Thermal Engineering of Interfaces in Nanotechnology
A Study of Alloys, 2D Materials, and Ferroelectric Oxides

Submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy
in
Mechanical Engineering

Dipanjan Saha
B.S., Mechanical Engineering, University of Connecticut
B.S., Biomedical Engineering, University of Connecticut

Carnegie Mellon University
Pittsburgh, PA
October 2019
Acknowledgements

First and foremost, I would like to thank my parents for encouraging me to pursue a PhD, and for continuously inspiring me with their tireless work ethic and personal standards of excellence. This dissertation would not have been possible without their love and unconditional support.

Next, I would like to thank the members of my committee: Professor Jonathan Malen (chair), Professor Alan McGaughey, Professor Jeffrey Weldon, and Dr. Abhishek Sharma. As my primary advisor, I have Professor Malen to thank for his unwavering support and for providing me with opportunities to gain breadth in materials deposition/characterization and device design/fabrication, in addition to gaining depth in nanoscale thermal transport. For this breadth of knowledge, I am also grateful to Professor Andrew Gellman’s mentorship and his students (Xiaoxiao Yu and Zhitao Guo) through our collaboration on two of my major projects, and Professor Feng Xiong/Yanhao Du’s collaboration in our graphene contact resistance work. As our collaborations continue past this dissertation, I remain optimistic that our work may someday make a major impact in the future of nanotechnology.

Finally, I would like to thank all of the friends who have been there for me throughout this PhD: Wee-Liat Ong, Sushant Kumar, Minesh Patel, Fransisco Ramirez, Olga Soto, Nathan Nakamura, Phil Smith, Raghav Garg, Steven Rich, Piyumi Wijesekara, Laisuo Su, Nina Meng, Xun Li, Tom Brubaker, Rishabh Shah, Hugh Li, Alex Christodoulides, Matt Bartnof, Turga Ganapathy, Jon Braaten, Mohamed Darwish, William Wei, Kevin Parrish, Todd Medema, and
many others. Additionally, I am grateful for the support received from my friends back home including Greg Reinhold, Emily Simonelli, Jonathan Hayon, and Anthony Renzullo.

Also, I would like to thank the sources of funding for the works presented in this thesis: the CMU Presidential fellowship and research grants from the National Science Foundation (NSF CBET 1403447), Carnegie Mellon’s Data Storage Systems Center (DSSC), and Northrop Grumman through the University Research Program.
The more electronic devices scale down into the nanoscale regime to achieve higher performance, the more important interfaces become to dissipating the increasing heating power generated through device operation, which negatively affects device performance and can even lead to critical failures of the technology. Phonon mediated transport across metal-nonmetal interfaces has been identified as an especially limiting thermal bottleneck. While the addition of metal layers at the interface with better vibrational matching to the nonmetal has been shown to significantly enhance interfacial thermal transport, in the context of device applications such an enhancement may not always be fully realized.

In this dissertation I will first present an overview of phonons, frequency domain thermoreflectance, and different nanotechnologies in order to demonstrate the importance of improving thermal transport at metal-nonmetal interfaces for device applications. Next, I will describe my work (in collaboration with Professor Andrew Gellman’s lab at Carnegie Mellon) on how the interdiffusion of extremely thin layers of Au on Cu progressively inhibits thermal transport across the metal-Al₂O₃ interface. I will then demonstrate how the experimental data was used to derive an analytical model to predict our unique diffusion profiles as a function of time, metal thicknesses, and permeabilities of the metal-metal interface to mass transport. Additionally, I will show how this analytical model can be utilized as an input to the Diffuse Mismatch Model to predict how interdiffusion lowers interfacial thermal conductance.
The second research project I will describe focuses on developing contacts to 2D materials, with the objective of being superior both thermally and electrically. This work was also performed in collaboration with Professor Gellman’s lab. This study is the first to investigate alloys as contacts to a 2D material, where my 2D material of interest was graphene which has some of the best-known material properties. Through this study, I determined that ~10 atomic percent palladium in nickel results in the largest reported thermal conductance of 114 MW/m²K to monolayer graphene supported by SiO₂. I will also present some of my preliminary data (in collaboration with Professor Feng Xiong’s lab/his student Yanhao Du at the University of Pittsburgh) to determine whether this alloy composition will be a higher performance electrical contact. This ongoing effort indicates the critical importance of using graphene with clean surfaces to reducing contact resistances.

For the final two sections of this thesis, I will describe my thermal conductivity measurements of the single crystal ferroelectric oxides SrTiO₃ and PbTiO₃ (performed in collaboration with Professor Francisco Rivadulla’s Lab at the University of Santiago de Compostela) which will demonstrate the surprising power of Ferroelectric Domain Walls (FEDWs) to significantly reduce the thermal conductivity of PbTiO₃ and SrTiO₃ by ≈60% at room temperature and a further ≈65% reduction from 275 K down to 225 K and temperatures below. Through these measurements I demonstrate that the thermal interfaces of FEDWs have incredible potential for future studies to actively control thermal conductivity.

Through the datasets presented in this dissertation, I experimentally answer important questions regarding thermal transport across interfaces with particular relevance to nanotechnology applications, and also open the door for interesting new questions to be answered by future research in this area.
# Table of Contents

Acknowledgements ........................................................................................................... iii
Abstract ................................................................................................................................. iv
List of Tables ....................................................................................................................... x
List of Figures ..................................................................................................................... x
List of Symbols/Abbreviations .......................................................................................... xvii

1 Phonons and Frequency Domain Thermoreflectance ............................................... 1
   1.1 Fundamental Terminology ......................................................................................... 1
   1.2 Frequency Domain Thermoreflectance ................................................................. 3

2 Thermal Interfaces at the Nanoscale ........................................................................... 7
   2.1 Introduction .............................................................................................................. 7
   2.2 Scientific Research on G .......................................................................................... 8
      2.2.1 $G_{p-p}$ at vibrationally mismatched surfaces .................................................... 8
      2.2.2 Interfaces between 3D and 2D materials ......................................................... 14
   2.3 Importance of Thermal Interfaces in Nanotechnology ......................................... 16
      2.3.1 Plasmonics-HAMR ......................................................................................... 16
      2.3.2 3D Architectures/Device Stacking ................................................................. 17
      2.3.3 Memristors ....................................................................................................... 18
      2.3.4 2D Devices ....................................................................................................... 20
   2.4 Integrating Thermal Research into Device Applications ....................................... 21

3 Interdiffusion of Adhesion Layers on Thermal Interface Conductance ................. 25
   3.1 Overview .................................................................................................................. 25
   3.2 Introduction ................................................................................................................ 26
   3.3 Results and Discussion ............................................................................................ 27
      3.3.1 Cu and Au film thickness ............................................................................... 27
      3.3.2 XPS depth profiles of annealed Au-Cu-Mo interfaces ................................ 28
      3.3.3 Heating time effect on interdiffusion ............................................................... 31
      3.3.4 Quantification areal surface composition and total sputtering depth .......... 32
      3.3.5 Thermal Interface Conductance ..................................................................... 33
   3.4 Modelling .................................................................................................................. 35
      3.4.1 Interdiffusion Composition Modelling ......................................................... 35
3.4.2 Interdiffusion Modelling Solution ............................................................................. 40
3.4.3 Molar quantification of Cu and Au measured by XPS depth profiling ...................... 43
3.4.4 Permeability Fitting .................................................................................................. 45
3.4.5 Thermal Interface Conductance Modelling .............................................................. 47
3.5 Methods ..................................................................................................................... 49
3.5.1 Preparation of layered Cu/Au sample ..................................................................... 49
3.5.2 EDX thickness characterization .............................................................................. 49
3.5.3 XPS depth profiling characterization .................................................................... 50
3.5.4 Thermal Interface Conductance Measurements ...................................................... 51
3.5.5 High Temperature Annealing ................................................................................ 52
3.5.6 Conductance Uncertainty Analysis ........................................................................ 52
3.5.7 Metal Thermal Conductivity Calculation ............................................................... 53
3.6 Conclusion ................................................................................................................. 53

4 Maximizing Alloy Graphene Interface Conductance....................................................... 55
4.1 Overview ................................................................................................................... 55
4.2 Statement of Contributions ....................................................................................... 55
4.3 Introduction ............................................................................................................... 56
4.4 Results/Discussion ..................................................................................................... 61
4.4.1 Metal Selection/Characterization .......................................................................... 61
4.4.2 Thermal Measurements ......................................................................................... 62
4.4.3 TEM Imaging .......................................................................................................... 66
4.4.4 Electrical Measurements ....................................................................................... 69
4.5 Methods ..................................................................................................................... 72
4.5.1 Graphene Acquisition ............................................................................................ 72
4.5.2 Thermal Sample CSAF Deposition ....................................................................... 72
4.5.3 EDX Metal Characterization ................................................................................ 73
4.5.4 Electrical Sample Patterning and CSAF Deposition .............................................. 74
4.5.5 CSAF Post Deposition Anneal .............................................................................. 77
4.5.6 Thermal Measurements ......................................................................................... 78
4.5.7 Electrical Measurements ....................................................................................... 79
4.6 Conclusion ................................................................................................................. 81
### 5 Reduction of Thermal Conductivity in Epitaxial SrTiO$_3$ Thin Films by Ferroelectric Domain Walls

5.1 Overview .................................................................................................................. 83 
5.2 Contributions to Dissertation Material ...................................................................... 83 
5.3 Introduction .............................................................................................................. 84 
5.4 Motivation to study SrTiO$_3$ .................................................................................... 85 
5.5 Results ...................................................................................................................... 87 
  5.5.1 Vacancy Scattering ............................................................................................... 87 
  5.5.2 Disentangling Thermal Interface Conductance ...................................................... 88 
  5.5.3 Thermal Conductivity .......................................................................................... 91 
  5.5.4 Approximation of Domain Sizes ............................................................................ 92 
5.6 Methods .................................................................................................................. 94 
  5.6.1 Sample Fabrication ............................................................................................... 94 
  5.6.2 Temperature Dependent Measurements of Thermal Conductivity ..................... 95 
5.7 Conclusion .............................................................................................................. 96

### 6 Record Reduction in Thermal Conductivity Through Phonon Scattering from Ferroelectric Domain Walls in PbTiO$_3$

6.1 Overview .................................................................................................................. 97 
6.2 Contributions to Dissertation Material ...................................................................... 97 
6.3 Introduction .............................................................................................................. 98 
6.4 Results and Discussion ............................................................................................. 99 
  6.4.1 PFM ......................................................................................................................... 99 
  6.4.2 TEM ........................................................................................................................ 101 
  6.4.3 Effect of Domain Wall Periodicity on Thermal Conductivity ................................. 103 
6.5 Methods .................................................................................................................. 106 
6.6 Conclusion .............................................................................................................. 109

### 7 Summary and Outlook

7.1 Interdiffusion of ultra-thin metal films on $G$ at metal-dielectric interfaces ............ 111 
7.2 Alloy contacts to 2D materials .................................................................................. 112 
7.3 Temperature dependent FEDWs on thermal conductivity of SrTiO$_3$ ..................... 113 
7.4 Ferroelectric domain walls on thermal conductivity in strained PbTiO$_3$ ............... 113

### 8 References

ix
**List of Tables**

- *Table 3-1. FDTR measurement uncertainty* .................................................. 52
- *Table 6-1. Debye Temperatures of Ferroelectric Oxides and Substrates* ............ 108

**List of Figures**

- *Figure 1-1. Chain of atoms with displacements representing a phonon mode.* ........ 2
- *Figure 1-2. Phonon dispersion (left), and phonon density of states (right). Modified from [3]. * ........................................ 3
- *Figure 1-3. Schematic of FDTR reproduced from [12].* ........................................ 5
- *Figure 1-4. Fit (blue line) of experimental FDTR phase lag vs heating frequency data (red points) for Au on Al₂O₃.* ............................................................. 6
- *Figure 2-1. Simulated phonon dispersion (left) and DOS (right) for two materials where the overlapping region in the DOS defines the available conduction pathways for a phonon transmitting across the interface. Reproduced with permission [3].* ................... 11
- *Figure 2-2. Experimental enhancement of $G$ between Au/Al₂O₃ through adhesion layers. Reproduced with permission [24].* ..................................................... 12
- *Figure 2-3. Thermal interface conductance between metals in contact with nonmetal substrates plotted against metal Debye temperature. For studies involving a metal intermediate layer sandwiched between a metal and nonmetal, the $\Theta D$ of the intermediate layer was used for the horizontal axis.* [15,24,26,45–48] ................................................................. 13
- *Figure 2-4. Thermal interface conductance between metals and single layer 2D materials supported by SiO₂ substrates [50–54].* ......................................................... 15
- *Figure 2-5. Simple schematic of Heat Assisted Magnetic Recording technology. The diameter of the “peg” at the bottom of the Au Near-Field Transducer is ~50nm in diameter, the same size as* .......
the heating spot in the recording media, allowing for this technology to record at smaller spot sizes than the diffraction limit of visible light [68]. Schematic reproduced from [69].

Figure 2-6. Simplified model of the oxygen vacancy migration in the first memristor.

Figure 2-7. a) Schematic of a graphene field effect transistor. B) Reduction in current saturation due to joule heating in the device and hence the importance of heat dissipation out of the channel into the substrate and contacts, the latter of which becomes more important as the device footprint shrinks. Reproduced from [85].

Figure 3-1. Color contour map of the Cu adhesion layer thickness across the Au-Cu film on an Al₂O₃ substrate. Thickness was measured using EDX on a 13×13 point grid.

Figure 3-2. Contour map of the Cu adhesion layer thickness as measured using EDX at 36 points (black dots) across the Au-Cu film on Mo.

Figure 3-3. XPS depth profiles of (a) Au and (b) Cu measured for an 8 nm Cu film with 39 nm of Au deposited on top. The underlying substrate is Mo. The first indication of Cu diffusion across the Au-Cu interface is observed after annealing at 440 K. At this temperature, the Cu is uniformly distributed across the thickness of the Au overlayer. At 520 K, the Au and Cu have fully alloyed. All measurements were conducted on a single sample.

Figure 3-4. XPS depth profiles measured at 20 nm Cu thickness and 46 nm Au thickness, where Cu, Au, and Mo through-plane composition measured as a function of Ar+ sputtering depth (nm) on the film for as-deposited, after annealing at 460 K for 20 minutes, 60 minutes, and 240 minutes, and finally at 520 K for 20 minutes.

Figure 3-5. Measurements of G vs Cu adhesion layer thickness for the films as-deposited, and after subsequent heating to 360 K, 440 K, 460 K, 480 K, and 520 K for 30 minutes. The values of G for the as-deposited films are within the error of literature values for pristine films [24].
Values of $G$ after annealing at 360 K are similar to those for the as-deposited film. A significant decrease in $G$ occurs after annealing at 440, 460, and 480 K. At 520 K, $G$ has reached its minimum, in good agreement with the literature values for a fully intermixed alloy [26].

Figure 3-6. Depiction of interdiffusion in the metal bilayer where Cu is deposited on a dielectric and capped with Au. According to this schematic, as Cu diffuses to the left and Au to the right, the total thickness is constant but the thickness of each side changes, moving the position of the Au-Cu interface denoted by the black dashed line. The rate at which each species crosses the interface is dependent on the permeability (function of temperature) of the interface to that species, the composition, and time. Once a species crosses the interface, it uniformly distributes itself on that side of the interface.

Figure 3-7. Time dependent at. % Cu on right, according to Figure 4 schematic, and $G$ calculated using the Diffuse Mismatch Model (described in the next section). The majority of interdiffusion and $G$ decrease occurs within the first 250 minutes of annealing at 460 K for a 41 nm Au film deposited on a 10 nm Cu film.

Figure 3-8. Fitting of experimental Cu atomic concentrations to determine the position of the interface between Au rich and Cu rich regions for 46 nm of Au on 25 nm of Cu after annealing at 460 K for 20 minutes.

Figure 3-9. Permeability fitting of experimental molar concentrations in Cu rich region for 46 nm of Au and 25 nm of Cu at 460 K. The boundary defining the Cu rich region is taken as the step in the Heaviside function (sample shown in Figure 3-8). The concentrations to the right of this boundary are used to determine the experimental molar concentrations.

Figure 3-10. DMM predictions of $G$ compared with experimental values. The shaded region depicts a 30% error in both permeabilities.
Figure 4-1. Theory of electronic contact resistance at graphene metal interfaces. a) Electron transmission is a two-step process from the metal to the graphene doped by the contacts, and then from the doped graphene to the uncontacted graphene in the channel. b) Transmission from the metal to the graphene involves tunneling through a Schottky barrier at the interface. The width of the barrier is the equilibrium distance $d_{eq}$. $\phi_M, \Delta V, \phi_G, \Delta EFM$ are the metal work function, the built-in potential difference across the barrier, the monolayer graphene work function, and the difference between the Dirac-point and Fermi level in the doped graphene, respectively. Reproduced with permission from [155].

Figure 4-2. $R_C$ for Cr, Ni, Au and Pd on graphene. Pd has the lowest $R_C$ despite having the same effect on the graphene’s work function underneath the contact as Au. Pd’s superiority to Au is attributed to better adhesion to the graphene. Reproduced from [156].

Figure 4-3. $G_T$ vs Debye Temperature of metals in contact with graphene. For contacts of a metal/adhesion layer, the Debye temperature of the adhesion layer was used. [51–53]

Figure 4-4. Binary phase diagram for Ni-Pd alloys. The red line signifies the annealing temperature to be used in this study to explore any potentially interesting effects from the alloy FCC phase separating by being in a miscibility gap. Modified from [178].

Figure 4-5. Sample fabricated for high throughput measurements of $G_T$ as function of NiPd alloy composition, and Cr adhesion layer thickness (left). Measurements of $G_T$ represent the thermal junction composed of graphene and its two adjacent interfaces, highlighted by the red border (right).

Figure 4-6. Measurements of thermal conductance ($G_T$) as a function of Ni-Pd alloy composition and Cr thickness (colored lines) showed a peak at zero adhesion layer thickness and ~10 at. % Pd in Ni. Data for a second sample with no Cr adhesion layer (black squares) reproduced the
thermal trend from the original sample well. Extrapolation of $G_T$ data to pure Ni shows good agreement with Reference [51] values (black stars). Inset shows a fit of phase lag vs frequency data at the peak conductance.

Figure 4-7. High resolution TEM image of 10 at. % Pd in Ni directly in contact with graphene on SiO$_2$ where an enhancement of $G_T$ was observed.

Figure 4-8. High resolution TEM image of ~60 at. % Pd in Ni with a 2 nm Cr adhesion layer, directly in contact with graphene on SiO$_2$, where an enhancement of $G_T$ was not observed.

Figure 4-9. $I_D$-$V_D$ curves show that current saturation was not occurring at 200 mV bias. Channel lengths are defined by the legend.

Figure 4-10. $R_C$ data for ten linear TLM devices patterned onto the graphene. Atomic percent Pd in Ni is given in the legend. While prominent features were observed at the Dirac point, no trend with alloy composition was observed and devices of redundant alloy composition showed inconsistent $R_C$ results, indicating the presence of contaminants at the metal-graphene interface that were nonuniformly distributed between devices.

Figure 4-11. Ni thickness map (left), atomic percent Ni in Pd as shown by the colorbar (right) acquired from EDX analysis.

Figure 4-12. Identification of graphene nanoribbon areas for TLM devices by optical microscopy.

Figure 4-13. ES patterning process. a) Fiduciary metal markers (purple) were patterned onto the graphene sample. Nanoribbon locations used to define placement of ten TLM devices (red) where NiPd CSAF composition would vary in the horizontal direction. b) Graphene was etched away in the shaded green area by O$_2$ plasma, followed by an EBL patterning step to define the metal contacts (orange). c) Ni-Pd CSAF deposition and liftoff with magnified image of metal
contacting the graphene nanoribbon. d) Lower magnification image depicts where measurement probes would make contact to pairs of pads separated by each graphene channel of varying length. Images courtesy of Yanhao Du.

Figure 4-14. Thermal conductivity of the thin film CSAF determined from 4-point probe measurements. Literature values obtained from [188].

Figure 4-15. Resistance data across each channel length for device F8 as a function of back gate voltage. Forward and backward gate sweeps are shown.

Figure 4-16. Linear trends observed in $R$ vs channel length for device F10 at a backgate voltage (relative to the Dirac peak) of -4 V.

Figure 5-1. Polarization hysteresis loop defining ferroelectrics.

Figure 5-2. Perovskite structure of SrTiO$_3$ (top left), strain imposed by different substrates (bottom left), and effect of temperature and strain on ferroelectric state modified from [192] (right).

Figure 5-3. Minimal effect on thermal conductivity of oxygen vacancy concentration as correlated to oxygen pressure during deposition.

Figure 5-4. Demonstration of film thermal conductivity extraction at 175 K.

Figure 5-5. Total interface conductance as a function of temperature.

Figure 5-6. Thermal conductivity of SrTiO$_3$ on LSAT and DyScO$_3$. A sharp decrease in thermal conductivity is observed as the film becomes fully ferroelectric on the DyScO$_3$ substrate.

Figure 5-7. Estimation of FE domain sizes of SrTiO$_3$ on DyScO$_3$ as a function of temperature.

Figure 5-8. (Top) Diagram of material stack where $\kappa_{eff}$ describes the junction thermal conductivity extracted from fitting the solution to the heat diffusion equation to experimental phase vs frequency data (example-bottom).
Figure 6-1. PFM amplitude images of PbTiO$_3$ on SrTiO$_3$ with (a) and without (b) the SrRuO$_3$ buffer electrode. In (a) the film is entirely one FE domain, whereas in (b) the film has a chaotic distribution of domains of polarization either up or down.

Figure 6-2. PFM amplitude images of PbTiO$_3$ strained by epitaxial growth on (a) DyScO$_3$, (b) TbScO$_3$, (c) GdScO$_3$, (d) SmScO$_3$. In each case alternating layers of domains are shown by thinner striations within larger regions known as superdomains, an example of which is outlined in red in (d).

Figure 6-3. TEM imaging showing different Ti displacement directions in two different FE domains.

Figure 6-4. Cross sectional TEM imaging shows the angle of FEDWs for PbTiO$_3$ grown on DyScO$_3$ and GdScO$_3$.

Figure 6-5. Thermal conductivity and FEDW periodicity for PbTiO$_3$ as a function of strain. A top view schematic is provided to show the FEDW orientations for the film on each substrate.

Figure 6-6. Comparison of experimental data from this work to thermal conductivity accumulation functions of PbTiO$_3$ from DFT calculations [201,202]. Inset) Fitting to Equation 6.2 to calculate thermal resistance of FEDWs in PbTiO$_3$.

Figure 6-7. Data from PbTiO$_3$ films on SrRuO$_3$ buffer layer on SrTiO$_3$ substrate used to determine $R_{int}$. Thin black lines demarcate a 95% confidence interval of the fitted line.

Figure 6-8. Fits where red denotes the $R_{Tot}$ method and blue is the self-consistency check method on (a) on SrRuO$_3$/SrTiO$_3$ (b) on DyScO$_3$. 

xvi
List of Symbols/Abbreviations

- CSAF-Compositionally Spread Alloy Film
- CVD-Chemical Vapor Deposition
- DMM-Diffuse Mismatch Model
- DOS- Density of States
- EBL-Electron Beam Lithography
- EDX-Energy Dispersive Xray [Spectroscopy]
- ES-Electrical Sample
- FDTR- Frequency Domain Thermoreflectance
- FE- Ferroelectric
- FEDW-Ferroelectric Domain Wall
- $G, G_T$-Thermal Interface Conductance
- HAMR- Heat Assisted Magnetic Recording
- $k, \kappa$ -Thermal Conductivity
- PFM-Piezo Force Microscopy
- $R_C$- Electrical Contact Resistance
- $R_{Dw}$-Domain Wall Resistance
- SEM-Scanning Electron Microscope
- TEM-Transmission Electron Microscope
- TLM- Transmission Line Measurement, Transfer Length Measurement
- TS-Thermal Sample
- XPS-Xray Photoelectron Spectroscopy
- $\Theta_D$-Debye Temperature
- $\phi$- Ferroelectric domain size
- $\omega$-Phonon Frequency
- K- Phonon Wavevector
CHAPTER 1

Phonons and Frequency Domain Thermoreflectance

1.1 Fundamental Terminology

It is very common in doctoral work for new PhD students to make advancements on the work of previous PhD students. Doing so requires meeting their predecessors at the edge of what they had known before diving into the unknown. In that vein I aim to provide a simple orientation on a few fundamental terms from the nanoscale heat transfer community, in the form that I wished to have had at the start of my PhD. For further details I defer to the bibles of Kittel [1] and Chen [2], which are helpfully comprehensive reference materials but can be initially overwhelming when prescribed to new PhD students studying thermal transport.

To begin, imagine yourself standing at the front of a large lecture hall full of students before class has started. As the students wait for class to begin they naturally begin chatting with each other. What do you hear standing at the front of the room? Probably a dull roar of meaningless noise. But in actuality you know that it’s not meaningless. It’s actually made up of very meaningful conversations.

An analogy can be made to thermal energy in a material. If you were to look at the motion of the atoms in a solid at a given temperature, it would seem totally random and meaningless. However, the “random” motion of the atoms can be deconstructed into sinusoidal waves of different frequencies (like in a fourier transform), and in the same way the meaningless noise in the lecture hall can be deconstructed into different conversations. Each sinusoidal wave of its own characteristic frequency is described as a phonon mode. For a 1D chain of atoms represented as a mass spring system in Figure 1-1, where the atoms are the open circles and the springs connecting
them are shown in gray, the displaced atoms are shown in black, and the phonon mode is depicted in red. Atomic displacements perpendicular to the 1D line are referred to as *transverse modes* (as seen in Figure 1-1), and displacements along the 1D line are *longitudinal modes*. The spatial periodicity of the phonon mode is described by its *wavevector*, \( \mathbf{K} \). And although Figure 1-1 shows a snapshot of the phonon mode with respect to time, it will also have a temporal periodicity described by its *frequency*, \( \omega \).

![Figure 1-1. Chain of atoms with displacements representing a phonon mode.](image)

Referring back to the lecture hall analogy, there will be multiple people who have the same characteristic pitch, and similarly there will be multiple of each phonon mode in a given material. How many of each phonon mode exists in the material is described by a *phonon density of states*.

For a given material, the phonon density of states is determined from a *phonon dispersion*. A phonon dispersion essentially describes the relationship between the frequency and wavevector...
of each phonon mode in a material, for a given direction in wavevector space. An elucidating example derivation of a phonon dispersion can be found in Kittel [1]. An example phonon dispersion and density of states is depicted in Figure 1-2. As shown, two different materials will have different dispersions and phonon density of states (vibrational spectra).

![Figure 1-2. Phonon dispersion (left), and phonon density of states (right). Modified from [3].](image)

By understanding the nature of phonons and how nanoscale material systems can be designed to manipulate them, technologies can be engineered to exhibit desired thermal behaviors.

### 1.2 Frequency Domain Thermoreflectance

To experimentally study thermal transport at the nanoscale, the measurements described in this thesis were collected using the noncontact optical pump-probe technique of Frequency Domain Thermoreflectance (FDTR) [4]. Here an overview of the technique is provided, and specific FDTR parameters/fitting will be described in each chapter as relevant to each experiment.
Also contained in each chapter will be comparisons to other published experimental data, collected primarily using Time Domain Thermoreflectance (TDTR) [5–7], and 3-omega (3\(\omega\)) [8]. All three techniques are comparably appropriate for studying thermal transport in thin films and interfaces [9].

A schematic of FDTR is diagrammed in Figure 1-3. Two continuous wave (CW) lasers (Coherent Inc.) at 488 nm (blue) and 532 nm (green) serve as the “pump” and “probe. The CW blue pump laser has its intensity sinusoidally modulated by an electro-optic modulator at a frequency \(f_1\), in order to apply periodic heating to the sample’s surface, which is coated with a Au transducer layer. The Au transducer layer is used because it has a large change in reflectance in response to changes in temperature at our FDTR wavelengths [10], as quantitively described by the coefficient of thermoreflectance. The thickness of the Au layer is generally \(~70\) nm, so that it is thicker than the optical penetration depth of the pump and probe lasers [11], and therefore heating only occurs in the surface layer.
When the periodic heat flux is applied to the sample, a periodic temperature response is induced, with a phase delay that depends on the thermal properties of the sample and heating frequency. The property of thermoreflectance can be utilized to detect the periodic temperature response by reflecting the CW green probe laser from the Au surface, where the reflected beam is intensity modulated by the periodic reflectance profile. Collecting the reflected pump and probe beams with a photodiode allows a lockin (Zurich HF2) to determine the phase delay between the periodic heating and temperature response for each heating frequency. Heating frequencies used in my experiments were 30 logarithmically spaced points between 100 kHz and 5 MHz.
The phase versus heating frequency data are then fit to a solution of the heat diffusion equation for layered structures [7] where the unknown parameters in the solution include the thermal properties sought by the measurement. It is ideal to only be fitting to one parameter due to multiple combinations of parameters yielding fits with sufficiently small mean squared error. A representative fit is shown in Figure 1-4.

Using this technique provides a noncontact method to determine thermal properties in very thin films. This is possible because the thermal penetration depth \((L_p)\) of the technique makes the measurements sufficiently sensitive to the thermal properties of the thin films and their interfaces rather than being dominated by the thermal properties of the orders of magnitude thicker supporting substrates. \(L_p\) is mathematically described by Equation 1.1 and physically defined as the distance into the material that the temperature is \(e^{-1}\) of the surface temperature. An experimentally relevant example calculation gives the \(L_p\) into \(\text{Al}_2\text{O}_3\) [13] as \(\sim874\) nm at a heating frequency of 5 MHz.

\[
L_p = \sqrt{\frac{\alpha}{\pi f_1}} \quad 1.1
\]
CHAPTER 2

Thermal Interfaces at the Nanoscale

2.1 Introduction

Studying the interface between two materials sounds like it might be the most mind-numbing topic a doctoral dissertation could be written about, especially when transport dynamics are typically dominated by bulk materials rather than the interfaces between them, the latter of which have a negligible volume by comparison. However, you’d be wrong. Interfaces should NOT be underestimated because they become a significant resistance to thermal transport as device length scales shrink down to the nanometer regime. For example, comparing the Kapitza length (length of material providing an equivalent thermal resistance to the interface) of Si [14] in reference to an Al/Si interface [15] is ~1 um, orders of magnitude larger than the nanometer sized device the interface would belong to.

To further understand these thermal interfaces, this chapter will begin with an overview of existing scientific research on thermal transport across interfaces of various material systems, followed by a discussion of different technologies where the thermal engineering of these interfaces is critical. For a more comprehensive review of published research on thermal interface conductance ($G$; aka thermal boundary conductance symbolized as TBC or $h$; also referred to as Kapitza conductance) I defer to References [16–19] which were published as recently as 2019.

Developing an understanding/appreciation for the importance of thermal transport across interfaces is encouraged to all researchers in the nanosciences, as the lines between specific disciplines begin to blur at the nanoscale. The multidisciplinary challenges facing the next generation of higher performance nanotechnology will demand a better integration of these
communities through the inclusion of thermal management considerations into device architecture, as opposed to adding thermal management systems as an afterthought.

2.2 Scientific Research on $G$

The three types of thermal energy transport across interfaces can be described as being transmitted from electrons to electrons (metal-metal interfaces), electrons to phonons (some metal-nonmetal interfaces), and phonons to phonons (metal-nonmetal and nonmetal-nonmetal). These are denoted $G_{e-e}$, $G_{e-p}$, and $G_{p-p}$.

Phonon to phonon energy transfer across interfaces is far more thermally resistive than electron to electron energy transfer [19]. In regards to $G_{e-p}$, the dominant perspective is that it is not significant across metal-nonmetal interfaces according to experimental evidence where metals and semimetals of similar vibrational spectra had similar $G$ to a diamond substrate [20,21]. However, first principles work on TiS$_2$/Si has argued that electron-phonon interactions between the metal and nonmetal provide an equal contribution to $G$ as phonon-phonon interactions [22]. Thus the current conclusion is that whether $G_{e-p}$ makes a significant contribution depends on the specific interfacial materials and the value of the volumetric electron-phonon coupling coefficient between the metal’s electrons and nonmetal’s phonons [23].

2.2.1 $G_{p-p}$ at vibrationally mismatched surfaces

The thermal energy carriers across metal/nonmetal and nonmetal/nonmetal interfaces are primarily phonons [22–24], due to a lower concentration of free electrons in dielectrics and semiconductors. Predictions of $G_{p-p}$ can be made using the following general equation, derived
from a calculation of the phonon flux across an interface with the simplifying assumption that both materials of the interface have isotropic phonon dispersions [25],

\[ G_{p-p} = \frac{1}{8\pi^2} \sum_j \int_{\omega_{j,A}} (\hbar \omega_{j,A}) (K_{j,A}^2) (\zeta^{A\rightarrow B}) \left( \frac{\partial n}{\partial T} \right) d\omega_{j,A} \]  

(2.1)

where the integral is taken for each phonon of frequency \( \omega \) within material A with polarization \( j \), \( \hbar \) is the reduced Planck constant, \( K_{j,A} \) is the phonon’s wavevector, \( \zeta^{A\rightarrow B} \) is the transmission coefficient (i.e. the phonon’s probability of transmission from A to B), and \( \frac{\partial n}{\partial T} \) is the partial derivative of the Bose-Einstein distribution with respect to temperature. While this representation takes the integral with respect to phonon frequency [26], it is also common to see this formulation in literature described with respect to phonon wavevector [24,25].

A fundamental limitation of this formulation is that it is inappropriate for interfaces between materials that are perfectly vibrationally matched. For example, if an imaginary interface were created by drawing a plane within a perfectly crystalline material, \( G_{p-p} \) should be infinity but the \( G_{p-p} \) calculated by Equation 2.1 gives a finite value. Such a scenario of perfect vibrational matching is observable at interfaces such as grain boundaries and the boundaries between ferroelectric domains (regions of changing polarization in a ferroelectric material). And so while this formulation is not a good analytical predictor of phonon transport in these kinds of interfaces, other more suitable approaches have been published in literature, such as Molecular Dynamics (MD) and theoretical modeling [27–33].

The description of transport across the interface is captured in the term \( \zeta^{A\rightarrow B} \). The two major analytical models deriving expressions for \( \zeta^{A\rightarrow B} \) are the Acoustic Mismatch Model (AMM)
and the Diffuse Mismatch Model (DMM). The distinguishing feature between them is that the AMM is more appropriate at temperatures below 30 K because the phonons excited at these temperatures have wavelengths longer than the roughness of the interface. Therefore, the interface can be treated as a plane where the phonons scatter specularly. Contrast this with the DMM where interface roughness does come into consideration and phonons are scattered diffusely, with no memory of their incoming polarization and trajectory after scattering at the interface [25,34].

Since most thermal transport applications are above 30 K, here I will focus on the DMM. For the DMM, there have been multiple formulations of $\zeta^{A\rightarrow B}$ [25,35,36] with different simplifying approximations and whether the scattering is elastic (phonon frequency is conserved) or inelastic. For phonon transport across metal/nonmetal interfaces, it is commonly assumed that scattering is elastic [24,26] and $\zeta^{A\rightarrow B}$ is defined as

$$\zeta^{A\rightarrow B} = \frac{\sum [K_{jB}(\omega)]^2}{\sum [K_{jB}(\omega)]^2 + \sum [K_{jA}(\omega)]^2}. \quad (2.2)$$

For frequencies larger than the lower of the maximum phonon frequency (aka the cutoff frequency) common to the two materials, $\zeta^{A\rightarrow B} = 0$. The closer the cutoff frequencies are between two materials, the more phonons will participate in transporting heat across the interface and the higher $G$ will be. This point is depicted in Figure 2-1 where the overlap between DOS in materials A and B can be seen in Figure 2-1b and the shaded area in red denotes non-participating phonon frequencies in elastic collision processes.
The cutoff frequency for a material is characterized by its Debye temperature ($\Theta_D$) [37]. The difference in maximum phonon frequencies (and therefore $\Theta_D$) between the two materials essentially describes the vibrational mismatch between them, and with the right thermal engineering design-choices presents an opportunity to improve $G_{p-p}$.

One of the major approaches to improve $G_{p-p}$ is through better vibrational matching by thermal bridging. Thermal bridging is the insertion of an intermediate layer ($M_C$) between two materials ($M_A$ and $M_B$) where the intermediate layer material has phonon density of states that overlap with each of its neighbors better than they do with each other. This enhances thermal transport because the better the overlap between two materials, the more conduction channels available to a particular phonon with a frequency that falls in the overlap region, assuming that transmission across the interface is still an elastic scattering event [3].

Figure 2-1. Simulated phonon dispersion (left) and DOS (right) for two materials where the overlapping region in the DOS defines the available conduction pathways for a phonon transmitting across the interface. Reproduced with permission [3].
Achieving significantly higher $G_{p-p}$ through the addition of an intermediate metal layer has been demonstrated experimentally. As shown in Figure 2-2, in the work of Jeong et al. it was demonstrated that adding as little as 1.5 nm of Cu and Cr resulted in a two and four-fold increase in $G$ between Au and Al$_2$O$_3$, respectively. While the introduction of an intermediate metal layer does add an additional interface to thermal transport, heat is primarily carried by electrons between the metals and so that thermal resistance is small [24]. Enhancement was also shown for a Ni adhesion layer inserted between Au and Al$_2$O$_3$, where better electron-phonon coupling improved $G$ by providing another channel for energy transfer, in addition to the better vibrational matching mechanism [38].

![Figure 2-2](image)

Figure 2-2. Experimental enhancement of $G$ between Au/Al$_2$O$_3$ through adhesion layers. Reproduced with permission [24].

Other factors besides vibrational matching that influence $G$ are interfacial bonding strength and roughness. The relative effect of each varies with the material system involved. For example, O’Brien et al. demonstrated that inserting a nanomolecular monolayer between SiO$_2$ and either Au
or Cu more than doubles $G$ due to improved interfacial bonding, despite higher vibrational mismatching [39]. Additional MD and experimental evidence of significantly higher $G$ through better bonding have also been observed [40–42]. On the other hand, interfacial roughening has been demonstrated to decrease $G$ [43,44]. This point is further elucidated in Figure 2-3 for different metals on commonly used nonmetallic substrates where the $\theta_D$ of the substrate is listed in the legend. As can be observed, better $\theta_D$ matching generally leads to higher $G$, but with mixed success. For example, a wide spread in $G$ can be observed for different studies involving Al on Al$_2$O$_3$ and diamond.

![Figure 2-3. Thermal interface conductance between metals in contact with nonmetal substrates plotted against metal Debye temperature. For studies involving a metal intermediate layer sandwiched between a metal and nonmetal, the $\theta_D$ of the intermediate layer was used for the horizontal axis. [15,24,26,45–48]](image-url)
2.2.2 Interfaces between 3D and 2D materials

Despite 2D materials like graphene having exceptionally high thermal conductivity [49], one of the major challenges in thermal transport involving such materials is getting heat into and out of them (across their interfaces). A review of published $G$ for different metals on single layer MoSe$_2$ or graphene on SiO$_2$ are shown in Figure 2-4 [50–54]. Inspection of this data clearly shows that $G$ is not as sensitive to Debye temperature matching as 3D metals/nonmetals from Figure 2-3. These data were all collected using the experimental technique of Time Domain Thermoreflectance (TDTR), a similar pump-probe technique to FDTR.

It is worth noting that this area of research is still relatively young, hence the experimental data presented in Figure 2-3 for metals on single layer 2D materials on SiO$_2$ substrates (for the fairest comparison) is limited to MoSe$_2$ and graphene, but future studies can expand this dataset to include other 2D materials like MoS$_2$, WS$_2$, WSe$_2$, etc. [55].
Publications concerning 2D materials thermally interfacing with 3D materials specific to theory [56–59] and molecular simulations [19,60–62] have primarily focused on nonmetal substrates instead of metal contacts for the 3D material, but have made important contributions to our understanding of how 2D materials interact with their neighbors. For example, the extremely high in-plane thermal conductivity of suspended graphene results from a surprisingly large contribution by out of plane flexural phonon modes [63], which have suppressed contributions when the graphene is supported due to strong interactions with the supporting substrate [64].
Simulations of even lower dimensional materials have also raised interesting questions about 2D/3D interfaces. For example, using MD and the wave packet method, Shi et al. [65], demonstrated that phonon transport from a 1D carbon nanotube to a 2D graphene sheet is attributable to elastic scattering with mode conversion. It is worth noting that the 1D/2D interface may be elastic due to the sparsely peaked nature of a 1D material’s DOS and so applying this method could lead to interesting phenomena in 3D/2D interfaces where the DOS are not as sparsely peaked in phonon frequency.

2.3 Importance of Thermal Interfaces in Nanotechnology

2.3.1 Plasmonics-HAMR

Plasmonics are electronic devices that rely on the manipulation of plasmons, the collective excitation of electrons. One of the major technological challenges in plasmonics is thermal stability [66]. In the worst-case scenario, temperatures can reach the melting temperatures of the metals resulting in a critical failure of the technology. For example, in Heat Assisted Magnetic Recording (HAMR) shown in Figure 2-5, surface plasmon polaritons are generated on the surface of a gold nanostructure called a Near Field Transducer (NFT) and migrate to the bottom of the NFT’s stem in order to deliver very focused heat to an underlying magnetic media where data storage occurs. However, the temperature of the NFT can become so high during this process that the structure melts, irreversibly destroying the device. Hence it is critical to dissipate the heat generated in the NFT into the surrounding dielectric media, but a bottleneck thermal resistance can be found at the interface between them [67]. Therefore, thermal engineering of the interface for sufficient heat dissipation is crucial to this technology.
2.3.2 3D Architectures/Device Stacking

A very promising direction for the future of electronics is vertically stacking devices. With the shrinking of transistors in accordance with Moore’s law, intra-node lengths are becoming short enough for quantum tunneling effects to leak current in the device’s OFF state and become severely detrimental to performance. If devices cannot be further shrunk within the plane of the wafer, then the obvious strategy to increase computing density is through vertical integration. Vertical stacking has already seen implementation, where the Package on Package (PoP) method
has been stacking memory chips onto logic chips. Since both components are constantly intercommunicating, vertical integration results in significant leaps in performance [70].

One of the major roadblocks to vertical integration is dissipating the heat generated within the stack. Due to the high density of interfaces, 3D integration is a field where optimization of interfacial thermal transport will have a significant impact on achieved performance [71]. More specifically, within vertically integrated packages the majority of the thermal energy is transferred from chip to chip via metal interconnecting solder bumps. Hence, the type of thermal interface of interest is metal/nonmetal (solder bump/chip) and overcoming this thermal bottleneck would increase the limits on the number of chips that can be stacked together [70].

2.3.3 Memristors

Memristors [72] take the advantages of device stacking CPUs and memory one step further by integrating their functionality into one device, and are a low power consuming alternative to traditional CMOS architectures. Furthermore, memristors are non-volatile (they do not lose their memory state when power is cut to the device). Hence, memristors could supplant technologies like DRAM (dynamic random-access memory) which require a long bootup process when power is restored as information is transferred from the hard drive back to memory.

Publication on the first memristor occurred in 2008 [73,74] at Hewlett Packard. The original device sandwiched TiO$_2$ between Pt electrodes as depicted in Figure 2-6. The TiO$_2$ layer consisted of two regions, one doped with a high concentration of oxygen vacancies and one without. As an electric field was applied across the TiO$_2$ layer, the charged oxygen vacancies drifted toward the Pt electrode on the undoped side. When the oxygen vacancies reached the Pt electrode, a conductive channel had been formed between the electrodes effectively shorting the
device and putting it into its ON state. When the electric field polarity was reversed, the oxygen vacancies migrated in the opposite direction, disconnecting the conductive channel and putting the device into its OFF state.

Figure 2-6. Simplified model of the oxygen vacancy migration in the first memristor.

Due to the dependence of oxygen vacancy diffusivity on temperature, thermal transport plays an important role in memristor performance. In the analytical modeling work of Singh et al. a 33% reduction in switching delay time was calculated when the operating temperature of a TiO$_2$ memristor was increased from 200 K to 400 K [75]. MD simulations by the team that invented the memristor at Hewlett Packard also showed that elevated temperatures aid vacancy diffusion, but additionally showed that a competing effect appears in that localized temperature gradients can disrupt the conductive oxygen vacancy filament and make device performance unstable [76]. Considering these memristor devices are at the nanoscale, the thermal conductance of the interface between the metal electrode and oxide plays a significant role in device performance. For example,
in a sub-nanosecond switching memristor that included a 7 nm tantalum oxide layer [77] the Kapitza length for tantalum oxide [78] using an Al/Al₂O₃ interface [15] (experimental metal/TaOₓ G data was unavailable) is ~15 nm (about twice the oxide thickness) and varies with the oxygen concentration of the oxide film.

2.3.4 2D Devices

After the isolation of mechanically exfoliated graphene by Geim and Novosolev in 2004 [79], 2D materials emerged as a thrilling new frontier in nanotechnology development. With record breaking measurements of thermal conductivity [49,80], electron mobility [81] and exciting optical properties [82] all within a single atomic layer of carbon atoms, graphene in particular was expected to revolutionize the electronics industry. However, graphene’s unique properties also brought major engineering challenges like: the lack of a bandgap has made it incompatible for applications of digital logic, there have been difficulties in scaling-up material fabrication while maintaining industrial quality standards, and contact conductance has remained inadequate for certain high-performance applications [83]. While the research community has expanded into other 2D materials like transition metal dichalcogenides in order to circumvent the first two challenges, contact engineering remains critical to achieving low electrical resistance and dissipating the heat that negatively affects performance [84]. The importance of adequate heat dissipation in 2D materials has been demonstrated by Islam et al. [85]. Islam’s simulated current saturation data due to self-heating of a graphene field effect transistor (GFET) are shown in Figure 2-7. As current flows through the device, joule heating reduces the device’s current saturation limit. Evidence of heating effects have also been experimentally observed where hotspots appear
in graphene through device operation and must be dissipated primarily out of the contacts as the device’s footprint on the supporting substrate shrinks in smaller devices.

![Image](image.png)

Figure 2-7. a) Schematic of a graphene field effect transistor. B) Reduction in current saturation due to joule heating in the device and hence the importance of heat dissipation out of the channel into the substrate and contacts, the latter of which becomes more important as the device footprint shrinks. Reproduced from [85].

### 2.4 Integrating Thermal Research into Device Applications

In Section 2.3 it was shown how thermal interfaces can have major impacts on the performance of future nanotechnologies like plasmonics, 3D devices, memristors and 2D devices. Although the research presented in Section 2.2 can inform design choices to alleviate detrimental thermal effects in these technologies, it is important to consider how well the benefits claimed in research will actually be realized when implemented into devices under operating conditions. Furthermore, optimizing performance in these technologies will entail identifying unique solutions that improve all relevant properties to device performance (electrical, thermal, and optical), or at
a minimum consideration of how certain design choices may have competing effects on different properties and how that would affect performance.

For example, in HAMR, 3D architectures, and memristors, enhancement of $G$ between metal-nonmetal interfaces could be achieved by inserting very thin layers of metals at the interface with better vibrational matching to the nonmetal. However, as joule heating occurs through the device’s operation and its temperature is elevated, enhanced interdiffusion would be expected between the metals. This raises the question, as the interdiffusion process occurs how will $G$ be affected? One of the most relevant experimental works was conducted by Hopkins et al. [86] and showed that $G$ decreases as the mixing layer thickness increases at a Cr/Si interface, but the effect of metal interdiffusion on $G$ in conditions that are technologically representative have yet to be studied and major questions remain. How will the enhancement in $G$ decay? Will enough unalloyed metal from the intermediate layer remain at the interface to observe a relatively prolonged enhancement in $G$?

It is important to remember that insertion of intermediate layers to improve $G$ also affects other properties related to device performance. Therefore, effects on all properties must be considered simultaneously. In HAMR for example, while the insertion of Cr or Cu would improve thermal conductance between the vibrationally mismatched Au and dielectric media, the potential tradeoff to consider is how the extinction length of the surface plasmon polaritons (SPP) on the Au would be affected, which is crucial to the core functionality of the technology. In the work of Chow and Bain [87], it was shown that inserting 1.2 nm of Cr at a Au/SiO$_2$ interface reduced the SPP propagation distance by 80% whereas Cu had very little effect on propagation distance due to its similar plasmonic properties to Au.
This multidisciplinary optimization is especially a limitation in 2D devices where one of the major hurdles to achieving high performance is insufficiently low electrical contact resistance; performance that will be made worse by poor thermal contact conductance. Fortunately, there are opportunities to co-optimize both by considering the study of alloys. Most research has been limited to pure metals, leaving the alloy design space as a relatively unexplored frontier. With alloys comes the possibility of finely tuning alloy composition, which will affect the interaction of the metal with the 2D material and could have different effects on phonon and electron transmission across the interface. This opens the possibility of using alloy composition to finely tune tradeoffs in thermal and electrical conductance to optimize performance for the specific 2D device application.

While the applications discussed thus far have viewed high thermal interface resistances as an obstacle to be overcome, are there applications where low $G$ can be positive? As shown in the work of Ihlefeld, *et al.* [88] active control of thermal interfaces can be achieved in ferroelectric materials to dynamically tune thermal conductivity and realize the thermal circuit element of a switch. The interfaces involved in achieving this were ferroelectric domain walls (FEDWs) which are the boundaries between regions of the material with different polarization direction. In Ihlefeld *et al.*’s work, the switching ratio achieved was limited to ~11% leaving the thermal community to wonder how much better thermal switching is possible? Furthermore, exactly how important are FEDWs to changes in thermal conductivity, since the interfaces are perfectly smooth and the materials across the interfaces are vibrationally identical?

It is the objective of this thesis to address each of these questions. This will be achieved through our study on interdiffusion in a Au/Cu bilayer and its effect on $G$ at the metal-Al$_2$O$_3$ interface. Additionally, we leveraged our experimental data to provide thermal engineers an
analytical model to predict interdiffusion, which we connected to the DMM to predict the effect on $G$ in order to help inform their device design choices. We also explored the alloy design space of thermal and electrical contacts on graphene, where we reproducibly demonstrated a peak in $G$ using a specific Ni-Pd alloy composition. This particular work also defined a new frontier in 2D material contact research where prior literature has been limited to pure metals. Finally, we demonstrated the potential for the thermal interfaces of FEDWs in strain engineered single crystal ferroelectric SrTiO$_3$ and PbTiO$_3$, which could be used for active control of thermal conductivity and would have potential applications in higher performance thermal switches than the current state of the art.

From a broader “big picture” perspective, it is through experimental investigations of interfaces in such a diverse set of materials that this dissertation aims to advance the sciences of interfacial thermal transport within the context of exciting nanotechnology applications.
CHAPTER 3

Interdiffusion of Adhesion Layers on Thermal Interface Conductance

3.1 Overview

The first systematic measurements on the impact of interdiffusion between a metal overlayer and adhesion layer, on the thermal interface conductance ($G$) at the metal bilayer-dielectric interface are reported. Composition depth profiles quantify the interdiffusion of a Au-Cu bilayer as a function of Cu adhesion layer thickness (0-10 nm), annealing time, and annealing temperature. Optical pump/probe measurements of $G$ quantify the effect of Au-Cu interdiffusion on thermal transport across the (Au-Cu)-$\text{Al}_2\text{O}_3$ interface. The enhancement of $G$ between Au and $\text{Al}_2\text{O}_3$ through the addition of a Cu adhesion layer decreases as Au-Cu interdiffusion occurs. For example, annealing a 41 nm Au film with a 4.7 nm Cu adhesion layer on $\text{Al}_2\text{O}_3$ at 520 K for 30 minutes, results in a 52 ±16% drop in $G$. An analytical model of the composition profile is derived with inputs of annealing time, temperature dependent permeabilities of the Au-Cu interface to each species, and the initial thicknesses of the Au and Cu layers. Integrating this model with a Diffuse Mismatch Model defines a new methodology for the prediction of $G$ that accounts for interdiffusion in metal bilayers on dielectric substrates, and can be used to evaluate the degradation of $G$ over a device’s lifetime.

Impact of Metal Adhesion Layer Diffusion on Thermal Interface Conductance,
3.2 Introduction

As increasingly complex electronic device architectures are developed, sufficient heat dissipation becomes ever more challenging. For example, in the field of 3D integration, device stacking leads to a high density of material interfaces, each of which can contribute a significant resistance to heat transfer [71]. In devices where these are metal-semiconductor or metal-dielectric interfaces, thermal transport is primarily a function of phonon transmission because the free electron density is low on the dielectric (or semiconductor) side of the interface [22–24].

Jeong, et al. showed that the insertion of metal adhesion layers which have a higher phonon density of states overlap with the dielectric than the overlayer metal’s overlap, significantly enhance thermal interface conductance ($G$) between the metal and dielectric [3,17,24]. Adding as little as 1.5 nm of Cu between Au and Al$_2$O$_3$ roughly doubles the value of $G$ with respect to that of Au-Al$_2$O$_3$. In comparison, Freedman et al. showed that at Au$_x$Cu$_{1-x}$-Al$_2$O$_3$ interfaces, the value of $G$ decreases as the Au content, $x$, increases [26]. While those two works quantify $G$ at the extremes of interdiffusion (no interdiffusion and complete interdiffusion), it is unknown how an intermediate value of interdiffusion would affect $G$, despite its potential to compromise the thermal benefits of adhesion layers over the lifetime of a device.

While there are pre-existing measurements on the effect of different metal compositions on $G$, [86,89,90] the outstanding research questions that this work addresses are how temperature treatment affects the interdiffusion of metal bilayer films on dielectric substrates, and how this interdiffusion affects $G$. Our experiments focus on interdiffusion of the Au-Cu adhesion layer system, and are compared to several published studies [91–95].

We report x-ray photoelectron spectroscopy (XPS) depth profiles and optical pump/probe measurements of $G$ for Au-Cu thin films of different Cu thicknesses that have been annealed at
temperatures in the range 320 K to 520 K for a period of 30 minutes. These data reveal how annealing temperature and Cu thickness affect the metal bilayer interdiffusion profiles and the subsequent effect on $G$. An analytical description is derived for the interdiffusion profiles as a function of time, temperature, and initial film thickness in thin Au-Cu bilayer films, and used as input to a Diffuse Mismatch Model (DMM) in order to predict $G$.

### 3.3 Results and Discussion

#### 3.3.1 Cu and Au film thickness

In order to investigate the effect of adhesion layer thickness on interdiffusion, two samples were fabricated with Cu wedges ($0 – 25$ nm in thickness) deposited on Mo and Al$_2$O$_3$ substrates and then covered them with a uniform film of Au ($\sim 40$nm). We then characterized the thicknesses of the Cu and Au layers using Energy Dispersive X-Ray (EDX) spectroscopy.

Figure 3-1 shows the lateral thickness distribution of the Cu adhesion layer across a 12 × 12 mm$^2$ area grid with 1 mm spacing, centered on the 14 × 14 mm$^2$ Al$_2$O$_3$ substrate. The maximum thickness of the Cu wedge was $23 \pm 1$ nm, and decreased linearly to zero across a distance of $\sim 6$ mm. The thickness of the uniform Au layer on top of the Cu wedge was $49 \pm 2$ nm.
The second sample was prepared on a Mo substrate in order to enable XPS depth profiling to study the interdiffusion between Cu and Au. The EDX map of the Cu film thickness deposited onto the Mo substrate is shown in Figure 3-2. Figure 3-2 shows the lateral thickness gradient of the Cu adhesion layer measured on a $10 \times 10$ mm$^2$ grid with 2 mm spacing, centered on the $14 \times 14$ mm$^2$ Mo substrate. The maximum thickness of the Cu wedge reaches $25 \pm 1$ nm, and decreases linearly with position to zero. The uniform thickness of Au was determined to be $39 \pm 1$ nm.

### 3.3.2 XPS depth profiles of annealed Au-Cu-Mo interfaces

Depth profiles of the Au-Cu bilayer film on Mo were obtained at various Cu thicknesses and after annealing the sample at temperatures in the range 320 K to 520 K. During depth profiling of multicomponent films, the surface composition measured by XPS can be influenced by the different Ar$^+$ sputtering rates for the individual alloy components [96–100]. This resulted in measured surface compositions that differ from the bulk composition [100–102]. During depth profiling of Au-Cu bilayers, the sputtering depth and the bulk composition at each depth were extracted from the XPS measured surface compositions and the calibrated Ar$^+$ sputtering rates for each component [103–105].

![Figure 3-2. Contour map of the Cu adhesion layer thickness as measured using EDX at 36 points (black dots) across the Au-Cu film on Mo.](image)
XPS depth profiles were obtained at four Cu thicknesses (25, 18, 8, and 0 nm) on the Au-Cu-Mo substrate to observe the interdiffusion between Au and Cu as a function of annealing temperature and time. XPS depth profiles measured at a Cu thickness of 8 nm are shown in Figure 3-3. Au, Cu, and Mo composition profiles were measured for the as-deposited bilayer and after each 30 minute vacuum anneal of the same sample at the temperatures of 320 K, 360 K, 440 K and 520 K. For the as-deposited film, the interdiffusion between Au and Cu is negligible at room temperature [106,107]. However, the width of the Au-Cu interface observed from the XPS depth profiling appears to be ~ 10 nm. This may arise for two reasons: (1) the momentum transfer induced by Ar$^+$ ion sputtering in the collision cascade region can result in atomic mixing of surface atoms; (2) the non-uniformity of the Ar$^+$ beam rastering across the 1 mm$^2$ sputtering area results in non-uniform rates of material removal. Experimental support for (2) can be seen in Figure 3-3 which reveals Mo signal at a depth of 35 nm, significantly shallower than the nominal combined metal film thickness of 47 nm. XPS profiles of the bilayer film obtained after heating at temperatures of 320 K and 360 K for 30 minutes were very similar to those obtained from the as-deposited film, indicating negligible interdiffusion of Au and Cu at temperatures ≤360 K. However, after annealing at 440 K, Cu had crossed the Au-Cu interface, and was uniformly distributed throughout the Au layer to form a Au-Cu alloy with an average of 8 at.% Cu. Subsequent annealing at 520 K for 30 minutes resulted in Au and Cu becoming completely interdiffused; forming a homogenous alloy with an average composition of 25 at.% Cu.
The uniform distribution of Cu in the Au rich region was also seen in the composition profiles generated by Rutherford backscattering spectrometry, performed by Aleshin et al. in their vacuum annealing experiments over the temperature range of 448 K to 523 K [92]. They attributed their profiles to grain boundary diffusion and we hypothesize that the same mechanism is at work in our films.

Interestingly, the XPS data of Figure 3-3 shows a buildup of Cu at the surface of the Au film after diffusing through the Au layer during heating at 440 K for 30 minutes. The same phenomenon was observed in the depth profiles at points on the sample with initial Cu thicknesses
of 18 and 25 nm and can also be seen in Figure 3-4. This observation is consistent with the experimental results of Aleshin et al. [92] and the surface accumulation work of Hwang et al. [108].

3.3.3 Heating time effect on interdiffusion

Figure 3-4. XPS depth profiles measured at 20 nm Cu thickness and 46 nm Au thickness, where Cu, Au, and Mo through-plane composition measured as a function of Ar+ sputtering depth (nm) on the film for as-deposited, after annealing at 460 K for 20 minutes, 60 minutes, and 240 minutes, and finally at 520 K for 20 minutes.

Once it was determined that 460 K was the heating temperature at which small amounts of diffusion occurred, a second set of experiments were conducted on a new sample to examine the heating time effect on the extent of diffusion after annealing at a fixed temperature 460 K. The XPS depth profiles were performed at five EDX characterized Cu thicknesses which are 28, 25, 20, and 0 nm. Figure 3-4 shows XPS depth profiles measured at 20 nm Cu thickness and 46 nm
Au thickness, where Cu, Au, and Mo through-plane composition have been measured as a function of Ar⁺ sputtering depth on the film for as-deposited and after annealing at 460 K for 20, 60, and 240 minutes.

Cu uniformly distributed into the Au layer with increasing Cu atomic percentages of 11.2, 18.2, and 23.1 with respect to each heating time. In addition, Cu atoms diffuse much faster into the pure Au layer compared to the diffusion rate of Au atoms into the Cu layer.

3.3.4 Quantification areal surface composition and total sputtering depth

In the Au-Cu binary system, the real composition was corrected from XPS measured surface composition by Equation 3.1 [103–105].

\[
\frac{C_{\text{Cu}}}{C_{\text{Au}}} = \frac{C_{\text{Cu}}^S}{C_{\text{Au}}^S} \times \frac{r_{\text{Cu}}}{r_{\text{Au}}} \tag{3.1}
\]

where \(C_i\) and \(C_i^S\) are the real composition and the surface composition for component \(i\), respectively, and \(r_i\) is the sputtering rate for component \(i\). Here \(\eta_i\) is constant and independent of composition. The Ar⁺ sputtering rate for each component was calibrated on pure Cu and Au thin film with known thicknesses, and were calculated to be 1.05 nm/s (Cu) and 1.75 nm/s (Au) at the same experimental conditions as described in Section 2.3. These calibrated Ar⁺ sputtering rate for Cu and Au are comparable with literature values for pure metals [109]. The total sputtering depth (\(r_{\text{total}}\)) can also be calculated by knowing the Ar⁺ sputtering rate and XPS surface composition for individual components using Equation 3.2 [103,110,111].

\[
r_{\text{total}} = r_{\text{Cu}}C_{\text{Cu}}^S + r_{\text{Au}}C_{\text{Au}}^S \tag{3.2}
\]
3.3.5 Thermal Interface Conductance

Using the laser pump/probe technique, Frequency Domain Thermo-Reflectance (FDTR) [112,113], $G$ was measured as a function of adhesion layer thickness and annealing temperature. Measurements of $G$ on the as-deposited film are shown in Figure 3-5 and agree within the uncertainty of the measured values reported by Jeong et al. [24]. As expected, $G$ rapidly increases as the thickness of the Cu adhesion layer increases from zero, and saturates at higher thicknesses (~4 nm of Cu). According to Jeong et al.’s model validated for both Cr and Cu adhesion layers, short wavelength phonons from Cu dominate thermal transport across the metal-dielectric interface. As thickness increases in the thin Cu region, longer wavelength phonons that also contribute to $G$ arise within the film. At higher Cu thicknesses, the additional long wavelength phonons have low density of states and thus contribute little to $G$ causing it to flatten out, as seen in Figure 3-5.

![Figure 3-5](image.png)

*Figure 3-5. Measurements of $G$ vs Cu adhesion layer thickness for the films as-deposited, and after subsequent heating to 360 K, 440 K, 460 K, 480 K, and 520 K for 30 minutes. The values of $G$ for the as-deposited films are within the error of literature values for pristine films [24]. Values of $G$ after annealing at 360 K are similar to those for the as-
A significant decrease in $G$ occurs after annealing at 440, 460, and 480 K. At 520 K, $G$ has reached its minimum, in good agreement with the literature values for a fully intermixed alloy [26].

After annealing at 360 K, $G$ is similar to that of the as-deposited multilayer films. This is consistent with the depth profiles of Figure 3-3 which show that there is negligible interdiffusion of the Au and Cu layers after annealing at 360 K. After annealing at 440, 460, and 480 K, the values of $G$ are notably lower than those obtained from the film annealed at 360 K. While the XPS data of Figure 3-3 shows that Cu diffuses into the Au, it is unclear from this figure whether Au is diffusing into the Cu region. Au diffusion into Cu is seen more clearly in Figure 3-4, where Au increasingly diffuses into the Cu as a function of annealing time. We hypothesize that this diffusion of Au into the Cu region is responsible for lowering $G$. This hypothesis was founded on the work of Freedman et al. which showed that at Au$_x$Cu$_{1-x}$Al$_2$O$_3$ interfaces, the value of $G$ decreases as $x$ increases [26]. Further comparison to Freedman’s work can be made since Figure 3-3 shows that our films are fully intermixed after annealing at 520 K. Using the as-deposited Au and Cu film thicknesses in our samples, the atomic fraction of Au was calculated and the values of $G$ from Freedman’s model at these concentrations were used to plot the open squares in Figure 3-5. The two sets of data (open squares and solid maroon squares) are in good agreement with one another, further corroborating that complete interdiffusion between Cu and Au has occurred at 520 K.
3.4 Modelling

In order to extend the use of our experimental data for thermal engineers to predict $G$ for other metal thicknesses and annealing temperatures, a simple composition model with an analytical solution has been developed and integrated with the Diffuse Mismatch Model to predict thermal interface conductance.

3.4.1 Interdiffusion Composition Modelling

Classical solutions to Fick’s Second Law for diffusion couples and thin films were inappropriate to model our composition profiles because their solutions are complimentary error functions and Gaussians, respectively, that decay to fixed boundary compositions far from the interface [114–117]. In contrast, the nature of diffusion in our thin films leads to uniform concentrations with boundary values that change as a function of annealing conditions. Specifically, Figure 3-3 clearly reveals that once the Cu atoms have crossed the Au-Cu interface, they distributed uniformly across the Au layer and Figure 3-4 indicates that when Au diffused across the Au-Cu interface, it could also be approximated to have a relatively uniform distribution across the Cu region. Relevant literature [118–125] were unable to represent these regions in our data.

Aleshin et al. [92] observed similar profiles, and suggested that diffusion along grain boundaries is the operative mechanism within the films. While Figure 2 and 3 of Aleshin’s work exhibited some uniform composition distributions similar to our data, their Au concentration in Cu decayed to zero and their Cu concentration in the Cu rich region maintained the initial concentration value, whereas ours did not. These differences prevent us from using the Whipple solution [119] to the Fisher model [118] and the Gilmer and Farrell solution for grain boundary
diffusion [126,127] as they did. These differences in composition profiles can be attributed to the thicknesses of their films: 200-250 nm of Cu and 45-70 nm of Au (Au diffusion in Cu study), and 800 nm of Cu and 60-120 nm of Au (Cu diffusion in Au study), whereas our Au was 45 nm and our Cu thickness ranged from 0-25 nm. For our thicknesses, interactions with free surfaces and substrate interfaces can be important [128]. Our bilayers can be best described as undergoing Type C grain boundary diffusion kinetics (diffusion along the grain boundaries dominate over diffusion from the grain boundary into the adjacent grains) [128,129] between two instantaneous sources (both films are too thin for either to be treated as semi-infinite) [130]. An approximate analytical solution has been described in the work of Hwang et al. [108,130–132], but also requires the assumption that the solute spreads along the surface after exiting the solvent, as is common in surface accumulation diffusion measurement techniques, but not observed in our Au diffusion into Cu data. This solution may be appropriate for modelling our data for Cu diffusion into Au, but would require additional details of the dimensions of the grain boundaries and Cu segregation factor at the interface.

Seeing that solutions presented in the literature were not well suited to describe our composition data, we derived a simple mass diffusion model in which spatial gradients in composition on either side of the Au-Cu interface are approximated to be zero and therefore, the major resistance to interdiffusion is at the interface itself, as depicted in Figure 3-6. This model is only applicable for materials where thicknesses are smaller than diffusion length scales, Type C kinetics are occurring, and the concentration of the uniform composition regions away from the bilayer interface are changing as a function of annealing time/temperature.
Figure 3-6. Depiction of interdiffusion in the metal bilayer where Cu is deposited on a dielectric and capped with Au. According to this schematic, as Cu diffuses to the left and Au to the right, the total thickness is constant but the thickness of each side changes, moving the position of the Au-Cu interface denoted by the black dashed line. The rate at which each species crosses the interface is dependent on the permeability (function of temperature) of the interface to that species, the composition, and time. Once a species crosses the interface, it uniformly distributes itself on that side of the interface.

The following two equations are generated to describe the net molar flux of Au and Cu, as a function of concentration difference across the interface for each species,

\[
\dot{n}_{\text{Cu,R}}(t) = -P_{\text{Cu}} \left( \frac{n_{\text{Cu,R}}(t)}{d_{\text{R}}(t)} - \frac{n_{\text{Cu,L}}(t)}{d_{\text{L}}(t)} \right) \\
\dot{n}_{\text{Au,R}}(t) = P_{\text{Au}} \left( \frac{n_{\text{Au,L}}(t)}{d_{\text{L}}(t)} - \frac{n_{\text{Au,R}}(t)}{d_{\text{R}}(t)} \right)
\]  

(3.3)  
(3.4)

where \( n_{\text{Au}} \) and \( n_{\text{Cu}} \) are the number of moles of Au and Cu per unit area in the plane of the interface, \( d \) refers to the thickness, the subscripts L and R designate the side of the interface in accordance with Figure 4, and \( P_{\text{Au}} \) and \( P_{\text{Cu}} \) are interfacial permeabilities to Au and Cu. These permeabilities describe the conductance of the interface to Au and Cu transport. The respective molar fluxes across the interface are equivalent to the molar flux of Cu leaving the right side and the molar flux of Au entering the right side of Figure 3-6, respectively.

The system described in Figure 4 can be thought of as having two containers of different gases separated by an infinitesimally thin membrane, where the membrane has a different
permeability to each species. Once a species crosses the interface it will distribute itself uniformly in the new container. The volumes of the containers are allowed to vary with time to capture the effect of the solid films getting thinner/thicker as the net flux across the membrane moves atoms from one side to the other.

As described in the work of Aleshin et al. [92], the physical mechanism of mass transport within each film is grain boundary diffusion. Once one species enters the grain boundary of the other, it rapidly diffuses along it. If the Au and Cu films are columnar grained, a possible reason that the dominant mass transport resistance occurs at the interface may be due to a mismatch of grain boundaries pathways between the films; an atom easily travels along a grain boundary in each film but needs to travel in-plane in the interfacial region to move from one grain boundary pathway to the other.

In Equation 3.3 and 3.4 there are six time-dependent unknowns. Two more equations relate the thicknesses to the number of moles of each species,

\[ d_{R}(t) = \frac{N_A a^3}{4} (n_{AuR}(t) + n_{CuR}(t)),\]  

\[ d_{L}(t) = \frac{N_A a^3}{4} (n_{AuL}(t) + n_{CuL}(t)),\]  

where \( N_A \) is Avogadro’s number and \( a \) is the average lattice constant of the conventional cell for a face centered cubic crystal structure (this relation is only valid if the two species have similar lattice constants). Substituting Equation 3.5 and 3.6 into Equation 3.3 and 3.4 yields

\[ \dot{n}_{CuR}(t) = -4 P_{CuR} \left( \frac{n_{CuR}(t)}{n_{AuR}(t) + n_{CuR}(t)} - \frac{n_{CuL}(t)}{n_{AuL}(t) + n_{CuL}(t)} \right),\]  

\[ \dot{n}_{CuL}(t) = -4 P_{CuL} \left( \frac{n_{CuL}(t)}{n_{AuL}(t) + n_{CuL}(t)} - \frac{n_{CuR}(t)}{n_{AuR}(t) + n_{CuR}(t)} \right),\]  

where \( P_{CuR} \) and \( P_{CuL} \) are the net fluxes of copper across the root and leaf films, respectively.
\[ \dot{n}_{\text{AuR}}(t) = \frac{4P_{\text{Au}}}{N_Aa^3} \left( \frac{n_{\text{AuL}}(t)}{n_{\text{AuL}}(t) + n_{\text{CuL}}(t)} - \frac{n_{\text{AuR}}(t)}{n_{\text{AuR}}(t) + n_{\text{CuR}}(t)} \right). \] (3.8)

Mass conservation relations

\[ n_{\text{AuL}}(t) = n_{\text{Au}} - n_{\text{AuR}}(t) \] (3.9)
\[ n_{\text{CuL}}(t) = n_{\text{Cu}} - n_{\text{CuR}}(t) \] (3.10)

are substituted into Equation 3.7 and 3.8 to yield two coupled differential equations, with two unknowns \( n_{\text{CuR}} \) and \( n_{\text{AuR}} \),

\[ \frac{N_Aa^3}{4P_{\text{Cu}}} n_{\text{CuR}}(t) = \left( \frac{-n_{\text{CuR}}(t)}{n_{\text{AuR}}(t) + n_{\text{CuR}}(t)} + \frac{n_{\text{Cu}} - n_{\text{CuR}}(t)}{n_{\text{Au}} - n_{\text{AuR}}(t) + n_{\text{Cu}} - n_{\text{CuR}}(t)} \right), \] (3.11)
\[ \frac{N_Aa^3}{4P_{\text{Au}}} \dot{n}_{\text{AuR}}(t) = \left( \frac{n_{\text{Au}} - n_{\text{AuR}}(t)}{n_{\text{Au}} - n_{\text{AuR}}(t) + n_{\text{Cu}} - n_{\text{CuR}}(t)} - \frac{n_{\text{AuR}}(t)}{n_{\text{Au}}(t) + n_{\text{Cu}}(t)} \right). \] (3.12)

Adding these two equations together produces

\[ \frac{\dot{n}_{\text{CuR}}(t)}{P_{\text{Cu}}} + \frac{\dot{n}_{\text{AuR}}(t)}{P_{\text{Au}}} = 0, \] (3.13)

which demonstrates that the rates at which Cu and Au cross the interface are proportional to the ratio of their respective permeabilities. Integrating both sides of this equation and substituting in initial conditions \( n_{\text{AuR}}(0) = 0 \), and \( n_{\text{CuR}}(0) = n_{\text{Cu}} \), yields

\[ n_{\text{AuR}}(t) = \frac{P_{\text{Au}}}{P_{\text{Cu}}} (n_{\text{Cu}} - n_{\text{CuR}}(t)), \] (3.14)

assuming that \( P_{\text{Au}} \) and \( P_{\text{Cu}} \) are independent of time. Substituting Equation 3.14 into Equation 3.11 and 3.12 results in the following two ordinary differential equations:
\[
\dot{n}_{\text{CuR}}(t) = \frac{4p_{\text{Cu}}}{N_A a^3} \left( -\frac{n_{\text{CuR}}(t)}{p_{\text{Cu}}/p_{\text{Cu}}(n_{\text{Cu}} - n_{\text{CuR}}(t)) + n_{\text{Cu}}} + \frac{n_{\text{Cu}} - n_{\text{CuR}}(t)}{n_{\text{Cu}} - n_{\text{CuR}}(t)} \right) \quad (3.15)
\]

\[
\dot{n}_{\text{AuR}}(t) = \frac{4p_{\text{Au}}}{N_A a^3} \left( \frac{n_{\text{Au}} - n_{\text{AuR}}(t)}{n_{\text{Au}} - n_{\text{AuR}}(t)} - \frac{n_{\text{AuR}}(t)}{n_{\text{AuR}}(t) - p_{\text{Au}}/p_{\text{Au}}n_{\text{AuR}}(t) + n_{\text{Cu}}} \right) \quad (3.16)
\]

The full analytical solutions to Equation 3.15 and 3.16 can be found in Section 2.4.2, as well as an approximation to the solution for easier implementation.

### 3.4.2 Interdiffusion Modelling Solution

The transcendental solution for moles of Cu on the right according to Figure 3-6 is

\[
t = c_1 \left[ c_2 n_{\text{CuR}}(t) + c_3 \ln \left( \frac{p_{\text{Cu}}/p_{\text{Cu}}n_{\text{Au}} + 1}{n_{\text{Cu}}} \right) n_{\text{CuR}}(t) - \frac{p_{\text{Au}}n_{\text{Cu}}}{p_{\text{Cu}}n_{\text{Cu}}} \right] + c_4 n_{\text{CuR}}^2(t) + c_5 \quad (3.17)
\]

and moles of Au on the right, found by plugging Equation 3.14 into Equation 3.17 is

\[
t = c_1 \left[ c_2 \left( n_{\text{Cu}} - \frac{p_{\text{Cu}}}{p_{\text{Au}}} n_{\text{AuR}}(t) \right) - c_3 \ln \left( \frac{p_{\text{Cu}}/p_{\text{Cu}}n_{\text{Au}} + 1}{n_{\text{Cu}}} \left( n_{\text{Cu}} - \frac{p_{\text{Cu}}}{p_{\text{Au}}} n_{\text{AuR}}(t) \right) - \frac{p_{\text{Au}}n_{\text{Cu}}}{p_{\text{Cu}}n_{\text{Cu}}} \right) + c_4 \left( n_{\text{Cu}} - \frac{p_{\text{Cu}}}{p_{\text{Au}}} n_{\text{AuR}}(t) \right)^2 \right] + c_5 \quad (3.18)
\]

where

\[
c_1 = \frac{-N_A a^3}{8 p_{\text{Cu}} (p_{\text{Cu}}/p_{\text{Cu}}n_{\text{Cu}} + n_{\text{Cu}})^3} \quad (3.19)
\]

\[
c_2 = 2 \left( \frac{p_{\text{Au}}}{p_{\text{Cu}}} - 1 \right) \left( \frac{p_{\text{Au}}}{p_{\text{Cu}}} n_{\text{Cu}} + n_{\text{Au}} \right) \left( \frac{p_{\text{Au}}}{p_{\text{Cu}}} n_{\text{Au}}^2 + \frac{p_{\text{Au}}}{p_{\text{Cu}}} n_{\text{Cu}} n_{\text{Au}} - n_{\text{Au}}(n_{\text{Cu}} + n_{\text{Au}}) \right) \quad (3.20)
\]

\[
c_3 = 2 \frac{p_{\text{Au}}}{p_{\text{Cu}}} n_{\text{Cu}} n_{\text{Au}}(n_{\text{Cu}} + n_{\text{Au}})^2 \quad (3.21)
\]

\[
c_4 = - \left( \frac{p_{\text{Au}}}{p_{\text{Cu}}} - 1 \right)^2 \left( \frac{p_{\text{Au}}}{p_{\text{Cu}}} n_{\text{Cu}} + n_{\text{Au}} \right)^2 \quad (3.22)
\]
\[ C_5 = -\left( \frac{P_{Au}}{P_{Cu}} \right)^4 n_{Cu} + (n_{Cu} + n_{Au})^2 \left( \frac{P_{Au}}{P_{Cu}} n_{Cu} \right)^2 + \frac{2P_{Au}}{P_{Cu}} n_{Cu} n_{Au} (n_{Au}^2 - n_{Cu}^2) - n_{Cu}^2 n_{Au}^2 - 2n_{Cu} n_{Au}^3 \] (3.23)

Approximations to the transcendental solutions, where negligibly contributing terms are eliminated, are

\[ t = \frac{-N_{Au}^3}{4P_{Cu} \left( \frac{P_{Au}}{P_{Cu}} n_{Cu} + n_{Au} \right)^3} \left[ C_1 + C_2 n_{CuR}(t) + C_3 \ln \left( \frac{P_{Au}}{P_{Cu} n_{Au}} + \frac{1}{n_{Cu}} \right) n_{CuR}(t) - \frac{P_{Au} n_{Cu}}{P_{Cu} n_{Au}} \right], \] and

\[ t = \frac{-N_{Au}^3}{4P_{Cu} \left( \frac{P_{Au}}{P_{Cu}} n_{Cu} + n_{Au} \right)^3} \left[ C_1 + C_2 \left( n_{Cu} - \frac{P_{Cu} n_{CuR}(t)}{P_{Au}} \right) + C_3 \ln \left( \frac{P_{Au}}{P_{Cu} n_{Au}} + \frac{1}{n_{Cu}} \right) \left( n_{Cu} - \frac{P_{Cu} n_{CuR}(t)}{P_{Au}} \right) - \frac{P_{Au} n_{Cu}}{P_{Cu} n_{Au}} \right], \] (3.25)

where the constants are

\[ C_1 = n_{Au}^2 n_{Cu} \left( n_{Au} \left( \frac{P_{Au}}{P_{Cu}} - 1 \right) \right. - \frac{n_{Cu}}{2}), \] (3.26)

\[ C_2 = \left( \frac{P_{Au}}{P_{Cu}} - 1 \right) \left( \frac{P_{Au}}{P_{Cu}} n_{Cu} + n_{Au} \right) \left( \frac{P_{Au}}{P_{Cu}} n_{Cu}^2 + \frac{P_{Au}}{P_{Cu}} n_{Cu} - n_{Au} \right) \left( n_{Cu} + n_{Au} \right), \] (3.27)

and

\[ C_3 = \frac{P_{Au}}{P_{Cu}} n_{Cu} n_{Au} \left( n_{Cu} + n_{Au} \right)^2. \] (3.28)

\( P_{Cu} \) and \( P_{Au} \) can be determined at a given temperature by fitting experimental XPS depth profile data for molar concentration of Au and Cu on the right side of the interface. Specifically, to determine the permeabilities of Cu and Au at 460 K, the molar concentrations of Cu and Au were calculated from the four XPS depth profiles after annealing times of 0, 20, 60, and 240 minutes at each Cu wedge thickness. The best-fit values for the permeabilities were \( P_{Cu} = 13.8 \times 10^{-13} \) m/s and \( P_{Au} = 6.7 \times 10^{-13} \) m/s. These were optimized by minimizing the sum squared error
between the full analytical solutions, (Equation 3.9 and 3.10 combined with Equation 3.17 and 3.18) and XPS-derived molar areal concentration values.

A plot of the time-dependent interdiffusion behavior, for a 41 nm Au layer on a 10 nm Cu layer using the permeabilities determined at 460 K, is shown in Figure 3-7. Both the approximate solution and the full solution are shown, with good agreement. The time dependent behavior of \( G \) is also shown in Figure 3-7, where \( G \) is calculated using the Diffuse Mismatch Model which will be described in Section 3.4.5. For this particular system, within 250 minutes at 460 K, a majority of the interdiffusion has occurred and a major decrease in \( G \) is evident.

Figure 3-7. Time dependent at. % Cu on right, according to Figure 4 schematic, and \( G \) calculated using the Diffuse Mismatch Model (described in the next section). The majority of interdiffusion and \( G \) decrease occurs within the first 250 minutes of annealing at 460 K for a 41 nm Au film deposited on a 10 nm Cu film.
3.4.3 Molar quantification of Cu and Au measured by XPS depth profiling

In the as-deposited Au-Cu bilayer film, the initial molar areal concentration for each Au and Cu layer can be quantified by EDX. However, as exemplified in Figure 3-4, the resolution of XPS depth profiling measured at the Au-Cu interface is about 15 nm, which could not represent the real sharpness of the Au-Cu interface. We locate the interface through a fit of a Heaviside step function to the Cu XPS profile. Given that a Heaviside step function has three fitting degrees of freedom

\[ y = a \cdot \text{heaviside}(x - b) + c, \]  
(3.29)

where the three degrees of freedom are a, b, and c, we were able to eliminate a degree of freedom by enforcing a molar conservation constraint as shown in the following derivation and using the same variables from Figure 3-6 and its accompanying derivation:

\[ x_L = \frac{n_{\text{Cu}L}}{n_{\text{Cu}L} + n_{\text{Au}L}} \rightarrow n_{\text{Au}L} = \frac{1 - x_L}{x_L} n_{\text{Cu}L} \]  
(3.30)

where \( x_L \) is the atomic percent of Cu in the Au rich region.

\[ d_L = \frac{N_A}{4} (n_{\text{Au}L} a_{\text{Au}}^3 + n_{\text{Cu}L} a_{\text{Cu}}^3) \rightarrow n_{\text{Au}L} = \frac{4d_L}{N_A a_{\text{Au}}^3} - \frac{n_{\text{Cu}L} a_{\text{Cu}}^3}{a_{\text{Au}}^3} \]  
(3.31)

Substituting Equation 3.30 into 3.31 and rearranging for \( n_{\text{Cu}L} \) yields

\[ n_{\text{Cu}L} = \frac{4x_L d_L}{N_A [(1 - x_L) a_{\text{Au}}^3 + x_L a_{\text{Cu}}^3]} \]  
(3.32)

and similarly

\[ n_{\text{Cu}R} = \frac{4x_R d_R}{N_A [(1 - x_R) a_{\text{Au}}^3 + x_R a_{\text{Cu}}^3]}, \]  
(3.33)
Substituting Equations 3.32 and 3.33 into the molar conservation equation

\[ n_{cu} = n_{cuL} + n_{cuR} = \frac{4}{N_A} \left[ \frac{x_L d_L}{(1 - x_L) a_{Au}^3 + x_L a_{Cu}^3} + \frac{x_R d_R}{(1 - x_R) a_{Au}^3 + x_R a_{Cu}^3} \right]. \] (3.34)

Since the total thickness of the two films \( L_T \) is the sum of \( d_L \) and \( d_R \), this can be substituted into \( d_R \) of Equation 3.34 and rearranged in terms of \( d_L \), where

\[ d_L = \frac{\left[ \frac{n_{Cu} N_A}{4} - \frac{x_R L_T}{(1 - x_R) a_{Au}^3 + x_R a_{Cu}^3} \right]}{(1 - x_L) a_{Au}^3 + x_L a_{Cu}^3} \left( \frac{x_L}{(1 - x_R) a_{Au}^3 + x_R a_{Cu}^3} \right). \] (3.35)

In Equation 3.29, \( a = (x_R - x_L) \), \( c = x_L \), and \( b = d_L \) which is a function of \( x_L \), \( x_R \) and system constants according to Equation 3.35. A sample fit of a Heaviside step function is shown in Figure 3-8.
Applying Equation 3.29 to the XPS depth profile data shown in Figure 3-4 for 20 nm of Cu, as well as depth profile data collected at initial Cu thicknesses of 28 and 25 nm, the molar concentration of Au and Cu in the Cu rich region were calculated as a function of time. Simultaneously fitting Equations 3.17, 3.24 and 3.18 to all three of these concentration profiles, yielded $P_{Cu}$ of $13.8 \times 10^{-13}$ m/s and $P_{Au}$ of $6.7 \times 10^{-13}$ m/s. The molar concentrations of Cu and Au
predicted by these values of permeability for 460 K are compared with the set of XPS data for 46 nm of Au and 25 nm of Cu in Figure 3-9.

![Graph showing molar amount of Cu in Cu rich region vs. time.](image)

**Figure 3-9.** Permeability fitting of experimental molar concentrations in Cu rich region for 46 nm of Au and 25 nm of Cu at 460 K. The boundary defining the Cu rich region is taken as the step in the Heaviside function (sample shown in Figure 3-8). The concentrations to the right of this boundary are used to determine the experimental molar concentrations.

The decrease of the Au experimental data point at 240 minutes relative to 60 minutes is explained by a decrease in the thickness of the Cu rich region as Cu leaves this region to enter the Au rich region. As Equation 3.31 shows, the molar amount of Au on a given side is dependent upon two competing factors: the thickness of that side and the molar amount of Cu on that side. After 240 minutes of annealing, while the amount of Cu in the Cu rich region has continually
decreased, the thickness of the Cu-rich region has also decreased substantially relative to the other Au data points.

### 3.4.5 Thermal Interface Conductance Modelling

The Diffuse Mismatch Model (DMM) is used to predict $G$ at large temperatures relative to the Debye temperature of either interfaced material [15,24,133,134]. To model the Au$_x$Cu$_{1-x}$-Al$_2$O$_3$ thermal interface conductance, the DMM described in Freedman, *et al.* was employed. For the alloy, Freedman, *et al.* used a Born-Von Karman phonon dispersion that continuously varied based on alloy composition defined by Vegard’s law and the average atomic mass. This was paired with the experimentally measured phonon dispersion of Al$_2$O$_3$ [26]. Following Jeong *et al.*’s approach to calculating $G$ for adhesion layers, we treat phonon wavelengths smaller than the thickness of the adhesion layer as being transmitted from the adhesion layer to the dielectric, and larger wavelengths as being transmitted from the Au layer directly into the Al$_2$O$_3$ [24].

In order to make comparative predictions with experimental data, the analytical interdiffusion model was utilized to calculate the alloy composition of the two metal layers as a function of annealing time and temperature ($P_{Au}$ and $P_{Cu}$ are temperature dependent), for the as-deposited Cu thicknesses (0-10 nm) and Au thickness of interest (41 nm). The alloy compositions of each layer were then input into the DMM model. DMM predicted values of $G$ for the Au-Cu film as-deposited, after annealing at 460 K, and for the fully intermixed film after annealing at 520 K are shown in Figure 3-10, with experimental data for comparison. For the 460 K DMM, the permeabilities used were $P_{Cu} = 13.8 \times 10^{-13}$ m/s and $P_{Au} = 6.7 \times 10^{-13}$ m/s, and an interdiffusion time of 60 minutes. One hour was used because the sample was first annealed at 360 K for 30 minutes, 440 K for 30 minutes, and then 460 K for 30 minutes; the XPS data in Figure 3-3 shows that little
interdiffusion had occurred at 360 K, and the permeabilities were assumed to be similar at 440 K and 460 K. The shaded regions of the DMM demarcate a 30% error in the permeabilities, for both the $P_{\text{Cu}}$ and $P_{\text{Au}}$.

Although the DMM does not consider the quality of the interface, and so is a very rudimentary model for the prediction of $G$, the reasonable agreement with data shown in Figure 3-10 indicate that it can be useful to estimate thermal interface conductance for various interdiffusion conditions [34,45].

![Figure 3-10. DMM predictions of $G$ compared with experimental values. The shaded region depicts a 30% error in both permeabilities.](image-url)
3.5 Methods

3.5.1 Preparation of layered Cu/Au sample

Two layered samples of Cu and Au were prepared by evaporative deposition from Cu and Au e-beam sources onto a 14 × 14 mm, 2 mm thick, Mo substrate (Valley Design Corp.) and one 14 × 14 mm, 1 mm thick, polished Al₂O₃ c-plane (0001) dielectric substrate using a rotating shadow mask deposition tool [135]. The shadow mask is located between the substrate and Cu e-beam source, which produces spatially varying flux gradients, and deposits a wedge shape with a linear thickness gradient across the substrate. Mo substrate was used because it is a conductive material required for XPS measurements. Neither Cu nor Au will interdiffuse with Mo at an elevated temperature [136–138]. The Al₂O₃ wafer was selected for the dielectric substrate in thermal interface conductance measurements in order to make direct comparisons to literature reported measurements of interface conductance [24,26]. The substrates were cleaned with isopropanol and dried in air. The Cu wedge thin film was deposited at a rate of 0.2 nm/min under ultra-high vacuum (UHV), at a base pressure of 2 × 10⁻⁹ Torr and a temperature of 300 K. Next, a uniform thickness of Au film was deposited at a rate of 0.2 nm/min under UHV on top of the Cu wedge and a temperature of 300 K.

3.5.2 EDX thickness characterization

After deposition, the sample was transferred to a Tescan scanning electron microscope (SEM) with an Oxford Instruments X-mas 80 mm² detector for EDX characterization. The thicknesses of Au and Cu layers were mapped at 36 points on a 10 mm × 10 mm area grid with 2 mm spacing centered on the Mo substrate. The thicknesses of the Au and Cu layers were mapped
at 169 points on a 12 mm × 12 mm area grid, with 1 mm spacing centered on the Al$_2$O$_3$ substrate. The EDX spectra (0-10 keV) were collected by rastering a high voltage electron beam (20 keV) across a 50 µm × 50 µm area. The obtained spectra were used to quantify the thickness (<100 nm) of Cu and Au with the INCA ThinFilmID software. We assume that the Cu adhesion layer is sandwiched between the Au layer and the Mo/Al$_2$O$_3$ substrate, since the characterization depth of the electron beam is larger than 300 nm [139].

3.5.3 XPS depth profiling characterization

XPS depth profiling is a destructive technique that repeatedly measures local composition and removes material from the surface through ion sputtering. The local through-plane composition was measured at each sputtering depth with a characterization depth of ~1 nm. XPS depth profiles of layered Au-Cu samples were conducted at four selected Cu thicknesses characterized by EDX in a ThetaProbe surface analysis system (ThermoFisher Scientific Inc.). XPS depth profiles were obtained from the as-deposited bilayer films and at the same thicknesses after annealing at temperatures of 320, 360, 440 and 520 K for 30 minutes each. Al K$_\alpha$ radiation from a monochromatic X-ray source (1486.6 eV) was focused onto a 50 µm diameter beam spot. The x-ray photoelectron spectra were collected at binding energies with 10 eV ranges around the Cu 2$p_{3/2}$, Au 4$f_{7/2}$, and Mo 3$p_{3/2}$d peaks, which were used for quantifying the through-plane composition. The scanned area was sputtered across an area of 1 mm$^2$ by rastering a focused Ar$^+$ beam (3 keV) with a backfilled pressure of 1 × 10$^{-5}$ Torr between XPS measurements. These scans were gathered at an analyzer pass energy of 100 eV with a 0.01 eV step size. The peak area of XP spectra were determined by performing the Thermo “Smart” background subtraction and peak fitting with a fixed 30% Lorentzian and Gaussian line shape in the Thermo Advantage Processing
software. The relative atomic composition was calculated by applying Thermo sensitivity factors to adjust the peak areas.

3.5.4 Thermal Interface Conductance Measurements

Measurements of $G$ were made with the noncontact optical pump/probe method, Frequency Domain Thermo-Reflectance [4,112]. In FDTR, a 488-nm continuous wave pump beam has its intensity modulated by an electro-optic modulator (EOM) at a given frequency and is focused onto the surface of the sample. The modulated beam periodically heats the surface of the sample, and the temperature of the sample, in turn, oscillates at the same frequency but with a phase lag related to the sample’s thermal interface conductance. A coincident 532-nm continuous wave probe beam is reflected by the sample surface, and its intensity is modulated by the change in reflectivity, caused by the periodically changing temperature (i.e. thermoreflectance). The reflected modulated pump and probe beams are individually collected by a photodiode and the phase lag of temperature with respect to heat flux is determined by a lock-in amplifier. The phase lag between pump and probe is measured as a function of modulation frequency (at thirty logarithmically spaced frequencies between 100 kHz and 5 MHz). We fitted the solution to the heat diffusion equation for layered systems to this phase lag versus frequency data, where the only unknown parameter in the solution is $G$ [7].

While in some cases our films were thinner than the optical penetration depth of our pump and probe lasers [11], the data did not require special analysis because of the modulation frequencies used and the high thermal conductivity of the metal bilayer, in accordance with Figure 4 of the work done by Schmidt et al. [140]. Any light that did transmit through the metal bilayer did not contribute to the thermoreflectance signal due to Al$_2$O$_3$’s transparency. The possibility of
needing special analysis for oxidation of the Cu by the oxide substrate was eliminated because the Gibbs free energy of formation of Cu$_2$O is higher than that of Al$_2$O$_3$’s [141].

3.5.5 High Temperature Annealing

After using the micromanipulator to have FDTR scan across the sample and measure $G$ as a function of Cu thickness, the sample was annealed in an ultra-high vacuum environment with a base pressure of $2 \times 10^{-8}$ Torr. The sample was then rescanned with FDTR. By iterating between vacuum annealing and measuring thermal interface conductance, $G$ was determined as a function of initial Cu thickness and annealing temperature. The annealing temperatures for this sample were 360 K, 440 K, 460 K, 480 K, and 520 K with an annealing time of 30 minutes per anneal.

3.5.6 Conductance Uncertainty Analysis

The uncertainty of the values reported in Figure 3-5 result from uncertainty in the input parameters for the fitting analysis of $G$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Percent Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Spot Size</td>
<td>± 5%</td>
</tr>
<tr>
<td>Metal Thermal Conductivity [142]</td>
<td>± 5%</td>
</tr>
<tr>
<td>Metal Volumetric Heat Capacity</td>
<td>± 6%</td>
</tr>
<tr>
<td>Metal Thickness</td>
<td>± 10%</td>
</tr>
<tr>
<td>Al$_2$O$_3$ Thermal Conductivity</td>
<td>± 2%</td>
</tr>
<tr>
<td>Al$_2$O$_3$ Volumetric Heat Capacity</td>
<td>± 2%</td>
</tr>
</tbody>
</table>

Table 1 lists the uncertainty in the input fitting parameters. The uncertainty propagation involves fitting for $G$, as each parameter is varied positively and negatively by the listed uncertainty. The value of the error bars in Figure 3-5 were calculated by taking the residual sum
of squares; using the fitted thermal conductances for each parameter with the uncertainty listed in Table 1 in comparison to the fitted conductance from the nominal value [143].

### 3.5.7 Metal Thermal Conductivity Calculation

The metal thermal conductivity used to experimentally determine $G$ was calculated by utilizing the XPS depth profiles presented in Figure 3-3. For each annealing temperature, the alloy thermal conductivity for the composition at each depth was determined based on literature [142]. The depth between XPS measurements was used as the $L$ to calculate $R_{\text{thermal}} = L/k$. Summing the resistances across the composition of the films yielded the total thermal resistance of the interdiffused bilayer. Dividing the total thickness of the bilayer by the total thermal resistance produced the effective thermal conductivity used for the metal bilayer.

### 3.6 Conclusion

We present systematic measurements of metal overlayer and metal adhesion layer interdiffusion through the use of our XPS depth profiling measurements, and report the corresponding evolution of $G$ as a function of heat treatment temperature and Cu-adhesion layer thickness. Using our experimental depth profiling results we have derived an analytical model to describe the unique interdiffusion behavior in the thin film Au-Cu system. Utilizing this model for DMM calculations, we have created a method for electronic/thermal engineers to simulate interdiffusion in Au-Cu films, and roughly predict its impact on $G$ with a dielectric substrate, according to the thermal conditions of their devices and the initial film thicknesses. The methodology we present opens the door for future studies with different film thicknesses and other material combinations where the major resistance to interdiffusion is at the interface between metal
films. Such experiments would provide permeability values to use in the model for the prediction of the evolution of $G$ due to high temperature exposure.

Acknowledgements

The authors would like to thank Professor Greg Rohrer of the Materials Science and Engineering Department of Carnegie Mellon for helpful discussion and his review of this work. We also acknowledge support provided by the National Science Foundation (NSF CBET 1403447), the Data Storage Systems Center (DSSC) at Carnegie Mellon University, and Northrop Grumman through the University Research Program.
CHAPTER 4

Maximizing Alloy Graphene Interface Conductance

List of Abbreviations

CSAF - compositionally spread alloy film
EBL - electron beam lithography
EDX - energy dispersive x-ray spectroscopy
ES - electrical sample
FDTR - frequency domain thermoreflectance
$G_T$ - thermal conductance, inversely related to thermal resistance
$R_C$ - electrical resistance
TLM - transfer length measurement, also referred to as transmission line measurement
TS (1 and 2) - thermal sample

4.1 Overview

The high thermal and electrical contact resistances to graphene significantly limit its potential in high frequency short channel devices. While existing literature has exclusively focused on metal contacts to graphene, we conduct the first major study exploring alloy contacts to graphene through the utilization of high throughput fabrication and measurement techniques. We experimentally demonstrate that ~10 at. % Pd in Ni reproducibly achieved a maximum in thermal conductance, which is dominated by phonon transport. Experiments to determine whether this alloy composition has an electrical resistance corollary continue, but are limited by graphene quality at the time of dissertation publication.

4.2 Statement of Contributions

Dipanjan Saha: CSAF deposition, EDX, thermal measurements, graphene nanoribbon identification, electrical measurements, Raman spectroscopy, 4-point probe device fabrication and measurements
Yanhao Du: graphene nanoribbon identification, electrical device design/fabrication, Raman spectroscopy
Xiaoxiao Yu: CSAF deposition, EDX
Zhitao Guo: CSAF deposition, EDX
Mohamed Darwish: 4-point probe device design
Yunus Kesim: 4-point probe device fabrication and measurements

4.3 Introduction

In the pursuit of high-performance electronic device development from 2D materials [84], one of the major design hurdles is contact engineering to achieve sufficiently low electrical contact resistance [144–146] and high thermal conductance [52] \( (R_C \text{ and } G_T) \). Among 2D materials, one of the best known and well-studied is graphene [79,83]. Having one of the highest measured thermal conductivities [49,80] and electron mobilities [81], in addition to its remarkable optical properties [82,147], makes graphene a material with incredible potential for device applications if challenges like contact engineering can be overcome [148].

Contact engineering to graphene is especially important in high frequency short channel devices, where large \( R_C \) drastically counteracts the benefits of graphene’s exceptional electron mobility in the channel [144,149,150]. Large \( R_C \) also leads to joule heating and current crowding at the metal-graphene interface with detrimental thermal effects on device performance [151]. The heat generated at the interfaces, in addition to hotspot formation in the channel during device operation [152–154], must be increasingly dissipated out of the contacts as the device’s footprint on the substrate shrinks in short channel devices. However, this heat transfer is inhibited by small \( G_T \) at the graphene contact interface. In materials such as graphene, where electrons are the charge carriers and phonons are the majority heat carriers [80], contacts are needed that are superior in both electron and phonon transport [52] across the interface.
The theory of electron transport across metal graphene interfaces is depicted in Figure 4-1. Transmission of electrons across the interface first involves tunneling through the Schottky barrier between the metal and the doped graphene underneath the contact. The width of the Schottky barrier is the interatomic distance between the metal surface and graphene sheet. The barrier heights are determined by the metal’s work function, the graphene’s work function, and difference in energy between the Dirac point and Fermi level of the doped graphene. Electron transmission into the doped graphene is then followed by transmission to the uncontacted graphene in the channel [155].

A complication in graphene contact design is the varying effects different metals have on the graphene. For example, in the work of Song et al. [156] the work function of graphene underneath Ni (5.0 eV) and Cr (4.3 eV) contacts was pinned to the work function of the metal (fermi level pinning). However, graphene underneath Pd and Au had a constant work function...
value of ~4.62 eV. Comparing these to the work function of uncontacted graphene (4.89-5.16 eV) indicates how vastly different metal contacts can affect graphene’s properties. Despite both Pd and Au having similar work functions (5.12 and 5.1 eV) and the same effect on graphene’s work function under the contact, they have very different $R_C$ values as shown in Figure 4-2. Pd having the lower $R_C$ was attributed by Song et al. to its better wetting to graphene, whereas Au very easily delaminates, thus indicating the importance of contact adhesion over work function considerations when lowering $R_C$.

![Figure 4-2. $R_C$ for Cr, Ni, Au and Pd on graphene. Pd has the lowest $R_C$ despite having the same effect on the graphene’s work function underneath the contact as Au. Pd’s superiority to Au is attributed to better adhesion to the graphene. Reproduced from [156].](image-url)
The classical approach for designing thermal contacts where phonons are the primary heat carriers across the interface, is to match the vibrational spectrum of the two materials in contact. Materials that are vibrationally well matched have similar Debye temperatures. Graphene has a very high Debye temperature of 1287 K [157]. However, increases in the Debye temperature of the metal do not necessarily increase $G_T$, as shown in Figure 4-3. Additional factors such as the graphene conformance [54] and chemical functionalization of the interface [53,158] also have significant effects. For example, in the work of Hopkins et al. [159] graphene was chemically functionalized with oxygen atoms to enhance bonding to the Ti contact which resulted in $G_T$ being almost doubled.

![Figure 4-3. $G_T$ vs Debye Temperature of metals in contact with graphene. For contacts of a metal/adhesion layer, the Debye temperature of the adhesion layer was used. [51–53]](image)

The studies included in Figure 4-3 were limited to interfaces of metal/graphene/SiO$_2$. Measurements of metal/graphene/metal interfaces [160–162] are excluded. Graphene
encapsulated in metal likely exhibits higher $G_T$ than graphene on SiO$_2$ because it involves phonon transport between two materials of identical vibrational spectra with only a monolayer of carbon between them. Such a methodology would not be a fair comparison to the more technologically relevant metal/graphene/SiO$_2$ interfaces.

An obvious strategy to co-optimize both thermal and electrical transport at the metal-graphene interface is to improve the interfacial bonding of the metal to the graphene. The spectrum of metal graphene interaction is described as ranging from chemisorption (stronger) to physisorption (weaker). While the strongest chemisorption may naively be expected to be the best graphene contact metal, strong chemisorption can lead to high $R_C$ by reacting with the graphene underneath the contact to form a carbide [163]. Metals that physisorb to graphene are Al, Ag, Cu, Au, Pt and metals that chemisorb are Co, Ni and Pd (Pd weakly chemisorbs/strongly physisorbs) [164–168]. I hypothesize that the optimal interfacial bonding condition to lower $R_C$ to graphene may be achieved in the spectrum between strong physisorption and chemisorption.

Another common practice of enhancing the metal-graphene interaction is through the addition of thin adhesion layers, although there is a lack of consensus on the singular optimal adhesion layer material and its ideal thickness. The most common adhesion layers used are Cr and Ti with thicknesses ranging anywhere between 0.5 to 10 nm [144,156,169–172].

In terms of contact architecture, the majority of published work has been focused on “top contacts” where the metal sits on top of the graphene. Published data on patterned/etched graphene to contact the graphene at its edge [173–176] and double contacts (contact from top and bottom) [172] have reported low values of $R_C$, but the additional fabrication steps introduce complexity that lowers industrial appeal. Therefore, the identification of a superior top contact would be a revolutionary breakthrough in graphene contact engineering.
While published literature has primarily investigated pure metals as contacts to graphene, our work seeks to identify a superior alloy contact. Published literature has not explored the use of alloys thus far probably due to the overwhelming nature of the alloy contact design space. Utilizing high throughput deposition and measurement techniques, this study defines a new methodology to identify an alloy contact to graphene co-optimized thermally and electrically.

4.4 Results/Discussion

4.4.1 Metal Selection/Characterization

Our experimental exploration into the alloy design space investigated the binary alloy compositions of Ni and Pd, with a Cr adhesion layer exhibiting a thickness gradient. Cr was used as one of the two most common adhesion layers to graphene (Ti being the other) with varying thickness across the sample, in order to experimentally determine the optimal adhesion layer thickness. Ni was chosen because it chemisorbs to graphene [165], while Pd weakly chemisorbs/strongly physisorbs [164–167]. Both metals have compelling electrical contact properties to graphene as shown in Figure 4-2. Values for these and other contact metals organized by features such as deposition technique and type of graphene are well tabulated by Giubileo and Bartolomeo [177]. While both metals generally have an FCC structure according to Figure 4-4, based on the post-deposition annealing temperature certain binary alloy compositions experience phase segregation (miscibility gap). The annealing temperature was selected to include such compositions in order to explore potentially interesting effects on contact properties.
Figure 4-4. Binary phase diagram for Ni-Pd alloys. The red line signifies the annealing temperature to be used in this study to explore any potentially interesting effects from the alloy FCC phase separating by being in a miscibility gap. Modified from [178].

4.4.2 Thermal Measurements

Measurements of $G_T$ as a function of alloy composition and adhesion layer thickness for the sample shown in Figure 4-5 were collected using the optical pump-probe method of Frequency Domain Thermoreflectance (Chapter 1.2). Utilizing a micro-manipulator system, specific locations on the sample were measured that were cross-referenced with EDX for alloy composition and metal thicknesses.
Figure 4-5. Sample fabricated for high throughput measurements of $G_T$ as function of NiPd alloy composition, and Cr adhesion layer thickness (left). Measurements of $G_T$ represent the thermal junction composed of graphene and its two adjacent interfaces, highlighted by the red border (right).

Measurements of $G_T$ are reported in Figure 4-6. In the regions where the Cr adhesion layer is thickest (2-5nm), no significant effects of the Ni-Pd composition on $G_T$ were observed. These thicknesses were large enough for an alloy-graphene interaction to be unexpected. However, measurements of $G_T$ corresponding to a Cr thickness of 0.5 nm (~2 atomic layers of Cr) showed an increase in $G_T$ at 10 at. % Pd in Ni. Most notably, measurements taken in the region where the alloy is directly in contact with the graphene (no Cr) observed $G_T$ maximize to a value of 114±14 MW/m²K. Such a large value is almost double the highest reported thermal conductance at a metal/graphene monolayer/SiO$_2$ junction (Figure 4-3) [51].

Due to the surprising nature of these results, we sought to ensure its reproducibility through the fabrication of a second sample (Thermal Sample 2-TS2) with data shown by the black squares. The reappearance of the peak in $G_T$ illustrates that this feature is reproducible. While there was
some misalignment in the peaks of the two datasets as a function of alloy composition, this can be attributed to the positions of the EDX and thermal measurements not being perfectly coincident. Not shown for the sake of legibility are the horizontal error bars on the data which we estimate as ±3% Pd in Ni. Regardless, these two sets of data show a peak in $G_T$ at ~10 at. % Pd in Ni directly in contact with graphene.

Although we demonstrate the repeatability of these thermal measurements, the extensive effort to do so deserves commentary. TS2 was the thirteenth sample fabricated after TS1 (original sample). The major reproduction difficulty was attributed to poor graphene surface quality which was diagnosed by suppression of $G_T$ for all alloy compositions, indicating the presence of resist at the metal graphene interface from the transfer process of CVD graphene to the SiO$_2$ wafer by the commercial supplier. This resist residue could not be removed with H$_2$/Ar annealing and the only method to determine whether the amount of residue at the interface would be tolerable was through fabrication and collection of thermal measurements. Eventually we were able to produce a second sample with $G_T$ indicative of metal on graphene (TS2) but the effort revealed the importance of high surface quality graphene in thermal conductance measurements.

A repeat measurement on TS1 in the region without Cr, 2.5 years after it was first conducted, was able to reproduce the red data shown in Figure 4-6 (reproduced data not plotted). This suggests that the peak in $G_T$ was resilient to any Au diffusion into the Ni-Pd alloy between measurements and demonstrated the material stability of the sample.
Figure 4-6. Measurements of thermal conductance ($G_T$) as a function of Ni-Pd alloy composition and Cr thickness (colored lines) showed a peak at zero adhesion layer thickness and ~10 at. % Pd in Ni. Data for a second sample with no Cr adhesion layer (black squares) reproduced the thermal trend from the original sample well. Extrapolation of $G_T$ data to pure Ni shows good agreement with Reference [51] values (black stars). Inset shows a fit of phase lag vs frequency data at the peak conductance.

Comparing our $G_T$ maximum to a literature reported value of 300 MW/m²K at a Pt/amorphous SiO₂ interface [179] suggests that the ~10 at. % Pd in Ni alloy may have been creating pinholes in the graphene and directly contacting the amorphous SiO₂. We hypothesize that this may also have occurred for 0.5 nm of Cr, where the alloy would have to diffuse through the Cr to reach the interface, and thus a suppressed peak in $G_T$ was observed. An alternative hypothesis is that the alloy has superior bonding to the graphene without destroying it, and the addition of ~2 atomic layers of Cr suppressed the interaction of the alloy with the graphene.

While it is unclear exactly why this alloy composition resulted in such a high $G_T$, it is worth noting the enhanced $G_T$ corresponded exactly to where the phase of the alloy was expected to be a miscibility gap (FCC phase separation of the Ni and Pd). To further investigate why a peak in
$G_T$ was observed, Transmission Electron Microscopy (TEM) imaging was conducted to visualize the interactions of the CSAF with the graphene.

### 4.4.3 TEM Imaging

Transmission Electron Microscopy (TEM) imaging was done on the original thermal sample (TS1) to further experimentally investigate why a peak in $G_T$ was observed. First, the position on the sample corresponding to the composition of peak $G_T$ was sectioned out using a Focused Ion Beam technique. Next, high resolution TEM imaging was conducted and is shown in Figure 4-7. Unfortunately, the imaging was unable to identify the atomic structure of the graphene and how it may have been affected by the deposition of 10 at. % Pd in Ni. The only known depiction of a cross section of monolayer graphene was achieved by Norimatsu and Kusunoki [180,181]. Other attempts have been able to visualize multilayer graphene but report damage to monolayer graphene from the TEM electron beam [182–185].

The dashed red line in the figure serves as an approximate demarcation of the metal from the SiO$_2$, where the graphene monolayer should be. This is an approximation because inspection of the image reveals that the SiO$_2$ surface is not atomically flat. Additionally, we were unable to visualize the miscibility gap and resolve the dimensions of phase separated features due to lack of contrast between Pd and Ni atoms. However, the TEM images were able to show the crystalline structure of the CSAF directly in contact with the graphene. The 3 nm of CSAF at the interface appears to form a disordered region of relatively uniform thickness. Farther away from the interface the metal becomes ordered into FCC grains of various crystallographic orientation. From these images the possibility is raised that the disorder at the interface is responsible for the enhancement of $G_T$ to the graphene supported by disordered SiO$_2$.  

66
Figure 4-7. High resolution TEM image of 10 at. % Pd in Ni directly in contact with graphene on SiO$_2$ where an enhancement of $G_T$ was observed.

To determine whether the enhancement of $G_T$ was caused by the disordered atomic structure at the interface, TEM images were also collected for a region of the sample where an enhancement of $G_T$ was not observed (Figure 4-8). In this region, ~3 nm of Cr adhesion layer was present and disordering can also be seen close to the interface. However, since both images show
disorder at the interface but only the region imaged in Figure 4-7 showed an enhancement in $G_T$, it can be concluded that the chemical composition of the alloy is affecting transport to the graphene over effects of the interfacial crystalline structure.

Figure 4-8. High resolution TEM image of ~60 at. % Pd in Ni with a 2 nm Cr adhesion layer, directly in contact with graphene on SiO$_2$, where an enhancement of $G_T$ was not observed.
4.4.4 Electrical Measurements

After measuring such an astonishing peak in $G_T$, we next sought to determine whether such a corollary could be found with respect to electrical transport across the metal-graphene interface. I collected measurements utilizing the vacuum probe station in Professor Feng Xiong’s group at the University of Pittsburgh, with the support of his student Yanhao Du who also did the majority of ES fabrication work. Electrical contact resistance measurements were collected using ten linear TLM structures described in Section 4.5.4. The measurements were taken in a vacuum probe station at a pressure of $10^{-4}$ Torr. The channel lengths used to extract $R_C$ for each set of TLM devices were 1, 2, 4, 6, and 8 $\mu$m. The source contact was biased at 200 mV while the backgate was swept from ~ -40 to 40 V. The $I_D$-$V_D$ curve measured for one of the devices across each channel length is provided in Figure 4-9. The linear nature of the data demonstrates that current saturation was not occurring at a bias of 200 mV.
Figure 4-9. $I_D-V_D$ curves show that current saturation was not occurring at 200 mV bias. Channel lengths are defined by the legend.

Measurements of $R_C$ are shown in Figure 4-10 where the legend describes the at. % Pd in Ni extrapolated from EDX data associated with each TLM device (Figure 4-13a). No observable correlation between $R_C$ and alloy composition was observed. Furthermore, devices with similar compositions such as F7 and F9 or F8 and F10, which were intended for measurement redundancy, gave inconsistent results. For example, F7 has one of the lower $R_C$ profiles whereas F9 was in the middle range of datasets. The shapes of the curves were also widely inconsistent and should resemble the shape of F8, relatively symmetrical with a peak resistance at the Dirac point caused by a minimum of available states for the electron to tunnel into from the metal.
Figure 4-10. $R_c$ data for ten linear TLM devices patterned onto the graphene. Atomic percent Pd in Ni is given in the legend. While prominent features were observed at the Dirac point, no trend with alloy composition was observed and devices of redundant alloy composition showed inconsistent $R_c$ results, indicating the presence of contaminants at the metal-graphene interface that were nonuniformly distributed between devices.

The major inconsistency of this data suggests that the CVD graphene acquired from ACS materials must have had contaminants at the interface between the metal and graphene that were not uniformly distributed across the sample and were responsible for the variations observed in $R_c$. The magnitude of $R_c$ in our measurements fell within a reasonable range compared to literature values [150,155,156,170,186,187].
4.5 Methods

4.5.1 Graphene Acquisition

The graphene samples for thermal conductance measurements (TS1 and TS2) were CVD grown monolayer graphene on 90 nm SiO$_2$ on Si acquired from Graphene Supermarket. Electrical measurements were conducted on CVD grown monolayer graphene on 300 nm SiO$_2$ on Si acquired from ACS Materials (ES). The thinner oxide was more desirable for thermal measurements due to improved sensitivity to the thermal resistance ($1/G_T$) of the graphene interface junction. The thicker oxide was more desirable for electrical measurements due to reduced leakage current into the backgate, significantly improving the measurement sensitivity to $R_C$.

Prior to CSAF deposition, the TS samples were annealed at 250°C for four hours in 5% H$_2$ in Ar by volume (25 sccm H$_2$ in 475 sccm of Ar in a 2” diameter quartz tube) at atmospheric pressure to remove organic contaminants from the surface of the graphene.

4.5.2 Thermal Sample CSAF Deposition

The metal deposition process for TS1 involved three steps. First, a Cr wedge was deposited ranging in thickness from 0 to 5 nm. In the perpendicular direction of the Cr thickness gradient, Ni and Pd wedges were co-deposited to form an alloy film that continuously varied in alloy composition (CSAF). Thus, one sample enabled a high throughput study probing an entire spectrum of alloy compositions and adhesion layer thicknesses instead of needing to make multiple samples of uniform compositions. Finally, the sample was coated in 70 nm of Au, which was necessary to collect thermal measurements using FDTR. Fabrication of TS2 underwent a similar procedure but omitted the Cr wedge deposition step since the introduction of Cr only functioned
to suppress the observed peak in $G_T$. The deposition pressure was $10^{-9}$ and $10^{-8}$ Torr for TS1 and TS2 at a rate of 0.2 nm/minute.

### 4.5.3 EDX Metal Characterization

Prior to thermal measurements/electrical device liftoff the deposited metal thicknesses and alloy compositions were obtained from energy dispersive x-ray (EDX) spectroscopy. A thickness map of Ni, as an example, and the alloy composition map for TS1 are shown in Figure 4-11. As shown, the Ni wedge shows a relatively linear thickness gradient primarily in one direction. Due to a small spatial offset between the positioning of the graphene sample and the positions of the wedges, TS1’s alloy composition ranged from 0 to 70 at. % Pd in Ni.

![Figure 4-11. Ni thickness map (left), atomic percent Ni in Pd as shown by the colorbar (right) acquired from EDX analysis.](image)

The EDX system used was a Tescan scanning electron microscope equipped with an Oxford Instruments X-max 80-mm$^2$ detector. For the thermal sample, the thicknesses were mapped across a 9 mm x 9 mm area centered on the graphene with a 1 mm grid spacing. For the electrical
sample a 13 mm x 3 mm area with 1 mm grid spacing was used that did not overlap with the TLM devices, in order to avoid the risk of damage from the electron beam to the resist adhering to the graphene in the channel of the TLM structures, which in turn could damage the graphene.

The 0-10 keV EDX spectra were measured by rastering a 20 keV electron beam across a 50 x 50 um area at each point. Thicknesses were extracted through spectra fitting done by INCA ThinFilmID software. The fitting procedure for TS1 modeled the layers as Au, Ni-Pd CSAF, Cr, and graphene on an SiO$_2$/Si substrate. The same procedure was followed for TS2 and ES, with the exclusion of the Cr layer for the former and Au and Cr layers for the latter.

4.5.4 Electrical Sample Patterning and CSAF Deposition

The fabrication of ES was conducted primarily by Yanhao Du, a doctoral student in Feng Xiong’s group at the University of Pittsburgh. My contribution to ES was in CSAF deposition, EDX characterization, and nanoribbon identification (Yanhao performed this step on earlier ES samples as we iterated to improve device yield). The ES fabrication procedure first involved the patterning of the sample with metal fiduciary markers (to serve as spatial reference points) using Electron Beam Lithography (EBL). The resist used for EBL was PMMA 950K A4. Ten 6 $\mu$m by 30 $\mu$m graphene regions were spatially identified with respect to the fiduciary markers using optical microscopy, combined with image color filtering, as shown in Figure 4-12. Image filtering was necessary to better depict cracks, wrinkles, tears, and residues we needed to avoid.
Next, the regions of graphene to be removed by O$_2$ plasma etching were defined using EBL. These regions included the area outside of the nanoribbon where the metal of the TLM devices would reside. An H$_2$/Ar annealing step (4 hours at 300°C of 400 sccm 2.5% H$_2$ in Ar), followed to remove resist residue from the previous EBL step, and then a subsequent EBL step patterned the regions where the alloy contacts would be deposited. Images of the process are detailed in Figure 4-13.

Figure 4-12. Identification of graphene nanoribbon areas for TLM devices by optical microscopy.
Figure 4-13. ES patterning process. a) Fiduciary metal markers (purple) were patterned onto the graphene sample. Nanoribbon locations used to define placement of ten TLM devices (red) where NiPd CSAF composition would vary in the horizontal direction. b) Graphene was etched away in the shaded green area by O$_2$ plasma, followed by an EBL patterning step to define the metal contacts (orange). c) Ni-Pd CSAF deposition and liftoff with magnified image of metal contacting the graphene nanoribbon. d) Lower magnification image depicts where measurement probes would make contact to pairs of pads separated by each graphene channel of varying length. Images courtesy of Yanhao Du.

Being constrained to ten TLM devices signified a major reduction in measurement resolution as compared to our thermal measurements. As a result, we opted to not investigate the effect of Cr adhesion layer thickness on $R_C$ as was done in the thermal measurements. Furthermore,
the desired alloy composition range was intentionally limited to the most interesting alloy compositions from the thermal data, 0-30 at. % Pd in Ni CSAF deposited directly onto the graphene. The achieved compositions for our TLM devices were between 15-30 at. % Pd in Ni. The deposition pressure was $10^{-8}$ Torr at a rate of 0.2 nm/min.

### 4.5.5 CSAF Post Deposition Anneal

In order to establish equilibrium phases of the alloys, a post deposition anneal of all three samples at 180°C for one hour was completed. TS1 was vacuum annealed without breaking vacuum after the metals were deposited. TS2 broke vacuum before being vacuum annealed in a separate chamber due to a malfunctioning heating stage in the deposition chamber. Breaking vacuum between the deposition and anneal was not expected to affect interfacial transport since contaminants would have had no access point to the contact interface.

After the liftoff process (removed the metal features that were not part of the TLM devices), ES was vacuum annealed in a vacuum probe station at a pressure of $10^{-4}$ Torr for 1 hour at 180°C before electrical measurements were conducted in the same chamber. It was critical to not break vacuum between the anneal and ES measurements, because water vapor adsorbed to the graphene nanoribbon could shift the Dirac point outside of the backgate sweeping range, in addition to making the graphene channel more resistive and therefore reducing the sensitivity to contact resistance. Hence, annealing at 180°C was expected to desorb the water vapor while exposing the CSAF to the same total annealing temperature and duration as the thermal samples.
4.5.6 Thermal Measurements

Frequency domain thermoreflectance (FDTR) was used to measure $G_T$ as a function of the alloy’s composition that was in contact with graphene. Phase delay data between the reflected pump and probe beams was collected for 30 logarithmically swept pump modulation frequencies (100 kHz to 5 MHz) across each position of interest on the sample. The positions of interest corresponded to measurements from EDX, with linearly interpolated locations also measured in order to report higher resolution thermal vs composition data. Linear interpolation was appropriate because the spatial thickness gradient of the deposited metal wedges was also linear.

The thermal conductivity of the Ni-Pd CSAF layer with Cr adhesion layer needed for fitting of the FDTR data was determined through a sample fabricated with 4-point probe structures patterned onto a dielectric substrate. Electrical conductivities measured from each device as a function of alloy concentration and Cr wedge thickness were converted to thermal conductivities using the Wiedemann Franz law. The thermal conductivity data at zero Cr thickness is plotted in Figure 4-14 and shows good agreement with literature trends [188], which were also converted to thermal conductivities using the Wiedemann Franz law. As expected, the CSAF values were lower than the literature values due to the former being a thin film (phonon boundary scattering limits thermal conductivity in thin films) and the latter being for bulk values.
Figure 4-14. Thermal conductivity of the thin film CSAF determined from 4-point probe measurements. Literature values obtained from [188].

4.5.7 Electrical Measurements

Measurements of electrical contact resistance were collected by contacting with probes at contact locations across each channel length of each device and measuring the current flowing between probes at a bias of 200 mV while the backgate was swept from -40 to 40 V. Resistance was calculated using Ohm’s law and a sample measurement is shown in Figure 4-15 for device F8. The overlapping lines represent forward and backwards sweep where minor misalignment
was observed.

To calculate electrical contact resistance, the data was split into forward and backwards sweeps and for each sweep direction, the Dirac peaks were aligned to $V_{BG}=0$ (peak in resistance due to a minimum of free electrons when the Fermi level is at the tip of the Dirac cone). Then electrical resistance vs channel length was plotted for each backgate voltage (relative to the Dirac
peak), where the intercept of the linear trend was multiplied by the channel width and divided by 2 for the two contacting interfaces per measurement, in order to output $R_C$. The strongly linear nature of the fit shown in Figure 4-16 was observed of data for all 10 TLM devices at all backgate voltages.

![Figure 4-16](image.png)

**F10, $V_G$: -4**

Figure 4-16. Linear trends observed in $R$ vs channel length for device F10 at a backgate voltage (relative to the Dirac peak) of -4 V.

### 4.6 Conclusion

Through the usage of high throughput alloy deposition techniques, we have successfully demonstrated a reproducible peak in thermal conductance to graphene with an alloy contact of ~10
at. % Pd in Ni. This finding (114±14 MW/m²K) is the highest reported thermal conductance from a metal to graphene on SiO₂. Ongoing experiments will determine whether a corresponding result can be found with respect to electrical contact resistance. Nevertheless, the astonishing finding for thermal conductance identifies the alloy design space as an unexplored frontier awaiting potential discoveries of superior contact metals for graphene and other 2D materials.

Acknowledgements

The authors would like to acknowledge the contributions of TEM spectroscopy by Noel Tom Nuhfer in the Materials Characterization Facility at Carnegie Mellon, fabrication support from Isen Ozalp, Darshil Gala, Raghav Garg, Anna Kalmykov, and Wei Gong, and helpful discussion from Eric Pop.
CHAPTER 5

Reduction of Thermal Conductivity in Epitaxial SrTiO$_3$ Thin Films by Ferroelectric Domain Walls

5.1 Overview

In the ferroelectric material SrTiO$_3$, we experimentally observed that thermal conductivity can be drastically reduced in response to temperature and strain applied to the single crystal film by its DyScO$_3$ substrate. This reduction occurs as the film enters its fully ferroelectric state which is expected to produce a maximum density of ferroelectric domain walls that would be strong phonon scattering sites. These observations were contrasted to our thermal measurements of SrTiO$_3$ grown on LSAT, where the film does not exhibit such a drastic reduction in thermal conductivity because it does not become fully ferroelectric in the measured temperature regime (100 to 300 K). Therefore, these measurements show that strain engineering is a powerful method to utilize SrTiO$_3$ as a temperature dependent thermal conductivity switch.

A. Sarantopoulos, D. Saha, W.L. Ong, C. Magén, J.A Malen, F. Rivadulla
Reduction of Thermal Conductivity in Epitaxial SrTiO$_3$ Thin Films by Ferroelectric Domain Walls,
To be submitted to Physical Review Letters.

5.2 Contributions to Dissertation Material

- Alexandros Sarantopoulos- Pulsed laser deposition growth of films, temperature dependent thermal measurements
- Dipanjan Saha- temperature dependent thermal measurements
- WeeLiat Ong- temperature dependent thermal measurements
5.3 Introduction

Thus far in this thesis, the discussion has centered around phonon transport across interfaces pertaining to the surfaces of two different materials in contact. However, phonon transport can also be impeded by interfaces within a material, i.e. where the two sides of the interface are of the same material. For example, Wang et al. [189] showed that at room temperature, reducing the grain size in nanocrystalline Si from 550 nm to 64 nm reduces thermal conductivity from ~80 to ~9 W/m·K. Despite this powerful knob to control $\kappa$ with grain size, the formation and removal of grain boundaries obviously cannot be dynamically controlled.

However, ferroelectrics are a class of materials that can dynamically switch thermal conductivity [88]. A ferroelectric material is defined as having a polarization hysteresis loop, as shown in Figure 5-1. If the material initially starts at zero polarization, when an electric field is applied its polarization will follow the dashed curve shown in Figure 5-1 until it reaches the polarization saturation point $P_S$. Once this point is reached, changes in the electric field will trace the solid polarization hysteresis loop. This hysteresis property gives the material the ability to have a polarization even when an electric field is not being applied $P_R$, and is therefore of research interest in application areas like random access memory [190] and memristors [191].

On an atomic level, polarization of ferroelectric materials occurs because charged atoms are displaced within the ferroelectric material in certain directions. Regions having uniform polarization are called ferroelectric domains. The nucleation and growth of ferroelectric domains can be achieved through the application of an electric field, and can also be controlled through
temperature and strain [192]. Here we experimentally investigate the latter two control mechanisms. Achieving drastic changes in $\kappa$ as a function of temperature would make this a useful material as a thermal circuit element. And as will be discussed in this chapter and experimentally investigated further in Chapter 6, the formation and destruction of the boundaries between ferroelectric domains, also known as ferroelectric domain walls (FEDWs), will serve as powerful knobs to tune thermal conductivity since we will show that FEDWs are very strong phonon scattering sites.

### 5.4 Motivation to study SrTiO$_3$

Strontium titanate, SrTiO$_3$, is a well studied ferroelectric material [193] with the perovskite structure [194] depicted in Figure 5-2. This material is particularly interesting because its ferroelectric state is predicted to be strongly tuned by both temperature and strain as shown in Figure 5-2 [192]. This presents the opportunity to study how the transition from one ferroelectric state to another affects thermal conductivity. Hence, SrTiO$_3$ films were grown on (LaAlO$_3$)$_{0.3}$(Sr$_2$TaAlO$_6$)$_{0.7}$ – commonly referred to as LSAT- and DyScO$_3$ substrates to impose specific compressive and tensile strains shown by the orange and turquoise lines of Figure 5-2. Thermal conductivity measurements were taken over the temperature range of 300 to 100 K (denoted by arrows) in order to investigate how changes in the ferroelectric state, from the paraelectric to the ferroelectric transition regime, and from the transition regime to the fully ferroelectric state, respectively, would affect $\kappa_{film}$. 

85
Figure 5-2. Perovskite structure of SrTiO$_3$ (top left), strain imposed by different substrates (bottom left), and effect of temperature and strain on ferroelectric state modified from [192] (right).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSAT</td>
<td>-0.95%</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>0%</td>
</tr>
<tr>
<td>DyScO$_3$</td>
<td>+1.15%</td>
</tr>
</tbody>
</table>
5.5 Results

5.5.1 Vacancy Scattering

![Figure 5-3. Minimal effect on thermal conductivity of oxygen vacancy concentration as correlated to oxygen pressure during deposition.](image)

Before investigating how $\kappa$ would be affected by the ferroelectric state, it was necessary to determine the sensitivity of our measurements to other scattering mechanisms such as oxygen vacancies. As a separate study, the effect of oxygen vacancy density on thermal conductivity of the films on the different substrates was conducted by growing the films at three different orders of magnitudes of oxygen pressure. As shown by the data presented in Figure 5-3, for any given substrate, the thermal conductivity of the film hardly changes. In fact, it took an extreme case of SrTiO$_3$ on LSAT to be vacuum annealed at a pressure three orders of magnitude lower to observe an appreciable effect on thermal conductivity. Thus, it can be concluded that our measurements...
would be more sensitive to the strain imposed by the substrate than be overly sensitive to the concentration of oxygen vacancies.

5.5.2 Disentangling Thermal Interface Conductance

![Diagram](image)

Figure 5-4. Demonstration of film thermal conductivity extraction at 175 K.

In order to disentangle the effect of temperature and strain on the $\kappa_{film}$ of SrTiO$_3$ from the effect on $\kappa_{eff}$ (which includes $G$), thickness dependent measurements of the film were taken at each temperature. Since the characteristic time for heat diffusion ($t^2/\alpha$ where $t$ and $\alpha$ are the film thickness and thermal diffusivity) is much shorter than the heating period in FDTR, the
temperature profile in the film can be approximated as a steady state 1D solution. This approximation allows the measured thermal resistance to be decomposed into the resistance of the film and interfaces as described by Equation 5.1.

\[
\frac{t_{film}}{\kappa_{eff}} = \frac{t_{film}}{\kappa_{film}} + R_{int} \tag{5.1}
\]

Example thickness dependent thermal resistance data are shown in Figure 5-4 where the slope of each data set is the inverse of \(\kappa_{film}\) and the inverse of the intercept is \(G\). The linear nature of the data supports the validity of the steady state approximation and indicates that \(\kappa_{film}\) does not show a thickness dependence.

Measurements of \(G\) (which represents the two interfaces adjacent to the SrTiO\(_3\)) as a function of temperature are shown in Figure 5-5. Outlier data points were omitted and corresponded to temperatures that were very difficult to stabilize at with our cryogenic system. A surprising aspect of Figure 5-5 is the difference in \(G\) as a function of strain and the rapid decrease with decreasing temperature for the films on the LSAT substrate. The Debye temperature of SrTiO\(_3\) is 413 K [195], LSAT is 500 K and DyScO\(_3\)'s is similar at 520 K [196] indicating that the vibrational mismatch between the film and both substrates should be similar. Currently we hypothesize that the nucleation of FEDWs near the interface [197] may be responsible since the decrease in \(G\) on LSAT is observed in the transition from paraelectric to the FE transition regime.
Figure 5-5. Total interface conductance as a function of temperature.
5.5.3 Thermal Conductivity

![Thermal Conductivity Graph](image)

Figure 5-6. Thermal conductivity of SrTiO$_3$ on LSAT and DyScO$_3$. A sharp decrease in thermal conductivity is observed as the film becomes fully ferroelectric on the DyScO$_3$ substrate.

The thermal conductivities of the strained SrTiO$_3$ films as a function of temperature are shown in Figure 5-6. A $\approx 60\%$ reduction in thermal conductivity at room temperature was observed for the film on LSAT compared to the film on DyScO$_3$, where the ferroelectric states were paraelectric and within the ferroelectric transition regime, respectively.

Further inspection of the $\kappa_{film}$ of SrTiO$_3$ on LSAT as a function of temperature reveals that it could be fit well to a modified Callaway model [198,199] shown by the solid line. As a reminder, in the temperature range of these measurements SrTiO$_3$’s ferroelectric state was expected to be
either in the paraelectric or ferroelectric transition regime on LSAT, but was not expected to become fully ferroelectric. In contrast, the experimental $\kappa_{film}$ data on DyScO$_3$ showed a significant decrease relative to the model as the temperature approaches the regime where the film’s ferroelectric changed from the ferroelectric transition regime to the fully ferroelectric state. Once in the fully ferroelectric state, the $\kappa_{film}$ exhibited a nearly constant value. We hypothesize that this occurred because once the film entered the fully ferroelectric state, it had saturated its nucleation of ferroelectric domains and had also achieved peak density of FEDWs, which we experimentally demonstrate in the next chapter to be very strong phonon scattering sites.

5.5.4 Approximation of Domain Sizes

Applying a model developed by Nan and Birringer [29] (Equation 5.2) that estimates grain size from thermal conductivity data, to the $\kappa_{film}$ data for our FE material where the FE domains are treated like homogenously sized grains, allowed us to estimate FE domain sizes ($\phi$). In this model $\kappa_{film}$ is compared to the single FE domain case $\kappa_0$ for which we used the experimental thermal conductivity of the SrTiO$_3$ film on LSAT, and $R_{DW}$ is the thermal resistance of the FEDWs. In our calculations $R_{DW} \approx 5 \times 10^{-9}$ m$^2$K/W was used, which is the Kapitza grain boundary thermal resistance for SrTiO$_3$ and was comparable to the $R_{DW}$ reported by Hopkins et al. for ferroic BiFeO$_3$ [200].

$$\frac{\kappa_0}{\kappa_{film}} = 1 + \frac{2R_{DW}\kappa_0}{\phi}$$ (5.2)
The temperature dependent domain sizes are plotted in Figure 5-7. At room temperature the average FE domain size is 35 nm, of the same order as phase-field calculations of SrTiO$_3$ under similar strains. A constraint of Equation 5.2 is that it is only valid in the diffusive regime, i.e. when the phonon mean free path $\Lambda$ is smaller than the domain size $\phi$. First principles calculations of the thermal conductivity accumulation function at room temperature predict a 60-70% contribution to thermal conductivity from phonons with $\Lambda < 10$ nm [27,201], making the use of Equation 5.2 justifiable around room temperature. At temperatures below 250 K, $\phi < \Lambda$ which describes ballistic phonon transport where phonons propagate without thermal resistance within the domains, so that $\kappa_0 \rightarrow \infty$ and Equation 5.2 tends to $\phi = 2\kappa_{film}R_{DW}$. Inputting the same parameters previously used in Equation 5.2, $\phi \approx 7.5$ nm. The resulting conclusion is that the reduction of thermal conductivity on DyScO$_3$ in Figure 5-6 correlates well with the expected reduction in domain size (increase in FEDW density, and FEDWs are strong phonon scattering sites). Furthermore, it can be concluded that the minimum thermal conductivity saturates at low temperature due to the minimum in FE domain size and subsequently the maximum density of FEDWs being achieved.
5.6 Methods

5.6.1 Sample Fabrication

Samples were fabricated by the Rivadulla group using Pulsed Laser Deposition, a layer by layer deposition process capable of growing single crystal thin films. Prior to deposition, the substrates were thermally treated in order to achieve atomic flatness. Four samples on each substrate were grown where the thickness of the films ranged from 10 to 65 nm. These samples were all grown at an oxygen pressure of 100 millitorr.
5.6.2 Temperature Dependent Measurements of Thermal Conductivity

Thermal conductivity of each sample was measured by FDTR (Chapter 1.2). Prior to measurements, the samples were coated with a Au transducer layer and Cr adhesion layer as depicted in Figure 5-8. The samples were measured using a cryostat where the temperature was controlled through the combination of either liquid nitrogen or liquid helium (initial attempts tried to measure at temperatures below liquid nitrogen) and a PID heater.

Thermal conductivity measurements were taken from 100 to 300 K at 25 K increments. Data at each temperature were fitted to the solution to the heat diffusion equation for layered systems where temperature dependent properties were used for each layer. A depiction of the four layers and a sample fit are provided in Figure 5-8. The only unknowns for the solution were the thermal conductivity of the SrTiO$_3$ film and the conductances of its two adjacent interfaces. As denoted by $\kappa_{eff}$ in the figure, the interfaces were combined with the SrTiO$_3$ and treated as one junction in the solution and a series of thickness dependent measurements were used to extract the thermal conductivity of just the film.

Figure 5-8. (Top) Diagram of material stack where $\kappa_{eff}$ describes the junction thermal conductivity extracted from fitting the solution to the heat diffusion equation to experimental phase vs frequency data (example-bottom).
5.7 Conclusion

We demonstrated that in thin films of SrTiO$_3$, temperature can be used to drastically reduce thermal conductivity. Specifically, we were able to reduce thermal conductivity by $\approx 60\%$ at room temperature on DyScO$_3$ relative to LSAT, and also achieved a further $\approx 65\%$ reduction from 275 K down to 225 K and below on the DyScO$_3$ substrate. This was achieved by transitioning the film into the fully ferroelectric regime on DyScO$_3$, in contrast to the film grown on LSAT where it never becomes fully ferroelectric. And so, we have shown how SrTiO$_3$ on DyScO$_3$ can be actively utilized as a temperature dependent thermal conductivity switch.
Chapter 6

Record Reduction in Thermal Conductivity Through Phonon Scattering from Ferroelectric Domain Walls in PbTiO₃

6.1 Overview

The thermal conductivities of PbTiO₃ are reported as a function of strain, and the largest recorded reduction in thermal conductivity for a ferroelectric at room temperature was achieved (61%). This was accomplished through the engineering of ferroelectric domain walls (FEDWs) which are experimentally shown as the dominant mechanism of phonon scattering in these single crystal films. FEDW thermal resistances were calculated to be \( \approx (5.0 \pm 0.2) \times 10^{-9} \text{Km}^2\text{W}^{-1} \), on the same scale as the large thermal resistances of grain boundaries in oxides. Through these measurements we demonstrate the potential change in thermal conductivity that could be achieved with subsequent research into PbTiO₃ as an active thermal conductivity switching material.


Ferroelectric domain walls in PbTiO₃ are effective regulators of heat flow at room temperature, Accepted ACS Nano Letters October 2019.

6.2 Contributions to Dissertation Material

- Eric Langenberg- film growth, PFM, TEM
- Dipanjan Saha- thermal conductivity measurements
6.3 Introduction

As introduced in Chapter 5.2, FEDWs are interfaces between domains that can exist within ferroelectric materials and have the potential to significantly reduce thermal conductivity. While Ihlefeld et al. [88] was able to dynamically switch thermal conductivity by 11%, their films were polycrystalline and were therefore unable to realize the material’s upper limit of thermal conductivity and demonstrate the full conductivity reduction that the material would be capable of. Utilizing the deposition technique of Molecular Beam Epitaxy to grow single crystal films we investigated whether a larger range of thermal conductivity could be achieved in PbTiO₃ through strain engineering. Additionally, we sought to experimentally determine exactly how powerful FEDWs are as a phonon scattering mechanism in this material.
6.4 Results and Discussion

6.4.1 PFM

Figure 6-1. PFM amplitude images of PbTiO$_3$ on SrTiO$_3$ with (a) and without (b) the SrRuO$_3$ buffer electrode. In (a) the film is entirely one FE domain, whereas in (b) the film has a chaotic distribution of domains of polarization either up or down.

Figure 6-2. PFM amplitude images of PbTiO$_3$ strained by epitaxial growth on (a) DyScO$_3$, (b) TbScO$_3$, (c) GdScO$_3$, (d) SmScO$_3$. In each case alternating layers of domains are shown by thinner striations within larger regions known as superdomains, an example of which is outlined in red in (d).
Like atomic-force microscopy, piezo-force microscopy (PFM) involves the rastering of a surface with an atomically fine tip, except the PFM tip records deflections due to the polarization of the underlying material. PFM images of PbTiO$_3$ on various substrates are shown in Figure 6-2 to visualize the spatial distribution of domains of different polarization directions. Each of the polarized domains can be visualized as repeating units within superdomains, where the former are the striations within the latter that is demarcated by the red outline of Figure 6-2d. The self-organization of domains and superdomains are attributed to the film distributing the built-up elastic energy resulting from its strain.
Cross sectional TEM images of the PbTiO$_3$ films are depicted in Figure 6-3. The images are of two ferroelectric domains of different polarization directions, and the difference in polarization stems from the displacement directions of the titanium atom relative to its centrosymmetric position within each unit cell.
A wider field of view cross sectional TEM image is shown in Figure 6-4 and corroborates the existence of different polarization domains imaged through PFM. It also reveals differences in FEDW angles relative to the film’s cross plane direction. For the image on DyScO₃, all of the shown FEDWs are angled at 45° relative to the cross plane direction whereas on GdScO₃, the FEDW between the a₁/a₂ domain are parallel to the direction of heat flow.
6.4.3 Effect of Domain Wall Periodicity on Thermal Conductivity

The major results of this study are encapsulated in Figure 6-5, where the blue points correspond to domain wall periodicity (the average distance between FEDWs) and the red points represent measurements of thermal conductivity as a function of strain imposed on the PbTiO$_3$ film by each labeled substrate. An obvious correlation is observed between thermal conductivity
and domain wall periodicity. Through FEDW engineering, we demonstrated a 61% reduction in the thermal conductivity values of single crystal PbTiO$_3$ relative to the film grown on SrTiO$_3$. The single domain film was fabricated by epitaxial growth on SrTiO$_3$ with a 10 nm SrRuO$_3$ buffer electrode, compared to growth directly on SrTiO$_3$ which resulted in the c-up/down domains that were shown in Figure 6-1.

While the substrates incited different types of domains in the PbTiO$_3$ film, as shown in Figure 6-5, it can be concluded that the observed reductions in $\kappa$ are primarily due to phonon scattering from FEDWs and the higher the density of FEDWs the lower $\kappa$ will be. This scattering mechanism clearly dominates over other factors such as the polarization directions of the domains and the FEDW’s angle relative to the primary direction of heat flow.
Figure 6-6. Comparison of experimental data from this work to thermal conductivity accumulation functions of PbTiO$_3$ from DFT calculations [201,202]. Inset) Fitting to Equation 6.2 to calculate thermal resistance of FEDWs in PbTiO$_3$.

Comparing the predicted thermal conductivity accumulation function for PbTiO$_3$ from two different sources [201,202] shown in Figure 6-6 where ~70% of the heat is carried by phonons with a mean free path of 10 nm or less, while the shortest domain wall periodicity of 22 nm, provides an argument against the observed thermal conductivity reduction being caused by a truncation of the mean free path length of phonons, $\Lambda(\lambda)$, as described in Equation 6.1. Instead the argument is raised that FEDWs must have an intrinsic thermal resistance.

105
\[ k(\lambda) = \int_{0}^{\lambda} \frac{1}{3} C(\lambda) n(\lambda) \Lambda(\lambda) d\lambda \]  \hspace{1cm} (6.1)

To calculate the thermal resistance of FEDWs, the thermal conductivity of PbTiO\textsubscript{3} on each substrate ($\kappa$), the thermal conductivity in the single domain case ($\kappa_0$), and the domain wall periodicity ($d$), were provided as inputs to the model derived by Nan and Birringer [29] defined as

\[
\frac{\kappa_0}{\kappa} = 1 + \frac{2\kappa_0 R_{DW}}{d} \hspace{1cm} (6.2)
\]

The fit of this model to the experimental data is shown in the inset of Figure 6-6. The FEDW thermal resistance calculated was $R_{DW} \approx (5.0 \pm 0.2) \times 10^{-9}$ Km$^2$W$^{-1}$. This value is comparable to the $R_{DW}$ reported by Hopkins et al. for BiFeO$_3$ [200] and is also comparable the thermal resistance of grain boundaries, for example in the oxide yttria stabilized zirconia [203].

The observation that FEDWs have comparable thermal resistance to grain boundaries is worth noting. Grain boundaries are much more dramatic interfaces where the grains on each side of the boundary can have different crystal orientations. In comparison, our FEDWs exist in a single crystal material and so the crystal orientation is the same on both sides of the interface. Hence it is astonishing that the interruption to periodicity from the different displacement directions of one atom within the unit cell on each side of the interface can yield such a large thermal resistance.

### 6.5 Methods

Measurements of thermal conductivity were conducted using Frequency Domain Thermoreflectance which was described in Chapter 1.2.
Figure 6-7. Data from PbTiO$_3$ films on SrRuO$_3$ buffer layer on SrTiO$_3$ substrate used to determine $R_{\text{int}}$. Thin black lines demarcate a 95% confidence interval of the fitted line.

In order to determine the thermal resistance of the interfaces ($R_{\text{int}}$) and report only the film thermal conductivity ($k_{\text{film}}$), the total thermal conductivity was measured for three films of PbTiO$_3$ on SrTiO$_3$ with a SrRuO$_3$ buffer layer in between, varying the thickness of the PbTiO$_3$ layer (Figure 6-7). Fits to $R_{\text{Tot}}$ in the presence of SrRuO$_3$ considered its heat capacity in addition to the heat capacity of the PbTiO$_3$ itself.

The heat flux across the film thickness can be described by:

$$q = -\kappa \nabla T \approx -\kappa \frac{\Delta T}{L_{\text{film}}}$$  \hspace{1cm} (6.3)

where $L_{\text{film}}$ is the film thickness. In this case $L_{\text{film}} / \kappa$ is the total thermal resistance measured by FDTR and included the contribution from the film and the interfaces. Summing the thermal interface resistances into a single term, $R_{\text{int}}$:

$$\frac{L_{\text{film}}}{\kappa} = \frac{L_{\text{film}}}{k_{\text{film}}} + R_{\text{int}}$$  \hspace{1cm} (6.4)
A plot of \( \frac{L_{\text{film}}}{\kappa} \) versus thickness (Figure 6-7) provides the intrinsic thermal conductivity of the film and the interface resistance. The y-intercept of this plot gave the sum thermal resistance of the interfaces (\( R_{\text{int}} \)): the thermal resistance from the interfaces at each side of PbTiO\(_3\) plus the thermal resistance between the SrRuO\(_3\) and SrTiO\(_3\). This measured \( R_{\text{int}} \) was subtracted from the total thermal resistance of each sample, assuming that the other samples had similar \( R_{\text{int}} \). It is expected that this is the largest possible \( R_{\text{int}} \) value in our systems as the additional interface (between SrRuO\(_3\) and SrTiO\(_3\)) did not exist with the samples on other substrates. As shown in Table 6-1, the other substrates have higher Debye temperatures compared to SrRuO\(_3\) and SrTiO\(_3\), so the scandates have higher frequency phonon modes available to scatter into, if the scattering is inelastic. The similarity in the Debye Temperatures among the scandates indicates they should have similar interfacial thermal resistances with PbTiO\(_3\). Since \( i \) we consider the same \( R_{\text{int}} \) for each sample and \( ii \) an overestimated \( R_{\text{int}} \) subsequently overestimated \( \kappa_{\text{film}} \) (Equation 6.4), the actual thermal conductivity reduction by domain wall scattering may be even larger than what we conservatively reported.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Debye Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTiO(_3) [204]</td>
<td>337</td>
</tr>
<tr>
<td>SrRuO(_3) [205]</td>
<td>390</td>
</tr>
<tr>
<td>SrTiO(_3) [195]</td>
<td>413</td>
</tr>
<tr>
<td>DyScO(_3) [196]</td>
<td>520</td>
</tr>
<tr>
<td>TbScO(_3) [196]</td>
<td>524</td>
</tr>
<tr>
<td>GdScO(_3) [196]</td>
<td>529</td>
</tr>
<tr>
<td>SmScO(_3) [196]</td>
<td>533</td>
</tr>
</tbody>
</table>
$R_{\text{Tot}}$, was used to fit the experimental data instead of three parameters ($k_{\text{film}}$, its interface resistance with the metal transducer $R_1$, and its interface resistance with the substrate $R_2$), because multiple equally good fits were possible when the three parameters were co-fit. Nevertheless, the solution should be consistent with a more physically accurate three parameter fit. To check for self-consistency a three-parameter fit was done with the constraint that $R_2 = R_{\text{int}} - R_1$. This constrained fit yields low MSE, comparable to the $R_{\text{Tot}}$ fits. The resulting values of $k_{\text{film}}$ from this self-consistency check were within 15% of the values reported in Figure 6-5. The fits of the two methods are shown in Figure 6-8.

Figure 6-8. Fits where red denotes the $R_{\text{Tot}}$ method and blue is the self-consistency check method on (a) on SrRuO$_3$/SrTiO$_3$ (b) on DyScO$_3$.

### 6.6 Conclusion

We reported the largest reduction in thermal conductivity at room temperature in a ferroelectric material of 61% using only strain engineering. Additionally, we experimentally showed that the increased density of ferroelectric domain walls was the dominant mechanism responsible for achieving this large reduction. Hence, it has been demonstrated that interruptions
in periodicity as small as a different displacement direction of the atoms in the unit cell from one ferroelectric domain to the next in these single crystal materials were enough to scatter phonons and this will serve as a powerful mechanism to control thermal conductivity.
CHAPTER 7

Summary and Outlook

7.1 Interdiffusion of ultra-thin metal films on $G$ at metal-dielectric interfaces

The insertion of thin metal films at metal-nonmetal interfaces, where the inserted metal has better vibrational matching to the nonmetal, has been shown to significantly enhance $G$ where phonons are the major interfacial heat carrier. However, we have shown that this enhancement of $G$ is progressively lost as the metals interdiffuse into each other. Such a scenario would be expected in applications where the metals chosen have a risk of interdiffusion, and elevated device operating temperatures can be expected.

Utilizing high throughput techniques (XPS through the Gellman Lab in chemical engineering at Carnegie Mellon, and measurements of $G$ through our lab) we observed unique diffusion profiles where as one metal element diffused into the other, it uniformly distributed itself within that film and this alloying gradually lowered $G$. We used our experimental data to derive an analytical model to predict diffusion profiles at a given time, where the only inputs were the amount of each metal and the permeability (temperature dependent) of the metal-metal interface to each element. Integrating this diffusion model with the Diffuse Mismatch Model, we provide a tool for thermal engineers to make predictions of $G$ for their specific design choices where a risk of interdiffusion exists.

While this diffusion model was created to make our results more generalizable beyond Au and Cu, which have similar sizes, it remains unclear exactly where the cutoff in element sizes lies to determine which combination of elements will exhibit the same Type C kinetics this model would be limited to. Furthermore, future experimental work will be needed to investigate
whether surfaces would have similar effects on the diffusion profiles for other element combinations as was observed in our unique Au/Cu diffusion profiles, where the film thicknesses are smaller than the mass diffusion lengths [128]. As nanoscale technologies shrink further and further, using very thin metal layers, the answers to these questions will have major ramifications on thermal transport as we have shown with our study.

### 7.2 Alloy contacts to 2D materials

In our pursuit of better thermal and electrical contacts to graphene, we have identified ~10 at. % Pd in Ni as the alloy composition that resulted in the highest reported thermal conductance value of 114 MW/m²K for a metal on monolayer graphene on SiO₂. While we continue experimental work to determine if this “magic” alloy composition also has an electrical corollary, it is worth noting that at a minimum our high throughput methodology has defined a new way to investigate the previously unexplored frontier of alloy contacts to 2D materials, looking beyond the limited set of pure metals previously reported.

While we have been able to reproduce this very exciting peak in thermal conductance, its existence has also raised many important questions. Why does this alloy composition give us the thermal data it does/what is the alloy doing to the graphene? Our TEM measurements have been unable to answer this particular question, but future work in this area would provide insights for the identification of alloy compositions that are superior contacts for other 2D materials aside from graphene.
7.3 Temperature dependent FEDWs on thermal conductivity of SrTiO$_3$

We demonstrated the use of strain engineering of single crystal SrTiO$_3$ as a method to drastically reduce thermal conductivity by $\approx 60\%$ at room temperature and also the use of temperature to achieve a further $\approx 65\%$ reduction from 275 K down to 225 K and below. This was achieved through the increasing density of ferroelectric domain walls as SrTiO$_3$ became fully ferroelectric.

Unfortunately, we were unable to directly image the FE domains through temperature dependent PFM measurements. Such measurements would have experimentally provided more information on the nucleation of domains in the ferroelectric transition regime for different temperatures. According to the work of Barzilay et al. [197] FE domains more readily nucleate close to surfaces due to the accumulation of defects there. While our experimental results show that thermal conductivity at room temperature does not strongly depend on oxygen vacancy concentration, additional studies of temperature dependent measurements through the FE transition regime may provide insight on whether vacancy/defect engineering can be a way to further control FE domain nucleation.

7.4 Ferroelectric domain walls on thermal conductivity in strained PbTiO$_3$

Utilizing strain engineering, we demonstrated a 61% reduction in thermal conductivity in single crystal PbTiO$_3$. Furthermore, we experimentally showed that this reduction very strongly correlated with FE domain wall density, indicating that FEDWs are powerful phonon scattering sites with thermal resistances comparable to grain boundaries. The results of this work demonstrate that single crystal PbTiO$_3$ is a very promising material for the study of active thermal conductivity switching. Unfortunately, we were unable to actively switch our PbTiO$_3$
films due to the film being too electrically conductive, which we attribute to the presence of charged oxygen vacancies. Hence, future studies investigating active thermal switching will require single crystal PbTiO$_3$ grown with a lower density of oxygen vacancies. While a reduction in thermal conductivity as large as 61% may not be realized by the application of an electric field, the potential switching ratio may be greater than that achieved by Ihlefeld et al. of 11% [88].
References


[38] X. Li, W. Park, Y. Wang, Y. P. Chen, and X. Ruan, J. Appl. Phys. 125, 1 (2019).


(1993).


(2009).


[178] (n.d.).


127


