FUNCTIONAL MATERIALS FOR THERMAL REGULATION

BY

QIYE ZHENG

DISSERTATION

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Materials Science and Engineering in the Graduate College of the University of Illinois at Urbana-Champaign, 2017

Urbana, Illinois

Doctoral Committee:

Professor David G. Cahill, Chair and Director of Research
Professor Paul V. Braun, Chair and Director of Research
Assistant Professor Daniel P. Shoemaker
Associate Professor Elif Ertekin
ABSTRACT

Developing thermal management materials with greater functionality for the control of heat dissipation and regulation is a fundamental step to improve the performance in many engineering systems. This dissertation presents experimental studies of heat conduction in distinctive thermal functional materials with an emphasis on advancing understanding of the correlation between thermal conductivity \( \Lambda \) and specific microscopic mechanisms that are closely related to their applications. The primary tools for the studies presented in this dissertation are time-domain thermoreflectance (TDTR) for measurements of thermal conductivity of thin films and bulk materials and thermal conductance of interfaces.

The thermal conductivity of two dimensional materials is of interest for many applications, including energy storage, nanoelectronics and heat dissipation. I studied thermal conductivity of graphite thin films grown by chemical vapor deposition (CVD) on single crystal Ni (111) at temperatures between 825 and 900 °C. The cross-plane thermal resistance of Al/graphite/Ni structures is a linear function of graphite film thickness in the thickness range 20-140 nm corresponding to a thermal conductivity of \( \approx 3.3 \ \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1} \), \( \approx 50\% \) of the cross-plane thermal conductivity of highly-oriented pyrolytic graphite (HOPG). The in-plane thermal conductivity varies with deposition temperature between 650 and 1000 W m\(^{-1}\) K\(^{-1}\), and is 30-50\% of the in-plane thermal conductivity of HOPG. The reduced thermal conductivity in comparison to HOPG is attributed to a combination of grain boundaries, structural disorder and size effects. I described a figure-of-merit for flexible heat-spreaders and found that this figure-of-merit for CVD graphite outperform that of Au by a factor of 2.

In another layered material of MoS\(_2\), the anisotropic thermal conductivity can be modified by electrochemical intercalation differently in thin films with vertically-aligned basal planes and
natural bulk crystals. The change of thermal conductivity as a function of the degree of lithiation correlates with the stacking order of the layered structure and the lithiation-dependent semiconductor to metal phase transition as supported by Raman spectroscopy. Further, the ratio of the in-plane to through-plane thermal conductivity is enhanced by the disorder in bulk crystals. These results suggest that stacking disorder and mixture of phases is an effective mechanism to modify the anisotropic thermal conductivity of two-dimensional materials, opening a promising way for thermal management in two-dimensional materials based electronics.

In comparison to the above materials where electron is ignorable in heat transport, transition metal nitrides provide a model system where electron dominates and electron-phonon interaction is strong. I studied thermal conductivities of VNₓ/MgO(001) (0.76 ≤ x ≤ 1.00) epitaxial layers, grown by reactive magnetron sputter deposition, in the temperature range 300 < T < 1000. Data for the total thermal conductivity are compared to the electronic contribution to the thermal conductivity calculated from the measured electrical conductivity, the Wiedemann-Franz law, and an estimate of the temperature dependence of the Lorenz number \( L(T) \). The total thermal conductivity is dominated by electron contribution and varies between 13 W m\(^{-1}\) K\(^{-1}\) at \( x = 0.76 \) and 20 W m\(^{-1}\) K\(^{-1}\) at \( x = 1.00 \) for \( T = 300 \) K and between 25 and 35 W m\(^{-1}\) K\(^{-1}\) for \( T = 1000 \) K. The lattice thermal conductivity \( \kappa_{\text{lat}} \) ranges from 5 to 7 W m\(^{-1}\) K\(^{-1}\) at 300 K and decreases by 20% at 500 K. The low magnitude and weak temperature dependence of the lattice thermal conductivity are attributed to strong electron-phonon coupling in VN.

Finally, in search of materials with variable thermal conductivity, I studied temperature dependent thermal conductivity of Ni-Mn-In and MnₓMGe (M = Ni, Co) alloys across their magnetic and structural martensitic phase transitions. A sharp change in thermal conductivity is observed through the martensitic transition but not through the magnetic transition in Ni-Mn-In.
and Mn,MGe alloys. In Ni-Mn-In, Λ changes from 8 W m⁻¹ K⁻¹ at 300 K to 14 W m⁻¹ K⁻¹ at 400 K. The average rate of the thermal conductivity change in Ni-Mn-In and Mn₈NiGe in the 50 K range of their transition temperatures is faster than common metals and alloys including the conventional shape memory alloy of NiTi. The austenite phase electrical conductivity of Ni-Mn-In is around 100 μΩ-cm at 400 to 500 K, which is comparable with stainless steel. Both Λ and electrical conductivity are more than twice as large as the metal-insulator transition material of VO₂ thin film in its metallic state. By comparing the result with the electronic thermal conductivity calculated from the Wiedemann-Franz law I attribute the rapid change through the phase transition in the Λ to the in the electronic contribution in Ni-Mn-In. My work suggests that Ni-Mn-In and MnNiGe based alloys may serve as functional materials for thermal management applications that require a high-contrast variable thermal and electrical conductivity as well as large high-end conductivities.
ACKNOWLEDGMENTS

I would like to thank my advisors, Professor David Cahill and Professor Paul Braun, for giving me the opportunity to do research at such a wonderful place. I feel deeply grateful for their extraordinary patience, extensive and superb instruction, guidance and advice. Their guidance benefited my PhD education and will continue to help me in the future to pursue a profession. I also thank David for giving me the chance to stay for longer as a post-doc.

I would like to thank other members of my thesis committee, Professor Daniel Shoemaker and Professor Elif Ertekin, for contributing their valuable experience, intelligence and time. Professor Daniel Shoemaker has also offered helpful advice and comments to the research project we collaborated on.

It has been my privilege to work with such smart and motivated people at Illinois. I thank my fellow group members, Xu, Rich, Greg, Dongyao, Gyungmin, Xiaojia, Judith, Junwoo, Ella, Hyejin, Sushant, Jiung, Jingu, Junjie, Chunjie, Hailong, Jinyun, Runyu, Kaitlin, Eric, and many collaborators especially Shannon Murray, and Antonio Mei who provided samples. I would like to give special thanks to Jun Liu, and Zhu Diao, for their hand-on help and useful discussions. I gratefully acknowledge the help from the staffs in MRL especially Julio and Mauro for your training and help in using the characterization and growth instruments in MRL. I also appreciate Gaohua Zhu from Toyota for his guidance during my co-op at Toyota Technical Center and the collaboration later.

Finally, I want to thank my family and girlfriend Kexin for their support during my PhD studies. Thank you for your love and trust.
TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION ......................................................................................... 1

1.1 Motivation ........................................................................................................ 1

1.2 Background ....................................................................................................... 2

1.3 Outline of Thesis .............................................................................................. 7

CHAPTER 2: EXPERIMENTAL METHODS ................................................................. 9

2.1 Time-domain Thermoreflectance (TDTR) ......................................................... 9

2.2 Low Frequency Raman Spectroscopy .............................................................. 17

2.3 CVD Growth of Graphite ................................................................................ 28

CHAPTER 3: THERMAL CONDUCTIVITY OF GRAPHITE THIN FILMS GROWN BY
LOW TEMPERATURE CHEMICAL VAPOR DEPOSITION ON NI (111) ....................... 32

3.1 Introduction ...................................................................................................... 32

3.2 Experimental ................................................................................................... 34

3.3 Morphology and Structure of CVD Graphite .................................................. 35

3.4 Cross-plane and In-plane Thermal Transport of CVD Graphite ....................... 38

3.5 Raman Spectroscopy and Thermal Conductivity Mapping ............................. 44

3.6 Evaluation of CVD Graphite for Flexible Electronic Application .................... 46

3.7 Conclusion ....................................................................................................... 47

CHAPTER 4: TUNING THERMAL CONDUCTIVITY IN MOLYBDENUM DISULFIDE BY
ELECTROCHEMICAL INTERCALATION .................................................................... 49

4.1 Introduction ...................................................................................................... 49

4.2 Materials Characterization ............................................................................. 51

4.3 Thermal Conductivity of Li$_3$MoS$_2$ .............................................................. 55

4.4 Effect of Li Intercalation on Interlayer Spacing and Elastic Constant ............... 57

4.5 Effect of Li Intercalation on Thermal Conductivity ......................................... 61
CHAPTER 1

INTRODUCTION

1.1 Motivation

Heat transfer, including conduction, convection, and radiation, is one of the fundamental energy transport mechanisms in nature.[1-3] Thermal conductivity ($\Lambda$), the property of a material to conduct heat, evaluated primarily in terms of Fourier's Law, is an important intrinsic properties of materials and is critical in various engineering systems.[1,3,4] For some applications, thermal conductivity itself is a key metric, e.g. thermal barrier coatings, nuclear fuels, and thermoelectric materials for energy conversion.[5-7] For many other technologies, the ability to manipulate heat conduction, as an important part of thermal management, is vital for the overall performance of the system, such as high power and nanoscale electronic and optoelectronic devices, heat-assisted magnetic recording, phase change memory, batteries for electric vehicles, and internal combustion (IC) engine. [8-13]

In different engineering system, the demand for the functional materials for thermal management/regulation varies greatly. In thermal barrier coatings and thermoelectric materials, one wants the thermal conductivity to be as small as possible while in nanoscale electronics and semiconductor laser, a demand for efficient cooling requires materials with high thermal conductivity. In some other cases, such as high-power batteries and IC engine, one wants to keep the system working within a certain range of temperature and hence materials with the ability to switch between low and high thermal conductivity in response to the environment and the internal heat generation would be useful.
The objective of this dissertation is to advance understanding of thermal conductivity, $\Lambda$, in representative functional materials for thermal regulation and how $\Lambda$ is influenced by features such as nanoscale size effect, electrochemically introduced disorder, electron-phonon interaction and diffusionless solid-solid phase transition that are closely related to their engineering application.

1.2 Background

Thermal management within the overall design of electronic products is increasingly important. Each new generation of electronic devices squeezes more power and performance into ever-smaller packages which causes increasing power density and Joule heating that must be dissipated efficiently to prevent overheating of the device. More challenges arise in the thermal management of the emerging flexible/stretchable electronics, a field growing with the rise of mobile devices and touchscreen applications in the past two decades.[8,14] Here the circuit elements are built upon flexible polymer substrates such as polyimide (PI), polydimethylsiloxane (PDMS), polyethylene terephthalate (PET), or other similar materials which have very low thermal conductivity, in the 0.1–0.3 W m$^{-1}$ K$^{-1}$ range. Such a low thermal conductivity would cause thermal management issues or device damage even though the power density of these devices are smaller than those found in high performance computing.[8] Functional materials with both high thermal conductivity to dissipate heat and mechanical flexibility to accommodate the deformation would benefit the thermal management in these integrated flexible/stretchable electronics.

2D materials, layer-structured materials consist of atomic layers with strong intra-layer covalent bonding stacked together by weak van der Waals bonds typically show anisotropic thermal conductivity. For example, at 300 K, thermal conductivity is $\approx$2000 W m$^{-1}$ K$^{-1}$ in highly ordered pyrolytic graphite (HOPG) and $\approx$ 250 W m$^{-1}$ K$^{-1}$ in h-BN along their basal plane (in-plane) direction, while it is only $\approx$6 W m$^{-1}$ K$^{-1}$ in HOPG and $\approx$1.5-2.5 W m$^{-1}$ K$^{-1}$ in h-BN along the cross
plane direction.[15-18] For flexible devices on a low thermal conductivity, low glass transition temperature polymer substrate, this feature could be employed to prevent the local melting of the substrate underneath a region of high power density by directing the heat laterally to the heat sink.[8,18] In thin plate, the product of thermal conductivity and its thickness, \textit{i.e.} the thermal conductance, dictates the amount of heat a structure can transport in steady state. While few layer graphene was reported to have high thermal conductivity, 600 W m$^{-1}$ K$^{-1}$ on SiO$_2$, increasing their thickness is necessary to obtain a sufficient thermal conductance for use as a heat spreading layer in electronic devices.[19-21] The bending stiffness of a homogeneous plate would increase with the cube of its thickness which limit the thickness of 2D materials heat spreader. Thus, a figure of merit encompassing the bending stiffness and thermal conductivity would be useful to evaluate the performance of layered materials in flexible electronics.

In most crystalline semiconductors, dielectrics and some semimetals with low electrical conductivity (e.g. graphite), heat is carried predominantly by phonons, a wide spectrum collective vibration mode of the lattice,[4] which are scattered by defects, anharmonicity, and grain boundaries.[22-24] At a fixed temperature, their thermal conductivity is typically governed by the average distance phonons propagate without being scattered, \textit{i.e.}, the mean-free-path (MFP) as a function of phonon frequency and polarization. In the layered material of graphite, the mean free path of main heat carrier phonons, are around a few hundred nanometers in the cross-plane direction and around a micron in the basal plane direction. The anisotropic MFP and speed of sound of phonon give rise to highly anisotropic thermal conductivity in graphite. In addition strong size effects on the thermal conductivity exist in thin films graphite with tens of nanometer thickness and hundreds of nanometer lateral grain size.[25,26] A direct study of the anisotropic
thermal transport in CVD graphite thin film, would provide knowledge about the process-
structure-property relationship in this materials and its performance as a heat spreader.

Considering the different phonon MFP along the basal plane and cross plane direction in a 2D material, systematically introduced disorder tends to play different role in scattering phonon along the two distinct axes and changes the anisotropy of its thermal conductivity. Guest ions of small molecules, e.g. alkali metal ions, can be intercalated electrochemically into the van der Waals gaps in graphite and many transition metal dichalcogenide, e.g. MoS₂. Ion intercalation changes the electronic structure and induces structural and compositional disorder as it changes layer spacing, interaction strengths between adjacent layers, and phase transitions.[27-30] Such and similar disorder usually occurs during crystal growth, fabrication, and application of the devices (e.g., energy storage, thermoelectrics, and nanoelectronics), and can be characterize by Raman spectroscopy.[31-35] A systematic study of how ion intercalation changes the crystal structure and phase and how it affect anisotropic thermal conductivity of layered materials provide insight into the thermal performance of 2D materials in real application.

In metals with high electrical conductivity, heat is mainly carried by electrons while the phonon contribution to the thermal conductivity is relatively small and has a complex dependence on temperature, lattice anharmonicity, and the strength of electron-phonon coupling.[4,36,37] Typically, at temperatures greater than 1/3 of the Debye temperature, the lifetimes of phonons that dominate heat transport are limited by the anharmonicity of lattice vibrations.[38] Scattering of phonons by electrons is less important except at low phonon frequencies. Measurements of the thermal conductivity of alloys can often be used to determine the lattice thermal conductivity by introducing elastic scattering of electrons that suppresses the electronic component.[39,40] The high-temperature lattice thermal conductivities of metals with relatively weak electron-phonon
coupling are typically in good agreement with the assumption of lattice thermal conductivity limited by anharmonicity.[37]

Metallic transition-metal (TM) nitrides and carbides provide a contrast to metals for studying lattice thermal conductivities because their Debye temperatures are high and therefore the anharmonic phonon scattering rates are low, and electron-phonon coupling is strong.[41] A study of temperature dependent thermal and electrical conductivity of TM nitride with varying concentrations of nitrogen vacancies would enable the separation of the contribution from phonon and electron which is important parameters for their applications such as barrier coating. Such a work may also provide insights into the potential of TM nitride metal/semiconductor superlattices as high temperature materials for thermoelectric energy conversion.

In some engineering systems, thermal switches, i.e. device or materials that switch between roles of good thermal conductors and good thermal insulators on demand, are useful to maintain an optimal temperature of the system. Typically, thermal switches are realized by engineering methods and operate at low temperature (< 300 K). For example, gas gap and liquid gap thermal switches are often integrated into a cryocooler system to reduce the heat load to the dewar and hence the cryogen consumption in the liquid helium temperature range.[42-45] Differential thermal expansion based thermal switches have been proposed for space applications from the liquid nitrogen temperature range up to near 300 K.[46-48]

Alternatively, a thermal switch could also be realized by materials alone, either actively or passively controlled, which do not require complex engineering design. Active manipulation of thermal conductivity has been reported in many materials by means of chemical composition modification,[49-53] strain,[54-56] and electrical or magnetic field,[57-61] in the past decade. Passive thermal switch materials, on the other hand, are controlled by internal thermodynamic
variables of a system e.g. temperature, which leads to even further simplification of the engineering design and may serve large scale applications in vehicles and high power batteries.[13]

For example, in modern automobiles, the average fuel conversion efficiency of an IC engine is in the range of 35-40%, when the engine is completely warmed up with the lubricant temperature at around 100 °C.[62] However, it is only about 9% at the beginning when the engine is cold (with the lubricant below 25 °C) before it warms up to optimal temperature in 5-10 minutes.[63] Reducing the warm-up time for an engine could improve its overall efficiency. This require the heat transfer rate to be small below optimal temperature but high enough above that temperature to keep the engine within a range of such temperature for the best efficiency. Thus, passive solid state thermal switch materials that could display a high contrast and reversible change in thermal conductivity near 300 K could serve such purpose without significantly changing the current design of engines.

Changes in the thermal conductivity $\Lambda$ of common single-phase materials with temperature are typically gradual near room temperature. In some metallic alloys, e.g. Al, Ti alloys and transition metal carbides and nitrides, thermal conductivity $\Lambda \propto T$ due to strong elastic scattering of electrons by impurities and defects.[39,64-66] In dielectric crystals, (e.g. Si, Ge, Al$_2$O$_3$, and MgO), $\Lambda \propto T^{-1}$ due to Umklapp phonon-phonon scattering.[67-69] To realize sharp thermal conductivity change in a narrow temperature range, a solid-solid phase transition, such as magnetic transition and structural transition, is a possible solution.

Depending on whether the atoms travel a long distance through the phase transition, a solid-solid phase transition can be categorized as diffusive or diffusionless transition.[70] For the diffusive phase transition, such as amorphous-crystalline transition in chalcogenide glass (e.g. Ge$_2$Sb$_2$Te$_5$, GeAsSe, and As$_2$Se$_3$), the change in thermal conductivity is often irreversible due to
the nonequilibrium in the amorphous phase.[71-74] For diffusionless transition where phase change occurs without long-range diffusion of atoms, the variation in thermal conductivity accompanying the displacive structure transition is typically reversible.[75] As an important type of diffusionless phase transition, the martensitic transition (MT), characterized by coordinated displacement of atoms, can bring about a strong modification of density of states near Fermi surface, which may change the electrical conductivity dramatically.[76-80] One example is the martensitic type metal–insulator transition (MIT) in a number of transition metal oxides (e.g. VO$_2$, Ti$_2$O$_3$, and La$_{1-x}$Sr$_x$CoO$_3$) and perovskite oxides.[81-85] However, oxide MIT materials usually have small thermal conductivity (<10 W m$^{-1}$K$^{-1}$) in the metallic phase due to the relatively small electrical conductivity.[86,87]

To find passive thermal switch materials with large thermal and electrical conductivity contrast and high “on-state” thermal conductivity, metallic alloys with both MT and relatively large electrical conductivity could serve as potential candidates, e.g. metallic Heusler alloys and some MM’X type metallic compound with hexagonal Ni$_2$In-type structure.[88-92] Another candidate is the coupled structural and antiferromagnetic (AFM) to ferromagnetic (FM) transition in FeRh which accompanies a significant change in electrical conductivity.[93] Metallic alloys would benefit thermal switch devices where relatively high electron mobility and density of states are necessary.

### 1.3 Outline of Thesis

This thesis is organized as follows. In Chapter 2, I describe the experimental techniques time-domain thermoreflectance (TDTR) that I used to study heat transport in different thermal functional materials as well as its extension for thermal conductivity mapping. I also describe the
technique I implemented for low frequency Raman spectroscopy measurement and the chemical vapor deposition process of graphite thin film growth on Ni (111) substrate.

In Chapter 3, I present the anisotropic heat transport in CVD grown graphite thin films prepared with varied growth temperature and thickness which shows strong size effect along the cross-plane direction. By analyzing thermal conductivity and Raman spectroscopy mapping I attributed the reduced in-plane thermal conductivity to lateral grain boundary scattering. In Chapter 4, I present the thermal conductivity of lithium ion intercalated molybdenum disulfide (Li$_x$MoS$_2$) as a function of the degree of lithiation ($x$) in which the change of thermal conductivity correlates with the structural and compositional disorder, e.g., the stacking order of the layered structure and the lithiation-dependent semiconductor (2H) to metal (1T) phase transition. Most of the Chapter 3 has been published in Adv. Mater. Interfaces, 3: 1600234. (2016), and most of Chapter 4 has been published in Nat. Commun. 7: 13211 (2016).

In Chapter 5, I concentrate on the studies of heat and electron transport in transition metal nitride of VN$_x$ ($0.76 \leq x \leq 1.00$) as a function of temperature (from 300 to 1000 K). The lattice and electronic components to the thermal conductivity are separated by calculating the electronic contribution to thermal conductivity from the measured electrical conductivity, the Wiedemann-Franz law, and an estimated Lorenz number $L(T)$ as a function of temperature.

In Chapter 6, I present the thermal and electrical conductivity across MT in off-stoichiometric Ni-Mn-In Heusler alloys and Mn$_x$MGe ($M = \text{Co, Ni}$) metallic compound and evaluated their potential as thermal switch materials in comparison with common phase change materials. Chapter 7 is the conclusion of my thesis, where I summarize what I have learned about thermal transport in these distinct functional materials.
CHAPTER 2

EXPERIMENTAL METHODS

2.1 Time-domain Thermoreflectance (TDTR)

2.1.1 TDTR Setup

The main experimental technique used in this dissertation for measurements of thermal transport in materials is time-domain thermoreflectance (TDTR), a well-established, ultrafast optical pump-probe technique.[94-97] TDTR was first reported by in 1986 by Easley et. al. and Maris et. al. to measure the thermal transport properties of thin films.[98,99] Since the development by Cahill in early 2000s, TDTR and its extension of frequency domain thermoreflectance (FDTR) has seen widespread adoption in nanoscale heat transport research.[100-102]

In short, TDTR measures the thermal response of a sample to a train of pump pulses periodically modulated at frequency $f$ by detecting temperature induced changes in the intensity of a reflected probe beam. The schematic diagram of our TDTR system is shown in Fig. 2.1. The pump and probe laser in this system are generated from the pulse train output of a Ti:sapphire laser mode-locked at at 80 MHz, pumped by a 532 nm Nd:YVO solid state laser with power of 9.5 W. The Ti:sapphire laser output has a pulse duration of $< 400$ fs with wavelength tunable between 710-900 nm. The typical wavelength of 785 nm we use has an average power of around 1.2 W (with the Nd:YVO laser power = 9.5 W).

A combination of a half wave plate and optical isolator is used to attenuate the laser power. The attenuated laser beam is split by a polarized beam splitter (PBS) cube into a pump beam and
a probe beam. The relative energy distribution between the pump and probe beams is adjusted by the PBS and a half wave plate before it.

The intensity of the pump beam is modulated by an electro-optic modulator (EOM) which imposing an additional $f = 9.8$ MHz square wave profile on the 80 MHz pulse. This frequency can vary depends on the experimental needs, but in most cases the $1/f$ noise and the 80 MHz repetition rate result in a practical range of 1-20 MHz. The probe beam is delayed relatively to the probe beam by a delay stage in the pump beam optical path in the range of -0.1 to 4 ns.

**Figure 2.1** The schematics of the TDTR setup at University of Illinois.[95] Mode-locked Ti:sapphire pulse laser is split into pump and probe beams, which sequentially heat and measure the change in thermoreflectance of the sample. Optical filters and the short pass filter are used to eliminate the artifacts due to pump beam leaked into the Si photodiode. The sample is sometimes placed on heating stage for temperature dependent measurement as needed.

The vertically-polarized pump and the horizontally-polarized probe beam are then deflected by two PBSs in their own optical paths and focused by a long working distance objective lens on the surface of the sample. The reflected probe beam is collimated by the objective lens and focused on a fast Si photodiode by a convex lens with a focal length of 350 mm. The schematic diagram of the TDTR system can be found in previous literature.[95]
Before TDTR measurements, the sample is usually coated with a metal transducer layer of 70 to 120 nm by DC magnetron sputtering at room temperature. As the temperature of a material changes, the refractive index, and therefore, the reflectivity of the transducer layer also changes. Such change in reflectivity is described by the thermoreflectance coefficient \( \frac{dR}{dT} \), a basic property specific to a material depending on the illumination wavelength and the ambient temperature. Within a small range of temperature variation, the optical reflectivity \( R \) of the metal transducer is, to a good approximation, linearly dependent on the change in temperature:

\[
\Delta R = (\frac{dR}{dT}) \Delta T.
\]

The surface temperature change of the metal transducer \( \Delta T \) of the transducer is determined by periodic pulse laser heating of the pump beam and the heat conduction to the sample. Using metal transducer with large enough \( \frac{dR}{dT} \) (and reflectivity \( R \)), \( \Delta T \) can be monitored by the change of the reflected probe beam intensity as a function of time delay between pump and probe. This is where the name “time domain thermoreflectance” comes from.

The output of the Si photodiode is connected to a radio frequency (rf) lock-in amplifier locked to the modulation frequency \( f \) of the pump beam. To remove the harmonics components from the 80 MHz pulse in the output of the Si photodiode, a 30 MHz low pass filter is used. In addition, an inductor and a preamplifier is placed in series between the output of the Si photodiode, the 50 Ω input of the rf lock-in amplifier and the low pass filter to form a resonant circuit with the capacitance of the reversed biased Si photodiode. This resonant circuit mainly filters out the odd harmonics of the pump modulation frequency from the signal.

To prevent pump light from reaching the detector, several methods are implemented in the TDTR system. First, the vertically polarized pump light specularly reflected from the sample surface is strongly rejected by the PBS in the probe beam path. Second suppression of the pump beam leakage is realized by the so-called “two-tint” filtering which separate the wavelength of the
pump and probe from the broad band output of the Ti:sapphire laser by two sharp edge filters.[95] Finally, the probe beam is modulated at an audio frequency of 200 Hz with a mechanical chopper which shift the thermoreflectance signals carried by the probe pulses to 9.8 MHz ± 200 Hz. A pair of computer-based audio frequency lock-in amplifiers pick up the 200 Hz frequency demodulated by the rf lock-in amplifier locked at 9.8 MHz.

This double modulation effectively reduces spurious signals at 9.8 MHz read by the rf lock-in that are unrelated to the temperature excursions of the metal film, such as the coherent pick-up signal of the lock-in. Unfortunately, the capacitance of the Si detector changes slightly with the power of light incident on it which could generate spurious signal at 200 Hz, affecting measurements of sample with small thermoreflectance signal. Because of such non-linearity, it’s better to use high pump power than high probe power. I typically fix the pump and probe power ratio at around 2. Moving the chopper to the pump beam path may also help according to a prior work by Rich Wilson.[103]

The experimental TDTR data consists of the in-phase and out-of-phase voltages, $V_{in}(t)$ and $V_{out}(t)$ recorded by a Si photodiode and picked up by the double modulation process. In analysis, the data of normalized ratio, $-V_{in}(t)/V_{out}(t)$, is compared to a diffusive thermal model which is an exact numerical solution of the heat diffusion equation for a multilayer structure in cylindrical coordinates.[94] Parameters needed in the thermal model are the pump modulation frequency $f$, the repetition rate of the laser $\tau$, thickness of each layer $h$, their heat capacity $C$, and thermal conductivity $\Lambda$ (a symmetric rank 2 tensor), and the $1/e^2$ radius of the laser spot $w_0$. An interface with thermal conductance $G$ is modeled by a layer with a small thickness $h_i$ (1nm) and a small thermal conductivity $\Lambda_i$, $G = \Lambda_i/h_i$. 
Among these parameters, most of them are fixed during the fitting of one measurement, which are either measured independently or taken from the science and engineering literature. The thickness of the metal transducer is typically measured by picosecond acoustic, or X-ray reflectivity.[104] The thermal conductivity of the transducer layer is derived from Wiedemann-Franz law. If not measured using TDTR or other calorimetry technique,[105] literature values of heat capacity of each layer are used. The laser spot size are typically measured by the signal correlation scanned from spatially offsetting the pump and probe beam, i.e. the so-called beam offset method.[106] In its basic application for a bulk sample, the thermal conductivity of the sample, $\Lambda$, and the thermal conductance, $G$, of its interface with the metal transducer are derived from the best-fit to the ratio data of $-V_{in}(t)/V_{out}(t)$. In general, for bulk samples the shape of the decay of $-V_{in}(t)$ depends on thermal conductance and the average thermal conductivity of the sample within the distance heat travels in the maximum delay time. $V_{out}(t)$, depends on the average value of thermal conductivity over the distance heat travels in $1/f$. The result $\Lambda$ will equal the bulk thermal conductivity when the thermal model used to interpret the data is an accurate description of the problem.[107]

To gauge how a parameter influences the output of the model in TDTR, it is useful to calculate the sensitivity of the measurement to a parameter ($\alpha$), defined as $S_\alpha = \frac{\partial \ln(-V_{in}/V_{out})}{\partial \ln(\alpha)}$. [108] For example, the larger the value of $S_\Lambda$, the smaller the error propagated from the other parameters into $\Lambda$ of interest. If sufficiently small spot size and low modulation frequency are used such that the thermal penetration depth $d_p = \sqrt{\Lambda/(C\pi f)}$ becomes comparable or larger than the pump laser spot size, heat flow in the sample become two-dimensional, and the measurement sensitivity to thermal transport along the in-plane direction becomes high. With accurate value of the laser spot
size and cross-plane thermal conductivity, one can measure the in-plane thermal conductivity this way (See Chapter 3). But for some materials, such as high thermal diffusivity materials, attention must be paid to the non-diffusive heat transport near the interface causing spot size dependence of the TDTR measurements.[107,109]

2.1.2 Temperature Dependent Measurement by TDTR

In TDTR measurements of thermal conductivity as a function of temperature, an accurate control of the ambient temperature and material properties especially the heat capacity of the sample is necessary. To perform temperature dependent TDTR, I have used a simple home-built heating stage using joule heating of a small ceramic stage and a resistance thermal detector (RTD) to monitor the temperature. A commercial Instec\textsuperscript{TM} heating-cooling stage with proportional–integral–derivative controller has also been used in some experiments. A Pfeiffer pump station equipped with a turbo pump is used to keep the chamber in vacuum as needed. The 0.5 mm quartz window of the Instec\textsuperscript{TM} stage has transmission of around 96\% at 785 nm resulting in TDTR signal reduction by around 12\%.

To verify the accuracy of the temperature reading of the home build heating stage, I measured the thermal conductivity of MgO (001) single crystal substrates purchased from MTI between 300 to 600 K in vacuum with Al transducer (see Fig. 2.2(a)). My results are in reasonable agreement with literature values and tabulated values from our group by 3\omega method.[110] The commercial Instec\textsuperscript{TM} stage has been calibrated by comparing the temperature obtained from another temperature sensor mounted on the surface of the sample stage with reading of its own RTD thermometer. TDTR measurement of the thermal conductivity of thermal oxide SiO\textsubscript{2} (500 nm)/Si from room temperature to 83 K using this Instec\textsuperscript{TM} stage shows good agreement with literature data at temperature higher than \sim 150 K (see Fig. 2.2(b)).[111] As the stage is cooled, the sample directly mounted on it becomes the colder than the ambient air in the cryostat and hence the residue
water vapor would inevitably condense on the sample surface at low enough temperature no matter how high of vacuum is maintained. A thin layer of water on top of the Al transducer invalidate the thermal model used for the TDTR data analysis and causes severely inaccurate results of sample thermal conductivity at low temperature. In practice, I cut off low temperature measurement data at 150 K when using this stage to avoid this problem. At high temperature, 300 to 800 K, thermal conductivity of epitaxial VNₓ/MgO(001) obtained using Instec™ heating stage is found to be consistent with the results from the home-built stage.

**Figure 2.2.** Control measurements to verify the temperature sensor reading of heating stages. (a) Thermal conductivity of MgO (001) single crystal from MTI measured by TDTR (open circles), literature,[110] and by 3ω method from 300 to 600 K. (b) TDTR measured thermal conductivity of SiO2 compared with literature values from 83 to 300 K.[111]

### 2.1.3 Thermal Conductivity Mapping By TDTR

Typical TDTR measurement of thermal conductivity is performed over the full range of delay times, -0.02 < t < 3.6 ns for the analysis of the ratio data of $-V_{in}(t)/V_{out}(t)$ as a function of time. However, for bulk sample or thin film sample with uniform thickness, if the thermal conductance $G$ is not too small, the thermal conductivity of the sample can be measured using $-V_{in}(t)/V_{out}(t)$ at
a single delay time $t_0$. By scanning the pump and probe laterally on the sample with the delay time fixed at $t_0$ one can obtain the $-V_{in}(t_0)/V_{out}(t_0)$ profile. This ratio profile can be converted to the thermal conductivity map using the a function derived from the thermal model using the best-fit parameters at one spatial location and the thermal conductitivity values encompassesing the range of the region. Using a motorized translational stage, the thermal conductivity profile can be measured using TDTR with more time efficiently than measure at each position over the full range of delay times.[97,112] The acquisition speed is limited by the time constant of the computer-based lock-in amplifier. Since the thermoreflectance signal arises from the product of the pump and probe fluence, the effective spot size of the measurement is $w_0/\sqrt{2}$. The spatial resolution is approximately the larger value from $w_0/\sqrt{2}$ and thermal penetration depth $d_p$.[97,112]

Fig. 2.3 shows an example thermal conductivity mapping of a nonuniform boron arsenide (BAs) bulk crystal. The thermal conductivity of BAs, $\Lambda_{\text{BAs}}$, and the interface thermal conductance $G$ between 87 nm Al transducer and BAs are first measured using full time delay scan, averaged at 3 locations to be $\approx 140$ W m$^{-1}$ K$^{-1}$ and $\approx 70$ MW m$^2$ K$^{-1}$, respectively. The sensitivity coefficient $S_a$ of different important parameters as a function of delay time for this sample is shown in Fig 2.3(a). To reduce the effect of the variation of $G$ on the measurement, thermoreflectance signal $-V_{in}/V_{out}$ at 1800 ps (at which $S_G \approx 0$) is used. The thermal conductivity mapping is then obtained by converting the ratio signal using the thermal model as shown in Fig. 2.3(b). In the measurement, the voltage measured by a photodiode detector is also recorded, and is used to eliminate measured points on the map which are under 95% reflectance which give unreliable values for the thermal conductivity of the sample.
Figure 2.3. (a) Calculated sensitivity coefficients $S_\alpha$ for a TDTR measurement on a BAs crystal with $\Lambda_{\text{BAs}} = 140 \text{ W m}^{-1} \text{ K}^{-1}$ and $C_{\text{BAs}} = 2.13 \text{ J cm}^{-3} \text{ K}^{-1}$ coated with Al with a thickness of 87 nm, $\Lambda_{\text{Al}} = 180 \text{ W m}^{-1} \text{ K}^{-1}$, and $C_{\text{Al}} = 2.44 \text{ J cm}^{-3} \text{ K}^{-1}$. The $1/e^2$ radius of the laser spot is 5.1 $\mu$m for both pump and probe. (b) The thermal conductivity mapping of a BAs crystal derived from thermoreflectance signal $-V_{\text{in}}/V_{\text{out}}$ recorded at a pump-probe delay time of 1800 ps. Blank area are excluded due to too high roughness for TDTR (reflectivity lower than 95% of a reference Al/Si wafer sample) to obtain reliable data.

2.2 Low Frequency Raman Spectroscopy

2.2.1 Raman Spectroscopy Techniques for Detection at Low Frequency

Raman spectroscopy allows nondestructive characterization of materials based on their unique structure, symmetry, electronic environment and bonding characteristics and provide quantitative and qualitative analysis of the individual compounds.[113-115] It has become a useful characterization technique for various materials such as minerals,[116] biomaterials,[117] carbon materials,[118,119] and layered materials.[120,121] A lot of advanced technique have been developed to improve Raman spectroscopy based on experimental needs, such as surface enhanced Raman spectroscopy,[122] coherent anti-Stokes Raman scattering,[123] and time-
resolved incoherent anti-Stokes Raman scattering,[124] and techniques to obtain low frequency Raman (<50 cm\(^{-1}\)).[125,126]

Raman spectroscopy at low frequency has long been an indispensable tool in multiple areas of research in materials science. For example, low frequency “breathing” modes exists in various protein molecules depending on their specific conformation;[127] folded acoustic modes in the range 0–100 cm\(^{-1}\) can be utilized to assess the quality of semiconductor multilayered structures (superlattices);[128] in amorphous glasses, most of the Raman spectra contain a low frequency response called "boson peak";[129] mineral such as sulfur has several vibration modes between 0 and 250 cm\(^{-1}\); low frequency shear modes in layered materials such as graphite and MoS\(_2\) are correlated with the interlayer interaction.[121,130]

To obtain high signal-to-noise in Raman measurements, especially in the low frequency spectral region, it is necessary to block Rayleigh scattering from reaching the detector. There are two main classes of filter used for Raman spectroscopy: tunable filtering spectrometer and optical filters.

A tunable filtering spectrometer typically uses triple-spectrometer setup. The first two monochromators are used as to disperse both the Rayleigh and Raman scattered light. Then, the Rayleigh light is physically blocked, and the Raman scattered light is recombined. The Raman light is dispersed by the third spectrometer with subsequent detection. The advantages of using a triple spectrometer include a widely variable laser filtering range, and a compatibility with any number of laser sources. The filtering performance is also excellent allowing Raman analysis down to 4-5 cm\(^{-1}\).[126,131] However, such an instrument is often bulky and expensive and the usage of three dispersive gratings usually results in a low throughput of the desired Raman signal.
An alternative way to filter the Rayleigh light is to use an optical filter, i.e. notch filters or edge filters, to selectively block the laser line (Rayleigh scatter) while allowing the Raman scattered light through to the spectrometer and detector. An edge filter is a long pass (or short pass) optical filter which absorbs all light up to (or down to) a certain wavelength and transmits light with longer (or shorter) wavelength including the laser emission for the measurements of Stokes (or Anti-Stokes) Raman scattering. Today’s standard edge filters with ultra-steep edge between the absorbing and transmitting spectral region offer blocking of the light up to around 70 to 300 cm\(^{-1}\) for visible light.

A notch filter, on the other hand, is designed to transmit most wavelengths with little intensity loss while attenuating light within a specific wavelength range (the stop band) to a very low level. In Raman spectroscopy, a notch filters allows measurements to be made for both the Stokes and Anti-Stokes Raman scattering which is not possible for edge filters. Common notch filters using dielectric stack thin film can provides high rejection through destructive interference and reflection in the stop band. However, the stop band of a thin film notch filter is typically of a few nanometers wide (corresponding to a few hundred cm\(^{-1}\)) which is not small enough for low frequency Raman measurements. Some organic material based holographic notch filter has a finite lifetime, and will degrade with time.

### 2.2.2 Experiment Setup of Low Frequency Raman Spectroscopy

To achieve low frequency Raman down to \(\sim 10\) cm\(^{-1}\), I used a BragGrate\textsuperscript{TM} Raman filters set including one band pass filter (BPF) and three OD3 band notch filters (BNFs) in combination with single monochromator Raman system.[130,132] The schematic diagram of low frequency backscattering Raman setup is shown in Fig. 2.4. The excitation wavelength of this Raman system is 488 nm from a Spectra-Physics Cyan solid-state laser. The polarization of the laser is controlled by a \(\frac{1}{2}\) wave plate next to the laser source. The power of the laser before the
objective is adjusted by a graduated neutral density filter varying between ≈1 to 14 mW to avoid excessive sample heating and obtain good signal to noise ratio. The Raman backscattered signal was collected through a 20× objective (N.A. = 0.4) with laser spot size ≈10 μm at the sample surface and collected by an Acton Insight spectrometer (Princeton Instruments) with a 1200 g mm\(^{-1}\) grating.

**Figure 2.4.** Schematics of the low frequency Raman spectroscopy with BragGrate\(^\text{TM}\) Raman filters. Photos of the light imaged on a white paper placed after the 1\(^{\text{st}}\) and the 3\(^{\text{rd}}\) BNF show the diffraction pattern and the diffuse scattered Rayleigh light. Dashed blue arrows shows the direction of the rejected Rayleigh light. The tilting angles of the BNFs are exaggerated in the figure for the sake of clarity. The acceptable range of input angle is around 6 ± 1°.

For a common Czerny–Turner monochromator, the resolving power is approximately

\[ \Delta \lambda \approx \frac{bd(\cos(\theta))}{f} ,\] \[\text{[133]}\] where \(b\) is the minimum resolvable image size on the charge-coupled
device (CCD) in the spectrometer ~2 pixels (≈40 μm for our spectrometer), $d$ is the spacing of the grating grooves, $f$ the focal length of the concave mirror, and $\theta$ the angle between incident and diffracted light on the grating. A typical $\theta \approx 20^\circ$ would give $\Delta \lambda \approx 0.1$ nm corresponding to a dispersion power of 4.2 cm$^{-1}$/pixel at 488 nm. The measured spectral FWHM of the 488 nm laser with the smallest slit size of 10 μm is about 4 cm$^{-1}$. Therefore, the spectral resolution of this Raman system is $\approx 4$ cm$^{-1}$. While it should not improve spectral resolution if an entrance slit size of <40 μm is used,[133] I typically use the smallest slit size of 10 μm to maintain the best spectral resolution and to reduce the diffuse Rayleigh light noise (see discussion below).

The BragGrate™ Raman filters I used our low frequency Raman system are volume Bragg gratings (VBG), which are volume holograms formed by photo-induced modulation of the refractive index of the recording media. The media used here is a type of photo-thermo-refractive glass, a type of sodium-zinc-aluminum-silicate glass doped with Ag, Ce, and F which provides refractive index modulation after exposure to UV radiation followed by thermal development. According to the manufacturer, these filters are environmentally stable with no humidity degradation, and are stable to any type of optical radiation. After three years of usage in our 488 nm laser Raman system, there’s no noticeable degradation of the performance of the filters.

The BPF in Fig 2.4 is designed to provide both spatial and spectral filtering of the laser line in the upstream of the low frequency Raman setup. In low frequency Raman measurements, the laser spectral noise should be removed as close as possible to the laser line, a process called the laser line “clean up”. The noise may come from the amplified spontaneous emission (ASE) (which is incoherent laser radiation optically amplified by the process of stimulated emission in a gain medium), broadband fluorescence background or plasma line in the laser output. The
BragGrate™ BPF has a FWHM linewidth of ~5 cm\(^{-1}\), much smaller than the line width of 200-300 cm\(^{-1}\) in standard BPF, with suppression of background noise up to OD7.

I used three BNFs in series to filter the Rayleigh scattered light from the sample. These BNFs have spectral bandwidth FWHM of ~0.3 nm corresponding to ~12 cm\(^{-1}\) at 488 nm, much smaller than the value of 2-3 nm minimum bandwidth (~100 cm\(^{-1}\)) of a common thin film notch filter. The first BNF, BNF1, is used in the position of a beam splitter or a dichromatic mirror compared to common Raman system. When the laser is directed toward sample, (in the laser inject path), BNF1 acts as a bandpass filter and provide further cleaning of the laser line. When the light reflected from the sample pass through this filter on the return path, BNF1 reject the Rayleigh light (dashed blue arrow in Fig. 2.4). This configuration increases the optical throughput and provide lower laser spectral noise. BNF2 and BNF3 are used in “reject” configuration reflecting the Rayleigh light away from the spectrometer, aligned in opposite directions to avoid interference between filters.

For these VBG filters, the acceptable range of the input angle for good performance is narrow as required by the Bragg condition. The 488 nm BNF (input ~6 ± 1°, output - 6 ± 1°) and BPF (input ~8.5 ± 1°, output - 6 ± 1°) will provide OD3 suppression only when it is aligned with an accuracy better than 0.1°. Such alignment accuracy can be easily achieved with standard kinematic optical mounts such as a Thorlab™ KM100 optical mount.

Due to the small Bragg angle required by these Raman filters, I used four mirrors (M1 to M4 in Fig. 2.4) before BNF1. The alignment is not an easy task as one need to make sure that the laser is centered to the objective lens and perpendicular to the spectrometer slit, and that the Bragg angle condition of BNF1 is satisfied at the same time. Consequently, the angle of the incident laser before the BNF1 is restricted to 6° around relative to the horizontal line in Fig. 2.4. If only two mirrors
are used and the BPF is placed right before the BNF1, the incident angle of the laser on the BPF is also fixed. This would significantly increase the difficulty to arrange the BPF and the mirrors and make it impossible to mount the large heating stage mentioned in Section 2.1.2 which is necessary for temperature dependent Raman measurements. A slight bump on the BPF would affect the filter effect greatly (and the intensity of laser reflected from the filters would drop dramatically). Considering the angle restrictions, it is also very difficult to use three mirrors together with the BPF. Using four mirrors before the BNF1 make the alignment easier, and keep the BPF in a safe position.

2.2.3 Suppression of the Rayleigh Background Noise

The most challenging problem in this low frequency Raman system is the diffuse scattered light from the BNFs. Fig. 2.4 shows the scattering light of 488 nm laser through a BNF imaged on a screen. The black arc seen on the screen in the transmission image corresponds to the Bragg angle for the wavelength used. To align BNF or BPF for maximum suppression, the black arc should be centered around the transmitted beam to obtain best filter alignment. The bright blue area outside the black arc is due to diffuse Rayleigh scattering of laser on particles or disorder in the photo-thermo-refractive glass of the notch filters. If a portion of this light reaches the detector it will “overshadow” good Raman signal close to the laser line. Additional filtering of the Rayleigh stray light was found to be helpful to obtain the best low frequency Raman signal.

Fig. 2.5 (a) shows the results of low frequency Raman spectra of bulk MoS$_2$ crystal (from SPI) with several different methods to suppress the diffuse scattered Rayleigh light. In fact, only using 3BNFs could already significantly reduce the Rayleigh light, and allow the low frequency peak of the $E_{2g}^{2}$ mode at ~32 cm$^{-1}$ to be visible. However, the background noise is dominated by the broad Rayleigh line from the diffusely scattered light without any blocking method. Such background
noise overshadows the two 2nd order Raman Stokes scattering peaks of MoS$_2$ at around 150 cm$^{-1}$ and 190 cm$^{-1}$.

Several methods have been found to be effective to reduce the noise. Since the minimum slit size of the spectrometer (10 µm) is probably not small enough, the easiest thing to do is to add a simple optical iris with an aperture size smaller than the width of the black arc (Fig. 2.4(a)). The back focal plane aperture size of the 20x objective is about $2 \times N.A. \times f = 8$ mm, while the black arc width after 3 BNFs are about 4-5 mm. In Fig. 2.5(a), I used a small aperture size of ~4 mm to block the Rayleigh stray light. Although the aperture reduces the Raman signal far from the Rayleigh line by about 3-4 times (the 1st order $A_{lg}$ and $E_{2g}^1$ mode) it suppress the background noise at ±25 cm$^{-1}$, close to the $E_{2g}^2$ shear mode at 32 cm$^{-1}$, by about 15-20 times and allows the weak 2nd order peaks at 150 cm$^{-1}$ and 190 cm$^{-1}$ to be visible.

Since the diffuse scattered light present at two sides of the black arc and the Raman signal, a similar method is to add a vertical slit instead of an optical iris after BNF3. Using a 3-4 mm vertical slit (two pieces of sharp-edge thick black paper attached to an optical mount) parallel to the black arc can reduce the background noise at ±25 cm$^{-1}$ by a factor of 30-40 and keep the Raman signal at ~1/3 of the result without blocking. I used this method for the characterization of MoS$_2$ lithiation in Chapter 4. A stronger Raman signal throughput can be maintained if the aperture size is larger than 4 mm but the background noise would be much larger. A circular shaped metal dot (beam stop) with size matching the collimated laser beam between BNF1 and BNF2 could help to reduce the Rayleigh light, but not as effective as a vertical aperture. Using a spatial filter is possible to block the Rayleigh light but too hard to align and was found to be no better than an iris. A modification of the spectrometer slit to allow a smaller minimum width would be another solution to this problem but this is hard to implement.
The Raman scattered light from the sample is isotropic in space. The backscattered Raman light collected by the objective lens depends on the incident angle of the laser (which determine the position of the laser focused on the sample relative to the objective lens center) while diffuse scattered lights does not. Hence a third method to reduce the background noise is to slightly tilt the BNF1 upward or downward so that the reflected light is slightly off from the horizontal plane. This way, the Raman signal will hit a slightly higher or low position on the spectrometer camera and can be shifted away from the broadest part of Rayleigh line image on the camera. Tilting the BNF1 by \( \sim 1^\circ \) can suppress of background noise by a factor of 3 while maintain the Raman signal at \( \sim 2/3 \) (probably due to a worse focusing), as shown in Fig. 2.4(b).

If the low frequency Raman signal is not polarization dependent, I can put a polarizer (analyzer) before the spectrometer and use \( z(xy)z' \), geometry for detection,\[134\] \( i.e. \) set the polarizer to be perpendicular to the polarization direction of the incident laser (which is controlled by the \( \frac{1}{2} \) wave plate). In this configuration, the second polarizer can serve as another filter to attenuate the Rayleigh scattering signal which is usually with the same polarization as the laser beam. The example Raman data of MoS\(_2\) (Fig. 2.4(b)) shows that a 60-100 times suppression of the background noise at \( \pm 25 \) cm\(^{-1}\) can be realized and the Raman peak of \( E_{2g}^{\prime} \), remain \( 1/3 \) of the unblocked one. However, the \( A_{ig} \) peak and the two 2\(^{nd}\) order peak at \( \sim 450 \) cm\(^{-1}\) are lost since they are polarized along the direction perpendicular to the polarizer.

Fig. 2.5(b) and (c) shows the low frequency Raman of three different types of materials: sulfur, highly ordered pyrolytic graphite (HOPG, (001) plane), and MoS\(_2\) (001) plane obtained using a 4 mm iris aperture together with spectrum of Si (100) acquired by using a common long pass filter cut off at \( \sim 100 \) cm\(^{-1}\). The spectra are scaled to their characteristic high frequency peaks normalized to the values obtained without blocking diffuse scattered Rayleigh light. Several strong peaks at
low frequency can be observed in sulfur and the MoS$_2$ $E_{2g}^2$ is clearly seen. However, the graphite shear mode at 42 cm$^{-1}$ (C peak) is not observed.[130] The main reason is that the intensity of graphite C peak is too weak. According to a previous literature using the same type of BNFs,[130] the intensity ratio of I(C)/I(G) in graphite is 0.049 of and 0.025 for 633 nm and 532 nm excitation laser. Assuming I(C)/I(G) remains ~0.025 (which is probably an overestimation) for 488 nm laser, the G peak intensity of ~23 cps mW$^{-1}$ (~1/5 of the MoS$_2$ 1$^{st}$ order peaks) corresponds to a C peak intensity of ~0.58 cps mW$^{-1}$ in our Raman system. This intensity is comparable with intensity of background noise at low frequency. Even using a perpendicularly polarized detection, the C peak is not observable. A better suppression of the background noise with stronger Raman signal throughput is necessary to observe weak peaks in low frequency Raman.

A more recent product of nano-edge (longpass) filter has been shown to be able to obtain Raman signal down to 10 cm$^{-1}$ with twice stronger Raman throughput than three BragGrate$^\text{TM}$ BNFs.[135] However, my attempt to use this type of nano-edge filter for the detection of the weak graphite C peak failed because of a strong background noise at the lowest cut-off edge of the filter presumably from the noise of the laser source. Using four BragGrate$^\text{TM}$ band pass the rejective geometry to clean up the laser before it enters the objective lens still couldn’t solve the problem. This problem might be solvable in the future with the ever-developing technique in the field of optical filters.
Figure 2.5. (a) Raman spectra of bulk MoS$_2$ from MTI on its (001) plane from -200 to 500 cm$^{-1}$ acquired with no blocking of the diffuse scattered Rayleigh light (black line), placing a 4 mm iris (#1, red line) or vertical aperture (#2, blue line) after BNF3, tilting the BNF1 (#3, green line), and using perpendicular polarization (#4, magenta line). All spectra are collected with 10 μm slit size, 1200 g mm$^{-1}$ grating in 3 sec exposure time with 80 times repetition. The two combination mode of at M point of the Brillouin zone $E_{2g}^1$ (M)-$A_{1g}$ (M) and $A_{1g}$ (M)-$E_{2g}$ (M) at ~150 and 190 cm$^{-1}$ are labeled.[136] (b) Representative low frequency (-300 to 300 cm$^{-1}$) and (c) regular frequency (300 to 1800 cm$^{-1}$) Raman spectra of sulfur (black line), MoS$_2$ (red line) HOPG (blue line) obtained with 4 mm iris and scaled to the intensity without diffuse scattered Rayleigh light blocking. The Raman spectrum of Si(100) acquired by using a common long pass filter is also shown in (c) for comparison (green line).
2.3 CVD Growth of Graphite

The growth of highly ordered graphite on Ni by chemical vapor deposition (CVD) has attracted significant interest due to the relatively high solubility and diffusivity of carbon in Ni, the lack of Ni-carbide phases, and scalability of the process for large-scale production.[137-139] My work on planar CVD graphite layers is partly inspired by prior work on the graphite and few layer graphene foams by CVD deposition on Ni templates with ultralow density ~5 mg cm$^{-3}$, relatively high mechanical strength, and relatively high electrical and thermal conductivity compared to common foam with similar density.[140-144] In my own work (not described in this dissertation), I’ve utilized CVD to grow few layer graphene on 3D Ni inverse opal (fabricated using colloidal crystal) with 600 nm pore size for the fabrication of 3D V$_2$O$_5$@graphene@V$_2$O$_5$ graphene-sandwiched Li-ion battery electrode that shows high capacities, good cycle stability, and fast charge–discharge kinetics.[145] Here, 3D CVD few-layer graphene with interconnected structure serve as good electrical conductor with low volume fraction and short solid-state ion diffusion length.

CVD growth of graphite on a transition metal substrate with large carbon solubility is fundamentally different than deposition on chemically-inert substrates where carbonization and thermal recrystallization occurs mainly on the substrate surface.[146] Carbon atoms usually come from the catalyzed decomposition of precursor of gas phase such as CH$_4$ and C$_2$H$_4$ on the metal surface at elevated temperatures. The atomic carbon dissolves into the transition metal at the same time and diffuses inside. After a certain period of time for carbon deposition, the substrate is cooled down, and the solubility of carbon in the metal decreases and graphite nucleates and grows at the surface.[147,148] To be more specific, the solubility of carbon in Ni is 0.8 at. % at 900 °C and 0.4 at.% at 730 °C [139]. The diffusivity of carbon in Ni is 8.5×10$^{-8}$ cm$^2$ sec$^{-1}$ at 900 °C and 0.4×10$^{-8}$
cm² sec⁻¹ at 725 °C [139]. As carbon precipitates at the surface of the Ni, graphite is formed by nucleation and growth [139,147,149].

To advance the fundamental understanding of the structure-processing-property relations of CVD graphite layers with a focus on thermal conductivity, I grew graphite with thickness in the range 20-140 nm grown by CVD on single crystal Ni (111) substrates at temperatures between 825 and 900 °C. The film thickness is controlled by changing the dwell time at the carbon deposition temperature.

Carbon growth was performed on single crystal Ni substrates (<111> orientation, >99.99% purity, surface roughness <3 nm over 20×20 µm² area from MTI Corporation) to minimize inhomogeneities and film roughness generated by grain boundaries and variations of crystal orientation [150-152]. Carbon deposition was performed using an Atomate hot-wall CVD reactor with an ID = 22 mm quartz tube. A rotary vane pump was used, and a molecular sieve filter was placed between the pump and the chamber to minimize back streaming of oil vapors into the chamber. The pump exhaust is routed to a CDO (controlled decomposition oxidation) system. The Ni substrate was prepared for carbon deposition using a H₂ gas flow of 400 sccm at a pressure of ≈1 Torr for 30 min at 900 °C to reduce surface oxide. The substrate was then cooled to the carbon deposition temperature at 10 °C min⁻¹ while maintaining a 400 sccm H₂ gas flow. Carbon deposition was initiated by introducing a gas mixture of 90 sccm C₂H₄ and 180 sccm H₂ while holding the overall pressure at ≈1 Torr. Dwell times from 10 min to 170 min at several temperatures between 800 to 900 °C were used. Finally, after carbon deposition, the samples were cooled to room temperature at a rate of 10 °C min⁻¹ under 500 sccm of flowing Ar.

As the dwell stage temperature rises for the from 825 to 1050 °C, the decomposition rate of C₂H₄ and the diffusivity of C in Ni become larger. With the same dwell time and cooling rate, the
film thickness increases as the dwell temperature rises.[153] If the growth temperature is fixed, increasing the exposure time would increase the amount of C dissolved in the Ni substrate as long as it doesn’t saturate the whole 0.5mm Ni substrate. Thus, increasing the exposure time would also increase the film thickness if the cooling rate is fixed. However, graphite layer on Ni inevitably forms wrinkles as a result of the thermal expansion mismatch between Ni and graphite. (The linear dimensions of the Ni substrate contract by 1.4% on cooling from 900 °C to room temperature while graphite contracts by only 0.05%. [149,154,155]) A thick layer of graphite would cause tall wrinkles and leads to higher surface roughness which causes diffuse scattering of the laser used in the TDTR measurements and adversely affects the results. Since the growth rate increase rapidly with temperature, I limited the temperature of CVD growth to 900 °C at maximum and varied the thickness by changing growth time at 900 °C.

On the other hand, if the growth temperature is too low, the lateral diffusion of C on the metal surface is slow causing graphite to become much less uniform and even non-continuous, with few layer graphene between islands of thick graphite.[153] Carbon deposition temperatures in the range of 825 to 900 °C were found to produce graphite layers that are sufficiently smooth and uniform for measurements by TDTR. The typical rms roughness of these graphite layers on Ni substrate is on the order of 10 nm as measured by atomic force microscopy over an area of 20×20 μm². Characterization of the CVD graphite is presented in Chapter 3.

Although CVD graphite is grown on single crystal Ni (111), the film is not still not uniform with variation in the thickness (see Chapter 3). Carbon atoms tend to precipitation and nucleate at high reactivity Ni surface sites, such as step edges.[156,157] Using other inert element, such as Au, to decorate these reactive site could inhibit the graphite nucleation density, allowing more uniform and controlled growth of graphite.[158] I deposited 25-50 nm Au by e-beam evaporation
on Ni (111) surface and annealed the Au/Ni substrate at 950 C for 30 min to form solid solution of Au-Ni where Au atoms serve as passivating substitute at Ni edge site.[157,159] This process before the normal CVD growth mentioned above could enhance the uniformity of the graphite by a certain degree providing better coverage of C on the alloyed Ni(Au) substrate.

However, this method doesn’t solve the wrinkle problem. This method also suppresses the growth rate of graphite dramatically mainly because the C diffusivity in Ni(Au) alloy is smaller. [158] What’s worse, the Au alloying with Ni significantly change the Ni thermal conductivity from 90 W m\(^{-1}\) K\(^{-1}\) down to around 60 W m\(^{-1}\) K\(^{-1}\) (even if the Au concentration is small), similar to Ni alloying with Pt.[160] Measurements of the thermal conductivity of Ni(Au) alloy substrate after C is removed shows variation in different batches. The TDTR data fitting to the Al/graphite/Ni(Au) is not always good presumably due to the Ni(Au) surface with uncontrollable composition gradient resulted from the kinetic nature of the Au diffusion near the Ni surface during the high temperature growth process. Therefore, I didn’t use the data from graphite grown by this method in Chapter 3.
CHAPTER 3

THERMAL CONDUCTIVITY OF GRAPHITE THIN FILMS GROWN BY LOW TEMPERATURE CHEMICAL VAPOR DEPOSITION ON Ni (111)

Parts of this Chapter were published in “Thermal conductivity of graphite thin films grown by low temperature chemical vapor deposition on Ni (111),” Qiye Zheng, Paul V. Braun and David G. Cahill,[161] Adv. Mater. Interfaces, 3: 1600234. (2016)

3.1 Introduction

The high in-plane thermal conductivity[162,163] of graphite, \( \approx \)2000 W m\(^{-1}\) K\(^{-1}\), enables important applications of graphite in thermal management.[164-166] However, extremely high process temperatures are often needed to obtain highly-oriented graphite with high thermal conductivity. For example, synthetic highly-oriented graphite is typically formed at temperatures on the order of 2500 °C by pyrolysis of hydrocarbon gases (e.g., CH\(_4\), C\(_2\)H\(_4\)) or polymer (e.g., polyimide, polyacrylonitrile, polyvinylidene chloride) precursors[167-170]. Lower process temperatures often result in strongly disordered microstructures.[170] For example, at 900 °C, thermal decomposition of hydrocarbons on chemically inert substrates typically yields turbostratic carbon.[171]

However, if the substrate material is a transition metal that has a significant equilibrium solubility of carbon, highly-oriented graphite can be grown at temperatures below 1000 °C.[172] Due to the relatively high solubility and diffusivity of carbon in Ni, and the lack of Ni-carbide
phases the growth of graphite on Ni by chemical vapor deposition (CVD) allows for large-scale production of graphite thin film with controllable thickness.\cite{137-139}

CVD graphite has been used to produce graphite-based foams with ultralow density $\sim 5 \text{ mg cm}^{-3}$, relatively high mechanical strength, and high thermal conductivity.\cite{140-144} My work on planar CVD graphite layers is partly inspired by prior work on the production of graphite foams by CVD deposition on Ni templates.\cite{141} In this paper, I advance the fundamental understanding of the structure-processing-property relations of CVD graphite layers with a particular focus on thermal conductivity, and thereby advance their applications in thermal management.

A reduction in the thermal conductivity of a thin CVD graphite layer compared to bulk HOPG could come from both effects of microstructural disorder and the sample dimensions (e.g., thickness) on the mean-free-paths of the acoustic phonons that are the dominant carriers of heat. Graphite films grown on Ni typically contain structural defects (e.g., point defects, stacking disorder and dislocations) and surface roughness (e.g., wrinkles),\cite{137,149} and both these classes of defects may scatter acoustic phonons.

I use time domain thermoreflectance (TDTR) to study the thermal conductivity of graphite with thickness in the range 20-140 nm grown by CVD on single crystal Ni (111) substrates at temperatures between 825 and 900 °C. I vary the film thickness by varying the dwell time at the carbon deposition temperature. The crystallinity of the layers is characterized by X-ray diffraction and Raman spectroscopy. I examine film uniformity by mapping cross-plane thermal conductivity and the ratios of Raman spectroscopy peaks with a spatial resolution of $\approx 10 \mu\text{m}$. 
3.2 Experimental

The details of graphite CVD growth process are described in Chapter 2.

The cross-plane thermal conductivity of CVD graphite is measured by TDTR using a sample structure of graphite/Ni (g/Ni) subsequently coated by an 80 nm thick Al thin film by magnetron sputtering. For measurements of in-plane thermal conductivity, I transferred the as-grown graphite film to thermally-oxidized Si wafer and then coated the g/SiO$_2$/Si structure with a 70 nm thick film of Nb. The lower thermal conductivity of the Nb film ($\approx 30$ W m$^{-1}$ K$^{-1}$) in comparison to Al films ($\approx 160$ W m$^{-1}$ K$^{-1}$) improves the sensitivity of TDTR to in-plane thermal conductivity.

I utilized the so-called “bubbling transfer” method described previously to transfer graphite layers from the Ni substrate to the oxidized Si wafer [173]. I substituted poly(bisphenol A carbonate) (PC) for polymethyl methacrylate (PMMA) as the handle to reduce organic residue [173,174]. Briefly, the Ni substrate coated with graphite was first spin-coated with PC followed by curing. Then the PC/g/Ni sample (0.5×0.5 cm$^2$) was dipped into a NaOH (0.5 M) aqueous solution and used as the cathode of an electrolysis cell with a Pt foil counter electrode (3.0×3.5 cm$^2$). After a current of 0.5 A was applied for tens of seconds, the PC/graphite layer detached from the Ni substrate, driven by the formation of H$_2$ bubbles at the interface between graphite and Ni. The PC/graphite layer was stamped on the SiO$_2$/Si substrate and cleaned with water. The PC was then dissolved by chloroform and the sample was annealed in an Ar/H$_2$ flow for 1 h at 400 °C to remove residual PC.

In a TDTR measurement, the pump beam is modulated at a frequency of either 9.8 or 1.1 MHz by an electro-optical modulator (see section 2.1). For measurements of cross-plane thermal conductivity a 5× objective lens that focuses the laser beams to a 1/e$^2$ intensity radius of $\approx 11.7$ μm was used. For measurements of in-plane thermal conductivity a 20× objective lens that focuses
the laser beams to a $1/e^2$ radius of $\approx 3.0$ $\mu$m was used. Due to the high thermal conductivity of the Ni and Si substrates, the steady-state heating in the measurements is negligible, $<10$ K.

### 3.3 Morphology and Structure of CVD Graphite

Carbon deposition temperatures in the range of 825 to 900 °C were found to produce graphite layers that are sufficiently smooth and uniform for measurements by TDTR. Fig. 3.1(a) and (b) shows an example scanning electron microscopy (SEM) image and a typical X-ray diffraction pattern of a graphite film grown at a carbon deposition temperature of 900 °C. The dominant surface feature is a network of wrinkles, presumably created by the thermal expansion mismatch between Ni and graphite. Large amplitude wrinkles cause diffuse scattering of the laser used in the TDTR measurements and adversely affect the results; I therefore performed measurement on relatively smooth regions of the sample where the reflected laser intensity is $>95\%$ of the intensity reflected from a reference sample. At carbon deposition temperatures below 825 °C, the graphite coverage becomes progressively more non-uniform.[175] At carbon deposition temperatures above 900 °C, the film tends to form more pronounced wrinkles. Shorter deposition times at high temperature produce non-continuous films.
Figure 3.1. (a) Scanning electron microscopy image of 70 nm thick CVD graphite grown on a Ni (111) substrate at 900 °C. (b) Example x-ray diffraction data for CVD graphite. All CVD graphite layers produced by deposition temperatures between 825 and 900 °C are highly textured with the (001) plane parallel to the substrate surface. Using the Ni (111) peak position as an internal calibration, the lattice constant of the CVD graphite film is $c = 3.356 \, \text{Å}$, the same as HOPG to within the accuracy of my measurement. (c) Example picosecond acoustic data for the change in the in-phase signal as a function of the delay time $t$ between pump and probe pulses incident on an Al/graphite/Ni sample. $\Delta t_{\text{Al}}$ and $\Delta t_g$ are the round-trip times for an acoustic pulse to traverse the Al and graphite layers, respectively. (d) Graphite thickness versus the dwell time of the exposure of the Ni substrate to the gas precursor at different substrate temperatures. The red dashed line is the fitting to the data for the 900 °C growth using the empirical function $h = a + bt^c$ described in the text.
The graphite film thickness is determined by picosecond acoustics method described previously,[176,177] see Fig. 3.1(c). The transient reflectance signals exhibit small positive and negative peaks superimposed on the thermal decay at times corresponding to the arrival of acoustic pulses at the sample surface. Negative (positive) changes in the signal occur for pulses which undergo phase shifts of $\pi$ (zero) due to reflection from an interface with a material of lower (higher) acoustic impedance, $Z = \rho v$, where $\rho$ is the mass density and $v$ the sound velocity of the material.[176] Since $Z_{\text{Al}} = 1.7 \times 10^7$ N s m$^{-3}$,[178] $Z_{\text{graphite}} = 0.9 \times 10^7$ N s m$^{-3}$,[179,180] and $Z_{\text{Ni}} = 5.4 \times 10^7$ N s m$^{-3}$ [180] pulses reflected from the Al/graphite, graphite/Ni, and Al/air interfaces have phase shifts of $\pi$, zero, and $\pi$, respectively.

The time interval $\Delta t_{\text{Al}}$ between the first and second downward peaks corresponds to the time required for the acoustic pulse to traverse the Al layer twice. Correspondingly, the time $\Delta t_{\text{g}}$ between the first downward and upward peaks is the time required for the pulse to traverse the graphite layer twice. Based on a measurement of the graphite film thickness by atomic force microscopy, I determined the longitudinal speed of sound along the $c$-axis in CVD graphite to be $4.1 \pm 0.2$ nm ps$^{-1}$. The x-ray lattice constant suggest that CVD graphite has the same density of 2.26 g cm$^{-3}$ as HOPG; therefore, $c_{33} = 38 \pm 3$ GPa, in agreement with the reported value of $37.5 \pm 1$ GPa of HOPG.[179,181] This is expected because the $c_{33}$ elastic constant is weakly affected by rotational stacking disorder.[182] Using the longitudinal speed of sound $v_L$ for Al (6.42 nm ps$^{-1}$) and CVD graphite I can obtain their thicknesses at each point of TDTR measurement by calculating $h = (v_L \Delta t)/2$. An important advantage of picosecond acoustics for determining the film thickness is the fact that the graphite thickness is measured at the same location as the TDTR data.
I note that for a typical graphite layer grown at a deposition temperature of 900 °C, the thickness variation is on the order of 10% across the entire substrate dimension of ≈5 mm.

Fig. 3.1(d) summarizes the graphite thickness \( h \) as a function of the dwell time \( t \) of growth at different temperature with a fixed cooling rate of 10 °C min\(^{-1}\). Data for the 900 °C growth is fit to the function \( h = a + bt^c \), where \( a \), \( b \) and \( c \) are fitting parameters. I find \( c = 0.38 \), smaller than the value of 0.5 that is expected in the limit of slow cooling and complete precipitation of all of the carbon diffused into the Ni substrate during the dwell time.[183] Due to the finite cooling rate, some carbon is trapped in the Ni. As expected, the thickness of graphite decreases as the growth temperature decreases due to the decrease of solubility and diffusivity of carbon in Ni; the graphite thickness scales with the product of solubility and the square root of the product of diffusivity and dwell time.

### 3.4 Cross-plane and In-plane Thermal Transport of CVD Graphite

Representative TDTR data and model fitting for a 35 nm thick graphite sample grown at 900 °C measured in two configurations (Al/graphite/Ni, and Nb/graphite/SiO\(_2\)/Si) are shown in Fig. 3.2(a). The thermal model used for fitting includes parameters for the thermal conductivity, heat capacity, and thicknesses of the metal and graphite layers.[94] The most important fixed parameters in the model are the thermal conductivity and heat capacity of the single crystal Ni substrate (91 W m\(^{-1}\) K\(^{-1}\) and 3.95 J m\(^{-3}\) K\(^{-1}\)) and the heat capacity of graphite[180] (1.59 J m\(^{-3}\) K\(^{-1}\)).
Figure 3.2. (a) Example TDTR data (open circles) for a \( \approx 35 \) nm thick graphite film measured with the sample configuration of Al (80 nm)/graphite/Ni ("g" in the figure label denotes graphite), 5× objective lens, and 9.8 MHz modulation frequency (configuration A); and Nb (70 nm)/g/SiO\(_2\) (1 µm)/Si, 20× objective lens, and 1.11 MHz modulation frequency (configuration B). The data are compared to the predictions of my thermal model (solid lines). (b) Corresponding sensitivity parameters as a function of delay time for parameters of in- and cross-plane thermal conductivity (\( \Lambda_c \) and \( \Lambda || \)), Al/graphite and Nb/graphite interface thermal conductance (\( G_{Al/g} \) and \( G_{Nb/g} \)) and beam spot size (\( w_0 \)) for configuration A (without prime) and configuration B (with prime).

I define the sensitivity of the fit \( S_\alpha \) as the logarithmic derivative of \(-V_{in}/V_{out}\) with respect to each of the parameters (\( \alpha \)) to gauge how a parameter influences the output of the model. The larger the value of \( S_\Lambda \), the smaller the error propagated from the other parameters into the measured thermal conductivity. Fig. 3.2(b) shows the sensitivity of the fits in Fig. 3.2(a) to changes in the various parameters in the thermal model. Since the measurement cannot distinguish well between the thermal resistance of a thin layer and the thermal resistance between that layer and the substrate, I treated the graphite and the bottom interfaces as one effective layer and fit the data to two free parameters, the Al/graphite interface thermal conductance, and an effective thermal
conductivity of the graphite layer that includes the series thermal resistance of the graphite/Ni interface. The radius of the focused spot $w_0$ is determined to an accuracy of 6% using the dependence of $V_{in}$ on the spatial offset of the pump and probe beams at short delay time (50 ps) measured on a reference Al/SiO$_2$ sample.[184]

In configuration A, the sensitivity to the cross-plane thermal conductivity is $\approx 0.87$ to 0.7 and the sensitivity to the in–plane thermal conductivity is extremely small, 0.02. Therefore, I am able to use configuration A to accurately determine the cross-plane thermal conductivity, independently of the in-plane thermal conductivity.

I plot the measured thermal resistance of the graphite film, (the series thermal resistance of the Al/graphite interface, the graphite layer, and the graphite/Ni interface), as a function of film thickness in Fig. 3.3(a) and (b). Previously reported data for exfoliated graphite[79] are included for comparison. The thermal resistance is independent of the growth temperature (825-900 °C) to within the measurement uncertainties. The graphite thermal resistance follows an approximately linear dependence on film thickness over the range of film thicknesses studied (red dashed line in Fig 3.3(a)). The slope of this fit corresponds to thermal conductivity of $3.3 \pm 0.3$ W m$^{-1}$ K$^{-1}$. The $y$-axis intercept gives a total interface thermal resistance of $\approx 2.3 \times 10^{-8}$ m$^2$ K W$^{-1}$, i.e., a thermal conductance of $\approx 44$ MW m$^2$ K$^{-1}$, comparable to prior studies of the thermal conductance of an interface between graphite and Al $\approx 50$ MW m$^2$ K$^{-1}$ at 260 K. The thermal conductance of Ni/graphite was previously reported to be $\approx 120$ MW m$^2$ K$^{-1}$ at 300 K.[185,186]
Figure 3.3. Cross-plane thermal resistance of graphite films grown at 825, 850, 875 and 900 °C as a function of film thickness in (a) linear and (b) log-log scale along with previous experimental (filled symbols) and simulation (black dashed line) data.[26,79,187] I added a constant interface thermal resistance of $2.3 \times 10^{-8} \text{ m}^2 \text{ K W}^{-1}$ to the simulation data.[26] The red dashed line in (a) is a linear fit of the data for the sample grown at 900 °C. The 7-15% error in the measured data is shown as representative error bars in (a) and (b). In-plane thermal conductivity of CVD graphite films grown at different temperatures as a function of thickness in (c) linear and d) log-x scale together with data of exfoliated encased graphite in a previous work.[188-191] Measured bulk HOPG value is labeled as dashed line in (c) and (d).
My measurements of the cross-plane thermal resistance are comparable to measurements of exfoliated graphite in the ranges of thickness where the measurements overlap.\cite{79,187} My measurements of the thermal resistance are significantly smaller than the recent study by Harb \textit{et al.} of a 35 nm thick graphite film deposited by dc-bias-activated CVD at a temperature of 950°C and measured by time-resolved x-ray diffraction at room temperature of $\approx 5\times10^{-8}$ m$^2$ K W$^{-1}$.$\cite{192}$

Calculations of the cross-plane thermal conductivity of graphite by first-principles methods show that the thermal conductivity of graphite is suppressed when the thickness is comparable to the mean-free-paths of the phonons that are the dominant carriers of heat in the cross-plane direction.$\cite{26}$ I include the calculation of Fugallo \textit{et al.} in Fig. 3.3(a) and (b) by taking the inverse of their calculated values of thermal conductivity, multiplying by the thickness, and adding a constant interface thermal resistance of $2.3\times10^{-8}$ m$^2$ K W$^{-1}$ to account for the thermal resistances of the Al/graphite and graphite/Ni interfaces in the experiment. This comparison suggests that the thermal resistance of thin CVD can be adequately accounted for by the limits on the phonon mean-free-path imposed by the sample thickness. For thicker layers, $> 50$ nm, the slope of the measured thermal resistance is larger than the calculation.

I measured the in-plane thermal conductivities of CVD graphite and a comparison sample of HOPG (SPI-1 grade from Structure Probe, Inc.) using a Nb thin film as the TDTR transducer layer, a 20× objective lens, and 1.11 MHz modulation frequency, see Fig. 3.3(c) and (d). The thermal conductivity of the Nb thin film, $\approx 30$ W m$^{-1}$ K$^{-1}$, is derived from electrical conductivity and the Wiedemann-Franz Law. The thermal conductance $G$ of the graphite/SiO$_2$ interface is fixed at 80 MW m$^{-2}$ K$^{-1}$.$\cite{193}$ I fixed the cross-plane thermal conductivity $\Lambda_c$ of the sample at 3.3 W m$^{-1}$ K$^{-1}$ as determined from the cross-plane measurement. The Nb/graphite interface conductance $G_{\text{Nb/g}}$ and the in-plane thermal conductivity $\Lambda_{||}$ are the remaining two free parameters in the model. Since
the sensitivity to $\Lambda_c$ and $G_{\text{Nb/g}}$ are much smaller ($S<0.1$) than the sensitivity to $\Lambda_\parallel$ ($S \approx 0.45$), variations in the interface conductance and cross-plane thermal conductivity do not produce significant errors in the measurement of $\Lambda_\parallel$.

The magnitude of the in-plane thermal conductivity $\Lambda_\parallel$ is 30-50% of the conductivity of HOPG with weak dependence on the film thickness. As the CVD growth temperature is lowered from 900 °C to 825 °C, $\Lambda_\parallel$ decreases by 20-35%. This trend is different from the reported thermal conductivity of thinner exfoliated graphite from single layer (graphene) to $\approx$ 10 nm thick supported on SiO$_2$ where $\Lambda_\parallel$ scales with the thickness (see Fig. 3.3(d)), which is attributed to long intrinsic mean free paths of phonons in graphite and partially diffuse phonon-interface scattering in the supported graphite.[28, 29] In addition, the measured in-plane thermal conductivity of thick CVD graphite is in general larger than those exfoliated graphite which is essentially free of stacking disorder. From this comparison, I conclude that stacking disorder in CVD graphite is not an important factor in limiting the in-plane thermal conductivity. I suggest the crystallite size and defects in the graphite along the basal plane direction may serve as the major source of phonon scattering, rather than of boundary scattering from the top and bottom interfaces which is less pronounced in thick film of my experiment compared with multilayer graphene in previous works. This conclusion is supported by the observation of a trend of increasing thermal conductivity with increasing deposition temperature. If I assume that lateral grain boundaries are the dominate scattering mechanism, a comparison to boundary-scattering length-dependence of the BTE calculations[26] suggests that the grain size in the basal direction of CVD graphite is 200-500 nm, consistent with microscopy studies of few layer CVD graphene grown at similar temperature and my Raman measurements.[194]
3.5 Raman Spectroscopy and Thermal Conductivity Mapping

Figure 3.4. (a) Raman spectra of CVD graphite at several different locations (data of location A, B, C was multiplied by 10^2, 10^4, and 10^6 respectively); spectrum for HOPG is included for comparison. Weak peaks at ≈1903, 2070 and 2200 cm\(^{-1}\) labeled by black triangles are attributed to the combination modes from iTA (in-plane transverse acoustic) +LO (longitudinal optical), LA (longitudinal acoustic) + LO, and iTA + iTO (in-plane transverse optical) phonons respectively. The sharp peak at 2324 cm\(^{-1}\) is from nitrogen in the ambient air. (b) Map of the effective cross-plane thermal conductivity \(\Lambda_c\) and (c) the integrated peak intensity ratio (\(I_G/I_{2D}\)) of CVD graphite at same location on the sample. (d) \(\Lambda_c\) vs. \(I_G/I_{2D}\) of data points shown in (b) and (c).
To better understand the spatial homogeneity and variations in the microstructure of CVD graphite, I plot the Raman spectra of CVD graphite grown at 900 °C measured at different locations on the sample in Fig. 3.4(a). Typical peaks of D (defect-activated breathing mode at 1350 cm$^{-1}$), G (E$_{2g}$ mode at 1580 cm$^{-1}$), D’ (overtone of out-of-plane transverse optical phonon at 1750 cm$^{-1}$), D + D” (combination mode of a D phonon and a LA phonon at 2440 cm$^{-1}$), and 2D (overtone of D phonon at 2700 cm$^{-1}$) are observed.[195] Although the G peak intensity is similar for all locations on the CVD graphite, and for HOPG, the intensity of the 2D peaks of the CVD graphite varies significantly from almost 5 times that of HOPG (location A) to only $\approx 0.5$ of that of the HOPG (location C). The 2D peak in the Raman spectrum of multilayer graphene depends strongly on the relative rotation angle between basal planes due to changes in electronic band structure.[196-198] The low intensity peaks labeled by black triangles which are more pronounced at location A and attributed to phonon combination modes may also be related to incommensurate stacking.

The 2D peak of HOPG can be decomposed into two Lorentzian peaks centered at $\approx 2730$ cm$^{-1}$ and $\approx 2690$ cm$^{-1}$ due to a splitting in the $\pi$ electrons dispersion resulting from interlayer coupling. The 2D peak of CVD graphite sometimes shows an extra peak component at $\approx 2712$ cm$^{-1}$ and sometimes even a single peak at 2712 cm$^{-1}$ (location A). These peaks could be related to rotational disorder or turbostratic structure which weakens the interaction between the basal planes that suppresses the splitting in the $\pi$ electrons dispersion and produces a graphene-like Raman spectrum.[199] Averaged over large areas, the intensity of the D peak is <10% of the intensity of the G peak, suggesting an in-plane crystalline size (or distance between structural defects) on the order of a few hundred nanometers.[200,201] The D to G intensity ratio increases slightly to $\approx 0.12$ for samples deposited at 825°C.
My graphite films are not spatially uniform.[149] To gain insight on the magnitude of the inhomogeneities, I mapped and compared the thermal conductivity and Raman spectrum of a 50 nm thick CVD graphite layer across the same 100x100 µm² region of sample with a spatial resolution of ~10 µm, see Fig. 4(b) and (c). I mapped the thermal conductivity by scanning the position of the sample at a fixed pump-probe delay time (207 ps) and recording the thermoreflectance signal $-V_{in}/V_{out}$ at each point. I then used the thermal model and the parameters at one spatial location to calculate the function of thermal conductivities corresponding to the thermoreflectance ratios that encompasses the values I measured during scanning.[202] The effective cross-plane thermal conductivity (including the top and bottom interface of Al/graphite and graphite/Ni) has an average value of 1.26 W m⁻¹ K⁻¹ with a standard deviation of 0.2 W m⁻¹ K⁻¹. The ratio of the integrated intensity of G ($I_G$ from 1470 ~ 1670 cm⁻¹) and 2D ($I_{2D}$ from 2620 ~ 2820 cm⁻¹) peaks in Raman spectra has an average value of 1.33 ± 0.25 (for HOPG, this ratio is measured to be 1.17, suggesting a deviation from perfect Bernal stacking in CVD graphite). The maps of thermal conductivity and Raman spectra are compared in Fig. 4(d) using a scatter plot of values measured in each location. I do not observe a significant correlation between the local thermal conductivity and the local ratio of the Raman intensities.

3.6 Evaluation of CVD Graphite for Flexible Electronic Application

Finally, I consider the potential application of CVD graphite as a thermal management material in flexible electronics.[203,204] I consider a figure of merit $K$ that combines the thermal conductance of the layer $\Lambda h$ and the bending stiffness of the film, $EI = \frac{Mh^3}{12(1-\nu^2)}$, where $M$ is the
plane-strain modulus. I define $K = \frac{Nh}{(EI)^{\frac{1}{3}}} = \lambda \left(1 - \nu^2\right)^{\frac{1}{3}}$ as a figure-of-merit that is independent of thickness.[179,205] Using mechanical properties of HOPG, $M \approx 1.02$ TPa, $\nu \approx 0.16$, and the thermal conductivity of CVD graphite, $900 \text{ W m}^{-1} \text{ K}^{-1}$, I find $K_{\text{graphite}} \approx 89 \text{ W m}^{-1} \text{ K}^{-1} \text{ GPa}^{-\frac{1}{3}}$. Metal films are sometimes used as heat spreaders in flexible electronics. For Au and Cu thin films of $\approx 100$ nm, I find smaller values, $K_{\text{Au}} \approx 48 \text{ W m}^{-1} \text{ K}^{-1} \text{ GPa}^{-\frac{1}{3}}$ and $K_{\text{Cu}} \approx 51 \text{ W m}^{-1} \text{ K}^{-1} \text{ GPa}^{-\frac{1}{3}}$ which decreases as the film thickness is reduced as the metal thermal conductivities decrease.[206,207] It was reported that placing graphite quilts of a few nanometers thickness on top of GaN transistors in a high-power electronic could lower the hotspots temperature by $\approx 20$ °C when operated at $\approx 13 \text{ W mm}^{-1}$, outperforming the use of Au thin films.[208] Combined with soft-lithographic printing techniques,[209] CVD graphite layers might provide some advantage in thermal management of devices where flexibility of the layer is an important constraint.

3.7 Conclusion

In summary, I measured the thermal conductivity of CVD graphite thin films with various thicknesses ($\approx 20 \sim 140$ nm) grown on single crystal Ni (111) substrate at temperatures from 825 to 900 °C by TDTR. The cross-plane thermal resistance is a linear function of the film thickness, The effective cross-plane thermal conductivity of $\approx 3.3 \text{ W m}^{-1} \text{ K}^{-1}$ is smaller than the predictions of first-principles solutions of the Boltzmann transport equation at the upper end of the thickness range. I do not observe, however, a correlation between the cross-plane thermal resistance and microstructural defects that produce changes in the Raman spectra. The in-plane thermal conductivity of films grown at different temperatures varies between $\approx 650$ to $1000 \text{ W m}^{-1} \text{ K}^{-1}$. If
I attribute the reduction of thermal conductivity compared to HOPG to phonon scattering by lateral grain boundaries, a comparison to first-principles calculations suggests a grain size on the order of 300 nm. I define a figure-of-merit for flexible heat spreaders and find that CVD graphite has potential advantages over metal films for thermal management of flexible electronics.
CHAPTER 4

TUNING THERMAL CONDUCTIVITY IN MOLYBDENUM DISULFIDE BY ELECTROCHEMICAL INTERCALATION

Parts of this Chapter were published in “Tuning thermal conductivity in molybdenum disulfide by electrochemical intercalation,” Gaohua Zhu, Jun Liu, Qiye Zheng, Ruigang Zhang, Dongyao Li, Debasish Banerjee, and David G. Cahill,[52] Nat. Commun. 7: 13211 (2016)

4.1 Introduction

Two-dimensional (2D) layer-structured materials consist of atomic layers with strong intra-layer covalent bonding stacked together by weak van der Waals bonds. Transition metal dichalcogenides (TMD), an important class of 2D materials, have attracted extensive research interest recently due to their unique electronic and chemical properties.[210] In particular, MoS$_2$ has been extensively studied for potential applications in nanoelectronics, optoelectronics and flexible electronic devices.[211-215] Although the thermal conductivity of single, few-layer, and bulk MoS$_2$ has been reported recently, the effects of structural and compositional disorders on the anisotropic thermal conductivity of layered materials, which usually occurs during crystal growth, fabrication, and application of the devices (e.g., energy storage, thermoelectrics, and nanoelectronics), have not yet been systematically characterized. [31-33]

Guest ions can be intercalated into the van der Waals gaps in MoS$_2$. Intercalation causes changes in the host material’s electronic structure and optical and electrical properties.[27] Intercalation can also induce structural and compositional disorder, including the change of layer spacing, interaction strengths between adjacent layers, and phase transitions.[28-30] The amount
of the intercalated ions can be controlled by the potential in the electrochemical process. Therefore, intercalation provides an effective way to systematically vary the structural and compositional disorder of many 2D materials and enables investigations of how disorder affects their thermal conductivity.

To understand how thermal transport properties can be affected by different crystalline orientations and structural disorder, thermal conductivity of both pristine and lithium ion intercalated bulk and thin film MoS\(_2\) are studied. The MoS\(_2\) basal planes in the bulk sample are oriented parallel to the surface, whereas, in the thin film sample, the MoS\(_2\) basal planes are vertically aligned. The thermal conductivity of lithium intercalated MoS\(_2\), Li\(_x\)MoS\(_2\), with different degrees of lithium ion intercalation (x) were measured by time-domain thermoreflectance (TDTR). It’s found that lithiation strongly modifies the thermal conductivity of MoS\(_2\) with drastically different effects on different forms of MoS\(_2\) due to the differences in crystalline orientation and initial structural disorder.

The most striking observation is that the thermal anisotropy ratio, the ratio of in-plane to through-plane thermal conductivity, in bulk Li\(_x\)MoS\(_2\) crystals increases from 52 (x = 0) to 110 (x = 0.34) as a result of lithiation-induced stacking disorder and phase transitions. The increase in thermal anisotropy with increasing disorder is counter-intuitive: previous studies show that structural disorder should decrease the thermal anisotropy ratio.[216,217] The enhanced thermal anisotropy ratio in Li\(_x\)MoS\(_2\) bulk crystal is likely due to the drastic differences in the in-plane and through-plane length scale of the lithiation-induced disorder.
4.2 Materials Characterization

The MoS$_2$ thin film samples with vertically-aligned basal planes were grown by rapid sulfurization of a Mo thin film.[218] Bulk samples of MoS$_2$ were obtained by mechanical exfoliation of bulk MoS$_2$ crystals (SPI Supplies). The cross-sectional transmission electron microscopy (TEM) image in Fig. 4.1(a) reveals that the thin film thickness is $\approx$200 nm after chemical vapor deposition (CVD) growth and the MoS$_2$ atomic layers are predominantly aligned perpendicular to the substrate with the edges of the MoS$_2$ layers exposed to the surface. A typical plan view TEM image of the vertically-aligned MoS$_2$ thin film is shown in Fig. 4.1(b). The thin film is polycrystalline with randomly oriented strip-like or columnar grains. The cross-sectional area of those columnar grains is approximately 10 nm wide and several tens of nanometers long. Bulk MoS$_2$ samples, with typical thickness of 10-20 $\mu$m, were prepared by standard Scotch tape assisted mechanical exfoliation method. A plan view TEM image of the bulk MoS$_2$ sample is shown in Fig. 4.1(c), where the high-quality atomic plane of MoS$_2$ can be seen.

![Figure 4.1](image)

**Figure 4.1.** TEM images of MoS$_2$ bulk crystals and thin films (a) Cross-sectional TEM image of the MoS$_2$ thin film with vertically-aligned basal plane. The scale bar is 20 nm. (b) Plan-view TEM image of the MoS$_2$ thin film. The scale bar is 10 nm. (c) Plan-view TEM image of the bulk MoS$_2$ crystal. The scale bar is 2 nm.
Figure 4.2. Raman spectra for bulk and thin film MoS$_2$ samples prior to lithiation at (a) low frequencies, (b) high frequencies. The y-axis is the signal intensity normalized by laser power (S/P) in the unit of counts per second per milliwatt (cps mW$^{-1}$). The bulk spectrum is shifted up by 50 cps mW$^{-1}$. Raman spectra for bulk Li$_x$MoS$_2$ samples at different degrees of lithiation ($x=0$, 0.34, and 0.68) at (c) low frequencies, (d) high frequencies. The $x=0.34$ and $x=0$ spectra are shifted up by 65 and 130 cps mW$^{-1}$, respectively.
Further structural analysis of bulk and thin film MoS\(_2\) samples prior to lithiation were carried out by X-ray diffraction (XRD) and Raman spectroscopy. In XRD, bulk samples show a strong (002) peak located at \(2\theta = 14.4^\circ\) and (004), (006), (008) peaks with decaying magnitudes, indicating that the basal planes of the bulk sample are parallel to the surface. The thin film samples have two peaks located at 32.8\(^\circ\) and 58.5\(^\circ\), which are due to the diffraction from (100) and (110) planes of individual columnar grains, consistent with my conclusion from the TEM images that the basal planes are vertically-aligned (see details in Fig. 4.5). In contrast to the bulk sample, (002) peak is not observed in the XRD spectrum of the thin film sample because the normal to the (002) planes is parallel to the substrate surface.

Fig. 4.2(a) and (b) present the Raman spectra of the bulk and thin film MoS\(_2\) samples. To probe the low frequency interlayer \(E^{2g}_{2g}\) phonon mode, I used three reflective volume Bragg grating filters (BragGrate\textsuperscript{TM} notch filters) in combination with a single-pass monochromator to access frequency shifts as small as \(~10\) cm\(^{-1}\) (as described in Chapter 2). The \(E_{1g}\) mode (286 cm\(^{-1}\)) is observed only in the thin film samples while the \(E^{2g}_{2g}\) mode (32 cm\(^{-1}\)) is only present in the bulk samples, as expected. According to the Raman selection rules, the \(E_{1g}\) mode is forbidden in backscattering experiment on the basal plane of bulk MoS\(_2\).[219,220] However, when the incident light scatters on the surface of edge-terminated MoS\(_2\), the corresponding scattering Raman tensor undergoes a rotation transformation, leading to a non-zero differential scattering cross-section and hence the \(E_{1g}\) mode can be observed. The observation of the \(E_{1g}\) mode in thin film samples therefore indicates that the basal planes of MoS\(_2\) are vertically aligned, consistent with the TEM and XRD data. The absence of the \(E^{2g}_{2g}\) mode (which is not forbidden by selection rules) in thin film samples is probably due to the randomly oriented columnar grains and stacking disorder in CVD-grown samples. In addition, although both \(A_{1g}\) at 383 cm\(^{-1}\) and \(E^{1g}_{2g}\) at 408 cm\(^{-1}\) modes are
present in bulk and thin film MoS$_2$, the peak intensity of the out-of-plane $A^1_{g}$ mode is similar to that of the in-plane $E^1_{2g}$ mode in the bulk sample and approximately 3 times that of the $E^1_{2g}$ mode in the thin film sample under the same measurement condition. Such preferred excitation of an out-of-plane mode is also consistent with the vertical-aligned crystal texture of the thin film sample considering the polarization dependence of the Raman scattering cross-section.[218]

![Figure 4.3. Initial discharge curves for thin film (black) and bulk (red) MoS$_2$ samples, compared with data by Wang et al. (dashed line) for thin film Li$_x$MoS$_2$.][221]

Electrochemical intercalation of lithium ions in both bulk and thin film MoS$_2$ was carried out using galvanostatic discharge process by Dr. Gaohua Zhu to study how lithiation affects the thermal conductivity differently in MoS$_2$ samples with different orientations. The intercalation process in the range of 1.1 to 3.0 V can be described as reaction (1)

$$\text{MoS}_2 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{MoS}_2 \quad (~1.1 \text{ V vs. Li/Li}^+, \ 0 \leq x \leq 1) \quad (1)$$

The discharge curves for thin film and bulk MoS$_2$ samples are shown in Fig. 4.3 Upon lithium ion intercalation, a well-defined plateau is observed at potentials between 1.1 and 1.2 V, as the
host lattice of MoS\(_2\) undergoes a phase transition from 2H to 1T phase.[222] The voltage dip at the initial stage of the discharge curve for bulk MoS\(_2\) sample is caused by the mass transport limitation of lithium ions. The voltage gradually recovers when the lithium ion transport is facilitated by the defects formed during intercalation. The voltage dip was not observed in the discharge process of thin film MoS\(_2\), which can be attributed to the high density of the edge sites in edge-terminated thin film samples.

By controlling the length of the time of charging, and hence the amount of charge relative to specific charge capacity for full intercalation of 167 mA h g\(^{-1}\), vertically-aligned Li\(_x\)MoS\(_2\) thin film (x = 33 at\%, 46 at\%, 68 at\% and 100 at\%) and lithiated bulk samples (20 at\%, 40 at\%, 60 at\%, 80 at\% and 100 at\%) with various lithiation degrees (x) were prepared. [222] The actual amount of Li in a fully lithiated bulk MoS\(_2\) sample is measured by inductively couple plasma mass spectroscopy (ICP-MS) measurements were performed on one. The actual x in other bulk Li\(_x\)MoS\(_2\) samples is then scaled by the same factor of 0.86.

4.3 Thermal Conductivity of Li\(_x\)MoS\(_2\)

MoS\(_2\) samples (schematics shown in Fig. 4.4(a)) were characterized using TDTR partly by Dr. Jun Liu to determine the change in thermal conductivity caused by lithium ion intercalation. The TDTR data of both thin film and bulk Li\(_x\)MoS\(_2\) samples are presented as a function of x in Fig. 4.4(b). The through-plane thermal conductivity of thin film Li\(_x\)MoS\(_2\) decreases monotonically from \(\approx3.4\) W m\(^{-1}\) K\(^{-1}\) (x = 0) to \(\approx1.7\) W m\(^{-1}\) K\(^{-1}\) (x = 1) with increasing lithium content. The through-plane thermal conductivity of bulk Li\(_x\)MoS\(_2\) decreases first from \(\approx2.0\) W m\(^{-1}\) K\(^{-1}\) (x = 0) to \(\approx0.4\) W m\(^{-1}\) K\(^{-1}\) (x = 0.34) and then increases to \(\approx1.6\) W m\(^{-1}\) K\(^{-1}\) (x = 0.86). The in-plane thermal
conductivity follows a similar trend, which decreases from \( \approx 105 \text{ W m}^{-1} \text{ K}^{-1} \) \((x = 0)\) to \( \approx 45 \text{ W m}^{-1} \text{ K}^{-1} \) \((x = 0.34)\) and then increases to \( \approx 80 \text{ W m}^{-1} \text{ K}^{-1} \) \((x = 0.86)\).

Figure 4.4. Thermal conductivity measurement of \( \text{Li}_x\text{MoS}_2 \) samples (a) Schematics of bulk and thin film \( \text{Li}_x\text{MoS}_2 \) samples for TDTR measurements. (b) Thermal conductivity of \( \text{Li}_x\text{MoS}_2 \) samples with different degrees of lithiation \(x\). Blue squares: through-plane thermal conductivity of thin film MoS\(_2\); black squares: through-plane thermal conductivity of bulk MoS\(_2\); black open squares: in-plane thermal conductivity of bulk MoS\(_2\). The minimum thermal conductivity for bulk
and thin film samples are plotted as black and blue dashed lines, respectively. The total uncertainties of the measured thermal conductivity are calculated by taking into account the systematic errors that propagate from uncertainties in the film thickness, laser spot size, and thermal properties of the transducer film and substrate.

To understand the drastic decrease of thermal conductivity, minimum thermal conductivity $\Lambda_{\text{min}}$ of thin film Li$_x$MoS$_2$, isotropic with randomly oriented columnar grains, is calculated a simplified model by Cahill and Pohl at the high-temperature limit using speed of sound from picosecond acoustic and surface acoustic method and atomic density from Rutherford backscattering spectrometry (RBS).[223] In the bulk Li$_x$MoS$_2$ samples, however, the strongly anisotropic structure introduces a significant phonon focusing effect,[224] which suppresses the through-plane average group velocity due to the relatively high in-plane group velocity. Thus the minimum thermal conductivity of bulk Li$_x$MoS$_2$ is calculated based on a modified minimum thermal conductivity model recently proposed by Zhen et al. (Equation S(7) in their supplementary material) to calculate the.[225] The calculated minimum thermal conductivity of bulk and thin film Li$_x$MoS$_2$ is plotted in Fig. 4.4(b) as dashed lines. Both measured through-plane thermal conductivity of bulk and thin film Li$_x$MoS$_2$ is higher than the predicted minimum thermal conductivity, which suggests a significant fraction of the phonons in these samples are propagating modes.

### 4.4 Effect of Li Intercalation on Interlayer Spacing and Elastic Constant

Lithium ion intercalation into van der Waals gap could change the thermal transport of MoS$_2$ due to several distinct mechanisms. First, the 2D layer spacing might change as a result of lithiation.[28,29,222] In addition, a recent theoretical work finds that intercalating lithium ions in
between the van der Waals layers enhances the binding energy through orbital hybridizations between cations (lithium ions) and anions (MoS$_2$).[226] Therefore, the interactions between the adjacent layers in Li$_x$MoS$_2$ could be different as a result of the layer spacing change and the electrostatic interaction between Li ions and S atoms. Second, the intercalated lithium donates electrons to MoS$_2$, which changes the oxidation states of Mo, and hence the electronic properties of MoS$_2$.[227,228] Last, as intercalation proceeds, MoS$_2$ goes through a phase transition from semiconductor 2H phase to metallic 1T phase.[222]

The increase of electrical conductivity caused by the phase transition from the semiconductor 2H to metallic 1T phase cannot explain the changes in the in-plane thermal conductivity of bulk Li$_x$MoS$_2$. A recent study shows the in-plane electrical conductivity of the metallic phase (1T) LiMoS$_2$ is $\approx 300$ S/cm, approximately 500 times that of the semiconducting phase (2H) MoS$_2$. The corresponding electronic contribution to the total thermal conductivity, predicted by the Wiedemann-Franz law, is only 0.2 W m$^{-1}$ K$^{-1}$ in LiMoS$_2$. Such a small increase cannot be the predominant mechanism to account for the in-plane thermal conductivity change in bulk Li$_x$MoS$_2$ from 45 to 80 W m$^{-1}$ K$^{-1}$ for $x=0.34$ to 0.86.
Figure 4.5. XRD characterization of Li$_x$MoS$_2$ samples (a) XRD spectra for MoS$_2$ thin film samples on sapphire substrate. The two diffraction peaks coincide with the standard X-ray diffraction powder patterns of MoS$_2$ (100) and (110). Therefore, the dominant lattice orientation in the MoS$_2$ thin film samples are (100) and (110). The diffraction peak at 32.8° and 58.5° corresponds to a lattice constant of 2.73 Å and 1.58 Å, respectively. (b) Lattice spacing $d$ between MoS$_2$ layers in bulk MoS$_2$ samples. The error bars are calculated by taking into account the experimental errors and the systematic errors that propagate from uncertainties in the fitting of XRD spectra. The inset plot is the change of MoS$_2$ (002) peak position with x in Li$_x$MoS$_2$. 
Figure 4.6 The effective elastic constant $C'_{33}$ (square) and $C'_{44}$ (diamond) of thin film Li$_x$MoS$_2$ with different degrees of lithiation $x$. $C'_{33}$ decreases from 147 GPa ($x = 0$) to 121 GPa ($x = 1$). $C'_{44}$ increases from 22 GPa ($x = 0$) to 32 GPa ($x = 0.34$) and then decreases to 18 GPa ($x = 1$). As comparison, the $C_{33}$ of bulk Li$_x$MoS$_2$ samples (circle) are also plotted. $C_{33}$ gradually changes from 52 GPa ($x = 0$) to 58 GPa ($x = 0.86$) with a transition point at $x \approx 0.34$. The error bars are calculated by taking into account the experimental errors and the systematic errors that propagate from uncertainties in the Al film thickness, Li$_x$MoS$_2$ film density, and the input elastic constants.

XRD spectra for bulk Li$_x$MoS$_2$ samples with different amount of lithium ion intercalation ($0 \leq x \leq 0.86$) are performed to determine the amount of layer spacing change due to lithium ion intercalation. Samples were placed inside an air-tight sample holder with a beryllium (Be) window in an argon-filled glovebox before they were transferred out for XRD characterization. Fig. 4.5(b) shows that the layer spacing is 6.16 Å and 6.19 Å for pristine MoS$_2$ and Li$_{0.86}$MoS$_2$, respectively, a 0.5% change in lattice constant within the measurement uncertainty ≈0.6%. The weak dependence of lattice constant on lithium content is consistent with the fact that the effective ionic radius of lithium ion[230] (76 pm) is slightly smaller than the octahedral site in the van der Waals
gap of in MoS$_2$. Assuming, an effective ionic radius of S$^{2-}$ as 1.84 Å, and close packing of S$^{2-}$ atoms, the radius of the octahedral site is 76 pm. My measurement on the layer spacing of Li$_{0.86}$MoS$_2$ agrees with a recent observation reporting on minimum interlayer distance in LiMoS$_2$, 12.32 Å.

Elastic properties of Li$_x$MoS$_2$ is measured using pump-probe techniques to help understand the thermal conductivity change in my samples. Polycrystalline MoS$_2$ thin films with vertically-aligned basal planes are transverse isotropic, which has five effective independent averaged elastic constants: $C'_{11}$, $C'_{12}$, $C'_{13}$, $C'_{33}$, and $C'_{44}$. Fig. 4.6 plots the effective $C'_{33}$ and $C'_{44}$ elastic constants of thin film Li$_x$MoS$_2$. The elastic constant $C'_{33}$ of Li$_x$MoS$_2$ thin film decreases from 147 GPa ($x = 0$) to 121 GPa ($x = 1$). Even though the density of Li$_x$MoS$_2$ thin films increases 11% from $x=0$ to $x=1$, the decrease of longitudinal speed of sound from 5720 m/s to 4930 m/s (measured by picosecond acoustics) dominates the decrease of $C'_{33}$. The elastic constant $C'_{44}$ increases from 22 GPa ($x=0$) to 32 GPa ($x=0.34$) and then decreases to 18 GPa ($x=1$). One possible explanation for the of elastic constant behavior in the thin film Li$_x$MoS$_2$ is the combined effect of increasing binding energy due to the intercalation of lithium ions and increasing structural and compositional disorder (e.g., point defects and mixture of phases).

The elastic constants of bulk Li$_x$MoS$_2$ samples $C_{33}$ are also plotted in Fig. 4.6. $C_{33}$ gradually changes from 52 GPa ($x = 0$) to 58 GPa ($x = 0.86$) with a transition point at $x \approx 0.34$, which suggests a phase transition in bulk Li$_x$MoS$_2$.

### 4.5 Effect of Li Intercalation on Thermal Conductivity

To study the effect of changes in lattice spacing and elastic constants on the thermal conductivity, I applied the Leibfried-Schlamann (LS) equation to predict the phonon thermal conductivity of Li$_x$MoS$_2$, which corresponds to the intrinsic thermal conductivity due to phonon-
phonon scattering. The LS equation takes the form of \( \Lambda = \frac{B'M\omega_D\delta}{T\gamma^2} \), where \( M \) is the mass of a unit cell, \( \delta^3 \) corresponds to atomic volume, \( T \) is temperature, \( \gamma \) is the Grüneisen parameter for the relevant direction of heat transfer, \( \omega_D \) is the Debye frequency for the relevant direction of heat transfer, and \( B \) is an amalgam of physical constants.[232] Using the Debye frequency defined as \( \omega_D = \nu_D k_D \), where \( k_D \) is the Debye cutoff vector, \( \nu_D \) is the speed of sound, I can express the thermal conductivity \( \Lambda = \frac{B'M}{T\gamma^2\delta^2} \left( \frac{C_{ij}}{\rho} \right)^{1.5} \), where \( B' \) is a constant, \( C_{ij} \) is the elastic constant, and \( \rho \) is the density. Considering a 4% increase in atomic mass, 11% increase in density, 18% decrease in the effective elastic constant \( C_{33}' \), 0.5% increase in lattice spacing for \( \text{Li}_x\text{MoS}_2 \) thin films from \( x=0 \) to 1, the LS equation predicts a 33% decrease in the through-plane thermal conductivity, if I assume that the change in Grüneisen parameter is negligible. Since TDTR measurement shows that through-plane thermal conductivity of thin films \( \text{Li}_x\text{MoS}_2 \) decreases continuously from \( \approx 3.4 \) to \( \approx 1.7 \) W m\(^{-1}\) K\(^{-1}\) from \( x=0 \) to 1, the softening of the lattice should be counted as one of the major contributors to the thermal conductivity reduction in \( \text{Li}_x\text{MoS}_2 \) thin films.

Similarly, for the bulk samples, if I consider the changes of elastic constants, lattice spacing, density, and atomic mass in a unit cell to be 11%, 0.5%, 3.3%, 3.8%, respectively from \( x = 0 \) to \( x = 0.86 \), the through-plane thermal conductivity is estimated to increase by \( \approx 14\% \). Under the same assumptions, the through-plane thermal conductivity of \( \text{Li}_x\text{MoS}_2 \) should increase \( \approx 5\% \) from \( x=0 \) to \( x=0.34 \). Such a small change and different trends indicate the lattice expansion and elastic constant change cannot explain the drastic thermal conductivity change in bulk \( \text{Li}_x\text{MoS}_2 \) samples.

I used Raman spectroscopy to further characterize lithiation-induced structural and compositional disorder of bulk \( \text{Li}_x\text{MoS}_2 \) to gain more insights about other phonon scattering
mechanisms that could lead to the thermal conductivity change. All bulk Li$_x$MoS$_2$ samples except pristine MoS$_2$ were loaded inside the glovebox into a home-made air-free sample holder sealed by O-ring and screw-on connectors and measured through the glass window of the holder. As shown in Fig. 4.2(c) and (d), the intensity of the low frequency peak at ~32 cm$^{-1}$ corresponding to the E$_{2g}^2$ shear mode in 2H-MoS$_2$ decreases as the degree of lithiation (x) increases. The decreasing peak intensity of E$_{2g}^2$ mode is attributed to the increasing amount of stacking disorder resulted from the lithium ion intercalation. In the 2H to 1T phase transition, the stacking of Mo atom planes change from ABA (two molecular layers per unit cell) to AA (one molecular plane per unit cell).[233,234]

As the atomic structure of the MoS$_2$ layer changes from prismatic aBa (2H) structure to octahedral aBc (1T) (upper letters correspond to Mo planes, lowercase letters correspond to the S planes),[235] the high frequency E$_{2g}^1$ and A$_{1g}$ modes redshift from 383 to 377 cm$^{-1}$ and 408 to 402 cm$^{-1}$ respectively, as the lithium content increases from x = 0 to x = 0.86. The observed redshift is mainly attributed to the intralayer shift of the S atom during the 2H to 1T phase change.[236]

Interestingly, I found that the A$_{1g}$ mode peak splits into two peaks at 402 and 408 cm$^{-1}$ while the E$_{2g}^2$ peak slightly broadens in the x = 0.34 sample suggesting the coexistence of 2H and 1T phases. The peak splitting was related to the Davydov pairs of the optical phonon branches due to the splitting of intralayer modes caused by the interlayer interaction when the lithium content is below x = 0.34.[234] I do not yet have a good understanding why the split of E$_{2g}^2$ peak is not clearly observed in x = 0.34 sample but it may be related to the intermediate atomic structure in the not-completed phase-change process. Both high and low frequency Raman spectra provide an evidence of the simultaneously increasing stacking disorder and mixture of phases during lithiation.

As a result of coexistence of two phases and increasing stacking disorder, phonon boundary scattering increases and thermal conductivity in both through-plane and in-plane directions
decrease until the largest degree of disorder is reached at $x \approx 0.34$. As intercalation proceeds, the bulk MoS$_2$ sample becomes increasingly dominated by the 1T phase ($0.34 < x < 0.86$) and the phonon boundary scattering become less important, and hence the thermal conductivity starts to increase again.

The most striking observation here is that the thermal anisotropy ratio of the bulk Li$_x$MoS$_2$ increases from 52 ($x = 0$) to 110 ($x = 0.34$) with increasing disorder. This trend of thermal anisotropy ratio change with respect to the structural defects or disorder is indeed counter-intuitive and beyond any previous works. For example, a recent study of graphene oxide films by Renteria et al. shows an increase of thermal anisotropy ratio attributed to decreasing disorder after annealing.[217] Luckyanova et al. found that the thermal anisotropy ratio decreases with interface atomic mixing in superlattices.[216] The thermal anisotropy ratio of a disordered WSe$_2$ crystal is similar well-ordered WSe$_2$ crystals at $\approx 30$.[237, 238] Measurements of lithiated MoS$_2$ bulk crystal demonstrate that lithiation-induced stacking disorder and phase transition can increase the thermal anisotropy ratio.

The original thermal conductivity measurement of bulk MoS$_2$ by Dr. Jun Liu published in Ref [52] did not consider the modulation frequency dependence in TDTR for this material. However, as noted by Jiang et al. the non-equilibrium between low and high frequency phonons may contribute extra interface thermal resistance and cause the cross-plane thermal conductivity obtained from TDTR to show frequency dependence, i.e. a failure of Fourier’s law.[239]

I measured the apparent thermal conductivity of bulk MoS$_2$, provide by Jiang et al. coated with Al sample (which could possibly be obtained from a different mine from the sample measured in Li intercalation experiments) using TDTR. The result shows frequency dependence with a large increase from 2.3 to 3.6 W m$^{-1}$ K$^{-1}$ as the modulation frequency decrease from 9.3 to 1.1 MHz.
Such a strong frequency dependence suggests a possible underestimation of the thermal conductivity in the cross-plane direction. The results for Li intercalated MoS$_2$ may be more complicated depending on how disorder introduced by intercalation change the spectral distribution of phonon thermal conductivity in the in-plane and cross-plane direction.[107] Presumably, as the stacking disorder and grain boundaries becomes more prominent, the scattering between non-equilibrium phonons of different frequency become less important and the measured cross-plane thermal conductivity of Li$_x$MoS$_2$ of large $x$ would be closer to intrinsic values. More systematic investigation of the intrinsic cross-plane thermal conductivity of MoS$_2$ and Li$_x$MoS$_2$ with a comparison of MoS$_2$ from different mines is necessary. However, the in-plane thermal conductivity doesn’t seem to show frequency dependence.[239] Thus the trend of the in-plane thermal conductivity as a function of Li content is believed to be reliable. If this is the case, the thermal anisotropy ratio at $x = 0$ would be even smaller and the effect of intercalation on the change on this ratio would be more significant.

Phonon-phonon and phonon-boundary scattering are the two possible major scattering mechanisms in the bulk Li$_x$MoS$_2$ samples. As discussed above, I estimated the change of the intrinsic lattice thermal conductivity that is limited by phonon-phonon interactions due to the changes in elastic constants and atomic densities. The predicted change in the intrinsic phonon-phonon scattering rates is small and I therefore exclude changes in phonon-phonon scattering as the dominant mechanism in lithiated bulk Li$_x$MoS$_2$. The combination of Raman spectroscopy data—and the pronounced change in the thermal conductivity of bulk samples—suggest that phonon scattering in the bulk Li$_x$MoS$_2$ is dominated by phonon-boundary scattering due to stacking disorder created by the phase transition.
In highly anisotropic layered materials, boundary-limited phonon mean-free-paths in the in-plane and through plane directions can differ by orders-of-magnitude due to the combination of phonon-focusing effects and divergent length scales of disorder in the in-plane versus through-plane directions. When boundary scattering dominates the phonon mean-free-paths, phonon focusing produces anisotropic phonon mean free path even in cubic crystals.[240] A recent modeling study[241] demonstrates that thin films of graphite can maintain their high in-plane thermal conductivity even for film thickness as small as 10 nm. In other words, in highly anisotropic crystals, boundary scattering along the \(c\)-axis has only a minimal effect on the \(ab\)-plane thermal conductivity. Further experimental evidence of this effect comes from a recent experimental study[242] of CVD-grown graphite thin films where the phonon mean-free-paths are different by more than an order of magnitude: the in-plane phonon mean free path is \(\approx300\) nm and the through-plane mean free path is \(<20\) nm.

Although a sophisticated phonon transport modeling is needed to rigorously analyze how different phonon branches are affected by boundaries and other forms of disorder, it’s possible to estimate how the boundary-limited phonon mean-free-paths in the \(c\)-axis \(L_c\) and in the \(ab\)-plane \(L_{ab}\) change with \(x\) by comparing my measured thermal conductivities with previous studies. Comparing the measured in-plane thermal conductivities of bulk \(\text{Li}_x\text{MoS}_2\) to the thermal conductivity of a single layer MoS\(_2\) with a varied characteristic length of phonon boundary scattering, predicted by a first-principle based Boltzmann transport equation (BTE) calculation suggests \(L_{ab}\) decreases from \(>1\) \(\mu\)m to \(\approx200\) nm for \(x=0\) to 0.34.[243] Similarly, the comparison between measured through-plane thermal conductivity of bulk \(\text{Li}_x\text{MoS}_2\) and that predicted by first-principle based BTE calculations suggests \(L_c \approx 200\) nm at \(x=0\).[244] The lowest through-plane thermal conductivity in bulk samples is comparable to that of turbostratic nano-crystalline MoS\(_2\)
thin films deposited by magnetron sputtering.[232] In the turbostratic thin film samples, the length of coherent stacking is unknown but should be less than the grain size $\approx 5$ nm.[245] The similar stacking disorder in bulk samples $\text{Li}_x\text{MoS}_2$ suggests the $L_c \approx 5$ nm at $x=0.34$. A plausible explanation for this pronounced phonon mean-free-path difference is that the lithium ions are much easier to diffuse along the in-plane direction compared with the through-plane direction. As a result, the density of disorder caused by lithium ion intercalation is less pronounced along the in-plane direction. Both $L_c$ and $L_{ab}$ reach their minimum values with the maximum mixing of the two phases at $x=0.34$.

Lastly, it’s noticed that the through-plane thermal conductivity of thin film $\text{Li}_x\text{MoS}_2$ sample is much lower than the in-plane thermal conductivity of the bulk $\text{Li}_x\text{MoS}_2$ sample, and the trends of change in through-plane thermal conductivity are different for bulk and thin film $\text{Li}_x\text{MoS}_2$ samples. Compared to bulk MoS$_2$, the basal planes in $\text{Li}_x\text{MoS}_2$ thin films contain high density of defects, especially point defects and oxygen impurities introduced during the chemical vapor growth process of the thin sample. Defects can significantly reduce the thermal conductivity of 2D materials by enhancing the phonon scattering as pointed out by a few simulations, resulting in much lower through-plane thermal conductivity.[19,246,247] The different trend of thermal conductivity change in thin $\text{Li}_x\text{MoS}_2$ can be explained by the high level of defects. Although the semiconductor 2H to metallic 1T phase transition also occurs in the thin film sample, unlike the bulk sample, the thermal conductivity of defective thin film $\text{Li}_x\text{MoS}_2$ is more sensitive to the lattice softening rather than stacking disorder.[247] Based on elastic constants results and estimation by LS equation, I attribute the decreasing trend of thermal conductivity in the $\text{Li}_x\text{MoS}_2$ thin film with increasing lithium content $x$ to the softening of the lattice with increasing lithium content and the increased phonon boundary scattering at the grain or phase boundaries.[248]
4.6 Conclusion

In summary, the anisotropic thermal transport in bulk crystal and CVD grown thin film MoS$_2$ samples with different amounts of lithium ion intercalation is measured by TDTR. Intercalation impacts thermal transport in bulk and thin film samples differently, depending on the crystalline quality of the 2D structure. While the thermal conductivity in the bulk sample can be effectively modified by introducing stacking disorder and mixture of phases, which significantly increases phonon-boundary scattering, the thermal conductivity change in the defective thin film sample is strongly affected by the lattice softening. Moreover, it’s found that lithiation tends to reduce the phonon mean free path more along the through-plane direction in Li$_x$MoS$_2$, rather than the in-plane direction, until the largest degree of disorder is reached at $x$≈0.34, leading to a significant increase in the thermal anisotropy ratio. Through lithium intercalation, I present an example for modifying the thermal conductivity and thermal anisotropy ratio over a wide range in MoS$_2$. This work provides insight on the impact of structural and compositional changes (e.g., disorder, layer spacing, and interfaces) on 2D materials applications, such as nanoelectronics, where thermal management is crucial.
CHAPTER 5

PHONON AND ELECTRON CONTRIBUTIONS TO THE THERMAL CONDUCTIVITY OF VNₓ EPITAXIAL LAYERS

Parts of this chapter were published in “Phonon and electron contributions to the thermal conductivity of VNₓ epitaxial layers,” Qiye Zheng, Antonio B. Mei, Mohit Tuteja, Davide G. Sangiovanni, Lars Hultman, Ivan Petrov, J. E. Greene, and David G. Cahill.[249] Phys. Rev. Materials 1: 065002

5.1 Introduction

As discussed in Chapter 1, metallic transition-metal (TM) nitrides and carbides provide a contrast regime to common metals for studying lattice thermal conductivities because their Debye temperatures are comparatively high and therefore the anharmonic phonon scattering rates are low, and electron-phonon coupling is comparatively strong.[41] The spectral integral of the Eliashberg function \( \alpha^2 F(\omega) \) yields a measure of the electron-phonon coupling strength:

\[
\lambda = 2 \int \alpha^2 F(\omega) \omega^{-1} d\omega .
\]

For TM nitrides and carbides, \( \lambda \) is between 0.6 and 0.9, large values compared to common metals such as Al (\( \lambda = 0.44 \)), Cu (0.13), Au (0.17), and Ti (0.38).[250-253] The primary goal of this work is to determine the lattice contribution to the thermal conductivity of VN through studies of the thermal conductivity of stoichiometric VN and VNₓ with varying concentrations of nitrogen vacancies.

In Fig. 5.1(a), I compare representative data for the total thermal conductivities of elemental metals to selected data for TM nitrides and carbides. The temperature dependence of the thermal conductivity of TM nitrides and carbides has been discussed previously.[262,266] Fig. 5.1(b) summarizes the electrical resistivity of the same set of elemental metals and TM nitrides and carbides. In most cases, at temperatures greater than the Debye temperature $\Theta_D$, the resistivity can be approximated as $\rho \approx \rho_0 + B + AT$, wherein I have distinguished between the residual resistivity $\rho_0$ created by elastic scattering by defects and a phenomenological constant $B$ that describes the shift in the extrapolated intercept of $\rho$ at $T = 0$ K relative to $\rho_0$. 
The Wiedemann-Franz (W-F) law predicts that the electronic thermal conductivity can be expressed as

\[ \Lambda_{el} \approx \frac{L(T)T}{\rho} = \frac{L(T)T}{\rho_0 + B + AT}. \]

(5.1)

\( L(T) \) is the temperature-dependent Lorenz number. [267,268] At low \((T \ll \Theta_D)\) and high temperatures \((T \geq \Theta_D)\), \( L(T) \) approaches the Sommerfeld value of \( L_0 = 2.44 \times 10^{-8} \, \Omega \, \text{W} \, \text{K}^{-2} \). In pure metallic elements at \( T > \Theta_D / 3 \), the resistivity typically scales as \( \rho \approx AT \) and therefore \( \Lambda_{el} \approx L_0 / A \) is nearly constant.[4] However, in TM nitrides and carbides, \( \rho_0 + B \) is often large due to the high concentrations of point defects (e.g., oxygen and carbon impurities and nitrogen vacancies).[39,258] Thus, the W-F law predicts that \( \Lambda_{el} \) should increase with increasing \( T \) at elevated temperatures (Fig. 5.1(a)).

Due primarily to strong covalent bonds,[269] VN exhibits high melting temperature (2050 \(^{\circ}\)C), hardness (15.9 GPa), electrical conductivity (33 \( \mu \Omega\)-cm), and chemical stability.[269-271] As a consequence, VN films have been employed to enhance the properties of cutting and grinding tools, hard electrical contacts, cylinder linings, diffusion barriers, and rechargeable microbatteries and supercapacitors.[266,272-276] A better knowledge of VN thermal and electrical transport properties could improve materials design for new applications.

This work may also provide insights into the potential of TM nitride metal/semiconductor superlattices as high temperature materials for thermoelectric energy conversion. In my early work on (Zr,W)N/ScN superlattices, I attributed the minimum in the cross-plane thermal conductivity as a function of superlattice period to the intermixing of interfaces while a more recent work on TiN/Al\(_{0.72}\)Sc\(_{0.28}\)N attributed such a minimum to coherent phonon effects.[277,278] A better
understanding of the lattice thermal conductivity in metallic TM nitrides could provide an important parameter for determining the efficiency of thermoelectric materials.

5.2 Epitaxial Growth and Structure Characterizations

VN_x/MgO(001) layers are grown in a load-locked ultra-high-vacuum magnetically-unbalanced dc magnetron sputter deposition system from a 7.6-cm diameter, 99.95%-pure, V disk target in 20-mTorr N_2 atmospheres as described in Ref [279]. Film N/V ratios, determined by Rutherford backscattering spectrometry, are varied from 1.00±0.05 to 0.76±0.05 by increasing the growth temperature from 430 to 740 °C. The combination of x-ray diffraction ω-2θ and ϕ scans with selected-area electron diffraction and high-resolution cross-sectional transmission electron microscopy analyses demonstrate that the VN_x films are NaCl-structure epitaxial single-crystals which grow cube-on-cube (001)_VN_x||(001)_MgO and [100]VN_x||(100)_MgO with respect to the substrate.[280] Fig. 5.2(a) is a representative cross-sectional scanning transmission electron micrograph acquired near a VN/MgO(001) film-substrate interface along the [010] zone axis. The image contrast scales primarily with the square of the average atomic number down the electron column; as a result, the film, which contains V (Z=23), appears lighter than the substrate for which the element with the highest Z value is Mg (Z=12). The single-crystalline nature of the film is demonstrated by well-ordered VN lattice fringes, observed to be registered cube-on-cube with respect to MgO. Spectral density plots produced from intensity line profiles extracted parallel to the interface in the film and substrate regions (as shown Fig. 5.2(a)) are plotted in Fig. 5.2(b). The curves are reminiscent of diffraction patterns calculated using the kinematical approximation, with peaks at 4.14 and 4.21 Å corresponding to the in-plane lattice parameters of VN and MgO. That the peaks occur at different distances indicates the film is not fully strained, consistent with high-
resolution reciprocal lattice mapping analyses, see below.

**Figure 5.2.** (a) Cross-sectional scanning transmission electron micrograph acquired near the 192-nm-thick VN/MgO(001) film-substrate interface along the [010] zone axis. (b) Spectral density plots produced from intensity line profiles extracted parallel to the interface in the film and substrate regions along the blue (VN) and orange (MgO) lines respectively. The abscissa in (b) is doubled to account for the two atomic columns per conventional NaCl-structure unit cells along the [010] projection. (c) and (d) High-resolution reciprocal-lattice maps, acquired with CuKα radiation, about the symmetric 002 and asymmetric 113 reflection from stoichiometric VN/MgO(001) in (a).
Out-of-plane \((a_\perp)\) and in-plane \((a_\parallel)\) lattice parameters of the epitaxial VN\(_x\)(001) films are obtained from high-resolution reciprocal lattice maps (HR-RLM) around symmetric 002 and asymmetric 113 reflections. Fig. 5.2 (c) and (d) shows representative HR-RLMs, acquired using Cu \(K\alpha\) radiation, around the 002 and 113 reflections of the stoichiometric VN/MgO(001) plotted as logarithmic isointensity contours as a function of in-plane \(Q_x\) and out-of-plane \(Q_z\) reciprocal-lattice vectors. The relaxed lattice parameters \(a_0\) of VN\(_x\) epitaxial layers are determined from \(a_\perp\) and \(a_\parallel\) through the relationship \(a_0 = a_\perp \left(1 - \frac{2\nu(a_\perp - a_\parallel)}{a_\parallel(1 + \nu)}\right)\) in which the Poisson ratio, \(\nu = 0.23\), is derived in our previous work on epitaxial VN/MgO(001) [280]. \(a_0\) decreases from 4.14 Å at \(x = 1.00\) to 4.09 Å at \(x = 0.76\) (see Table I), in good agreement with previous studies of bulk and sputter-deposited VN\(_x\) [280-283]. VN(001) in-plane \(\xi_\parallel\) and out-of-plane \(\xi_\perp\) x-ray coherence lengths, which serve as measures of crystalline quality, are obtained from the width of symmetric 002 reflections parallel \(Q_x\) and perpendicular \(Q_z\) to the diffraction vector \(\mathbf{k}\) through the relationships: \(\xi_\parallel = 2\pi / |\Delta Q_x|\) and \(\xi_\perp = 2\pi / |\Delta Q_z|\). From the results shown in Fig. 5.2, \(\xi_\parallel = 23\) nm and \(\xi_\perp = 44\) nm. \(\xi_\parallel, \xi_\perp\) values depend, in addition to structural quality,[265] on film thickness.[265,284] Stoichiometric epitaxial Group-IVB TM nitrides TiN/MgO(001), ZrN/MgO(001), and HfN/MgO(001), grown under conditions similar to those of the present Group-VB VN(001) layers, exhibit \(\xi_\parallel\) values of 86,[285,286] 18,[286] and 22 nm,[287] respectively.

The thicknesses of the VN\(_x\) epitaxial layers are determined using RBS atomic areal density and HR-RLM lattice parameters to within \(\pm 5\%\). For the five samples measured, the thickness varies from 160 to 229 nm (see Table I). The thickness of the stoichiometric VN sample is 192
nm, which is close to the value of 194 nm obtained using picosecond acoustics with the previously-reported longitudinal sound velocity \( v_{001} = 9.8 \text{ km s}^{-1} \).[280] The complex index of refraction of VN is \( n \approx 1.49+3.44i \) at 785 nm as measured by ellipsometry, corresponding to an optical absorption depth of \( \alpha^{-1} = \frac{\lambda}{4\pi k} = 18 \text{ nm} \), consistent with recent results on the optical properties of VN/MgO(001).[279]

**Table 5.1.** Composition \( x \), growth temperature \( T \), areal density, relaxed lattice constant \( a_0 \), film thickness \( h \), mass density \( \rho \), and longitudinal sound velocity \( v_{001} \) of epitaxial VN\(_x\) samples.

<table>
<thead>
<tr>
<th>( x )</th>
<th>( T ) (°C)</th>
<th>V (( 10^{18} \text{ cm}^{-2} ))</th>
<th>N (( 10^{18} \text{ cm}^{-2} ))</th>
<th>( a_0 ) (Å)</th>
<th>( h ) (nm)</th>
<th>( \rho ) (g cm(^{-3}))</th>
<th>( v_{001} ) (km s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>430</td>
<td>1.08</td>
<td>1.08</td>
<td>4.14</td>
<td>192</td>
<td>6.06</td>
<td>9.8</td>
</tr>
<tr>
<td>0.93</td>
<td>509</td>
<td>1.15</td>
<td>1.07</td>
<td>4.13</td>
<td>195</td>
<td>6.04</td>
<td>9.3</td>
</tr>
<tr>
<td>0.88</td>
<td>589</td>
<td>1.28</td>
<td>1.12</td>
<td>4.11</td>
<td>209</td>
<td>6.04</td>
<td>8.0</td>
</tr>
<tr>
<td>0.84</td>
<td>636</td>
<td>1.44</td>
<td>1.21</td>
<td>4.10</td>
<td>229</td>
<td>6.03</td>
<td>7.3</td>
</tr>
<tr>
<td>0.76</td>
<td>740</td>
<td>1.06</td>
<td>0.81</td>
<td>4.09</td>
<td>160</td>
<td>5.98</td>
<td>7.3</td>
</tr>
</tbody>
</table>

### 5.3 Transport Properties Measurement of VN\(_x\)/MgO

A modified time-domain thermoreflectance (TDTR) method, which required no additional transducer layer to be deposited on the sample surface, was used to measure the thermal conductivity of epitaxial VN\(_x\) thin films.[94,95] The pump beam is modulated at a frequency of 4.1 MHz by an electro-optical modulator. This frequency is lower than the typical 10 MHz modulation used in my previous TDTR studies and was chosen to enhance the sensitivity to VN thermal conductivity (see Fig. 3). The pump and probe beams are focused on the sample through a 5× objective lens to a 1/e\(^2\) intensity radius of \( \approx 10.7 \mu\text{m} \). The total beam power of 15 mW creates
a steady-state temperature rise of ≈4 K at room temperature and 8 K at 1000 K. (See section 2.1 for other details.) Based on the measured film thickness and the picosecond acoustic signal from TDTR,[280], I also derived the longitudinal speed of sound \( v_{001} \) in the five VN\(_x\) samples to a precision of ±0.4 km s\(^{-1}\) (Table 5.1).

In a conventional TDTR measurement, the sample is coated with a 60-90 nm metal transducer which provides the thermoreflectance signal. At the beginning of these studies, I tried using Pt as the transducer layer. However, a dramatic change in the interface thermal conductance between Pt and VN\(_x\) was observed at \( T > 700 \) K. I tentatively attribute this observation to reduction of the native oxide at the Pt/VN\(_x\) interface by the VN\(_x\) layer. This uncontrolled change in interface conductance often led to inconsistent measurements. Therefore, I instead studied bare VN\(_x\) films without an additional transducer layer. The room-temperature thermoreflectance \( \frac{dR}{dT} \) of VN\(_x\) is 2.2×10\(^{-5}\) K\(^{-1}\) at 785 nm, significantly smaller than for Al or TiN, but still sufficient for TDTR measurements.[288,289]

Temperature-dependent VN\(_x\) TDTR measurements from 300-1000 K are performed by mounting the VN\(_x\)/MgO(001) specimen on a heater stage in a vacuum chamber and monitoring the sample temperature with a Pt resistance thermometer. To minimize sample oxidation, the chamber was pumped with a turbo-molecular pump. The electrical resistivity \( \rho \) of the VN\(_x\) films was measured from 300 to 500 K by the Van der Pauw method using a heating stage in ambient air. To confirm the reliability of the data measured in ambient, I also performed Van der Pauw method resistivity measurements of the VN\(_{0.84}\) sample from 300 to 920 K using a high vacuum furnace in a vacuum better than 5 × 10\(^{-7}\) Torr. The resistivity \( \rho \) vs. temperature from 300 to 500 K obtained from the two facilities agrees to within 1%. The lateral dimensions of the other samples are too small to be measured with the high vacuum system.
Figure 5.3. Example TDTR data: \(-V_{in}/V_{out}\) vs. delay time (open circles) for the 192-nm-thick epitaxial stoichiometric VN/MgO(001) film measured at 300 K and 1000 K. Data (black open circles) are compared to the predictions of the thermal transport model described in the text (red solid lines) with the optical absorption length and the thermal conductivity of the VN layer as free parameters.

Representative TDTR data and model fitting for a 192-nm-thick stoichiometric VN sample measured at 300 K and 1000 K are shown in Fig. 5.3. The thermal transport model used for fitting includes parameters for the thermal conductivity, heat capacity, and thickness of the VN\(_x\) layers, and the MgO substrate, the thermal conductance of the VN\(_x\)/MgO interface and the thicknesses of the optical absorption layer.[94] In TDTR data analysis, the thermal conductivity of the VN\(_x\) layer and thickness of the optical absorption layer are used as free parameters for fitting. The thickness of the VN\(_x\) layer is measured by RBS. The MgO substrate thickness of 0.5 mm is essentially semi-infinite for my TDTR measurements at 4.1 MHz modulation frequency.[108] The VN\(_x\)/MgO interface thermal conductance is measured separately on a sample specifically designed to
optimize that measurement (see below). The thermal conductivity and heat capacity of the single-crystal MgO(001) substrate and the temperature and composition-dependent heat capacity of VN$_x$ are taken from references. [110,290] The reference volumetric heat capacity of stoichiometric VN at its Debye temperature of 800 K (see below) is 4.72 J cm$^{-3}$ K$^{-1}$,[290] in good agreement with the Dulong Petit value of $3Nk_B \approx 4.67$ J cm$^{-3}$ K$^{-1}$ calculated using the measured lattice constants at room temperature and the thermal expansion coefficient from the literature.[290,291] At 300 K, the VN volumetric heat capacity from the reference is 3.58 J cm$^{-3}$ K$^{-1}$. I also measured the thermal conductivity of the same MgO substrate used for VN$_x$ growth by conventional TDTR with an 80-nm Al coating. The measured MgO thermal conductivity results from 300 to 600 K agree with reference data to within 5%.[110]

Figure 5.4. Calculated sensitivity parameters in TDTR measurements as a function of delay time at (a) 300 K and (b) 1000 K for important parameters used in modeling 192-nm-thick VN/MgO: VN thermal conductivity and heat capacity ($\Lambda_{VN}$ and $C_{VN}$), absorption layer thickness and VN thickness ($h_{abs}$ and $h_{VN}$), VN/MgO interface thermal conductance (G), and MgO substrate thermal conductivity and heat capacity ($\Lambda_{MgO}$ and $C_{MgO}$).
Figs. 5.4(a) and (b) show the sensitivity (See section 2.1 for definition) of the fits in Fig. 5.3 to changes in the various parameters in the thermal-transport model for VN$_x$/MgO. TDTR measurements of thick VN$_x$ films have moderate sensitivity to $\Lambda_{VN}$ (0.25-0.4) because the thermal resistance for heat transport through the thickness of the VN$_x$ film is larger than the thermal resistance of the VN$_x$/MgO interface; i.e., $h/\Lambda_{VN} > G^{-1}$. The measurement sensitivity to interfacial thermal conductance G is small ($|S_G| < 0.05$) so long as G is large ($> 0.7$ GW m$^{-2}$ K$^{-1}$). This limits the error propagation from my estimate for G: a 20% error in G propagates into only an ≈3% error in VN$_x$ thermal conductivity. With increasing temperature from 300 to 1000 K, the thermal diffusivity of the VN layer, $D = \frac{\Lambda_{VN}}{C_{VN}}$, increases by ≈20%, while the effusivity of MgO substrate $\varepsilon = \sqrt{\Lambda C}$ decreases by ≈30%. These changes in thermal properties produce pronounced variations with temperature in the TDTR signal sensitivity to the VN thickness.

Since the thickness of the absorption layer $h_{abs}$ and the thermal conductivity of VN$_x$, the two free parameters in the model fitting, have maxima in their sensitivity at short (< 300 ps) and long (> 1 ns) time delays, respectively, I could obtain their values relatively independently. The TDTR measurement of the absorption layer thickness is 18±3 nm for all VN$_x$ samples at all temperatures, e.g. $h_{abs}$ obtained in Fig. 5.3 is 18 nm at 300 K and 20 nm at 1000 K. This result agrees with the room temperature ellipsometry measurement of the imaginary part of the refractive index for VN$_x$ of varied compositions [279]. To independently measure the thermal conductance of the VN$_x$/MgO interface (G), I prepared a thinner 29-nm-thick VN/MgO(001) sample that enables higher sensitivity to G. I coated this sample with an 80-nm-thick layer of Al by magnetron sputtering to avoid artifacts that are sometimes encountered in TDTR studies of semi-transparent layers. By annealing the Al/VN/MgO sample overnight at 750 K in air, I obtained a metallic contact between
Al/VN, presumably due to the reduction of the native oxide at the Al and VN interface by the VN layer; *i.e.*, I hypothesize that oxygen at the Al/VN interfaces diffuses into the bulk of the VN film during annealing. The Al/VN and VN/MgO interface thermal conductances are measured to be $\approx 1.1 \pm 0.3 \text{ GW m}^{-2} \text{K}^{-1}$ and $\approx 0.8 \pm 0.2 \text{ GW m}^{-2} \text{K}^{-1}$, respectively. The thermal conductances of the two interfaces are both weakly temperature dependent from 300 to 700 K. The value of $G_{\text{VN/MgO}}$ is close to that of epitaxial TiN/MgO(001), $G \approx 0.7 \text{ GW m}^{-2} \text{K}^{-1}$ at room temperature.[289] Although the diffusion of surface oxide changes the interface thermal conductance, I do not expect the oxygen diffusion into bulk VN$_x$ to significantly affect the thermal and electrical conductivity measurements using bare VN$_x$. Variations in the thermal conductivity and absorption layer thickness of VN$_x$ samples in three repeated TDTR measurements are less than 4%, smaller than the measurement uncertainty. The electrical resistivity of VN$_{0.84}$ measured in a high-vacuum system after the TDTR measurement to 1000 K also shows good agreement with the resistivity results between 300 and 500 K obtained earlier (see Fig. 5.6(a)). A vanadium oxide layer of 1 to 3 nm corresponds to an oxygen areal density of $\approx 10^{16} \text{ cm}^{-2}$.[292] Even if all the oxygen from the surface diffuses into the bulk, it will result in $\approx 1 \text{ at\%}$ concentration of extra oxygen in the VN$_x$ layer. Assuming the effect of the 1 at\% oxygen is similar to 1 at\% N vacancies in VN$_x$, the change in electrical and thermal conductivity should be below experimental uncertainty, consistent with what I observed.
5.4 **Electron and Phonon Contribution to Thermal Conductivity of VN\(_x\)**

I plot data for the thermal conductivity of VN\(_x\) as a function of temperature and composition \(x\) in Fig. 5.5. The thermal conductivities increase monotonically over the temperature range \(300 < T < 1000\) K and decrease with increasing N vacancy concentration. The temperature dependence of the thermal conductivity becomes slightly stronger with decreasing \(x\). Over this temperature range, \(\Lambda\) increases by a factor of 2 for \(x = 0.76\), and increases by a factor of 1.7 for \(x = 1.00\).
Figure 5.6. (a) Electrical resistivity of VN$_x$/MgO(001) layers as a function of temperature measured in ambient air (open symbols) and high vacuum (blue line). Previously published data for a stoichiometric epitaxial VN/MgO(011) film deposited by the same method (solid line) together with a linear extrapolation of this data (dashed line) are included for comparison.[265] The blue line is the result for VN$_{0.84}$ measured with a different four-point probe system in a high-vacuum furnace as described in the text. (b-f) The same thermal conductivity of VN$_x$ films as in Fig. 5.5 (filled black symbols) and their electronic thermal conductivity calculated from corresponding electrical resistivity by the W-F law with a constant Lorenz number $L = L_0$ (black open symbols = $\Lambda_{el}$) and $L = L(T)$ (red open symbols = $\Lambda_{el}^c$ from Eq. (5)) [293] as a function of temperature from 300 to 1000 K. The black and red dashed lines are $\Lambda_{el}$ and $\Lambda_{el}^c$ calculated via the W-F law with $L = L_0$ and $L = L(T)$ obtained from a linear extrapolation of the electrical resistivity data (open symbols) from 300 to 500 K. $\Lambda_{el}$ calculated from $\rho(T)$ with the same 300 K resistivity as the stoichiometric VN sample and the TCR for epitaxial VN at 250-300 K in previous work
**Figure 5.6.** (cont.) [265] is also included in (b) (blue dashed line). The blue solid line in (e) shows the converted $\Lambda_d$ values for VN$_{0.84}$ from the direct high vacuum measurement result in (a) (blue line) from 300 to 920 K.

In Fig. 5.6(a), I plot my measurements of the electrical resistivity $\rho$ of VN$_x$ as a function of temperature. The VN$_x$(001) room-temperature resistivity, $\rho_{300K}$, increases from 42 to 73 $\mu\Omega$-cm as $x$ decreases from 1.00 to 0.76. The data for stoichiometric VN(001) are larger than the reported $\rho_{300K}$ value of 33 $\mu\Omega$-cm for VN/MgO(011).[265] This larger resistivity suggests that the VN(001) sample may be slightly off-stoichiometry or contaminated by a small amount of carbon or oxygen that is not detectable in the RBS measurements. The electrical resistivity of VN$_{0.84}$ measured in a high-vacuum furnace shows a linear behavior up to 920 K, consistent with the measurement from 300 to 500 K, which justifies the linear extrapolation of the data of lower temperature measurements. Such behavior is different from the temperature-dependent resistivity in a previous report on VN$_{0.92}$ powder with 8 at% oxygen which displayed an irreproducible anomaly at ~720 K due to the electrically active oxygen.[294]

The resistivity $\rho$ increases with temperature due to the increasing strength of electron-phonon scattering. The temperature coefficient of resistivity (TCR) over this temperature range, defined as $(\rho_{300K} - \rho_{300K}) / \Delta T$, increases from $3.6 \times 10^{-8}$ $\Omega$ cm K$^{-1}$ to $6.9 \times 10^{-8}$ $\Omega$ cm K$^{-1}$ as $x$ increases from 0.76 to 1.00.

I calculated the Debye temperature, $\Theta_D$, using Houston’s method [295] and the elastic constants measured in my previous work on stoichiometric VN.[280] $\Theta_D \approx 800$ K. The longitudinal elastic constant decreases with decreasing $x$ (see Table 5.1). If I assume that all 3
independent elastic constants of VN$_x$ have the same dependence on $x$, then $700 < \Theta_B < 800$ K for $0.76 < x < 1.0$. The scaled temperatures in my work are therefore $0.4 < \frac{T}{\Theta_B} < 1.4$.

5.5 Separation of phonon and electron contribution to thermal conductivity

To understand the temperature-dependent behavior of $\Lambda$, I first apply the W-F law with a constant Lorenz number

$$\Lambda_{el}(T) \approx \frac{L_0 T}{\rho} = \frac{L_0 T}{(\rho_0 + AT)},$$

(5.2)
in which $L_0$ is the Sommerfeld value of Lorenz number $L_0 = 2.44 \times 10^{-8}$ $\Omega$ $W$ $K^{-2}$. $\Lambda_{el}(T)$ results from Eq. (5.2) for each VN$_x$ sample are compared to the total thermal conductivities measured by TDTR in Figs. 5.6(b)-(f). I conclude that the thermal conductivity of VN$_x$ between 300 to 1000 K is predominantly electronic in origin.

An empirical relationship between the electrical resistivity $\rho$ and thermal conductivity $\Lambda$ of metal alloys was suggested by Smith and Palmer and is often used to predict the thermal conductivity of alloys from measurements of the electrical resistivity [296]

$$\Lambda = \frac{CL_0 T}{\rho} + \Lambda_L,$$

(5.3)
in which $CL_0$ is the effective Lorenz number and $\Lambda_L$ is the lattice thermal conductivity; $C$ and $\Lambda_L$ are free parameters that are adjusted to fit the data. The Smith-Palmer equation is often a good description of the thermal conductivity of alloys, although significant deviations were observed by us in some Ni solid solutions.[160] Furthermore, application of the Smith-Palmer equation assumes that the Lorenz number does not depend strongly on temperature or alloy composition.
and that the lattice thermal conductivity does not depend on composition [112]. Nevertheless, I expect that the Smith-Palmer plot shown in Fig 5.7 provides a useful first estimate of the Lorenz number and lattice thermal conductivity. The linear fit of Fig. 6 gives $C = 0.90$ and $\Lambda_L = 5 \text{ W m}^{-1} \text{ K}^{-1}$.

![Figure 5.7. Smith-Palmer plot, see Eq. (2), for VN$_x$ from 300 to 500 K.](image)

At the next level of sophistication, I consider the temperature dependence of the Lorenz number $L$. With the assumptions of spherical Fermi surfaces, equilibrium phonon distributions, a Debye phonon spectrum, and the predominance of normal processes for electron-phonon scattering,[4,297] the theoretical expression for the Lorenz ratio, $L_{th}(T)/L_0$ as a function of temperature is [36,298]
Here, \( k_F \) is the Fermi wave vector, \( \Theta_D \) and \( q_D \) are the Debye temperature and Debye wave vector, respectively. The Debye integrals \( J_n \) are defined as

\[
J_n \left( \frac{\Theta_D}{T} \right) = \int_0^{\Theta_D/T} \frac{x^n e^x}{(e^x - 1)^2} dx .
\]  

(5.5)

Eq. (3) has been used to understand the electronic thermal transport in metals and alloys.[37,297] The second term in the denominator involving \( k_F / q_D \) is due to electron-phonon inelastic small-angle scattering (vertical processes). The third term is a correction that accounts for situations where large-angle scattering can reverse the electron direction without restoring the distribution back to equilibrium.[297] Electron-impurity scattering is included as \( \rho_{imp} / A \) in the equation.

In Fig. 5.8, I plot the Lorenz ratio as a function of reduced temperature as predicted by Eq. (3) and give comparisons to experimental results for several metals. The similarity of the Lorenz ratios for Cu, Ta, Nb, and ThN is striking [37,293,299]. Here, the red line shows \( L_{th}(T) / L_0 \) for an ideal free-electron-like monovalent metal where \( k_F / q_D = 2^{-1/3} \). The drop in \( L_{th}(T) \) when the temperature is decreased below \( \Theta_D \) is caused by the dominance of inelastic vertical scattering of electrons by phonons. At high temperature, the greater probability of large-angle quasi-elastic scattering between electrons and high energy phonons reduces the deviation between \( L(T) \) and \( L_0 \). A higher level of impurity (large \( \rho_{imp} / A \)) results in a stronger elastic scattering of electron,
reducing the deviation of $L_{th}(T)$ from the Sommerfeld value. Impurity scattering dominates at low temperature when electron-phonon scattering is weak.

![Graph showing temperature variation of the Lorenz function normalized to the Sommerfeld value from experiments and theory as a function of reduced temperature for Cu, Ta, Nb, and ThN.](image)

**Figure 5.8.** Temperature variation of the Lorenz function normalized to the Sommerfeld value from experiments and theory as a function of reduced temperature for Cu,[37,299] Ta,[299] Nb,[299] and ThN.[293] Lorenz function, $L_{th}(T)$, calculated from Eq. (4) where $k_F \ell q_D = 2^{-1/3}$ assuming the impurity term $\rho_{imp} / A = 0$ (red solid line) and $\rho_{imp} / A = 0.1$ (red dashed line) are also included for comparison.

Due to the lack of detailed knowledge about the electron-phonon coupling constant, Fermi wave vector, and residual resistance of my samples, a direct calculation of $L(T)$ for VN$_x$ using Eq. (5.4) is not possible. Considering the relatively small difference among $L(T)$ values for normal metals shown in Fig. 5.8, I approximate the Lorenz function of VN$_x$ with $L(T)$ interpolated from a similar NaCl-structure TM nitride, ThN, which also shows an increasing thermal conductivity with increasing temperature over a similar range.[293]
Since static point defects typically elastically scatter electrons of different energy with equal effectiveness, the W-F law with $L(T) = L_0$ is usually valid for the residual resistivity due to point-defect scattering. Assuming negligible deviation from Matthiessen’s rule, \textit{i.e.} different scattering processes are independent of each other,[300] an improved model by adding the thermal resistance from electron-phonon and electron-defect scattering based on the temperature-dependent Lorenz function follows as[40,299]

$$
\Lambda_{el}^c = \left( \frac{\rho_i}{L(T)T} + \frac{\rho(x) - \rho_i}{L_0 T} \right)^{-1}.
$$

(5.6)

$\rho_i$ is the electrical resistivity of defect-free VN which is derived from subtracting the 9 $\mu\Omega$-cm difference in $\rho_{300K}$ between the stoichiometric VN in my previous work [265] and the VN in this work and the 2 $\mu\Omega$-cm residual resistivity of VN in Ref. [265] from the $\rho$ of the stoichiometric VN. $\rho(x)$ is the resistivity of VN$_x$ with N vacancies.

Applying Eq. (5.6) to VN$_x$, I obtain the corrected electronic thermal conductivity $\Lambda_{el}^c$ as a function of temperature. As shown in Figs. 5.6 (b)-(f), $\Lambda_{el}^c$ is 20-30\% smaller at 300 K than $\Lambda_{el}$ calculated with $L_0$ and approaches $\Lambda_{el}$ at high temperature. As the concentration of nitrogen vacancies increases, \textit{i.e.}, as $x$ decreases, the difference between $\Lambda_{el}^c$ and $\Lambda_{el}$ decreases because the elastic scattering of electrons by defects becomes stronger, hence the contribution from the second term in Eq. (5) becomes larger.

In Fig. 5.9(a), I plot the total thermal conductivity $\Lambda$ and my two calculations of the electronic component, $\Lambda_{el}$ and $\Lambda_{el}^c$, for VN$_x$ as a function of composition at three temperatures. The total and electronic thermal conductivities decrease as the vacancy concentration increases, and tends
to flatten out at high vacancy concentration, a behavior similar to what has been observed in other TM carbides and nitrides.[266]

**Figure 5.9.** (a) Thermal conductivity ($\Lambda$, black filled symbols) of $\text{VN}_x$ films as a function of composition $x$ at representative temperatures and 300 K electronic thermal conductivity with constant Lorenz number $L = L_0$ (black open symbols = $\Lambda_{el}$) and $L = L(T)$ (red open symbols = $\Lambda_{el}$ from Eq. (5)) [293] (b) Lattice thermal conductivity $\Lambda_L$ as a function of temperature and composition derived from $\Lambda_L = (\Lambda - \Lambda_{el})$.

I plot the $\text{VN}_x$ lattice thermal conductivity derived by subtracting the electronic component $\Lambda_L = (\Lambda - \Lambda_{el})$ in Fig 5.9(b). For all samples, $\Lambda_L$ constitutes approximately 35-40% of the total thermal conductivity at 300 K and decreases as temperature increases, contributing 20-25% to the total thermal conductivity at 500 K. $\Lambda_L$ values derived this way are approximately 20-30% smaller than those derived from the W-F law with the Sommerfeld Lorenz number at 300 K and are comparable to the lattice thermal conductivity of closely related materials, such as ThN and TaC, at high temperature.[39,64] However $\Lambda_L$ is still small compared to estimates of the lattice thermal conductivity of TiC and ZrN in the intermediate and high temperature ranges.[40,64,277]
attribute this to relatively stronger electron-phonon scattering in VN and the significant contribution of phonon scattering by N vacancies.

$\Lambda_L$ in VN$_x$ does not show a $\Lambda_L \propto 1/T$ relation characteristic of anharmonic three phonon interactions (see Fig. 5.9(b)). In Makinson’s transport theory for metals,[36] the lattice thermal conductivity obtained from electron-phonon scattering alone should be nearly independent of temperature at $T > 0.6\Theta_D$. For the temperature range of my measurements, $(0.4 < \frac{T}{\Theta_D} < 0.7$ in Fig 5.9(b)) the weak temperature dependence of $\Lambda_L$ indicates that the thermal resistance from electron-phonon scattering is of the same order as the thermal resistance from anharmonic phonon interactions.

As seen in Fig. 5.9(b), when the vacancy concentration increases, the lattice thermal conductivity $\Lambda_L$ decreases and has a weaker dependence on temperature. In the high-temperature limit of a Debye model with the assumption of phonon scattering rates that scale quadratically with phonon frequency, the lattice thermal conductivity limited by point-defect scattering is

$$\Lambda^p_L = \Lambda^i_L \frac{\omega_0}{\omega_D} \tan^{-1}\left(\frac{\omega_D}{\omega_0}\right).$$

(6)

$\Lambda^i_L$ is the lattice thermal conductivity of intrinsic phonon scattering, $\omega_D$ is the Debye frequency, and $\omega_0$ is a characteristic frequency at which the phonon point-defect scattering rate is equal to the phonon-phonon scattering rate.[37,301] Eq. (5.7) predicts $\Lambda^p_L \propto T^{-1/2} \varepsilon^{-1/2}$ when point-defect scattering is strong and $\Lambda^p_L \propto \varepsilon^{-1}$ when point-defect scattering is weak, in which $\varepsilon$ is proportional to the point-defect concentration.[301,302] Therefore, $\Lambda^p_L$ is expected to become smaller as the vacancy concentration increases and should have a weaker temperature dependence than $\Lambda^i_L$. I
also note that the longitudinal sound velocity in VN\textsubscript{x} decreases with increasing vacancy concentration (see Table 5.1) which reduces the velocity of acoustic phonons. This lattice softening with decreasing x may also contribute to the trend of decreasing lattice thermal conductivity with decreasing x.

### 5.6 Conclusion

In summary, I measured the temperature-dependent thermal conductivity from 300 to 1000 K of epitaxial VN\textsubscript{x}/MgO(001) (0.76 < x < 1.00) thin films by TDTR and compared the result with the electronic thermal conductivity calculated from the Wiedemann-Franz law. The increase in the thermal conductivity in the temperature range of my measurement is predominantly electronic in origin. The relatively low lattice thermal conductivity and its weak temperature dependence are attributed to strong electron-phonon coupling in VN\textsubscript{x}. Increasing vacancy concentration was found to reduce both the electron and lattice thermal conductivities and lead to weaker temperature dependence for the lattice contribution to the thermal conductivity.
CHAPTER 6

HIGH CONTRAST THERMAL CONDUCTIVITY SWITCH IN Ni-Mn-In AND MnₓMGe (M = Co, Ni) ALLOYS

Ni-Mn-In Parts of this chapter will be published in “Room-Temperature High Contrast Thermal Conductivity Switch in Ni-Mn-In Heusler Alloys” by Qiye Zheng, Gaohua Zhu, Zhu Diao, and David G. Cahill, in preparation. MnₓMGe parts of this chapter will be published in “Thermal Conductivity Switch and Magnetic Martensitic Transition in Ni-Mn-In MnₓMGe (M = Ni, Co)” by Qiye Zheng, Shannon Murray, Paul V. Braun, Daniel P. Shoemaker, and David G. Cahill, in preparation.

6.1 Introduction

Passive thermal switch materials controlled by temperature could benefit thermal management in a variety of systems such as internal combustion engines, catalytic conversions and batteries with the advantage of simple engineering design and the potential of scale-up.[12,13,303] To find reversible passive thermal switch materials with large thermal and electrical conductivity contrast and high “on-state” thermal and electrical conductivity, metallic alloys with MT are potential candidates.[88,89]

The family of Ni-Mn based Heusler alloys have attracted a lot of attention since the discovery of the magnetic shape memory effect in Ni₂MnGa.[304,305] In off-stoichiometric Ni-Mn-X (X = Ga, In, Sn, Sb) alloys, a L₂₁ cubic high-temperature parent austenite phase transforms into a structurally modulated low symmetry martensite phase through MT upon cooling. The MT is also accompanied by different types of magnetic transformation.[306-309] The complex behavior of structural and magnetic phase transitions in Ni-Mn-X alloys induced either by temperature,
magnetic field or hydrostatic pressure gives rise to interesting physical properties such as thermoselasticity, (magnetic) shape memory effect, magnetocaloric effect, and changes in transport properties.[304,305,310-316]

The off-stoichiometric Heusler alloy Ni$_{50}$Mn$_{50-x}$In$_x$ undergoes a martensitic phase transformation between the L2$_1$ structured austenite and monoclinic structure of martensite with MT temperature, $T_m$, spread in a large range of $120 \text{ K} < T_m < 770 \text{ K}$ when Ni composition is around 50 and $5 < x < 16$. [317-320] Notably, $T_m$ of around 300-400 K with thermal hysteresis $< 25 \text{ K}$ can be achieved when $14 < x < 16$. [317] ~40-60% changes in the electrical conductivity through the MT has been reported when $14 < x < 16.3$ in single- and polycrystalline Ni$_{50}$Mn$_{50-x}$In$_x$ at temperature from 130 to 300 K.[315,321,322]

Recently, the ternary metallic compounds MM’X with hexagonal Ni$_2$In-type structure at room temperature have also attracted much attention due to their rich magnetic and structural properties.[90-92] As members of the MM’X family of compounds, the stoichiometric MnCoGe (MnNiGe) alloy displays ferromagnetic (antiferromagnetic) properties at room temperature with Curie (Neel) temperature $T_C \approx 345 \text{ K}$ ($T_N \approx 346 \text{ K})$. [91,323] In the paramagnetic region the MnCoGe (MnNiGe) alloy undergoes a martensitic structural transition at around $T_m \approx 420 \text{ K}$ (470 K) from the Ni$_2$In-type hexagonal structure (space group P6$_3$/mmc) to the TiNiSi-type orthorhombic structure (space group Pnma). Notably, a change in the electrical conductivity in the MnCoGe$_{0.985}$In$_{0.015}$ bonded with 3.9 wt % epoxy binder has been reported.[90] Whether the thermal conductivity would also show a large increase through the structural transition is a question of interest to this study. Another question is whether the spin disorder scattering of electron and phonon, which changes across the magnetic phase transition,[324,325] would also influence the thermal conductivity.
Here I report time-domain thermoreflectance method (TDTR) measurement of an up to 80% change in total thermal conductivity $\Lambda$ across the temperature induced martensitic phase transition with $320 \text{ K} < T_m < 370 \text{ K}$ in $\text{Ni}_{50}\text{Mn}_{50-x}\text{In}_x$ alloys (nominal composition of $14 < x < 14.7$) and a 20-40% change of $\Lambda$ in $\text{Mn}_x\text{MGe}$ ($M = \text{Ni, Co}$ nominal composition of $0.99 < x < 1.02$) from 300 to 700 K. The electrical resistivity of Ni-Mn-In alloys measured by the van der Pauw method shows more than 40% decrease as they transform from martensite of poor metal to metallic austenite. The large change in electrical and thermal conductivity in Ni-Mn-In is significantly different from the behavior of stoichiometric Heusler alloy of $\text{Ni}_2\text{MnGa}$ with only a 10% change below 300 K.[326]

Electronic thermal conductivity calculated from the electrical conductivity and the Wiedemann-Franz law indicates the sharp increase in $\Lambda$ in Ni-Mn-In alloys is originated from the dramatic change in the electronic contribution while the lattice thermal conductivity remains nearly constant. I further analyzed the potential of Ni-Mn-In alloys and $\text{Mn}_x\text{MGe}$ alloys as thermal switch materials by comparing their average rate of change in dimensionless $\Lambda$ as a function of temperature with other common materials.

6.2 Sample Preparation

Bulk polycrystalline Ni–Mn–In alloys are prepared by Dr. Gaohua Zhu from Toyota using arc melting in a protective argon atmosphere from 99.9% pure constituents. The samples were annealed at 1173 K for 24 h under argon atmosphere. The $\text{Mn}_x\text{MGe}$ ($M = \text{Ni, Co}$) samples are synthesized using solid state reaction from powder elements at around 1000 °C by Shannon Murray from Prof. Daniel Shoemaker’s group at UIUC.

To prepare a smooth surface for TDTR measurement, the $\text{Mn}_x\text{MGe}$ sample of irregular shape with dimension of a few millimeter were embedded in crystal bond and mechanically polished. After removing the crystal bond with acetone immersion and sonication, the sample was further
rinsed by IPA and ethanol. The Ni-Mn-In alloys sample is cut into thin plate of 0.2 to 0.4 mm by wire saw and mechanically polished. All samples are then coated with Al of around 80 nm by DC magnetron sputtering. I pay extreme attention to the smoothness of the sample surface. I compare its reflectivity at 785 nm laser wavelength with that of an Al coated silicon wafer. The Al coating for the Ni-Mn-In alloy sample and the silicon wafer are carried out in the same sputtering run. Only samples showing a reflectivity > 95% of that of the silicon wafer are selected for the TDTR measurement of thermal conductivity.

6.3 Characterization Methods

X-ray diffraction of the Ni-Mn-In alloys is conducted by our collaborator at Evans Analytical Group using a Bruker D8 Vantec micro-diffractometer equipped with a micro-focus copper x-ray tube with Montel optics monochromator, a Vantec 500 2-D area detector and laser alignment system. The stage was oscillated in the x and y directions and rotated in the Phi direction around the area of interest to increase the number of crystallites brought into diffracting conditions. XRD data was collected by a coupled 0-2θ scan. Unlike traditional point detectors, the 2D detector accepts diffraction from crystallites oriented in a wide variety of tilt angles with respect to the incident x-ray beam. This results in reasonable diffraction intensity even though the spot size analyzed is very small. The X-ray powder diffraction of Mn$_x$MGe alloys was performed by Shannon Murray but not shown here.

The thermal analysis of the magnetic and martensitic phase transition behavior of the powder Mn$_x$MGe sample are characterized by Shannon Murray using TA Instrument Q20 Differential Scanning Calorimeter from 193 to 823 K with a ramping rate of 20°C min$^{-1}$. I measured the temperature dependent magnetization of all Mn$_x$MGe and Ni-Mn-In alloy samples using Quantum
Design Magnetic Property Measurement System (MPMS 3) from 4 to 400 K under low field of 0.01 T.

To determine the actual composition in Ni-Mn-In samples, inductively coupled plasma mass spectroscopy (ICP-MS) measurements are performed by Dr. Gaohua Zhu at Toyota. The atomic composition is calculated by measuring the element masses in the bulk (total mass=0.5 g). The measured compositions are in reasonable agreement with the intended values (see Table 6.1). The compositions of the MnₓNiGe alloys are determined by X-ray fluorescence, but further verification of the results is in progress.

Time-domain thermoreflectance method was used to measure the thermal conductivity of Ni-Mn-In and MnₓMGe alloys. (see section 2.1 for details)

Temperature-dependent TDTR measurement from 300-600 K are performed by mounting the specimen on a heater stage and monitoring the sample temperature with a Pt resistance temperature detector. In the heating and cooling process, I hold at each temperature for 2 minutes to stabilize the temperature of the sample before measurements. The total laser beam power of 15 mW creates a steady-state temperature rise of <8 K at room temperature and <5 K at 530 K. The steady state heating is added to the sample temperature in the analysis and plotting TDTR data.

In the TDTR data analysis, the thermal conductivity of the bulk samples and the thermal conductance of the Al/alloy interface, G, are the only two parameters that are adjusted for curve fitting. G is measured to be around 120 to 180 MW m⁻² K⁻¹ in these alloys, typical for Al/metal interface with thin surface oxide. For TDTR data fitting use the heat capacity documented in a previous work for Ni-Mn-In alloys with similar compositions (Ni₉₅Mn₃₅In₁₅₂) at low temperature, and fix the heat capacity above 300 K at 3.37 J cm⁻³ K⁻¹, an average value before and after the phase transition.[318] A fixed C value is used to avoid the error from the inaccurate
measurement of $C$ near a phase transition from calorimetry. The room temperature $C$ of Ni$_{49.5}$Mn$_{35.2}$In$_{15.2}$ in the literature is close to the value calculated using the Dulong-Petit law of $C = 3Nk_B = 3.2$ J cm$^{-3}$ K$^{-1}$ where $N$ is the atomic density for the martensite phase for the martensite phase. Since the Debye temperature of Ni$_{49.5}$Mn$_{35.2}$In$_{15.2}$ in the literature was measured to be $\approx 316$ K and is insensitive to the 1-3 % change in the composition, the heat capacity change after the phase transition is small, < 3% from 300 to 400 K.[327] For Mn$_x$MGe, heat capacity of 3.1 J cm$^{-3}$ K$^{-1}$ derived from the the Dulong-Petit law is close to the value of 3.12 J cm$^{-3}$ K$^{-1}$ measured by PPMS in Mn$_{1-x}$Fe$_x$CoGe ($x < 0.2$) and 3.2 J cm$^{-3}$ K$^{-1}$ in (MnCo)$_{1-x}$Ge ($x = 0.02$) at room temperature.[325] The Debye temperature of (MnCo)$_{1-x}$Ge ($x = 0.02$) is around 398 K. Hence, I approximate heat capacity of Mn$_x$MGe in the temperature range of TDTR measurement with a constant value of 3.2 J cm$^{-3}$ K$^{-1}$. Generally, for a bulk sample, TDTR method measures the sample thermal effusivity, $(\Lambda C)^{1/2}$. When $C$ is fixed, a peak in the sample heat capacity as a function of temperature is also manifested as a peak in the apparent thermal conductivity if the temperature oscillation, $\Delta T$, is large. For these alloys, $\Delta T < 0.2$ K in my measurement condition of laser power.

The electrical resistivity of the Ni-Mn-In samples from 300 to 500 K are measured by the van der Pauw method using a Stanford Research System SR830 lock-in amplifier and a home-built probe station equipped with Signatone tungsten carbide probes and a heating stage. A custom-made circuit is used to switch the current/voltage contacts as well as reverse the bias polarity. Typically, a 1.00 V(rms), 13 Hz sine wave output is applied to the circuit, which is converted to a 6.7 mA(rms) bias current through the sample using a total bias resistance of 150 $\Omega$. To eliminate any residual phase error, I measured a 20 nm platinum film on sapphire and set the phase to a value (typically $\sim 0.6$ deg) to minimize the out-of-phase reading. Using this setup, I measured the resistivity of an 80 nm Al film on thermally oxidized Si wafer to be 3.27 $\mu\Omega$-cm. This is consistent
with the result of 3.31 µΩ-cm measured by a commercial Signatone collinear four-point probe connected to a Keithley 2000 multimeter. I also measured a resistivity of 72 µΩ-cm for a 304 stainless steel, which is in agreement with the literature value of 74 µΩ-cm. The MnₓMGₑ (M = Ni, Co) samples are too small to mount probes for electrical resistivity measurements.

The electrical resistivity of all Ni-Mn-In samples are also measured in a Quantum Design physical properties measurement system (PPMS® Dynacool) by using the van der Pauw method with 8 mA current from 4 to 400 K. As the PPMS system only has two signal channels for resistance measurement, samples are measured in van der Pauw geometry from the perpendicular geometry without switching the side of current and voltage. The PPMS data is then scaled by matching the room temperature result with the probe station. The major sources of error in the resistivity obtain from the both of the methods are the sample thickness variation (3-6%) and the location of the probes (1-3%). The uncertainty in the input voltage resulting from the 1/f noise from the lock-in is around 1.5%. The error in the bias resistance (1%) also contributes. The total error in the probe station measurement amounts to about 6%.
6.4 Structure and Magnetic Properties of Ni-Mn-In Alloys

![X-ray diffraction data](image)

**Figure 6.1.** X-ray diffraction data (black line), the Rietveld refinements (red line) and the residue (blue dashed line) of the four Ni-Mn-In alloys measured at 300 K.

Fig. 6.1 shows the room temperature x-ray diffraction data of the four Ni-Mn-In alloys. Rietveld refinements based on modulated 6M monoclinic structure are also presented which shows good agreement with experimental result.[320] The deviation might be caused by residue austenite phase in the sample or martensite phase of different modulation period (such as 10 M monoclinic) which is sensitive to the composition.[76,320] However, the austenite phase fraction
in the sample at room temperature is too low to be accurately identified. Unit cell parameters determined by Rietveld refinement are shown in Table 6.1. A high temperature measurement of sample A at 500 K shows XRD pattern matches the L2₁ cubic (not shown).

The martensitic transition for a particular Heusler alloy is related to its electronic structure, which can be accounted for experimentally by examining the valence electron concentration, \( e/a \).[328-330] An examination of the physical properties as a function of \( e/a \) provides a useful guide for tailoring materials to a specific interest. The \( e/a \) of the four Ni\(_{50}\)Mn\(_{50-x}\)In\(_x\) alloys calculated as the atomic concentration weighted sum of the number of valence electrons in Ni (3d8 4s2), Mn (3d5 4s2), and In (5s2 5p1) is also given in Table 6.1. The increment of electron concentration is due to an increase in atomic percentage of Mn and/or In. According to previous works, the range for transitions from austenite to martensite is around \( e/a = 7.9 \), consistent with my observation.[317,328]

Table 6.1. Compositions of the Ni\(_{50}\)Mn\(_{50-x}\)In\(_x\) determined by ICP-MS analysis, unit cell parameters, the valence electron concentrations per atom \( e/a \), the martensitic transition temperature \( T_m \) and the width of the hysteresis from electrical resistivity measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>x</th>
<th>Composition</th>
<th>Lattice constants at 300 K</th>
<th>( e/a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>14</td>
<td>Ni(<em>{51.7})Mn(</em>{34.3})In(_{13.9})</td>
<td>4.42 5.52 12.90 86.62</td>
<td>8.00</td>
</tr>
<tr>
<td>B</td>
<td>14.3</td>
<td>Ni(<em>{50.7})Mn(</em>{35.0})In(_{14.3})</td>
<td>4.42 5.55 13.02 86.57</td>
<td>7.95</td>
</tr>
<tr>
<td>C</td>
<td>14.5</td>
<td>Ni(<em>{50.3})Mn(</em>{35.6})In(_{14.1})</td>
<td>4.44 5.53 12.95 86.22</td>
<td>7.94</td>
</tr>
<tr>
<td>D</td>
<td>14.7</td>
<td>Ni(<em>{50.3})Mn(</em>{34.8})In(_{14.9})</td>
<td>4.41 5.52 12.93 86.53</td>
<td>7.91</td>
</tr>
</tbody>
</table>
Table 6.1. (cont.) Curie temperatures of the martensite phase \( (T_c^M) \) and the austenite phase \( (T_c^A) \) determined by thermomagnetization curve.

<table>
<thead>
<tr>
<th>( T_m ) (K)</th>
<th>( \Delta T_m ) (K)</th>
<th>( T_c^M ) (K)</th>
<th>( T_c^A ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>366</td>
<td>9</td>
<td>123</td>
<td>303</td>
</tr>
<tr>
<td>343</td>
<td>12</td>
<td>140</td>
<td>302</td>
</tr>
<tr>
<td>336</td>
<td>7</td>
<td>166</td>
<td>315</td>
</tr>
<tr>
<td>321</td>
<td>7</td>
<td>183</td>
<td>307</td>
</tr>
</tbody>
</table>

The temperature dependence of magnetization, \( M(T) \), of the four Ni-Mn-In alloys were characterized using a Quantum Design Magnetic Property Measurement System (MPMS® 3) from 4 to 400 K in an applied field of 10 mT upon heating and cooling, as shown in Fig. 6.2. Upon cooling, the martensitic transition of the crystal lattice occurs first, corresponding to a small change in the magnetization with a hysteresis between the cooling and heating cycle. The characteristic transition temperatures at which martensite appears \( (M_s) \), and austenite annihilates \( (A_f) \), are indicated in the figure. The martensitic transition temperature \( T_m \) derived from the arithmetic mean of \( M_s \) and \( A_f \) is consistent with the \( T_m \) obtained from the electrical conductivity vs. temperature measurements (as demonstrated in Table 6.1) within 5 K. \( T_m \) increases as \( e/a \) becomes larger, in line with Ni-Mn-X (Ga, In, Sn, Sb) Heusler alloys which can be attributed to the stabilization of the modulated monoclinic phases with increasing \( e/a \) as predicted by first principle calculations.[328,329,331,332] The difference of the magnetization of between the two phases is small compared to Ni-Mn-In alloys of different composition and \( e/a \). [316]
Figure 6.2. Temperature dependence of magnetization, $M(T)$, of Ni-Mn-In alloys in an applied field of 10 mT. Red lines are from heating cycle and blue lines are from cooling cycle. The temperatures at which martensite appears ($M_s$), austenite annihilates ($A_f$), and the Curie temperature of the martensite and austenite phases are labeled in the figure.

A second feature in $M(T)$ occurs at around 310 K (about 20 K below $M_s$) and the hysteresis between heating and cooling curves persists to temperatures below 70 K. This suggests that the martensitic transition is not fully completed, and austenite coexists in the sample even below the ‘apparent’ martensitic transition temperature. The temperature corresponds to this feature is
assigned to the Curie temperature of the magnetic transition in the residual austenite phase, $T_c^A$, which remains relatively stable as $e/a$ changes.[316] Below 200 K, the martensite phase experiences another magnetic transition, from the paramagnetic to the ferromagnetic phase at a Curie temperature of $T_c^M$. A decrease of $T_c^M$ with increasing $e/a$ is observed, in agreement with previous results for Ni-Mn-X (Ga, In, Sn, Sb) Heusler alloys.[328,331]

### 6.5 Magnetization and Calorimetry Characterization of Mn$_x$MGe Alloys

![Figure 6.3](image)

**Figure 6.3.** Temperature dependence of magnetic susceptibility of (a) Mn$_x$NiGe and (b) Mn$_{1.01}$CoGe measured upon heating in 10 mT field. Previous data of stoichiometric MnNiGe is also shown for comparison.[333]

Representative data of the temperature-dependent susceptibility in the presence of 10 mT for Mn$_x$NiGe with $x = 0.99, 1.00, 1.01, 1.02$ are plotted in Fig. 6.3. Upon cooling, the martensite phase shows a magnetic transition from the paramagnetic (PM) state to the antiferromagnetic (AFM) state at a Néel temperature $T_N$ near 347 K (for stoichiometric MnNiGe) in agreement with previous reports.[91,333,334] The magnetic moments of 2.8 $\mu_B$ are only localized on the Mn atoms and

103
form an AFM spiral structure leading to a relatively low magnetization.[334,335] The step in curve near 200 ~250 K correspond to the AFM to AFM transformation from single to of a double spiral structure according to a previous neutron diffraction measurement.[334] The increase of Neel temperature as Mn composition x increases is presumably related to the change of exchange interactions in the Mn moments when the lattice configurations is changed. The temperature dependent magnetization data of the Mn_{1.01}CoGe shows a ferromagnetic (FM) to paramagnetic transition at Curie temperature $T_c$ around 350 K in agreement with a literature report.[325]

![Figure 6.4](image)

**Figure 6.4.** (A) 1\textsuperscript{st} cycle differential scanning calorimetry of Mn$_x$NiGe ($x=0.981$, 0.985, 0.995, 1.018) between 193 to 823 K. (d) Phase diagram of Mn$_x$NiGe based on the transition temperatures derived in DSC and magnetometry experiments. In (d), the error bars indicate the range of phase transition hysteresis between heating and cooling.

To further characterize the structural and magnetic transition, differential scanning calorimetry (DSC) was used to measure the Mn$_x$NiGe samples; the results shown in Fig. 6.4(a). The two neighboring peaks in each curve correspond to magnetic and martensitic transitions. $T_N$ is determined from the peaks at lower temperature and the martensitic transitions $T_m$ from the peak
at higher temperature upon heating or cooling. The two types of transitions have the same sign of the enthalpy change upon heating and cooling, but the 1st order martensitic transitions are broader in temperature. The hysteresis during heating and cooling is larger in the martensitic transition.

Based on the DSC and magnetometry measurements, the Mn$_3$NiGe phase diagrams are proposed as shown in Fig. 6.4(b). Upon heating, the martensite phase Mn$_3$NiGe first transforms from AFM to PM and then structurally transforms from PM martensite to PM austenite. In the alloy system, $T_m$ change from 370 K to around 500 K as x increase from 0.981 to 1.018. Higher Mn composition, which probably corresponds to more Mn substitution of Ni site according to X-ray fluorescence, leads to an increase of martensitic transition temperature. In addition, the hysteresis between the peak in heating and cooling in thermal cycle becomes larger as x increases.[336] The degree of chemical ordering in the microstructure, caused by the different substitutions on different positions, and its effect on the width of the effective 3d bands and bonding strength may play a role.[91,92]
Figure 6.5. Temperature dependence of electrical resistivity in Ni-Mn-In alloys. The results obtained in thermal cycle by PPMS (solid lines) between 4 to 400 K are compared with the measurements using the probe-station (black open circles) from 300 to 500 K upon heating. The resistivity vs. temperature measurements of sample B is repeated 5 times to study the training effect. The black dashed line in (c) is a repeated measurement from 250 to 400 K of sample C as the initial data was noisy in that temperature range. The red line in (d) is a measurement in 9 T magnetic field. Representative error bars in the probe station measurement are also labeled.
The electrical resistivity $\rho$ of Ni-Mn-In alloys is shown in Fig. 6.5. I observed an abrupt change in $\rho$ by around 40-50% with a small hysteresis of 7 to 12 K as a result of martensitic and reverse martensitic transition, consistent with literature report of Ni-Mn-In alloys with similar compositions.[322] The austenite phase resistivity is around 100 to 130 $\mu\Omega$-cm comparable with the common shape memory alloy NiTi and stainless steel.[337,338] At 100 < $T$ < 200 K, the resistivity of Ni-Mn-In alloys shows a broad peak which is correlated with Curie temperature of the martensite at which the rate spin disorder scattering of electron changes.[285,339] At high temperature, the resistivity remain almost flat with temperature coefficient of the resistivity on the order of $10^{-2}$ $\mu\Omega$ cm K$^{-1}$ presumably due to a relatively large residual resistivity in these alloys.

The results from PPMS and probe station are in good agreement: the difference in the transition temperature is smaller than 2 K and the difference in austenite phase $\rho$ are within the error bars for samples A, C and D. The relatively large deviation of high temperature resistivity in sample B is presumably caused by the asymmetry of the sample shape. I repeated thermocycle of resistivity measurements using PPMS on sample B, the sample of the highest residual resistivity and high magnetization presumably due to a relatively large amount ferromagnetic impurity.[284] Five times of thermocycle (sometimes also referred to as training) between 250 to 400 K after the initial cycle between 4 to 300 K shows no noticeable change in $\rho$ or the hysteresis. A weak training effect in both transport and magnetization in Ni-Mn-In is important for their applications as thermal switch.

Two possible mechanisms contribute to the poor-metal to metal transition through MT in Ni-Mn-In. The first one is the modification of electron density of states near the Fermi level originated from the lattice structure symmetry change which changes the carrier concentration in the alloy.[79,80,340,341] The second is the change of the electron scattering rate by the change in
twin boundary density or phonon. In fact, twin boundaries appear in all the martensitic phases of other Huesler alloys but in many of them, such as Ni$_2$MnGa, the behavior is very different.[287,326,342] This suggest that the change in electron density of states might be important. Such a conclusion is supported by density functional theory (DFT) calculations which demonstrate an increase of electron DOS near the Fermi level in Ni$_{50}$MN$_{35}$In$_{15}$.[322,343] To investigate the contributions from the two mechanism, further characterization of the electron carrier concentration by Hall measurement is in progress.

Applying 9 T magnetic field to sample D reduces its $T_m$ by 9 K corresponding to a $\frac{dB}{dT} \approx 1$ T K$^{-1}$ which indicate a weak field dependence on the magnetic field compared to Ni-Mn-In of different compositions.[344] The change in transition temperature ($\Delta T$) induced by a change in magnetic field ($\Delta B$) is approximately given by the Clausius–Clapeyron relation in the magnetic phase diagram as $\frac{dB}{dT} \approx -\frac{\Delta S}{\Delta M}$, where $\Delta M$ and $\Delta S$ are the differences in magnetization and entropy change between the austenite and martensitic phases, respectively.[76] Since both of the martensite and austenite are paramagnetic at $T_m$, the change in the magnetization is only about 1000 A/m for sample D which in turn gives a small entropy change of around 0.1 J K$^{-1}$ m$^{-3}$.[345] [344] The weak field dependence of the transport properties benefits the stability of Ni-Mn-In alloys in practical application. It’s also noted that the slope of $\rho(T)$ changes near 350 K in 9 T, which is possibly due to the shift of the austenite phase Curie temperature from 307 K to a temperature higher than the $T_m$. 
Figure 6.6. Temperature dependence of thermal conductivity of Ni-Mn-In (a) sample A, (b) sample B from 300 to 530 K and (c) sample C, (d) sample D from 150 to 530 K upon heating and cooling. Red symbols (open squares, open circles, filled circles) are representative data from the heating cycle collected from different locations on the same samples. Blue open squares stand for data collected during cooling run. Electronic thermal conductivity calculated from the measured electrical conductivity and the Wiedemann-Franz law from PPMS (black lines) and probe station (black open circles) are demonstrated. Corresponding error in the total and electronic thermal conductivity are labeled at representative data points.
I plot the temperature dependence of the thermal conductivity during heating for Ni-Mn-In alloys in Fig. 6.6. The magnitude of room temperature thermal conductivity is approximately 8 Wm$^{-1}$ K$^{-1}$ without significant dependence on the composition. A distinct sharp change of around 30%-60% (with the peak from heat capacity excluded) occurs near $T_m$ with the inflection point of the $\Lambda$ change within 6 K of the $T_m$ determined by electrical measurements. At 400 K (above $T_m$), the austenite phase $\Lambda$ is around 13 to 15 W m$^{-1}$ K$^{-1}$, a value dramatically larger than those in oxide MIT materials such as VO$_2$.\[84] $\Lambda$ increases with rising temperature almost linearly in both martensite and austenite phases. A previous work reported a similar sharp change in thermal conductivity of Ni$_{50}$Mn$_{33.7}$In$_{16.3}$ single crystal but at a much lower transition temperature of around 150 K.\[322] The thermal hysteresis between heating and cooling near $T_m$ is about 10 to 15 K which is consistent with the width of the hysteresis loop in $\rho$.

The variation in measurements performed at different location on samples is most significant near the transition temperature but becomes less pronounced around 50 K above $T_m$. In location where the transition is smeared, I didn’t observe sharp peak induced by heat capacity. The variation is possibly caused by the different amount of austenite in the region of TDTR measurement or the premartensitic transition observed in similar Ni-Mn-In based alloys (induced by magnetoelastic coupling between the magnetic and structural transition).\[346] As indicated by the magnetization measurements, small fraction of austenite phase coexists with martensite in Ni-Mn-In alloys near 300 K below $T_m$ which may result from the inhomogeneity of the composition or strain.\[76,347] Compared to the resistivity measurement data which is a result averaged over the whole sample, TDTR only measures the volume within the laser spot size of 10.1 $\mu$m and a thermal penetration depth $L_p = \sqrt{\Lambda/\pi f C} \approx 400$ nm near the sample surface, where $f$ is the modulation frequency and
C is the volumetric heat capacity of the sample. Hence, TDTR results are more sensitive to local properties or inhomogeneity.

The resistivity from the heating run has a pronounced peak originates from the peak in the real heat capacity during the laser pulse induced phase transition. The peak during cooling is not observed since the temperature oscillation created by the 9.1 MHz modulated pump laser pulses is only 0.1 K which is smaller than the MT hysteresis of around 10 K.[348] Hence the sample could not be heated to temperature for martensite to austenite transition by laser during cooling. The peak in heating and lack of peak in cooling agree with heat capacity measurement of some alloys with martensitic transition resulting from the relaxation process associated with the first-order phase transition.[349,350] Due to a low fraction of the austenite phase, I didn’t observe a sharp peak at near $T^A_C$.

I estimate the electronic thermal conductivity by the Wiedemann Franz law $\Lambda_e \approx LT / \rho(T)$ using a Sommerfeld value of $L= L_0 = 2.44 \times 10^{-8} \, \Omega \, \text{W} \, \text{K}^{-2}$. As shown in Fig. 6.6 the change in the total thermal conductivity in the 150-500 K temperature range is dominated by the electronic contribution. The lattice thermal conductivity remains nearly constant around 4 to 6 W m$^{-1}$ K$^{-1}$ in different samples above 300 K. The sharp change in $\Lambda_e$ resemble the shape of the total thermal conductivity in both the magnitude and temperature hysteresis. Hence, I attribute the increases in the thermal conductivity of Ni-Mn-In through the martensitic transition to the change of the electronic contribution. Since the temperature dependence of $\rho(T)$ in the austenite phase is weak, the increase in the electronic thermal conductivity is nearly proportional to temperature leading to an almost linear behavior of $\Lambda$. This result is quite different from the almost flat curve of $\Lambda$ below 300 K in the prior report for Ni$_{50}$Mn$_{33.7}$In$_{16.3}$ because the $\rho(T)$ below Curie temperature of the austenite phase still increases with temperature rapidly due to electron-magnon scattering.[322]
6.7 Thermal Conductivity of Mn\textsubscript{x}MGe Alloys

Figure 6.7. Temperature dependence of apparent thermal conductivity in Mn\textsubscript{x}NiGe (x from 0.981 to 1.021) from 300 K to 700 K (black symbols). Different symbols in each plot correspond to measurement done on different pieces of sample from a same batch. The heating and cooling cycle measured on the sample in Mn\textsubscript{1.018}NiGe are shown as red and blue open diamond symbols. The data near the magnetic phase transition around 350K is not shown in all data to better demonstrate the overall thermal conductivity behavior through martensitic transition.
I plot the temperature dependence of the thermal conductivity between 300 to 700 K for Mn$_x$NiGe in Fig. 6.7. The scattered data for samples with the same composition is mainly attributed to the anisotropy of the crystal in both martensite (TiNiSi-type orthorhombic) and austenite phase (Ni$_2$In-type hexagonal). I measured thermal conductivity on different pieces of samples with random orientations. Upon heating, a sharp peak near 350 K appear corresponding to the sharp magnetic phase transition originated from the peak in the real heat capacity during the phase change. However, I noticed that the thermal conductivity doesn’t change after the sample is fully turned into PM state; i.e. the magnetic transition does not effectively change the thermal conductivity in Mn$_x$NiGe. At higher temperature, the thermal conductivity shows another increase without peak behavior corresponding to the broad martensitic structural transition with relatively large hysteresis.[84] The large hysteresis of around 100 K is demonstrated in the heating and cooling measurement in Fig. 6.7(f). Due to the large intrinsic strain induced by the a 2.7% change in unit cell volume through the MT,[91] the small chunks of polycrystalline samples tend to crack as the sample is heated and cooled across the MT. Thus, I could rarely obtain a full thermal cycle data of the TDTR measurement in these samples.

In general, a higher Mn content, in addition to increase the $T_m$, also enhances the magnitude of increase in thermal conductivity through the martensitic transition and the higher the transition temperature. The most rapid increase is observed in Mn$_{1.014}$NiGe which changes by $\sim$40% from $\approx$11 to $\approx$15.5 W m$^{-1}$ K$^{-1}$, in 575 K $<$ $T$ $<$ 625 K a (see below for more a quantitative comparison). The inflection points of the step-like increases in the thermal conductivity data correspond to $T_m$ which are consistent with DSC results.
Figure 6.8. Temperature dependence of apparent thermal conductivity in Mn$_x$CoGe ($x=1.005$, 1.01, 1.015, 1.02) from 300 K to 600 K during heating.

I plot the temperature dependence of the thermal conductivity during heating for Mn$_x$CoGe in Fig. 6.8. In contrast to Mn$_x$NiGe, no peak (see Figure 3 (b)) appears near its Curie temperature of about 350 K for magnetic phase transition probably due a weak peak in heat capacity from magnetic contribution. In all Mn$_x$CoGe samples an increase in thermal conductivity corresponding to the broad martensitic structural transition is observed, similar to Mn$_x$NiGe. The sharpest
increases are observed in Mn$_{1.015}$CoGe and Mn$_{1.02}$CoGe which changes by ~25-30% from 450 to 550 K.

Although the size of the Mn$_x$MGe samples are too small for electrical conductivity measurement, the discussion in Section 6.6 suggest the change in the total thermal conductivity through MT in Mn$_x$MGe may also results from electronic contribution. This tentative conclusion is supported by the large relative change in electrical resistivity in MnCoGe across the MT.[351]

6.8 Evaluation of Thermal Conductivity Switch in Ni-Mn-In and Mn$_x$MGe

To evaluate the MT induced thermal conductivity change in Ni-Mn-In and Mn$_x$MGe alloys for thermal switch application, I define an average logarithmic rate of change in thermal conductivity in a certain temperature range as: $Z = \frac{\partial \ln \Lambda}{\partial \ln T}$. The larger the absolute value of $Z$ the faster the change in thermal conductivity. For materials with phase transition, I calculated the average value of $\langle Z \rangle = \left( \frac{\partial \ln \Lambda}{\partial \ln T} \right) \approx \left( \frac{T \Delta \Lambda}{\Lambda \Delta T} \right)$ in the range of approximately $T^* \pm 25$ K where $T^*$ is their corresponding phase transition temperature (the baseline value of the sharp peaks in Ni-Mn-In alloys are taken). The data of $\langle Z \rangle$ for Ni-Mn-In, Mn$_x$MGe (M = Ni, Co) alloys, and $Z(T)$ and $\langle Z \rangle$ for some common materials between 300 to 600 K is illustrated in Fig 6.9. Largest value of $\langle Z \rangle$ is used if multiple data sets exist.
Figure 6.9. Logarithmic rate of change in thermal conductivity, $Z$ as defined in the main text for Ni-Mn-In alloys (black filled circles), $\text{Mn}_x\text{NiGe}$ (blue open squares), $\text{Mn}_x\text{CoGe}$ (red open circles), Cu,[180] 304 stainless steel,[332] Ni-22 at%Cr alloy,[76] Si,[345] $\text{SiO}_2$,[111] natural type-IIa diamond,[338] NiTi (this work and [350]), $\text{VO}_2$ (nanobeam).[87] and $\text{VO}_2$ thin film (tf).[84] Literature data of materials without transition are shown as solid lines for metals and dashed lines for dielectrics.

Above 300 K, the $Z$ value of dielectrics crystals of Si and diamond and good metals such as Cu are typically negative indicating a decreasing thermal conductivity as temperature rises. Poor metals alloys such as stainless steel alloy and Ni-22 at%Cr alloys show a stable small positive $Z < 0.8$, corresponding to a nearly linear $\Lambda$ as a function of temperature. The curve for amorphous dielectric $\text{SiO}_2$ also positive. In comparison, $Z$ values for phase transition materials of NiTi, $\text{VO}_2$, Ni-Mn-In, and $\text{MnXGe}$ are relatively large positive numbers as a result of the sharp change in thermal conductivity within a narrow temperature window. The $Z$ for Ni-Mn-In alloys is larger than that for the conventional MT material of NiTi and NiCr and stainless steel alloys. The largest
value of Z is around 3.2 for Ni-Mn-In sample C which means a 10% change in temperature would lead to ~30% change in thermal conductivity on average in the transition temperature region. Except VO₂ thin films, Ni-Mn-In shows the fastest rate of change in thermal conductivity among materials examined.

6.9 Conclusion

In summary, I measured the temperature dependent thermal conductivity of magnetic and martensitic phase transitions materials of Ni-Mn-In and MnₓMGe (M = Ni, Co) alloys from 130 to 700 K using time-domain thermoreflectance (TDTR). A sharp change in thermal conductivity is observed through the structural martensitic transition (near room temperature for Ni-Mn-In) but not through the magnetic transition in Ni-Mn-In and MnₓMGe alloys. The average rate of the change of Λ in Ni-Mn-In and MnₓNiGe in the 50 K range of their transition temperatures is faster than common metals and alloys including the conventional shape memory alloy of NiTi. By comparing the result with the electronic thermal conductivity calculated from the Wiedemann-Franz law I attribute such a rapid change in the thermal conductivity to the electronic contribution in Ni-Mn-In. In addition, the austenite phase thermal and electrical conductivity in Ni-Mn-In are about 14 W m⁻¹ K⁻¹ and ~100 μΩ-cm respectively near 400 K which are both more than twice as large as VO₂ thin film in metallic state and comparable with stainless steel. [84,337] A similar austenite phase thermal conductivity of around 12 to 17 W m⁻¹ K⁻¹ and a lower values 8 to 10 W m⁻¹ K⁻¹ of at about 600-700 K were measured in MnₓNiGe and MnₓCoGe, respectively. The transport properties in Ni-Mn-In alloys are insensitive to the training of thermal cycle and external magnetic field. In all these alloys, the phase transition temperature can be adjusted by the alloy composition. Therefore, Ni-Mn-In and MnNiGe based alloys may serve as potential materials for
room temperature thermal switch devices with large “on state” electrical and thermal conductivity where high contrast in thermal conductivity and electron carrier concentration are necessary.
CHAPTER 7

CONCLUSIONS

Thermal management in different engineering system requires functional materials with different heat transport properties. An understanding of how thermal conductivity \( \Lambda \) is correlated with the microscopic characteristics of the material is important for their application. Time-domain thermoreflectance (TDTR) is a powerful tool for the study of nanoscale thermal transport in various materials system. Combining TDTR with other materials characterization techniques such as Raman spectroscopy, X-ray diffraction, and the conventional yet useful four-probe electrical resistivity measurement, I studied thermal transport physics in several representative functional materials.

I measured the thermal conductivity of CVD graphite thin films with various thicknesses (\( \approx 20 \sim 140 \) nm) grown on single crystal Ni (111) substrate at relatively low temperatures from 825 to 900 °C by TDTR. The effective cross-plane thermal conductivity of \( \approx 3.3 \text{ W m}^{-1}\text{K}^{-1} \), obtained from thermal resistance as a function of film thickness, is about half of that in HOPG. The reduction can be explained by size effect at the lower end up to 50 nm compared to predictions of first-principles solutions of the Boltzmann transport equation (BTE). However, the values are smaller than the BTE prediction at the upper end of the thickness range. Although stacking disorder may play a role in reducing the cross-plane thermal conductivity, I did not observe a correlation between the cross-plane thermal resistance and microstructural defects that produce changes in the high frequency Raman spectra. A better low frequency Raman technique to characterize the stacking disorder would be useful to understand the deviation. The in-plane thermal conductivity of films grown at different temperatures varies between 1/3 to 1/2 of the value of HOPG which
can be reasonably attributed to phonon scattering by lateral grain boundaries. I also define a figure-of-merit for flexible heat spreaders and find that CVD graphite has potential advantages over metal films for thermal management of flexible electronics.

Using electrochemical Li intercalation, the anisotropic thermal transport in bulk crystal and CVD grown thin film MoS$_2$ samples with different amounts of lithium ion is measured by TDTR. Intercalation impacts thermal transport in bulk and thin film samples differently, depending on the crystalline quality of the 2D structure. The thermal conductivity in the bulk sample can be effectively modified by introducing stacking disorder and mixture of phases as supported by Raman spectroscopy of the shearing mode, which significantly increases phonon-boundary scattering. The thermal conductivity change in the defective thin film sample is strongly affected by the lattice softening. Moreover, it’s found that lithiation tends to reduce the phonon mean free path more along the through-plane direction in Li$_x$MoS$_2$, rather than the in-plane direction. As a result, a significant increase in the thermal anisotropy ratio is observed with increasing Li content until the largest degree of disorder is reached at $x \approx 0.34$. This work demonstrates how the thermal anisotropy ratio can be controlled by systematically introduced disorder.

I measured the temperature-dependent thermal conductivity from 300 to 1000 K of epitaxial thin films VN$_x$/MgO(001) with varied N vacancy concentration ($0.76 < x < 1.00$) by TDTR. I compared the result with the electronic thermal conductivity calculated from the Wiedemann-Franz law. The increase in the thermal conductivity in the temperature range of my measurement is predominantly electronic in origin. The relatively low lattice thermal conductivity and its weak temperature dependence are attributed to strong electron-phonon coupling in VN$_x$. Increasing vacancy concentration was found to reduce both the electron and lattice thermal conductivities and lead to weaker temperature dependence for the lattice contribution to the thermal conductivity.
I studied the temperature dependent thermal conductivity of Ni-Mn-In and Mn₃MGe (M = Ni, Co) alloys across their corresponding magnetic and structural martensitic phase transitions. Thermal conductivity changes dramatically through the martensitic transition but not through the magnetic transition in Ni-Mn-In and Mn₃MGe alloys. The average rate of the change in Λ for Ni-Mn-In and Mn₃NiGe in the 50 K range of their transition temperatures is faster than common metals and alloys including the conventional shape memory alloy NiTi. By comparing the result with the electronic thermal conductivity calculated from the Wiedemann-Franz law I attribute such a rapid change in the thermal conductivity to the in the electronic contribution resulted from the change in electron density of states and the mobility in Ni-Mn-In. In addition, the austenite phase thermal and electrical conductivity in Ni-Mn-In are about 14 W m⁻¹ K⁻¹ and ~100 µΩ·cm respectively near 400 K which are both more than twice as large as than VO₂ thin film in metallic state and comparable with stainless steel.[84,337] My work suggest that Ni-Mn-In and MnNiGe based alloys may serve as potential materials for room temperature thermal switch devices with large “on state” electrical and thermal conductivity where high contrast in electron carrier concentration are necessary.
CHAPTER 8

BIBLIOGRAPHY


123


[103] R. B. Wilson, University of Illinois at Urbana-Champaign, 2015.