

Manipulating the Chemical Bond to Control Thermal Transport in Graphene and Low-Dimensional Carbon Films

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ABSTRACT

The high thermal conductivities exhibited by graphene and other low-dimensional carbon structures have generated tremendous potential for functional material solutions in a wide array of military applications. In this work, we present a series of studies focusing on experimental measurements of the thermal boundary resistance and thermal conductivity of low-dimensional carbon allotropes thin films in which the films are processed to introduce changes in the chemical bond at surfaces and interfaces. The atomic interactions are manipulated in such a way to increase to bond strength, which increases the thermal transport of these low-dimensional carbon-based films. We present studies on functionalized graphene, 2D Covalent Organic Frameworks (COFs), and a new allotrope of carbon recently discovered deemed “graphullerene” (a few layer superatomic cousin to graphene with remarkably increased thermal conductivity compared to fullerene thin films).

Keywords: *thermal conductivity, graphene, covalent organic framework, graphullerene, phonon transport, thermal boundary resistance, time domain thermorefectance, steady state thermorefectance*

1.0 INTRODUCTION

The high thermal conductivities exhibited by graphene and other low-dimensional carbon structures have generated tremendous potential for functional material solutions in a wide array of military applications [1], [2]. In particular, the unique properties of these carbon allotropes allow for tremendous efficiency in the transport of not only charge carriers but also thermal carriers (i.e., phonons) as well. For these reasons, carbon nanostructures, including graphene, are being pursued both for a variety of electronic applications and as an enabler of next-generation thermal solutions, making thermal transport properties of these materials and their interfaces key, such as thermal conductivity and thermal boundary conductance.

The key atomistic property that ultimately dictates the thermal transport in these low-dimensional carbon allotropes is the atomic bonding environment, which governs the phononic spectrum and intermolecular interactions, and the atomic defects that arise from processing of the carbon material to improve its optical, electrical or chemical properties. The introduction of atomic defects could often be viewed as deleterious to thermal transport due to the increased phonon scattering [3]. For example, C₆₀/C₇₀ fullerene compacts exhibit ultra-low thermal conductivities due to the weak intermolecular bonding at the fullerene / fullerene junctions [4], and functionalizing fullerene to create phenyl-C₆₁-butyric acid methyl ester (PCBM) based thin films results in further reductions in thermal conductivity and one of the lowest thermal conductivities ever reported for fully dense materials [5]-[10]. This is shown in Figure 1 [6], which plots the thermal conductivity of a range of materials at room temperature as a function of their atomic density, showing that PCBM exhibits the lowest thermal conductivity of any fully dense solid at room temperature. Further exemplifying the role of the chemical bond in the thermal conductivity of solids, it is notable that the highest thermal conductivity of any

fully dense three-dimensional solid is diamond. It is well known that graphene also exhibits such remarkably high thermal conductivities, often exceeding diamond [1],[2], [11]. Thus, the materials with the highest and lowest thermal conductivities are different forms of carbon.

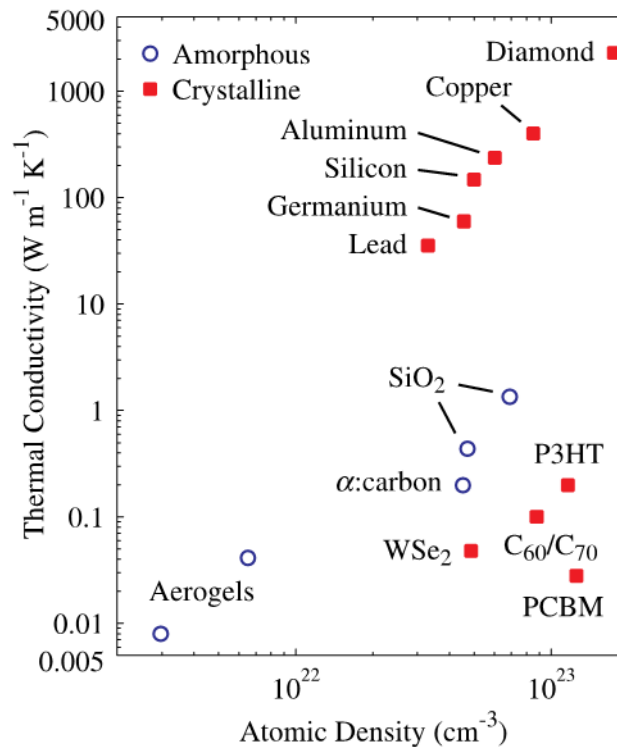


Figure 1: Thermal conductivity of a range of amorphous and crystalline solids, plotted as a function of their atomic density. Carbon-based materials exhibit some of the highest and lowest thermal conductivities. Figure from Duda et al. [6].

However, as the length scales of materials reduce to values below their thermal carriers' mean free paths, the thermal resistance at material boundaries and heterogeneous interfaces begins to become the dominant thermal resistance of the system, composite, or device [12], [13]. This Thermal Boundary Resistance (TBR), or its corollary to thermal conductivity, the Thermal Boundary Conductance (TBC), become the dominant thermal resistance and thermophysical transport properties, respectively, that dictate the thermal processes and temperatures of devices at these length scales [14] – [16].

The TBC as a function of temperature measured across various interfaces is shown in Figure 2 [15], including measurements on the TBC across Al/graphene (Al/SLG) interfaces [17]. The TBC across the TiN/MgO and Bi/diamond interfaces represent some of the highest and lowest phonon-dominated TBCs ever measured, respectively [18], [19]. Note that the electron-dominated TBC (Al/Cu and Pd/Ir) are roughly one order of magnitude higher than the phonon-dominated TBC [20], [21]. The additional data in Figure 2 (Al/Si, Al/SLG, and GaSb/GaAs interfaces) [17], [22], [23] represent experimental measurements, where imperfections and interfacial non-idealities impact the measured TBCs. The specific interfacial imperfection that was investigated in each material case is indicated by labels in Figure 2. Briefly, these three example interfaces show the effects of either roughness (Al/Si), bonding (Al/SLG), or dislocations (GaSb/GaAs) on the thermal boundary conductance. In the Al/Si case, a rougher substrate leads to a decrease in thermal boundary conductance. At the Al/SLG interfaces, by increasing the bonding between otherwise nonreacting Al films and SLG substrates, Al can bond covalently to the SLG, thereby increasing the thermal transport. At the GaSb/GaAs interfaces, the large lattice mismatch between the GaSb and GaAs leads to strain dislocations. The

number of dislocations can be controlled via the growth technique, and we observed that making a GaSb/GaAs interface with a higher number of dislocations per unit area results in a lower TBC. Along with these data, the equivalent conductances of various thicknesses of SiO₂ are indicated by the solid lines (this is equivalent conductance calculated by $h = k_{\text{SiO}_2}/d$, where d is the thickness of the SiO₂ and k is its thermal conductivity). Clearly, the structure and chemistry of the interface also impacts the TBC across graphene interfaces, much like the thermal conductivity of lower dimensional carbon structures discussed with respect to Figure 1.

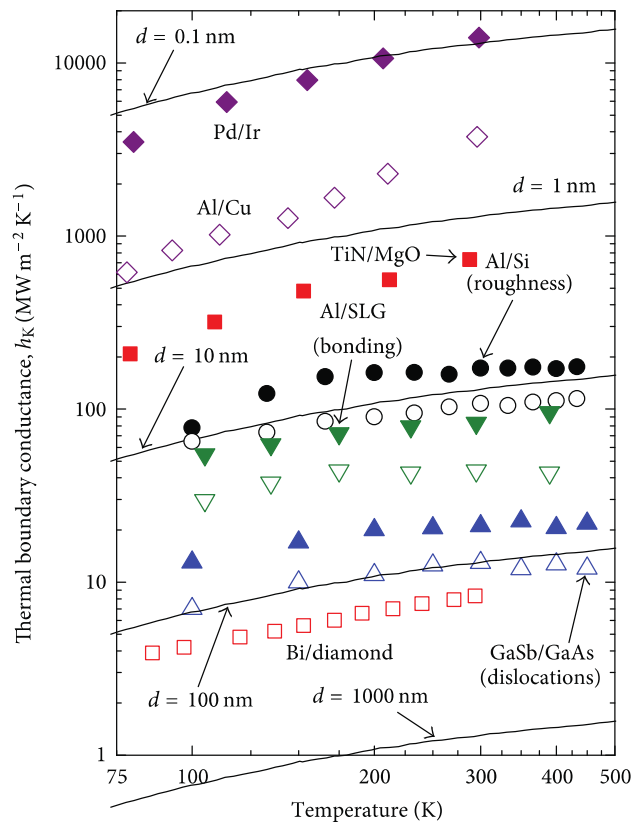


Figure 2: Thermal boundary conductance at various solid interfaces as a function of temperature. Typical values span over three orders of magnitude. For comparison, the equivalent conductances of various thicknesses of SiO₂ (d) are also shown. Figure from Hopkins [15].

Clearly, from the discussions above exemplified in Figure 1 and Figure 2, the ability to tailor the interatomic interaction and increase bonding at graphene interfaces or low-dimensional carbon molecule junctions could indeed result in improved thermal properties, thus providing a novel route to improve thermal conductivity and TBR in low-dimensional carbon allotropes with designer functional properties. In this work, we present a series of studies focusing on experimental measurements of the TBC and thermal conductivity of low-dimensional carbon allotropes thin films in which the films are processed to introduce changes in the chemical bond at surfaces and interfaces. The atomic interactions are manipulated in such a way to increase bond strength, which increases the thermal transport of these low-dimensional carbon-based films. We review studies on the TBC across functionalized and chemically modified graphene contacts (Section 3.0) [17], [24]-[26], 2D Covalent Organic Frameworks (COFs) (Section 4.0) [27], and a new allotrope of carbon recently discovered deemed “graphullerene” (a few layer superatomic cousin to graphene with remarkably increased thermal conductivity compared to fullerene thin films) (Section 5.0) [28]. Before discussing these works, we first discuss the measurement techniques used to determine the thermal resistances of these thin films and interfaces.

2.0 PUMP-PROBE THERMOREFLECTANCE FOR MEASUREMENTS OF NANOSCALE THERMAL RESISTANCES

The measurements of thermal properties (thermal conductivity and thermal boundary resistance) of the graphene and other thin low-dimensional carbon films were performed with various pump-probe thermoreflectance techniques [29]-[30], including Time Domain and Steady State Thermoreflectance (TDTR [31] and SSTR [32], respectively). These optical-based techniques are well-suited for measurements of thin films and spatially confined structures due to the implementation of focused lasers to source heat and monitor the temperature changes in the area of a focused laser spot.

3.0 CHEMISTRY EFFECTS ON THE THERMAL BOUNDARY CONDUCTANCE ACROSS GRAPHENE INTERFACES

In graphene devices, it is necessary for this two-dimensional material to be able to efficiently transport heat into the surrounding 3D device architecture in order to fully capitalize on its intrinsic transport capabilities. Therefore, the thermal boundary resistance at graphene interfaces is a critical parameter in the realization of graphene electronics and thermal solutions. In prior work by Hopkins et al. [17] and Walton et al. [25], we examined the role of chemical functionalization on the TBC across metal / graphene interfaces. Specifically, we studied plasma functionalized graphene with the functional groups used to control the graphene interfacial interactions. The addition of adsorbates to the graphene surfaces are shown to influence the cross-plane thermal conductance, as shown in Figure 3 [25]. This behaviour is attributed to changes in the bonding between the metal and the graphene, as both the phonon flux and the vibrational mismatch between the materials are each subject to the interfacial bond strength. These results demonstrate that plasma-based functionalization of graphene surfaces is a viable approach to manipulate the thermal boundary conductance.

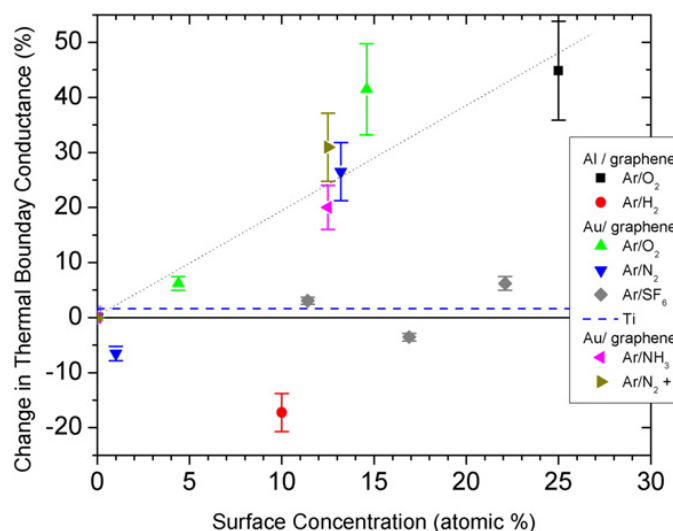


Figure 3: The change in thermal boundary conductance at aluminum-graphene (Al/SLG) and gold-graphene (Au/SLG) interfaces as a function of the type and concentration of functional groups at the interface prepared using operating backgrounds indicated in the legend (e.g., Ar/O₂). Also shown (dashed line) is the result for an interface prepared using a Ti thin film (i.e., Au/Ti/SLG). The presence of H- and F-functional groups as well as the Ti layer has little or negative impact on the thermal boundary conductance. The presence of O- and N- functional groups, however, tends to increase the thermal boundary conductance in proportion to the concentration of those groups (the dotted line). Figure from Walton et al. [25].

These results shown in Figure 3 motivate the following question: what role does metal contact chemistry have on the TBC across metal / graphene interfaces? In our prior work, we have shown that the TBC across Ti/SLG/SiO₂ largely depends on the oxide composition at the contact [26]. By varying the base pressure and the deposition rate of the encapsulating Ti layers, we demonstrated that the oxide composition in the Ti layer can be systematically changed (Figure 4 left panel) and, therefore, the resulting TBC across the graphene interface scale. Our results show that a faster deposition rate leads to lower oxide composition at the contacts, thus significantly increasing TBC, as shown in Figure 4 (right panel).

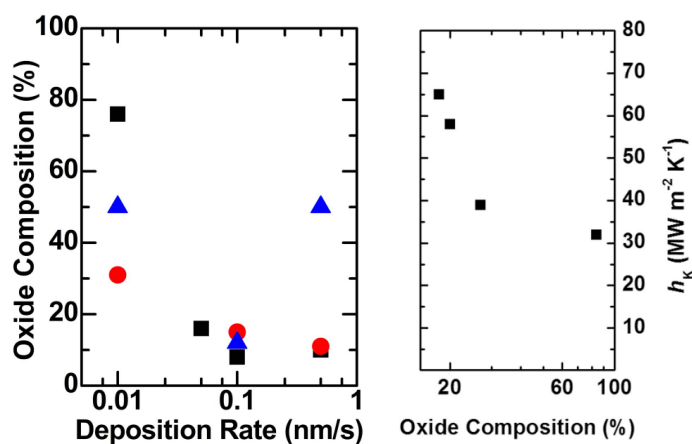


Figure 4: (Left) Ti oxide composition versus deposition rate SLG/SiO₂ samples. Each identical marker shape represents samples cut from the same piece of graphene. (Right) TBC across Au/Ti/SLG interfaces as a function of oxide composition in the Ti. Figures from Freedy et al. [26].

4.0 HIGH THERMAL CONDUCTIVITIES AND LOW DIELECTRIC CONSTANTS (LOW-K) OF THIN FILMS OF COVALENT ORGANIC FRAMEWORKS (COFs)

As the features of microprocessors are miniaturized, low-dielectric-constant (low-*k*) materials are necessary to limit electronic crosstalk, charge build-up, and signal propagation delay. However, all known low-*k* dielectrics exhibit low thermal conductivities, which complicate heat dissipation in high-power-density chips. Two-Dimensional (2D) Covalent Organic Frameworks (COFs) combine immense permanent porosities, which lead to low dielectric permittivities, and periodic layered structures, which grant relatively high thermal conductivities. However, conventional synthetic routes produce 2D COFs that are unsuitable for the evaluation of these properties and integration into devices. In our prior work by Evans et al. [27], we report on a series of high-quality COF thin films, which reveal that 2D COFs have high thermal conductivities (1 W m⁻¹ K⁻¹) with ultra-low dielectric permittivities (*k* = 1.6). These results show that oriented, layered 2D porous organic polymers are promising next-generation dielectric layers and that these molecularly precise materials offer tunable combinations of useful properties.

Compared to other organic or porous materials, 2D COFs have unusually high thermal conductivities (Figure 5). This finding is consistent with the structural regularity, large porosities, strong interlayer interactions and low heat capacities of 2D COFs. Molecular dynamics simulations give additional insight into the high anisotropic thermal conductivities of COF-5. We extract an anisotropy ratio of 3.4 between in-plane and cross-plane COF-5 thermal conductivities (hollow symbols in Figure 5). This anisotropy is valuable for thermally dissipative coatings, including in low-*k* dielectric layers, where device failure from thermal build-up can be mitigated. By this approach, we predict an in-plane thermal conductivity of 3.5 W m⁻¹ K⁻¹. These absolute thermal conductivities and anisotropy ratios are lower for 2D COFs than for other layered crystals, which likely arises as a function of periodic voids in their van der Waals surface.

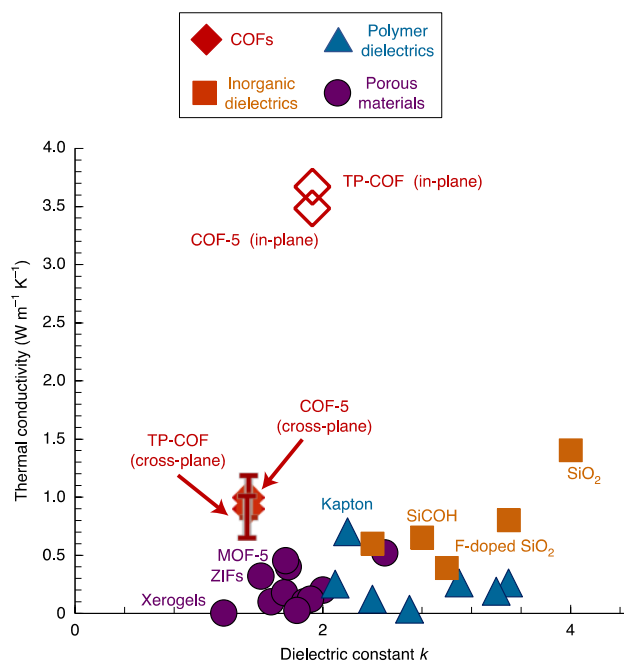


Figure 5: Meta-analysis of thermal conductivities in low- k dielectrics. Relation between thermal conductivity and dielectric constant for various materials. Filled diamonds are experimentally measured thermal conductivities and open diamonds are evaluated using computational techniques. Figure from Evans et al. [27].

The 2D COFs overcome the traditional trade-off between dielectric permittivity and thermal conductivity that is found in all known low- k dielectric materials (Figure 5). For example, dense amorphous metal oxides, such as Al_2O_3 or HfO_2 are relatively thermally conductive compared to low-density aerogels, which are thermally insulating owing to their porous structure and tortuous solid networks. Although the densities of 2D COFs are comparable to those of aerogels, their thermal conductivities are comparable to those of materials that are an order of magnitude denser, such as conventional amorphous metal oxide dielectrics. This relatively high thermal conductivity is most likely driven by the well-interfaced van der Waals contact of porous 2D polymers that are arranged as eclipsed stacks. Furthermore, we suspect that the thermomechanical properties of 2D COFs could be modulated by the introduction of molecular guests, as has been observed in other porous materials, which unlocks the possibility of responsive materials [33]. The combined thermal resistances of these COF films (including both thermal conductivity and thermal boundary conductances) highlight 2D COFs as low-thermal-resistance, ultra-low- k thin films relative to traditionally studied low- k dielectrics.

5.0 GRAPHULLERENE AND GRAPHULLERITES: A FEW LAYER COVALENT NETWORK OF FULLERENES WITH ENHANCED THERMAL CONDUCTIVITIES

The two natural allotropes of carbon, diamond and graphite, are extended networks of sp^3 -hybridized and sp^2 -hybridized atoms, respectively. By mixing different hybridizations and geometries of carbon, one could conceptually construct countless synthetic allotropes. In this work published by Meirzadeh et al. [28], we introduced graphullerene, a two-dimensional crystalline polymer of C_{60} that bridges the gulf between molecular and extended carbon materials. Its constituent fullerene subunits arrange hexagonally in a covalently interconnected molecular sheet. We explore the thermal conductivity of this material and find it to be much higher than that of molecular C_{60} , which is a consequence of the in-plane covalent bonding. Vibrational thermal transport is strongly impacted by the strength of the interatomic and intermolecular interactions. In

fullerene-based materials, the modification of intermolecular interactions has been shown to impact the vibrational scattering mechanisms affecting thermal conductivity (see discussion in Section 1.0). Figure 6b compares the room temperature thermal conductivity of mechanically exfoliated, thin, bulk graphullerite flakes with that of molecular C_{60} crystals. Unlike previous reports, in which chemical modifications of C_{60} resulted in reductions of thermal conductivity (see discussion in Section 1.0), the high in-plane order and the formation of intermolecular covalent bonds in graphullerite enhance thermal transport. Graphullerite shows a marked increase in k ($2.7 \text{ W m}^{-1} \text{ K}^{-1}$) that is nearly one order of magnitude higher than that measured in molecular C_{60} crystals ($0.3 \text{ W m}^{-1} \text{ K}^{-1}$). We note that this value for graphullerite is an average of all directions, as our technique is equally sensitive to thermal transport in both in-plane and cross-plane directions.

Molecular dynamics simulations provide fundamental insights into the vibrational thermal transport dynamics and the mechanisms that drive this order of magnitude increase in k . Figure 6b presents the molecular-dynamics-predicted thermal conductivity values for graphullerite along the three crystallographic directions between 100 K and 400 K. These simulations support the marked increase in thermal conductivity for the polymerized phase compared with that of molecular C_{60} . More specifically, the in-plane thermal conductivity (across the covalently bonded sheets) is more than one order of magnitude higher than the out-of-plane value, which is similar to that of molecular C_{60} crystals. The in-plane thermal conductivity of graphullerene is also highly anisotropic, with the b direction (along the $[2+2]$ inter-fullerene bonds) demonstrating the highest thermal transport. A comparison between the calculated vibrational spectra of C_{60} and graphullerite demonstrates that the 2D covalent bonding of C_{60} introduces many new vibrational modes throughout the spectrum (Figure 6c). These modes provide additional pathways for heat conduction, which results in an overall increase in thermal conductivity for graphullerite compared with molecular C_{60} .

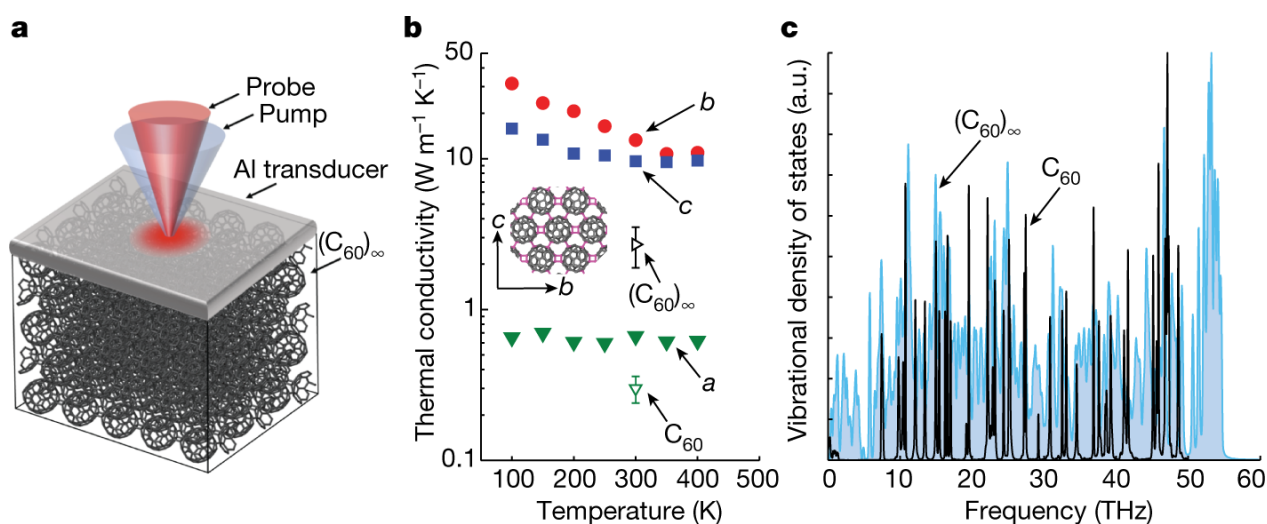


Figure 6: (a) Schematic of the thermal conductivity measurement. (b) Experimentally measured thermal conductivities of a few-micrometres-thick graphullerite flake at room temperature (black open triangle) and a molecular C_{60} single crystal (green open triangle). The filled symbols represent the non-equilibrium molecular dynamics predictions for the three crystallographic directions. (c) Vibrational density of states of molecular C_{60} and graphullerite showing additional modes throughout the vibrational spectrum for the 2D polymer phase. Figure from Meirzadeh et al. [28].



6.0 CONCLUSIONS

The key atomistic property that ultimately dictates the thermal transport in these low-dimensional carbon allotropes is the atomic bonding environment, which governs the phononic spectrum and intermolecular interactions, and the atomic defects that arise from processing of the carbon material to improve its optical, electrical or chemical properties. The ability to tailor the interatomic interaction can provide a novel route to improve thermal conductivity and thermal boundary resistance in low-dimensional carbon allotropes with designer functional properties. This work reviewed a series of studies focusing on experimental measurements of the thermal boundary resistance and thermal conductivity of low-dimensional carbon allotropes thin films in which the films are processed to introduce changes in the chemical bond at surfaces and interfaces. The atomic interactions are manipulated in such a way as to increase to bond strength, which increases the thermal transport of these low-dimensional carbon-based films. I reviewed our prior works on the TBC across functionalized and chemically modified graphene contacts (Section 3.0) [17], [24]-[26], 2D Covalent Organic Frameworks (Section 4.0) [27], and a new allotrope of carbon recently discovered deemed “graphullerene” (a few layer superatomic cousin to graphene with remarkably increased thermal conductivity compared to fullerene thin films) (Section 5.0) [28].

7.0 ACKNOWLEDGEMENTS

This work reviews a series of both historical and recent works reporting on the thermal properties of various low-dimensional carbon films and their interfaces, the research for which was funded via various programs in the United State Department of Defense. I appreciate support for my contributions to the research described in Sections 3, 4 and 5 from the Office of Naval Research (program manager: Dr. Mark Spector), Grant Numbers N00014-13-4-0528, N00014-15-12769, and N00014-20-1-2686. I also appreciate support for my contributions to the research on titanium chemistry effects on SLG TBC described in the later half of Section 3 from the Army Research Office (program manager: Dr. Pani Varanasi), Grant Number W911NF-16-1-0320.

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9.0 AUTHOR BIOGRAPHY

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