

Cross Plane Thermal Conductance of Graphene-Metal Interfaces

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ABSTRACT

We present an experimental study of cross-plane thermal conductance in metal-graphene-oxide stacks employing time-domain thermoreflectance (TDTR) measurements on Al/m/graphene/SiO₂ structures with monolayer graphene for varying adhesion metals *m*. Thermal conductance *G* in the range of 15-60 MWm⁻²K⁻¹ are found across several metals - a two-to-fourfold decrease over Al/m/SiO₂ reference values, charted against metal Debye temperature over a 274-630 K range, as well as electronic work function. The results of this study help with a better understanding of the roles of electron and phonon transport in thermal conduction across graphene-metal interfaces, revealing potential trade-offs between electrical contact resistance and heat management in graphene devices.

KEY WORDS: Graphene, thermal conductance, time-domain thermoreflectance, Debye temperature, metal work function

NOMENCLATURE

G thermal boundary conductance, Wm⁻²K⁻¹
T temperature, K
TBR thermal boundary resistance, m²KW⁻¹
c acoustic propagation velocity, m/s

Greek symbols

α transmission probability
 θ_D Debye temperature, K
 ψ_F work function, eV

INTRODUCTION

Graphene, a single-layer sheet of sp²-bonded carbon atoms, has been the subject of extensive research in recent years owing to its superlative electronic, mechanical and thermal properties. This includes repeated measurements of high in-plane thermal conductivities on both supported and suspended films, recording values of 2000-4000 Wm⁻¹K⁻¹ [1,2], as well as theoretical study of the implications of flexural (out-of-plane) transverse phonon modes with quadratic acoustic dispersion. Conversely, out-of-plane heat transfer to deposited metals or dielectrics has received less attention, despite significant implications for thermal management in graphene transistors [3], interconnects [4], or as interfacial materials to heat-sensitive memory materials [5].

A single previous study [6] performed time-domain thermoreflectance (TDTR) measurements on exfoliated 1-10 layer graphene flakes, transferred to SiO₂ substrates and contacted by a 2 nm Ti adhesion layer/100 nm Au optical transducer. Employing a model of series Kapitza conductances between graphene/metal and graphene/SiO₂ [7], the authors

found the former interface to dominate heat transport, producing a net conductance *G* of 25 MWm⁻²K⁻¹ (one-quarter the value for reference metal/oxide stacks) independent of the number of graphene layers present. Temperature invariance of this value for *T* > 100 K is consistent with acoustic-phonon dominated heat transfer, with negligible contribution from charge carriers for nominal metal contacts of intermediate electrical resistance. Metals with high Debye temperatures are therefore expected to optimize thermal coupling in the cross-plane direction.

The following aims to perform congruent analysis across a series of adhesion-layer metals (Table I), spanning a range of electron (work function) and phonon (Debye temperature) energies. Ti and Pd are noted for high wettability on graphene, commonly used as electrical contacts or adhesion layers for other electrode metals [8,9]. Surface interactions between graphene/transition metal interfaces have been researched extensively [10]. Interactions include changes to the band gap of graphene due to π -band interactions, lattice matching and surface buckling, and variations of surface interactions due to metal graphene surface separation. Nickel has been shown to interact strongly with graphene, with strong interactions with the π -band of graphene causing shifts in band gap, whereas palladium shows weak-to-strong surface interactions due to higher metal-graphene separation distances [10].

Table 1. Work function and Debye temperature of investigated adhesion-layer metals [11,12]

Metal	Pd	Ti	Al	Ni	Cr
Debye Temperature θ_D [K]	274	420	428	450	630
Work Function ψ_F [eV]	5.22	4.33	4.28	5	4.5

SAMPLE PREPERATION

Monolayer CVD-grown graphene was purchased from a commercial supplier (Graphene Supermarket) and pre-transferred to 1cm-by-1cm 285 nm SiO₂/Si chips. Commercial CVD graphene was investigated as a scalable alternative to higher-quality exfoliated flakes, with only monolayer films studied per the established independence of cross-plane thermal transport on interlayer graphite interaction.

Raman spectroscopy is an established characterization technique used to analyze a variety of carbon-based materials, including graphene, diamond, and carbon nanotubes. The Raman spectrum of graphene has two unique spectrum bands that allow for the determination of the number of layers of graphene, and one and to determine the number of defects

[13], enabling quick characterization of the structure and quality of the samples. Samples were measured using a WiTec 500 AFM/micro-Raman Scanning Microscope; two of the graphene chips were probed at 5 different locations across the surface of the chip, allowing for studying the general uniformity of the film across our substrate (sample spectrum in Fig 1). Measurements were taken at 100X objective with a 600-lines/mm grating, at a probe frequency of 532 nm. Care was taken to minimize the laser power to reduce local heating of the surface of our substrates. The G, 2D, and D lines were measured at 1601 cm^{-1} , 2708 cm^{-1} , and 1359 cm^{-1} respectively. High 2D:G intensity ratios confirmed monolayer coverage, with a D:G ratio less than 0.1 indicative of low defectivity for CVD-grown films [14].

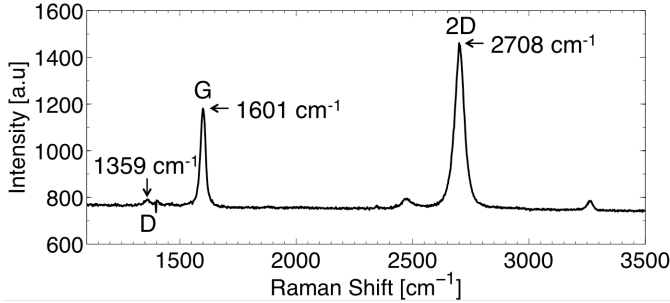


Fig. 1. Raman spectrum for monolayer CVD graphene on 285 nm SiO_2/Si chips collected post-cleaning. The high 2D:G intensity ratio confirms monolayer coverage, with low defectivity indicated by the low D:G intensity ratio.

Following cleaning in acetone and 2-propanol (see Appendix), samples were uniformly metalized in a Lesker PVD-75 electron-beam evaporator pumped to 5×10^{-7} Torr base pressure. 3 nm of adhesion metal was deposited at a low rate of 0.1 Å/s , to optimize film quality/increase grain size, followed by 45 nm of Al at 0.1 Å/s for the first 5 nm and 0.5 Å/s thereafter, without breaking vacuum. For the all-Al case, 50 nm was used, again employing the slower deposition rate for the first 8 nm. Atomic Force Microscopy was used to verify initial film thicknesses to $\pm 0.5 \text{ nm}$, limited largely by in-air oxidation of the top Al surface. Two graphene chips were metalized in every run, alongside a reference 285 nm SiO_2/Si chip. Figure 2 shows the vertical cross-sections of our samples.

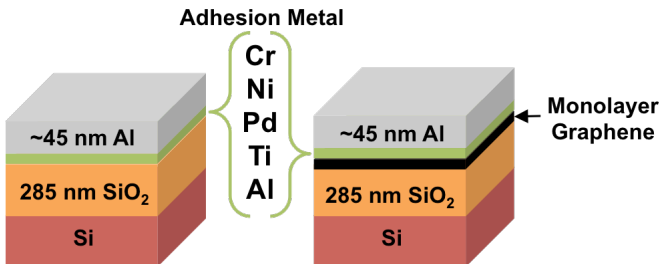


Fig. 2. Structures of metalized samples for TDTR measurements. 285 nm SiO_2/Si chips with and without monolayer graphene were uniformly metalized with 3 nm of adhesion metal followed by 45 nm of Al, except for the all-Al case for which 50 nm of Al was deposited.

THEORETICAL MODEL

The thermal conductance G of the $\text{Al}/m/\text{graphene}/\text{SiO}_2$ structures with monolayer graphene for varying adhesion metals m is attributed to the interfacial thermal boundary resistance of $m/\text{graphene}$, and $\text{graphene}/\text{SiO}_2$ interfaces acting in series. In terms of thermal boundary conductance, $G = TBR^{-1}$, we have

$$G^{-1} = G_{m/\text{graphene}}^{-1} + G_{\text{graphene}/\text{SiO}_2}^{-1} \quad (1)$$

For the $\text{Al}/m/\text{SiO}_2$ structures, the thermal conductance is attributed to the interfacial thermal boundary resistance of the m/SiO_2 interface.

$$G^{-1} = G_{m/\text{SiO}_2}^{-1} \quad (2)$$

The three main sources for interfacial thermal conductance are incomplete contact, near-interface disorder, and acoustic/diffuse mismatch. Since complete contact is common for thin-film systems, the interfacial thermal conductance can be approximated by the acoustic/diffuse mismatch model assuming near-interfacial disorder is negligible. The impact of near-interfacial disorder is difficult to generalize, but primarily depends on the quality of the initial stages of film deposition [15].

Even though electrons transport energy all the way to an interface, the transport of energy across an interface is limited by the transmission probability of phonons. At temperature, below 30K for solid-solid interfaces, the phonons wavelengths are long in comparison to the dimensions of the interface roughness. The acoustic mismatch model assumes the phonons are governed by continuum acoustics and the interface can be considered as a plane, so the transmission probability of phonons can be approximated using an acoustic analog of Fresnel equation. At higher temperatures, the phonon wavelength decreases and becomes comparable to the dimensions of the interface roughness. As a result, the phonons are reflected in a diffuse manner rather than in specular manner.

Since the temperature of the $\text{Al}/m/\text{graphene}/\text{SiO}_2$ and $\text{Al}/m/\text{SiO}_2$ structures are well above the 30K, the thermal conductance of the samples can be approximated using the diffuse mismatch model. The transmission probability of phonons from side i is given by [16]:

$$\alpha_i(\omega) = \frac{\sum_j c_{3-i,j}^{-2}}{\sum_{i,j} c_{i,j}^{-2}} \quad (3)$$

where $c_{i,j}$ is the acoustic propagation velocity from side i with mode j . For frequencies below the Debye cutoff frequency, the thermal boundary conductance is approximated by

$$G_{DMM}^{-1} = \left[\frac{\pi^2 k_B^4}{15 \hbar^3} \frac{1}{2} \frac{\sum_j c_{i,j}^{-2} \sum_j c_{3-i,j}^{-2}}{\sum_{i,j} c_{i,j}^{-2}} \right]^{-1} \cdot T^{-3} \quad (4)$$

The acoustic propagation velocities for the various adhesion metals and SiO_2 are known, while the acoustic propagation velocities for graphene are assumed to be

$c_{i,1} = 21.3 \text{ km/s}$ and $c_{i,2} = c_{i,3} = 13.6 \text{ km/s}$ based on previous literature [1]. The calculated thermal conductance of the Al/*m*/graphene/SiO₂ and Al/*m*/SiO₂ structures versus Debye temperature for the various adhesion metals *m* is shown in Figure 3. High thermal boundary conductance values are predicted by this model. A linear trend is expected for the thermal conductance vs. Debye temperature across graphene-metal interfaces due to the linear relationship between average acoustic propagation velocities and Debye temperature for the various adhesion metals *m*. However, minimal variation between different adhesion metals and uniformly smaller conductance is achieved in the presence of monolayer graphene as a result of the small variation in acoustic propagation velocities for the various adhesion metals relative to the large acoustic propagation velocities of graphene.

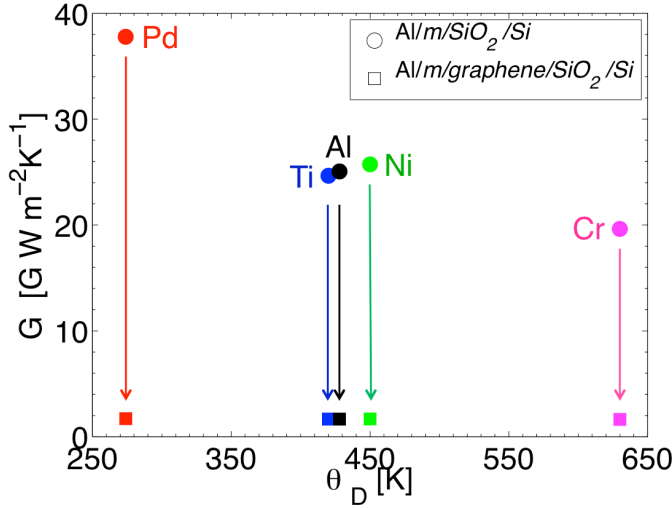


Fig. 3. Theoretical thermal conductance for Al/*m*/SiO₂ and Al/*m*/graphene/SiO₂ versus adhesion metal Debye temperature. In the presence of graphene, minimal variation between different adhesion metals and uniformly smaller conductance on the order of $2 \text{ GWm}^{-2}\text{K}^{-1}$ are achieved.

MEASUREMENT PROCESS

Time-domain thermoreflectance (TDTR) measurements are widely used for characterizing the thermal properties of thin film structures. The TDTR method is an optical technique that uses ultra short- pulses to generate a transient thermal response. The thermal response of the thin film structures depends on the film thicknesses, the heat capacity of the films, the thermal conductivity of the films, and the thermal boundary resistances. To investigate the effect on thermal conductance for the various adhesion metals *m*, TDTR measurements were performed on the Al/*m*/SiO₂ and Al/*m*/graphene/SiO₂ samples.

The TDTR system consists of a mode-locked Nd:YVO₄ laser that generates pulses ($\lambda = 1064 \text{ nm}$) at a repetition rate of 82-MHz. The pulses are separated into pump and probe beam components using a beam splitter. The pump beam is modulated at 2 MHz and converted to 532 nm, while the probe is delayed from the pump beam using a linear mechanical delay stage. Both the pump and probe beams are focused on the sample surface as shown in Figure 4. The heat deposited on the sample surface by the pump beam generates a transient

thermal response. The probe beam measures the temporal reflectivity of the surface, which is directly related to the temperature response.

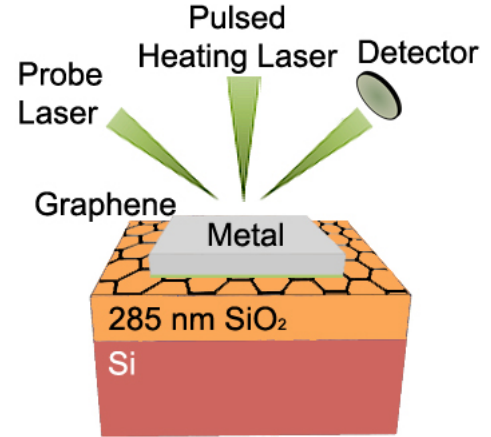


Fig. 4. Schematic of time-domain thermoreflectance measurements.

Five TDTR measurements were taken at two different spots on each sample except for the Al/Pd/graphene/SiO₂ sample for which TDTR measurements were taken at four different spots. The thermal response at each spot for each sample is simply the average of all five TDTR measurements. Since the thermal conductance of the samples is attributed to the interfacial thermal conductance acting in series, Figure 5a shows the assumed structure of the samples for deriving the thermal conductance of the samples. Figure 5b shows the representative TDTR normalized reflectance trace and curve fit.

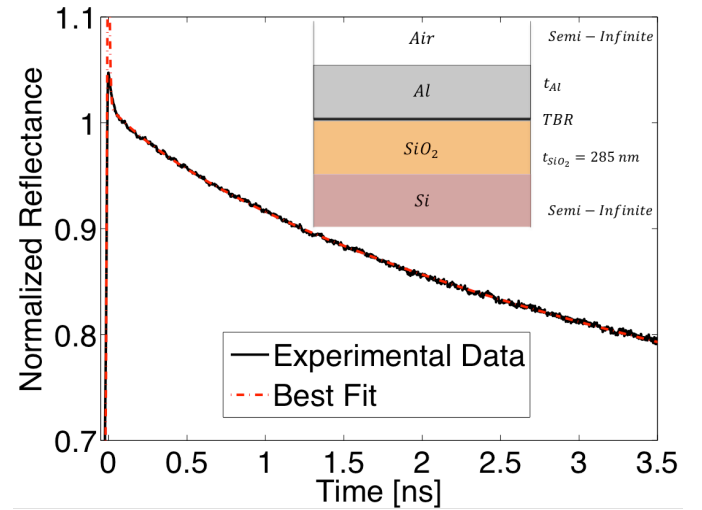


Fig. 5. Thermal resistance system for Al/*m*/SiO₂ and Al/*m*/graphene/SiO₂ and representative TDTR normalized reflectance trace for Al/*m*/SiO₂ and Al/*m*/graphene/SiO₂ samples, along with best-fit curve.

The fitting parameters of the TDTR measurements for the Al/*m*/SiO₂ samples were the Al/SiO₂ thermal boundary resistance and transducer conductivity. Using the measured transducer conductivity, the fitting parameter for the Al/*m*/graphene/SiO₂ samples was the Al/SiO₂ thermal

boundary resistance. The metal thickness was taken to be $45+3$ [Al+m] nm for Ni, Cr, Ti, Pd and 50 nm for Al based on AFM measurements. The specific heat of the transducer film was approximated by a thickness weighted average.

RESULTS AND DISCUSSION

Figures 6a and 6b present measured thermal conductance for Al/m/graphene/SiO₂ and Al/m/SiO₂ stacks for the various metals, plotted against the electronic work function and Debye temperature of the adhesion-layer metal m . Across all metals, a two-to-fourfold decrease in thermal conductance is observed in the presence of monolayer graphene, commensurate with previously reported trends measured on Ti/Au metalization layers [6]. This overall trend is consistent with additional contributions from interfacial Kapitza resistances at metal/graphene and graphene/oxide boundaries. Decreased overall thermal conductances are reported, on the order of tens of $\text{MW m}^{-2}\text{K}^{-1}$ for this transducer/substrate combination.

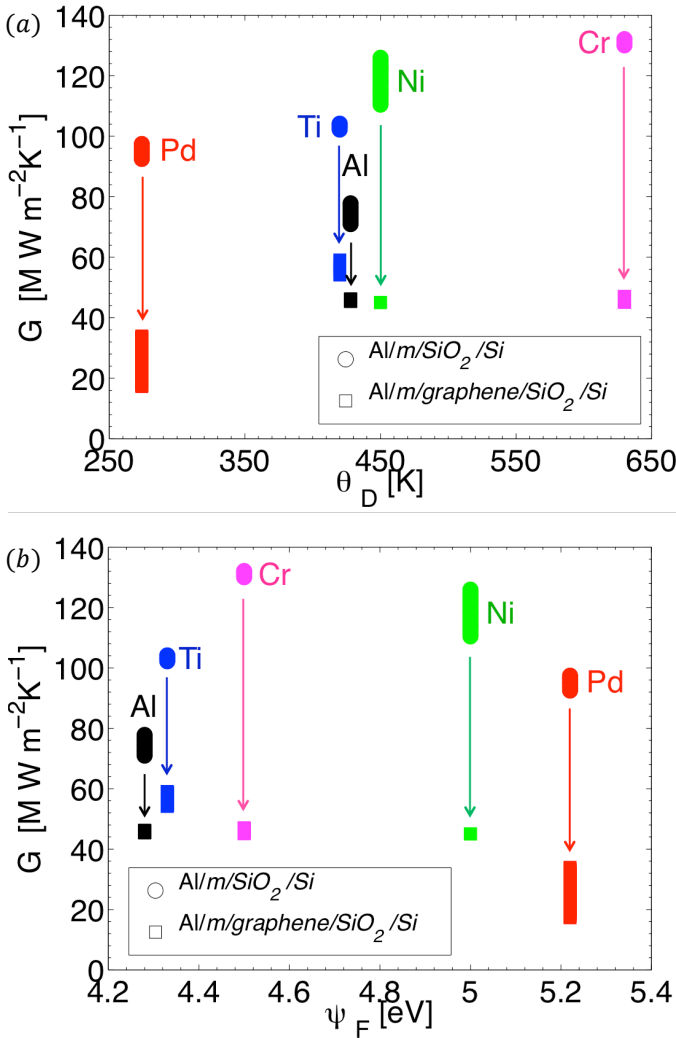


Fig. 6. Measured thermal conductance for Al/m/SiO₂ and Al/m/graphene/SiO₂ versus (a) adhesion metal Debye temperature and (b) adhesion metal work function.

Examining measured conductance versus metal electronic work function (Fig. 6b) no trend is present. In the absence of further data points across an intermediate range of energies

closer to above graphene's Dirac-point work function of 4.6 eV [9], an electron contribution to cross-plane thermal conductance is not apparent. Comparatively, a plot of G versus metal Debye temperature in Fig. 6b demonstrates a monotonic incline in thermal conductance with θ_D . A second-order dependence on interface-quality in presumably uniform thin films is suggested by the deviation in Al vs. Ti resistances, with the latter offering improved thermal conductance from better physical adhesion.

The correlation of thermal conductance with metal Debye temperature reveals potential design trade-offs between heat management and electrical-contact-resistance in graphene devices. Palladium, cited for good adhesion and efficient carrier injection to carbon nanomaterials [8, 9], presents a high thermal resistance from its low acoustic phonon energies (θ_D of only 274 K). Ni ($\theta_D = 450$ K) and Cr ($\theta_D = 630$ K) offer improved thermal conductance alongside work functions more closely matched to graphene's Dirac point, although electrical contact resistances suffer from poor physical wettability. Graphitic-interfacial layers [17] emerge as a prospective solution, shown to improve adhesion and carrier injection from such high- θ_D metals as Ni, without introducing excessive impedance for cross-plane heat flow, per the demonstrated invariance of G_{Thermal} on the number of graphene layers [6].

CONCLUSION AND FUTURE WORK

In summary, we have conducted experiments measuring the cross-plane thermal conductance of thin-film metal stacks, detecting graphene interfacial layers through changes in thermal resistivity using time-domain thermorefectance measurements. Results have shown an overall decrease in the thermal boundary conductance with the addition of monolayer graphene in the metal-oxide stacks. We have found a correlation between the Debye temperature of the adhesion metal and the thermal boundary conductance, consistent with proposed models of acoustic-phonon dominated cross-plane heat transfer.

Future work will include investigating the temperature dependence of the thermal conductance of the graphene-interface layers. Growing graphene through CVD methods directly on a metal substrate would change the surface interfaces, which would allow for a better understanding of the relationship between contact quality and heat transfer. Detailed characterization and analysis of the metal film interfaces and adhesion layer would bring insight into potential metal/graphene surface interactions and heat transfer mechanisms.

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APPENDIX

Sample Fabrication Procedure

The 10 received chips of CVD-graphene on 285 nm SiO₂/Si, along with reference oxide/Si chips without graphene, were first cleaned as follows:

1. 60-minute bath in Acetone
2. 5 minute rinse in 2-Propanol
3. Blow-dry with N₂
4. 40-minute bake in 90°C bake-out oven

Visual inspection of graphene chips revealed consistent coverage with minor wrinkles and gaps, with cleaning removing blemishes from transfer polymer or ambient contaminants. Metalization parameters used for the 5 metals in the PVD-75 Electron-Beam evaporator are provided below:

Table 2. Sample Metalization Parameters

Metal	Source Purity	Beam Voltage	Mean Beam Current	Deposition Rate
Ti	99.995%	8 kV	26 mA	0.1 Å/s
Pd	99.95%	8 kV	40 mA	0.1 Å/s
Ni	99.99%	10 kV	46.5 mA	0.1 Å/s
Cr	99.95%	8 kV	5 mA	0.1 Å/s
Al	9.999%	8 kV	66-88 mA	0.1-0.5 Å/s