and squeeze out neighboring chains.[202] The in-plane dimension of the chains has been measured to increase with decreasing film thickness below certain times of the bulk radius of gyration.[203, 204] Consequently, the glass transition temperature [205-208] and thermal expansion coefficient[209] have been measured to change in ultrathin polymer films compared to their bulk counterpart. Though still on debate, the common agreement on the change of chain morphology in ultrathin polymer film is that the polymer chains are re-orientated and less entangled compared to that in bulk polymers when the thickness of the polymer thin films is much smaller than certain times of the radius of gyration of the polymer. The effective thermal conductivity of polymer thin film could be different from that of bulk polymers in two aspects: (1) the thermal conductivity of polymer thin film changes due to the change of chain orientation and chain entanglement; (2) the interfacial thermal conductance between polymer thin film and substrate changes due to a closer contact and a stronger interaction between polymer chains and the substrate. In this section, the effective thermal conductivity of polymer films from ultrathin to bulk-like is measured to show how the chain confinement affects the thermal transport in polymer thin films and explore the possible reasons for the size effect of the effective thermal conductivity. This study could be beneficial for the thermal management in macro- and microelectronics and photovoltaics with polymer thin films.

Three sets of polystyrene films were spin-coated on (100) *n*-type Si wafer with natural oxide. The polystyrene samples with different molecular weight were purchased from Scientific Polymer Products Inc.. Table V.3 shows the molecular weight and radius of gyration of the three sets of polystyrene films. The thickness of the spin-coated polystyrene thin films was measured by XRR and was from around 5 nm to 300 nm.

Sample set	Molecular weight (kg/mol)	Radius of gyration (nm)
1	2000	38
2	31.6	4.6
3	4	1.6

Table V.3 The molecular weight and radius of gyration of the three sets of polystyrene films

The thermal conductivity of polymer thin films was measured using the TTR method with the tri-layer configuration in Figure IV.2.1(b). The ~100 nm Al thin film was thermally evaporated on the spin-coated polymer thin films. Since the thickness of polymer films ranges from a few nanometers to hundreds of nanometers, a heat transfer analysis is needed to identify the thermal property that can be extracted by fitting. For example, when the thin film is ultrathin, the only thermal property extracted is the effective thermal conductivity or thermal resistance of thin film, which includes two interfaces between polymer film and its neighboring materials, and the intrinsic thermal conductivity of polymer thin film. When the thickness is on the order of 100 nm, the interfacial thermal conductance could be separated from the intrinsic thermal conductivity of thin film.

If the thermal resistance of thin film is the only thermal property extracted, the heat transfer model should be equivalent using the bi-layer and tri-layer configuration model, which assumes

$$\frac{d_3}{\kappa_{eff}} = \left(\frac{1}{G_2}\right)_{bi-layer} = \left(\frac{1}{G_2} + \frac{1}{G_4} + \frac{d_3}{\kappa_3}\right)_{tri-layer},$$
 (V.2.1)

where κ_{eff} is the effective thermal conductivity of the thin film with the thickness d_3 , the subscript means the variable is in the bi-layer configuration or tri-layer configuration. When the following four terms in Eq. (IV.2.13) can be neglected as,

$$\frac{\gamma_3\gamma_5}{\gamma_1G_4}n \ll \frac{\gamma_5}{\gamma_1},\tag{V.2.2a}$$

$$\frac{\gamma_3}{\gamma_1} n \ll \frac{\gamma_5}{\gamma_1}, \tag{V.2.2b}$$

$$\frac{\gamma_3\gamma_5}{G_2G_4}n \ll \frac{\gamma_5}{G_2},\tag{V.2.2c}$$

$$\frac{\gamma_3}{G_2}n \ll \frac{\gamma_5}{G_2},\tag{V.2.2d}$$

and the term n/γ_3 can be simplified as,

$$\frac{n}{\gamma_3} \approx \frac{d_3}{\kappa_3}, \qquad (V.2.2e)$$

the condition of Eq. (V.2.1) can be satisfied, which can be found by comparing the bi-layer model in Eq. (IV.2.9) and the tri-layer model in Eq. (IV.2.13). The equations from (V.2.2a) to (V.2.2e) can be summarized as the following three conditions,

$$\gamma_3 n \ll G_2 \text{ and } G_4, \tag{V.2.3a}$$

$$\gamma_3 n \ll \gamma_5, \tag{V.2.3b}$$

$$\frac{n}{\gamma_3} \approx \frac{d_3}{\kappa_3}.$$
 (V.2.3c)

114

When the thermal properties of thin film satisfy the Eqs. (V.2.3.a) to (V.2.3c), only thermal resistance can be extracted from the TTR measurement.

We can estimate the dominant thermal property of polystyrene thin films measured by the TTR method. When the thickness of polystyrene film is below around 40 nm, the measured thermal property at 2.08 MHz is only the thermal resistance of the polymer film, which is calculated using a thermal conductivity value of 0.15 W/mK, a heat capacity value of 1.24 J/cm³K, an interfacial thermal conductance (between polymer thin film and Al thin film or Si substrate) value of 10 MW/m²K. Therefore, the polystyrene film with thickness below 40 nm was fitted with the bi-layer configuration model where the effective thermal conductivity or thermal resistance was fitted. When the film thickness is around 200 nm, the film resistance (1.33 μ Km²/W) is much larger than the interfacial thermal resistance (0.1 μ Km²/W), where the interfacial thermal conductance is not sensitive in the measurement. When the thickness is between 40 nm to 200 nm, both the interfacial thermal conductance and the thermal conductivity of the film could be sensitive in the measurement.

Figure V.2.1 shows the sensitivity analysis and measurement procedure for the thermal properties of the set-1 polystyrene thin films as examples. Figure V.2.1(a) shows the TTR measurement signal of the set-1 18.5 nm-thick polystyrene film at 2.08 MHz. The fitting result of the effective thermal conductance is 4.55 MW/m²K. Figure V.2.1(b) shows the TTR measurement signal of the set-1 191 nm-thick polystyrene film at 0.98 MHz, 2.08 MHz, and 6.8 MHz. Figure V.2.1(c) shows the sensitivity analysis of measuring the set-1 191 nm-thick polystyrene film under modulation frequencies of 2.08 MHz and 6.8 MHz. Both of the interfacial thermal conductance G_2 and G_4 are not sensitive while the thermal conductance is not sensitive

in the measurement of films with the thickness on the order of 100 nm, the volumetric heat capacity and thermal conductivity of the polystyrene thin film can be simultaneously measured using multiple modulation frequencies, similarly as shown in Section IV.2. Figure V.2.1(d) shows the κ -*C* diagram that used to extract the thermal conductivity and volumetric heat capacity of the set-1 191 nm-thick polystyrene film. Figure V.2.1(e) show the sensitivity analysis of measuring the set-1 60 nm-thick polystyrene film under modulation frequencies of 2.08 MHz and 6.8 MHz. The thermal conductivity κ_3 of polystyrene thin film is sensitive under both modulation frequencies. The total resistance of the two interfaces G_2 and G_4 is sensitive under a modulation frequency of 2.08 MHz while the interfacial thermal conductance between polymer film and Si G_4 is sensitive under a modulation frequency of 6.8 MHz. Thus, all the three unknown thermal properties κ_3 , G_2 , and G_4 can be extracted. Figure V.2.1(f) shows the TTR measurement signal of the set-1 60 nm-thick polystyrene film at 2.08 MHz, 3.4 MHz, and 6.8 MHz.





Figure V.2.1.The sensitivity analysis and measurement procedure for the thermal properties of polystyrene thin films. (a) the TTR measurement signal of the set-1 18.5 nm-thick polystyrene film at 2.08 MHz. (b) the TTR measurement signal of the set-1 191 nm-thick polystyrene film at 0.98 MHz, 2.08 MHz, and 6.8 MHz. (c) The sensitivity analysis of measuring the set-1 191 nm-thick polystyrene film under modulation frequencies of 2.08 MHz and 6.8 MHz. (d) The κ -C diagram that used to extract the thermal conductivity analysis of measuring the set-1 60 nm-thick polystyrene film. (e) The sensitivity analysis of measuring the set-1 60 nm-thick polystyrene film under modulation frequencies of 2.08 MHz and 6.8 MHz. (f) The TTR

measurement signal of the set-1 60 nm-thick polystyrene film at 2.08 MHz, 3.4 MHz, and 6.8 MHz.

Table V.4 shows the measured thermal conductivity and volumetric heat capacity of three polystyrene films with the thickness larger than 100 nm. As shown in the sensitivity analysis in Figure V.2.1(c), only the thermal conductivity and volumetric heat capacity of the polymer thin film is sensitive and can be fitted. Both the thermal conductivity and volumetric heat capacity of the three polystyrene films are close to each other, which agree with the bulk values of thermal conductivity and volumetric heat capacity of polystyrene.[210] Table V.5 shows the measured thermal conductivity and interfacial thermal conductance of three polystyrene films with thickness around 60 nm. The thermal conductivity κ_3 of the polystyrene film and the interfacial thermal conductance G_2 between Al film and polystyrene film are the same with three sets of ~60 nm-thick polystyrene films. The interfacial thermal conductance G_4 between polystyrene film and Si substrate changes with different sets of polymers.

Table V.4 Thermal conductivity and volumetric heat capacity of three polystyrene films with thickness larger than 100 nm.

R_g (nm)	<i>d</i> (nm)	κ_3 (W/mK)	$C (J/cm^3K)$
1.6	191	0.154	1.24
4.6	184	0.152	1.24
38.0	302	0.152	1.25

R_g (nm)	<i>d</i> (nm)	κ_3 (W/mK)	$G_2 (\mathrm{MW/m^2K})$	G_4 (MW/m ² K)
1.6	60	0.154	18.01	8.65
4.6	56	0.153	20.47	8.81
38.0	62	0.155	19.35	16.28

Table V.5 Thermal conductivity and interfacial thermal conductance of three polystyrene films with the thickness around 60 nm.

Figure V.2.2 shows the measurement results of the effective thermal conductivity of the polystyrene thin film samples as a function of the film thickness and the ratio of the film thickness to the radius of gyration. Figure V.2.2(a) shows that the effective thermal conductivity of polystyrene films decreases first and then increases with decreasing thickness of the polystyrene film. An orange dash line is also drawn to show the effective thermal conductivity of polystyrene film assuming that both the thermal conductivity and interfacial thermal conductance do not change. For the polystyrene films with radius of gyration less than 5 nm (set-2 and set-3), the measured effective thermal conductivity agrees with the orange dash line when the thickness is larger than 50 nm and deviates from the orange dash line when the thickness is smaller than 50 nm. For the polystyrene film with radius of gyration as 38 nm (set-1), the measured effective thermal conductivity agrees with the orange dash line when the thickness is larger than 200 nm and deviates from the orange dash line when the thickness is smaller than 200 nm. Apparently we find that the effective thermal conductivity increases compared to the bulk value (orange dash line) when the thickness decreases below certain times of the radius of gyration of bulk polystyrene. Figure V.2.2(b) shows the effective thermal conductivity of polystyrene films plotted as a function of the ratio of the film thickness d to the radius of gyration R_g . A larger ratio

 d/R_g indicates a more chain confinement effect in the polystyrene thin film. All the points deviate from the orange dash line in Figure V.2.2(a) follow a line $\kappa_{eff} = 0.135 (d/R_g)^{0.957}$ in Figure V.2.2(b). The effective thermal conductivity κ_{eff} increases with decreasing d/R_g following this line till $d/R_g = 10$.



Figure V.2.2. The measurement results of the effective thermal conductivity of the polystyrene thin film samples as a function of (a) the thickness d of the film, (b) the ratio of the film thickness to the radius of gyration d/R_g . The orange dash line in (a) is calculated assuming that both the thermal conductivity and interfacial thermal conductance do not change.

Based on all the measured results in Table V.4, Table V.5, and Figure V.2.2, we can analyze how the chain confinement affects the thermal properties of polystyrene thin films. The effective thermal conductivity of polymer thin film could be different from that of bulk polymers due to the chain confinement effect by a different intrinsic thermal conductivity of polymer thin film or a different interfacial thermal conductance between polymer thin film and the substrate. As shown in Figure V.2.2, the effective thermal conductivity of set-1 polystyrene films with certain confinement (the ratio d/R_g is around 3 – 6) still follows their corresponding bulk values (orange dash line) when the thickness is from 100 nm- 300 nm. When the thickness of polymer thin film is larger than 100 nm, the intrinsic thermal conductivity of thin film dominates the effective thermal conductivity. Therefore, the intrinsic thermal conductivity of polystyrene films does not change when polymer chains are confined. Such a conclusion is also supported by the fact that the measured thermal conductivity of the 60 nm-thick set-1 polystyrene film with d/R_g around 1.6 is the same with the set-2 and set-3 polystyrene film with much larger values of d/R_g (12 and 37.5). The interfacial thermal conductance between the polystyrene thin film and substrate starts to play a role in the effective thermal conductivity when the thickness of polymer thin film is less than around 60 nm, where the measured effective thermal conductivity increases compared to the bulk value (orange dash line). Thus, the increase of the interfacial thermal conductance between polystyrene thin film and Si substrate should be the main reason for the increase of the effective thermal conductivity. Such a conclusion is also confirmed by the measurement results shown in Table V.5, where the interfacial thermal conductance between polystyrene thin film and Si substrate G_4 increases with the increasing chain confinement d/R_g . The polymer chains are re-orientated, becoming more parallel to the surface, and less entangled compared to that in bulk polymers when the thickness of the polymer thin films is much smaller than the radius of gyration of the polymer. Therefore, the interfacial thermal conductance between polystyrene thin film and substrate increases due to a closer contact and a stronger interaction between polymer chains and the substrate, which is the main reason for the increasing effective thermal conductivity measured.

V.3 Summary of this chapter

In this chapter, the thermal properties of the nanostructured polymers, including hybrid organic-inorganic thin films and polystyrene thin films, are measured using the ultrafast pumpand-probe system. The cross-plane thermal conductivity and volumetric heat capacity of hybrid organic-inorganic zincone thin films enabled by MLD processes and alternate ALD:MLD processes were measured using the frequency-dependent TDTR method. The thermal conductivity of MLD zincone film with DEZ/HQ sequence is higher than that of MLD zincone film with DEZ/EG sequence, due to the critical role of flexibility that the backbones (EG or HQ) play in the structural morphology and thermal conductivity of the zincone thin films. In the ALD:MLD zincone film, the alternate-layering structure with very different atomic configurations between the ALD atomic flake layers and the MLD molecular layers strongly scatters phonons, which reduces the thermal conductivity to be much lower than that of the MLD zincone films with the same organic component. Much lower thermal conductivity values are obtained in ALD/MLD-enabled hybrid organic-inorganic zincone thin films compared to that of the ALD-enabled W/Al₂O₃ nanolaminates reported by Costescu et al.,[192] which suggests that the dramatic material difference between organic and inorganic materials may provide a route for producing materials with ultralow thermal conductivity.

The measurement of the ultrathin polymer thin films shows that the effective thermal conductivity increases when the thickness of the polymer is much smaller than around ten times of the radius of gyration. The interfacial thermal conductance between polymer thin film and the substrate increases due to a closer contact and a stronger interaction between polymer chains and the substrate, which is the main reason for the increasing effective thermal conductivity

measured. The measurement results of those nanostructured polymers show the effect of structure parameters of the organic materials on thermal transport, which could be used for further design the devices that utilize organic or hybrid organic-inorganic materials.

CHAPTER VI FUTURE WORK

The simulation and characterization work in this thesis could be extended to study more features of nanostructured polymers. In this thesis, the chain parameters of the polymers have been shown to strongly affect the thermal conductivity of polymer chains. To further study the properties of polymer chains, the relationship between mechanical property and thermal property in organic materials could be found through molecular dynamics simulations since both mechanical properties and thermal properties of polymer chains are related to the backbone flexibility, bond strength, and the chain orientation. In addition, how each interaction in the polymer chain (bond-stretching, bond-bending, dihedral interaction) affects the thermal and mechanical properties remains a question. The simulation work could provide insights on the structure-property relationship and thermal transport mechanism in organic materials. Furthermore, the preliminary study on the hybrid organic-inorganic zincone thin films shows the dramatic difference between organic and inorganic materials could render materials with ultralow thermal conductivity. This work could be extended to a systematic study by changing the ratio of organic and inorganic components or searching more combinations for organic and inorganic materials. Moreover, if the hybrid materials with aligned chains or ordered structures can be fabricated using ALD/MLD, those materials could also be potentially used for thermal management.

The pump-and-probe system has been improved to be able to simultaneously measure anisotropic thermal conductivity, heat capacity, and interfacial thermal conductance. In addition, the pumping from backside measurement setup has been tested and ready for study of complicated materials. Based on this improved characterization system, the study of hybrid organic-inorganic materials or even more classes of materials could be more systematic. For instance, the organic-inorganic nanocomposites and the organic-inorganic superlattices could be excellent platforms to study thermal transport across organic-inorganic interfaces, and also as potential materials for thermoelectrics and thermal insulation. Moreover, the study of ordered/aligned organic/inorganic materials (e.g. nanowire arrays, molecular 2-D or 3-D architecture) could bring a new perspective to understand the thermal transport in those materials and provide materials with improved performance.

Another interesting direction to follow is to develop high-efficiency thermoelectrics and high-level thermal rectification using inorganic-organic interfaces and nanocomposites that are low-density, low-cost, and easy to synthesize. Despite the progress in material synthesis and electronic property measurement of conductive polymer-based materials, the fundamental understanding of the interrelationships among electrical and thermal transport across inorganic-polymer interfaces is completely lacking. The systematic study through both experimental and theoretical approaches the thermal and thermoelectric transport phenomena in conductive polymers, the inorganic-polymer interfaces and nanocomposites could be beneficial. Both planar and nanostructured interfaces of inorganic-organic materials can be fabricated and the electrical, thermal, and thermoelectric transport properties can be probed simultaneously to understand the multi-carrier transport and interactions of electrons and phonons. The insight on the fundamental transport mechanisms will be employed to develop high-efficiency inorganic-organic thermoelectric nanocomposites and to design inorganic-polymer thermal rectifiers that could enable new generations of phononic computing devices.

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APPENDIX

Appendix I. Frequency-domain Response of the Surface Temperature Change

We present in detail the calculation of the frequency-domain response of the surface temperature change in the real space, which is obtained by solving the heat conduction equation for a Gaussian heat source on a multiple layer of materials and weighting the temperature distribution at the top surface by the Gaussian intensity distribution of the probe beam. Similar calculations can be also found in the literature.[144, 146, 159]

A.I.1. Single layer and interface

Considering a cylindrical heating spot on the metallic transducer, which absorbs laser heating, the heat conduction equation can be written as the following for each layer:

$$\frac{\kappa_r}{r}\frac{\partial}{\partial r}\left[r\frac{\partial\tilde{\theta}(r,z)}{\partial r}\right] + \kappa_z\frac{\partial^2\tilde{\theta}(r,z)}{\partial z^2} = C\frac{\partial\tilde{\theta}(r,z)}{\partial t}, \qquad (A.I.1)$$

where *r* is the radial coordinate, *z* is the cross-plane coordinate (in the depth direction), *t* is time, $\tilde{\theta}$ is the temperature, *C* is the volumetric heat capacity, and κ_r and κ_z are the in-plane and crossplane thermal conductivity, respectively.

To solve the equation with radial symmetry, the zeroth-order Hankel transform is performed to simplify Eq. (A.I.1), which yields[162]

$$-\kappa_r x^2 \theta(z) + \kappa_z \frac{\partial^2 \theta(z)}{\partial z^2} = C \frac{\partial \theta(z)}{\partial t}, \qquad (A.I.2)$$

where x is the transform variable, and θ is the temperature in Hankel transform. In the thermoreflectance measurement, the heating pulses are modulated by a frequency ω_0 , and the response are extracted from the probe laser beam at the frequency ω_0 by a lock-in amplifier, so a solution of Eq. (A.I.2) is sought in the frequency domain:

$$\theta = u \exp[i(\omega t - \xi)], \qquad (A.I.3)$$

where u is a function of z only, and ζ is an arbitrary constant. Substituting Eq. (A.I.3) into Eq. (A.I.2), we have

$$\frac{\partial^2 \theta(\omega, z)}{\partial z^2} = q^2 \theta(\omega, z), \qquad (A.I.4)$$

where

$$q = \sqrt{\frac{\kappa_r x^2 + iC\omega}{\kappa_z}} . \tag{A.I.5}$$

The general solution of Eq. (A.I.4) is

$$\theta(z) = \alpha \exp(qz) + \beta \exp(-qz), \qquad (A.I.6)$$

$$F(z) = -\alpha \kappa_z q \exp(qz) + \beta \kappa_z q \exp(-qz), \qquad (A.I.7)$$

where α and β are constants, and $\theta(z)$ and F(z) are the temperature and heat flux at the point *z*. Let θ and *F* be the temperature and heat flux at the face z=0 and let θ' and *F'* be their values at the face z=d. The relation between these four quantities θ , *F*, θ' and *F'* can be expressed as

$$\begin{bmatrix} \theta'\\ F' \end{bmatrix} = \begin{bmatrix} \tilde{A} & \tilde{B}\\ \tilde{C} & \tilde{D} \end{bmatrix} \begin{bmatrix} \theta\\ F \end{bmatrix}.$$
 (A.I.8)

By substituting Eq. (A.I.6) and (A.I.7) into Eq. (A.I.8), α and β can be eliminated, and we can easily get

$$\widetilde{A} = \widetilde{D} = \cosh(qd), \ \widetilde{B} = -\sinh(qd)/(\kappa_z q), \ \widetilde{C} = -\kappa_z q \sinh(qd).$$
(A.I.9)

When heat diffuses through an interface, there should be a temperature difference between its two sides, and the only necessary property is the interface thermal conductance G, which could be defined by

$$F = F' = G(\theta - \theta'). \tag{A.I.10}$$

In matrix form Eq. (A.I.10) will become

$$\begin{bmatrix} \theta' \\ F' \end{bmatrix} = \begin{bmatrix} 1 & -1/G \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \theta \\ F \end{bmatrix},$$
(A.I.11)

Eq. (A.I.8) and (A.I.11) are the heat transfer solutions for a single layer with thickness of d and an interface, respectively.

A.I.2. Multilayer

In a multilayer structure with *n* parallel layers inside,[164] the temperature θ_{j+1} and heat flux F_{j+1} on the bottom side of the *j*th layer should be the product of the temperature θ_j and heat flux F_j on the top side with a matrix M_j , *i.e.*,

$$\begin{bmatrix} \theta_{j+1} \\ F_{j+1} \end{bmatrix} = \begin{bmatrix} A_j^+ & B_j^+ \\ C_j^+ & D_j^+ \end{bmatrix} \begin{bmatrix} \theta_j \\ F_j \end{bmatrix} = M_j \begin{bmatrix} \theta_j \\ F_j \end{bmatrix}.$$
 (A.I.12)

Multiple layers are handled by multiplying the matrices for each individual layers in sequence. Therefore, the temperature θ_{n+1} and heat flux F_{n+1} of the bottom side of the multilayer stack can be expressed by

$$\begin{bmatrix} \theta_{n+1} \\ F_{n+1} \end{bmatrix} = \begin{bmatrix} A^+ & B^+ \\ C^+ & D^+ \end{bmatrix} \begin{bmatrix} \theta_1 \\ F_1 \end{bmatrix},$$
 (A.I.13)

where

$$\begin{bmatrix} A^{+} & B^{+} \\ C^{+} & D^{+} \end{bmatrix} = M_{n}M_{n-1}...M_{1}, \qquad (A.I.14)$$

and θ_l and F_l are the temperature and heat flux on the top side of the multilayer stack. If the heat flux is applied to the top surface of the first layer, and the *n*th layer is assumed to be semi-infinite or adiabatic, which means $F_{n+l}=0$, the top surface temperature will be given as

$$\theta_1 = -\frac{D^+}{C^+}F_1,$$
 (A.I.15)

from Eq. (A.I.13), where C^+ and D^+ are calculated via Eq. (A.I.14).

A.I.3. Frequency-domain response of surface temperature change

The pump pulse heats the top surface and gives the top boundary condition as the cylindrical heat flux distribution

$$\tilde{I}_{pump}(r) = \frac{2Q_{pump}}{\pi R_{pump}^2} \exp(\frac{-2r^2}{R_{pump}^2}),$$
(A.I.16)

Which after taking the Hankel transform will give

$$F_{1}(x) = I_{pump}(x) = \frac{Q_{pump}}{2\pi} \exp(\frac{-x^{2}R_{pump}^{2}}{8}), \qquad (A.I.17)$$

where Q_{pump} is the power absorbed from pump laser, and R_{pump} is the $1/e^2$ radius of pump intensity distribution as a Gaussian spot. Inserting Eq. (A.I.17) to Eq. (A.I.15) yields the surface temperature

$$\theta_{1}(x) = -\frac{D^{+}}{C^{+}} \frac{Q_{pump}}{2\pi} \exp(\frac{-x^{2} R_{pump}^{2}}{8}).$$
(A.I.18)

The surface temperatures are measured by thermoreflectance, *i.e.*, the change in the reflectivity, which depends on the temperature change. This change in reflectivity is measured by changes in the reflected intensity of a probe laser beam. Let Q_{probe} be the power of probe beam and let R_{probe} be the $1/e^2$ radius of probe intensity distribution as a Gaussian spot. The thermoreflectance response H(x) contained in reflected probe beam should be the product of surface temperature θ_1 and thermoreflectance coefficient v, and weighted by the probe intensity distribution, considering the cylindrical spreading effects,[159]

$$H(x) = \nu \frac{Q_{probe}}{2\pi} \exp(\frac{-x^2 R_{probe}^2}{8}) \theta_1(x) = -\nu (\frac{D^+}{C^+}) \frac{Q_{pump} Q_{probe}}{4\pi^2} \exp[\frac{-x^2 (R_{pump}^2 + R_{probe}^2)}{8}].$$
(A.I.19)

The frequency-domain response $H(\omega)$ of the surface temperature change in real space can then be found by taking the inverse Hankel transform of Eq. (A.I.19):

$$H(\omega) = v \frac{Q_{pump}Q_{probe}}{2\pi} \int_0^\infty x(-\frac{D^+}{C^+}) \exp\left[\frac{-x^2(R_{pump}^2 + R_{probe}^2)}{8}\right] dx.$$
(A.I.20)

Appendix II. Sample fabrication and characterization of zincone thin films

A.II.1 Sample fabrication

The zincone thin film samples were fabricated on a *p*-type (100) Si wafer. A 1 nm alumina adhesion layer was deposited at 150° C by the atomic layer deposition (ALD), which serves as the seed layer to promote molecular layer deposition (MLD) growth. The surface reactions for ALD Al₂O₃ can be described as[177]

$$AlOH^* + Al(CH_3)_3 \rightarrow AlOAl(CH_3)_2^* + CH_4$$
(A.II.1)

$$AlCH_{3}^{*} + H_{2}O \rightarrow AlOH^{*} + CH_{4} , \qquad (A.II.2)$$

where the asterisks denote the surface species. The Al_2O_3 ALD growth occurs during the alternating exposures to trimethylaluminum (TMA) and H_2O . The main driving force for the efficient reactions is the formation of a very strong Al-O bond.

Zincone MLD process uses zinc precursors that can be matched with aliphatic and aromatic organic precursors.[179] For instance, diethyl zinc (DEZ) can react with diols such as ethylene glycol (EG) and hydroquinone (HQ). The surface reactions for zincone MLD can be written as

$$ZnR^* + HOR'OH \rightarrow ZnOR'OH^* + RH$$
(A.II.3)

$$R'OH^* + ZnR_x \rightarrow R'OZnR_{x-1}^* + RH$$
 (A.II.4)

where the zinc alkyl molecule is ZnR_x and the diol is HOROH. The R_x is CH_3CH_3 ; the R is CH_3CH_3 for EG and C_6H_4 for HQ, respectively. Figure A.II.1 shows the schematics of the

chemical reaction sequence for type-A and type-B MLD zincone films and the type-C ALD:MLD zincone film.[179, 182] Type-A and type-B MLD zincone films are reacted with DEZ/EG (1:1) and DEZ/HQ (1:1) in sequence, respectively. ZnO can be deposited using ALD with DEZ and H₂O as the reactants, similar to ALD Al₂O₃. The type-C ALD:MLD zincone film is fabricated by alternating ZnO ALD and zincone MLD steps which uses DEZ/H₂O/DEZ/HQ (1:1:1:1) in sequence, as shown in Figure A.II.1(c).



(c)

Figure A.II.1. (a) Schematic two-step reaction sequence for type-A MLD zincone film using diethyl zinc (DEZ) and ethylene glycol (EG). (b) Schematic two-step reaction sequence for type-B MLD zincone film using DEZ and hydroquinone (HQ). (c) Schematic four-step reaction sequence for type-C ALD:MLD zincone film growth by alternating ZnO ALD using DEZ and H₂O and a similar MLD process for growth of type-B MLD zincone film using DEZ and HQ.

The chemicals and materials used in this work are the same as previous studies.[179, 182, 183, 185] DEZ (Zn(C₂H₅)₂) (minimum Zn 52.0 wt.%, product number 256781) was obtained from Sigma-Aldrich and used without further treatment. Deionized water (DI water) was used as the water source for ALD growth of alumina adhesion layer and ZnO. The organic material sources EG (purity 99.8%, product number 324558) and HQ (purity >99%, product number H9003) were purchased from Sigma-Aldrich. High purity Ar (99.999%) (National Welders Supply Co.) was used as the purge gas and carrier gas for reactants. The Si wafer was first wet cleaned in BakerClean JTB-100 solution and then rinsed with DI water and blown dry with N₂. ALD of ZnO layers and MLD of the zincone thin films were carried out in the same viscous flow vacuum reactor. A controlled temperature gradient was maintained along the entire gas flow path to prevent precursor condensation.[177, 179, 182, 183] The DEZ precursor and DI water were contained in stainless steel containers and evaporated at room temperature. The HQ and EG were contained in similar containers and evaporated at 80 °C. Ultra-high-purity Ar gas was used as the carrier gas and further purified by using a gas filter before entering the system. The flow rate of Ar carrier gas was $120 \text{ cm}^3/\text{min}$ with a steady-state process pressure of ~0.9 Torr monitored by a Baratron pressure gauge. [182, 183] The DI water, HQ, and EG were bled into the reactor using Ar carrier gas. The reactant dose amount was adjusted by either changing pulse time or by

changing the flow rate through the needle valve orifice. The organic and metal organic precursors were pumped through separate exhaust lines, which were controlled separately.

A.II.2 Grazing incidence X-ray diffraction (GIXRD) of zincone thin films

	θ()	β (rad)	L (nm)
(100)	31.765	0.011	13.15
(002)	34.394	0.018	8.60
(102)	36.193	0.017	9.05
(110)	56.603	0.020	8.43
(103)	62.757	0.028	6.10
(112)	67.842	0.028	6.21

Table A.II.1. Areal size estimation of the atom-thick ZnO flakes using Scherrer's formula.

The grazing incidence X-ray diffraction (GIXRD) scans were conducted on the zincone thin films using a high resolution X-ray diffractometer (Cu X-ray tube) from Bede Scientific to qualitatively analyze the crystallographic order. A collimator (Osmic Max-Flux) and a channel cut crystal restricted the Cu K α radiation to the Cu K α_1 emission at 0.154 nm. The GIXRD data were shown in Figure 2b in the main text. Both type-A and type-B MLD zincone films exhibit amorphous-like structure while type-C ALD:MLD zincone films exhibit crystalline-like behavor, with strong features of ALD ZnO. Additionally, as a first-order approximation, the areal size of the atomic-thick ALD ZnO flakes can be estimated from the Scherrer's formula,[195]

$$L = \frac{K\lambda}{\beta\cos\theta},\tag{A.II.5}$$

where *L* is the average size of the domain with crystallographic order, *K* is the dimensionless shape factor, which is usually set as 0.93,[195] λ is the X-ray wavelength, β is the peak width (in radian), which is usually characterized as the full width at the half maximum, θ is the GIXRD Bragg angle. Table A.II.1 shows the areal size estimation of the atom-thick ZnO flakes using Scherrer's formula. The areal size *L* of the atomic-thick ALD ZnO flake with the (100) orientation is estimated to be about 13 nm, while the areal sizes of other flakes are estimated to be around 6-9 nm.

A.II.3 Estimation of reactive site density and average growth rate

The ALD/MLD growth of materials on a reactive surface depends strongly on the substrate temperature, steric effects (*i.e.* each atom occupies a certain amount of space), the existence of double reactions, and surface reactive site density.[179, 184, 188] A double reaction happens if both reactive end groups on the monomers react with available surface sites, consuming and/or blocking surface reactive sites that would otherwise be available during the following surface reaction step. Such double reactions lead to the loss of reactive surface sites or the decrease of reactive site density and could result in a decreasing growth rate compared to the deposition without double reactions during ALD/MLD.

The *in situ* quartz crystal microbalance (QCM) measurements were used to monitor the mass gain of the organic (EG or HQ) components and the inorganic (DEZ) components during each MLD cycle.[183] The QCM measurement was performed in the viscous flow reactor using

a Maxtek TM400 thin film deposition monitor. Table A.II.2 shows the ratio of mass gain during the deposition of EG (HQ) to that of DEZ when fabricating the 43 nm-thick type-A MLD zincone film (136 nm-thick type-B MLD zincone film), which was measured at 150 °C by the QCM in the linear growth region (beyond the initial nucleation and growth region). For example, in the linear growth region, the measured mass gain during deposition of DEZ was 28.4 ng/cm² and the measured mass gain during deposition of HQ was 23.9 ng/cm² in the fabrication of the 136 nm-thick type-B MLD zincone film. The total mass gain is 52.3 ng/cm² per HQ/DEZ MLD cycle. The ratio of the measured mass gains for depositing HQ and DEZ is 23.9/28.4=0.84. The maximum/idealized ratio of the mass gain during HQ deposition to that of DEZ should equal the ratio of the molecular weight gained in the deposition of HQ to that of DEZ if all the reactive sites are available for the surface reaction. The idealized ratio for mass gain of HQ to that of DEZ in one HQ/DEZ MLD cycle is 80.03 (g/mol) / 93.4 (g/mol) = 0.856. The measured mass gain ratio of HQ to DEZ is always lower than the idealized ratio since certain percentage of the surface reactive sites is blocked by the HQ molecules. Comparing this measured ratio to the idealized ratio of mass gain of HQ to that of DEZ, we can estimate the reactive site density during one HQ/DEZ MLD cycle. The estimated reactive site density is 36.4% (0.24/0.66) and 98.1% (0.84/0.856) for the 43 nm-thick type-A MLD zincone film and 136 nm-thick type-B MLD zincone film, respectively. In the growth of type-C ALD:MLD zincone film, HQ in the MLD cycle can react with both the DEZ in the ALD cycle and the MLD cycle. It is rather challenging to estimate the ratio of mass gain of HQ to that of DEZ in one MLD cycle in the type-C ALD:MLD zincone film.

Table A.II.2. The ratio of mass gain during deposition of EG (HQ) to that of DEZ when fabricating the 43 nm-thick type-A MLD zincone film (136 nm-thick type-B MLD zincone film), which is measured at 150 °C by the QCM in the linear growth region. The reactive site density during one MLD cycle of the EG (HQ) and DEZ can be estimated by the measured ratio of mass gain divided by the idealized ratio of mass gain.

The ratio of mass gain	Measured	Idealized	Estimated reactive site density
EG/DEZ in 43nm-thick type-A	0.24	0.660	36.4%
MLD zincone film			
HQ/DEZ in 136 nm-thick type-B	0.84	0.856	98.1%
MLD zincone film		0.000	

Table A.II.3. The mass density, the average growth rate, the idealized linear growth rate, and the mass gain of the 43 nm-thick type-A MLD zincone film, 136 nm-thick type-B MLD zincone film, and 139 nm-thick type-C ALD:MLD zincone film.

	Density	Average growth	Mass gain	Idealized linear
	(g/cm^3)	rate (nm/cycle)	(ng/cm ² /cycle)	growth rate
				(nm/cycle)
43 nm-thick type-A	1.9	0.086	16.3	~0.69
136 nm-thick type-B	1.9	0.272	52.3	~0.84
139 nm-thick type-C	5.0	0.154	76.5	~1.06

Table A.II.3 shows the mass density, the average growth rate, the idealized linear growth rate, and the mass gain of the 43 nm-thick type-A MLD zincone film, 136 nm-thick type-B MLD zincone film, and 139 nm-thick type-C ALD:MLD zincone film. The average growth rate is calculated as the total thickness divided by the cycle number for each sample. The idealized linear growth rate is calculated as the length of the molecule vertically deposited per cycle. The growth rates of the three types of zincone thin films are much less than the idealized linear growth rate. The mass density of each film is estimated by the total mass gain during one cycle divided by the average growth rate, and confirmed by the X-ray reflectivity (XRR) measurement.