Modifying Surface Energy of Graphene via Plasma-based Chemical Functionalization to Tune Thermal and Electrical Transport at Metal Interfaces

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Abstract

The high mobility exhibited by both supported and suspended graphene, as well as its large in-plane thermal conductivity, has generated much excitement across a variety of applications. As exciting as these properties are, one of the principal issues inhibiting the development of graphene technologies pertains to difficulties in engineering high-quality metal contacts on graphene. As device dimensions decrease, the thermal and electrical resistance at the metal/graphene interface plays a dominant role in degrading overall performance. Here we demonstrate the use of low energy electron-beam plasma functionalization of oxygen, fluorine and nitrogen groups on graphene surfaces as a method to tune the thermal and electrical transport properties across gold-single layer graphene (Au/SLG) interfaces. We find that while oxygen and nitrogen groups improve the thermal boundary conductance ($h_K$) at the interface, their presence impairs electrical transport leading to increased contact resistance ($\rho_C$). Conversely, functionalization with fluorine has no impact on $h_K$, yet $\rho_C$ decreases with increasing coverage densities. These findings indicate exciting possibilities using plasma-based chemical functionalization to tailor the thermal and electrical transport properties of metal/2D material contacts.

Keywords: Graphene, Contacts, Functionalization, Thermal Boundary Conductance, Contact Resistivity
The remarkable electrical \([1-3]\) and thermal \([4-6]\) properties of single-layer graphene (SLG) have had a staggering impact on the research landscape over the past decade. Groups across the world in engineering, basic sciences and medicine have characterized and attempted to exploit these enhanced properties with the goal of revolutionizing their respective fields. One example is the field of graphene electronics where an incredible amount of research has focused on transistors, sensors and opto-electronics based on this material. While great progress has been made toward integrating graphene into many of these applications, there remain several practical issues that have hindered the large-scale development of graphene technologies and led to a migration away from this material to other 2-D structures such as MoS\(_2\). One such issue relates to difficulties associated with engineering high-quality metal contacts on graphene. \([7-9]\) For field effect transistors (FETs), there is a critical channel length below which the metal/graphene interface is the dominant resistance in the device, thereby limiting the on-current of the transistor. \([7,9]\). In order to scale-down graphene FETs for high device-densities, further minimization of the contact resistivity \((\rho_C)\) is required. While a great deal of work has been carried out in Refs. \([8-16]\) to reduce \(\rho_C\) via the choice of metal and processing conditions (i.e., resist removal and thermal annealing post-patterning), it is estimated that \(\rho_C\) must decrease by at least another order of magnitude before graphene FETs with channel lengths \(\leq 1\mu m\) can achieve the required performance characteristics. \([7,8]\)

Additionally, there are a multitude of device applications related to high-power RF and Microwave (MW) electronics where larger device geometries (length scales of 1-10 \(\mu m\)) dictate that larger values of \(\rho_C\) may be acceptable. Several groups \([17-20]\) have demonstrated graphene transistors with cutoff frequencies greater than 10 GHz, indicating their potential as a possible alternative to GaAs, InP and GaN in MW amplifiers, mixers, detectors, etc. While these results are promising, it has also been shown that Joule heating can have a profound effect on the saturation current and transient performance of graphene devices, potentially limiting their applicability for high-power applications. \([21-24]\) Because of this, the thermal transport between graphene and adjacent layers (i.e., substrate, gate dielectric, contacts, etc.) are critical parameters that must be well understood to ensure reliable and repeatable performance of future devices.
Without addressing these issues through development of novel, useful methods to tune thermal and electrical transport at these interfaces, the immense potential of graphene and other 2-D materials may never be fully realized. This work reports measurements of the thermal and electrical transport properties of chemically functionalized gold-single layer graphene (Au/SLG) interfaces. The cross-plane thermal transport is measured via Time Domain Thermoreflectance (TDTR) and the in-plane electrical transport is measured for two-terminal devices using a Keithley source-measure unit (SMU). Both properties are found to vary as a function of the percent coverage of functional groups on the graphene, providing an opportunity to tune the interfacial transport properties and subsequently offer increased flexibility for future device design.
Figure 1: Images (a)-(d) outline the patterning process used to fabricate functionalized contacts. (a) CVD-grown graphene previously transferred onto 300 nm of SiO$_2$ on p-type silicon is covered with a shadow mask (b) consisting of 16 identical TLM patterns, chemically etched into 25μm thick molybdenum stock (Towne Engineering, Inc.). The mask is affixed to the sample with kapton tape and loaded into the chamber for plasma functionalization (c) with a variety of adsorbates in the areas (red) that remain exposed. Following functionalization, the sample is loaded into a metal evaporator and 500 nm Au is deposited (d) onto the same areas that were functionalized previously. (e) Optical image of the TLM geometry used in this study after fabrication, including the measured distances between pads.

Single layer graphene was grown via low-pressure chemical vapor deposition (CVD) on copper foil and transferred to 300 nm SiO$_2$/Si substrates as outlined in Refs. [25-27]. Following transfer, x-ray photoelectron spectroscopy (K-Alpha XPS) and Micro-Raman spectroscopy were performed to confirm minimal residual and structural quality. Physical masks were affixed to the samples to define localized processing regions. These masks were made via chemical etching of 25 μm thick molybdenum stock by Towne Engineering, Inc. and consisted of sixteen TLM patterns per mask (See Figure 1 for pattern dimensions). The samples were then individually exposed to electron beam generated plasmas to introduce chemical moieties to the exposed areas. [27,29] While vari-
ous plasma sources have been used in the synthesis and modification of graphene. [30, 31] Electron beam generated plasmas are well-suited for chemical functionalization as they are capable of delivering a flux of reactive species while limiting the ion kinetic energies to a few eV. [32] Thus, they provide the ability to chemically modify the graphene without etching or introducing unwanted physical changes, which is an attribute that makes these plasma systems particularly attractive for the large scale processing of very thin or 2D materials. Fine control over coverage is achieved by increasing the operating pressure, which serves to increase the flux of reactive species delivered to the graphene surface. [33, 34] Patterning via physical masks rather than by lithographic processes was chosen to avoid damaging the structure during lift-off and minimize the affect of any residual photoresist on the measurements made in the study. [10]
Figure 2: (a) X-ray photoelectron spectra of the core level C1s of (from bottom to top) as-transferred, nitrogen, fluorine and oxygen functionalized graphene films at comparable surface coverages. (b) Raman spectra of (from bottom to top) as-transferred, nitrogen, fluorine and oxygen functionalized graphene films at comparable surface coverages.

Witness samples of pristine graphene from the same batch of CVD grown material were functionalized along with the masked samples to enable representative characterization of the graphene post-functionalization. Figure 2 depicts the X-Ray Photoelectron Spectroscopy (XPS) and Raman signatures acquired from graphene films that were functionalized with a variety of chemical functional groups at similar coverages. Figure 2a depicts the XPS spectra of as grown and chemically functionalized graphene films with different functional groups at similar surface coverages. The high-resolution C1s spectra confirms the chemical modification of graphene to be due to the introduction of oxygen, nitrogen and fluorine functionalities. De-convolution of the C1s attributes the subcomponents of pristine graphene to be sp\(^2\) C-C (284.4eV) bonding with a slight asymmetry associated to the presence of native oxygen functionalities (located at 286.3 eV). After functionalization, the XPS spectra show a variety of different chemical moieties for each functional group type. The nitrogen functionalized graphene film contained 13.2 at % total nitrogen, mostly in the form of N-sp\(^2\)-C and N-sp\(^3\)-C bonds, located at 285.5 eV and 287.6 eV respectively. An additional peak is observed at 288.8 eV which can be a combined contribution of C=N and C=O functionalities. The fluorinated sample contained a total of 16.9 at % total fluorine which is present in the...
form of C-CF (286.1 eV), C-F (288.6 eV), C-F$_2$ (290.8 eV) and C-F$_3$ (292.82 eV). Finally the oxygenated graphene sample contained 14.6 at % oxygen, in the forms of C-O (285.8 eV), C=O (287.3 eV), and O-C=O (288.7 eV) species.

Figure 2b depicts the characteristic Raman spectra of the as-grown graphene (black line) with the G (1570 cm$^{-1}$) and 2D (2700 cm$^{-1}$) graphene signature peaks. Conjugation of the six member ring structure of graphene can become disrupted when functional groups are introduced to the carbon structure due to electron sharing or sp$^3$-bond formation leading to sp$^3$ hybridization evident by the presence of a D (1350 cm$^{-1}$) peak while reducing the G and 2D peak intensities. Although the Raman spectra is for samples with comparable surface coverages, there are clear differences in the Raman signatures attributed to the differences in bonding types and their influence over the resulting structural configuration of graphene. Oxygen functionalities, for example, will pull the attaching carbon atom from the graphene plane more aggressively, leading to significant structural changes at the functionalized sites. Fluorine functionalities however, can maintain sp$^2$ hybridization at low F coverage, while sp$^3$ configuration is expected at larger F coverages. Raman spectroscopy is very sensitive to structural changes, therefore at comparable surface coverage, oxygen functionalities will show more pronounced D peaks since they perturb the sp$^2$ hybridization more drastically than nitrogen or fluorine functionalities. Combined, the Raman and XPS spectra of functionalized graphenes demonstrate that even at comparable surface coverages, the resultant atomically thin functionalized surface differs dramatically both structurally and chemically from each other, demonstrating the impact of a few adsorbates on the surface of graphene.

Two separate sets of samples were fabricated due to certain requirements regarding the thickness of the Au layer for the thermal and electrical parts of the study. These sets of samples were functionalized at different times and the deposition conditions were replicated as closely as possible. For the thermal studies, 90 nm of Au was deposited on the functionalized SLG samples for measurement via TDTR. For the electrical studies, 500 nm of Au was deposited on the functionalized samples to facilitate probing of the contact pads with kelvin (dual-tip) probes. Such a thick Au layer was required because of difficulties encountered while trying to probe the 90 nm pads.
in the thermal study. Due to the weak adhesion between the Au/SLG and SLG/SiO$_2$ interfaces, it is difficult to make electrical contact with the pads without deeply penetrating the Au film and perturbing the interface. While it was nearly impossible to consistently probe the 90 nm pads, we were able to make contact to the 500 nm Au pads much more effectively.
Figure 3: Metal/SLG thermal boundary conductance ($h_K$) versus atomic percent coverage of various adsorbates on single layer graphene. Coverages of approx. 13-15 at% oxygen or nitrogen result in a 25-40% enhancement in $h_K$, while functionalization with fluorine at coverages ranging from 11.4 - 22.1% yields no enhancement of $h_K$ compared to the Au/SLG baseline case.

Table 1: Atomic percent coverage of functional groups (if applicable) and the resulting thermal boundary conductance ($h_K$) for the samples investigated in the thermal part of the study.

<table>
<thead>
<tr>
<th>Interfacial Layer</th>
<th>Coverage (at. %)</th>
<th>$h_K$ (MWm$^{-2}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Au/SLG)</td>
<td>-</td>
<td>22.91</td>
</tr>
<tr>
<td>Titanium (Au/Ti/SLG)</td>
<td>100</td>
<td>23.29</td>
</tr>
<tr>
<td>Oxygen (Au/O/SLG)</td>
<td>4.4</td>
<td>24.33</td>
</tr>
<tr>
<td></td>
<td>14.6</td>
<td>32.41</td>
</tr>
<tr>
<td>Fluorine (Au/F/SLG)</td>
<td>11.4</td>
<td>23.61</td>
</tr>
<tr>
<td></td>
<td>16.9</td>
<td>22.10</td>
</tr>
<tr>
<td></td>
<td>22.1</td>
<td>24.33</td>
</tr>
<tr>
<td>Nitrogen (Au/N/SLG)</td>
<td>1.0</td>
<td>21.41</td>
</tr>
<tr>
<td></td>
<td>13.2</td>
<td>28.98</td>
</tr>
</tbody>
</table>
The samples fabricated for the thermal part of the study were measured using time-domain thermoreflectance (TDTR). [35] TDTR is a non-contact, optical pump-probe technique utilizing ultra-fast sub-picosecond laser pulses to characterize the thermal transport properties of nano structured materials and systems. The details of our measurement system and the analysis used to extract the thermal properties of interest from the data are provided in the Supporting Information. Figure 3 shows the thermal boundary conductance, $h_K$, across the metal-SLG interface as a function of surface coverage of the various functional groups on graphene (see Table 1 for exact values). In addition, $h_K$ was measured across the Au/SLG and Au/Ti/SLG interfaces with no added functional groups between the metal and graphene. The measured value of $23\pm0.7$ MW m$^{-2}$ K$^{-1}$ for the Au/SLG and Au/Ti/SLG interfaces agrees well with previous work, [36] and these results indicate that the inclusion of the Ti layer appears to have little to no effect on the thermal boundary conductance. Typically, Ti is used as an adhesion layer as it is more reactive than Au with a wide array of materials. Therefore, following other experimental works on the effect of interfacial bonding on thermal boundary conductance, [37–39] one would expect a larger thermal boundary conductance with an increase in bond strength. The results here likely indicate that the graphene surface reactivity is dominating the bonding environment and not the reactivity of the metal film, which we further assert below.

The type of functional group present at the Au/SLG interface clearly impacts the measured thermal boundary conductance in different ways, and the observed differences between the chemical moieties can be explained by considering the individual effects of the adsorbates on the surface energy of the SLG. In the case of fluorinated graphene, the formation of ionic C-F bonds with the out-of-plane $\pi$-orbital of the graphene have been shown to decrease the surface energy of the functionalized-SLG sheet. [27] This decrease in surface energy will negatively impact the adhesion between the metal and graphene. While the strong C-F bond should be beneficial from a phononic point of view on a local scale, the adhesion between the fluorine-functionalized SLG and the Au layer above remains weak, resulting in no net enhancement of $h_K$ across the interface. By comparison, plasma functionalization with oxygen [27] and nitrogen [29] have both been shown
to increase the surface energy, thereby making the functionalized SLG sheet more reactive. This is corroborated by work showing that the surface energy of graphene oxide is larger than that of graphene alone, \[40, 41\] resulting in increased reactivity. Here, the addition of oxygen or nitrogen functional groups increases the surface reactivity and thus improves adhesion of the metal contact to the functionalized graphene, resulting in an increased $h_K$.

We offered a similar explanation in our previous work \[39\] to describe the difference between oxygen and hydrogen functionalization at an aluminium-SLG interface, where we argued that oxygen provides a stronger coupling between graphene and Al via the formation of Al-O bonds, while hydrogen leaves the graphene surface inert. In that work, a 100\% increase in $h_K$ over the value for Al/SLG was observed at an Al/O/SLG interface with 25 at. \% coverage, while an Al/H/SLG interface of similar coverage exhibited a slight decrease in $h_K$. While the increase associated with oxygen in the present work is more modest, the enhancement in $h_K$ suggests that the transport across the metal-graphene interface can be heavily influenced by the reactivity of the graphene surface, particularly in the case of contacts made with less reactive metals such as Au. This implies that to design a metal/graphene contact for optimal thermal transport, the surface reactivity of the graphene is of utmost importance and can be more influential than the metal/graphene reactions.
Figure 4: Width-normalized contact resistivity ($\rho_C$) versus atomic percent coverage of various adsorbates on single layer graphene. The introduction of oxygen or nitrogen at coverages greater than 5 at % causes $\rho_C$ to increase dramatically. Conversely, while low coverages of ≈ 5 at % fluorine causes an increase in $\rho_C$, coverages greater than 5 at % cause $\rho_C$ to decrease with increasing coverage. Inset: Sheet resistance ($R_S$) of the graphene between the TLM pads due to doping of the graphene adjacent to the metal contacts that occurred while functionalizing the graphene via physical masks.
Table 2: Atomic percent coverage of functional groups (if applicable), sheet resistance ($R_S$) of the graphene between the contacts, and contact resistivity ($\rho_C$) for the samples investigated in the electrical part of the study.

<table>
<thead>
<tr>
<th>Interfacial Layer</th>
<th>Coverage (at. %)</th>
<th>$R_S (\Omega/\text{sq})$</th>
<th>$\rho_C (\text{k}\Omega\mu\text{m})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (Au/SLG)</td>
<td>-</td>
<td>110.75</td>
<td>7.04</td>
</tr>
<tr>
<td>Titanium (Au/Ti/SLG)</td>
<td>100</td>
<td>117.15</td>
<td>6.11</td>
</tr>
<tr>
<td>Oxygen (Au/O/SLG)</td>
<td>4.4</td>
<td>148.35</td>
<td>5.44</td>
</tr>
<tr>
<td></td>
<td>14.6</td>
<td>7945.50</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>19.0</td>
<td>21926.50</td>
<td>235</td>
</tr>
<tr>
<td>Fluorine (Au/F/SLG)</td>
<td>5.5</td>
<td>422.65</td>
<td>24.40</td>
</tr>
<tr>
<td></td>
<td>10.91</td>
<td>200.55</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>12.26</td>
<td>454.55</td>
<td>8.15</td>
</tr>
<tr>
<td>Nitrogen (Au/N/SLG)</td>
<td>9.6</td>
<td>256.60</td>
<td>20.74</td>
</tr>
</tbody>
</table>
To complement the thermal measurements, the width-normalized electrical contact resistance ($\rho_C$) at these functionalized metal-graphene interfaces were measured via the transfer length method (TLM). TLM is a widely used technique for measuring $\rho_C$ at a metal-semiconductor interface and details regarding our measurement equipment and the analysis of the data are provided in the Supporting Information. Figure 4 plots $\rho_C$ across the metal-SLG interface as a function of surface coverage for a similar set of samples to those investigated in the thermal part of the study. The value of $\rho_C$ for both Au/SLG and Au/Ti/SLG interfaces is essentially the same (see Table 2 for exact values). This is consistent with other measurements [8, 13] of the contact resistance between graphene and these metals, and highlights an auxiliary conclusion from this work; the inclusion of a titanium wetting layer between Au and SLG improves neither the thermal, nor the electrical transport across the metal/SLG interface. In the case of oxygenated graphene, $\rho_C$ increases by more than an order of magnitude with increasing coverage. For fluorinated samples, $\rho_C$ actually decreases with increasing coverage, approaching values observed in the non-functionalized contact case (Au/SLG and Au/Ti/SLG).

The differing trends in $\rho_C$ between functionalization with oxygen and fluorine are indicative of the potential to engineer electrical contacts on graphene via the introduction of these chemical moieties at the interfaces. Central works, both computational [42, 44] and experimental [9, 11, 45, 46] on metal-graphene contacts have shown that the choice of metal used for the contact has a significant impact on their transport characteristics. The doping of graphene directly underneath the metal, [42, 43] as well as in regions adjacent to the contacts [44, 46] due to 2D confinement can impede charge flow and result in undesirable behavior, such as contact resistance that can vary as a function of applied gate bias. [7, 9, 16] Ref. [9] suggests that the intentional doping of the graphene underneath the metal contacts through non-metal adsorbates may lead to an increased number of conduction modes, thereby enhancing both the cross-plane and in-plane conduction pathways and lowering the contact resistance. To this point, it is instructive to further explore the effects of adsorbates on the electronic structure of graphene to gain insight into their potential impact on $\rho_C$.

Calculations of the density of states (DOS) for oxygenated [47, 48] and fluorinated [49] graphene
highlight an important difference between the use of these two adsorbates. Functionalization with either adsorbate induces a band gap in the electronic structure that widens with increasing coverage. However, in the oxygen case, the Fermi Level remains positioned within the center of the band gap, and the resulting graphene is best characterized as being in a semiconducting state. An increase in the sheet resistance ($R_S$) is observed in the oxygenated samples due to the doping of the graphene adjacent to the metal contacts that occurred while functionalizing the graphene via physical masks (see inset of Figure 4 and the discussion in the Supporting Information). The positioning of the Fermi Level and reduction in mobility [50–52] due to adsorbates are two of the factors that can explain the 1-2 order of magnitude increase in $R_S$. Functionalization with fluorine is a bit different in that as coverage increases and the band gap widens, the Fermi Level moves into the valence band and the graphene remains semi-metallic. [49] This down-shift in the Fermi Level is attributed to the interaction of the $\pi$ orbitals of the carbon atoms with the p orbitals of the fluorine adsorbates and the electron localization that occurs in the C-F bond. While the fluorine adsorbates do lead to increased scattering and a corresponding reduction in mobility, [49] the increase in $R_S$ for fluorinated graphene is not as dramatic as the oxygenated case due to the position of the Fermi Level in the valence band.

The impact of these adsorbates on the transport properties of functionalized Au-SLG contacts is two-fold. First, the distortion of the electronic structure and the shift in position of the Fermi Level of the functionalized graphene will have a significant impact on the nature of the metal-graphene interaction outlined in Refs. [42, 43], as well as the transmission probability across the dipole created at the interface. [9] The resulting work-function of a functionalized metal-graphene contact will be different from that of a non-functionalized contact comprised of the same metal, with a difference of up to $\approx 1$ eV possible, depending upon the degree to which the adsorbates screen the chemical interaction between the metal and graphene. [42, 43] Second, the difference in work function between the metal-covered graphene and the graphene channel adjacent to the contact will affect the in-plane transport of carriers between the contact and channel regions. Some of the factors that contribute to such affects include charge density profiles that exhibit $pn$ junctions
within the transport path [44] and screening potentials that can extend for hundreds of nanometers into the channel. [11, 44, 46]

Based on these two effects, it would be reasonable to assume that the inclusion of adsorbates would serve to further increase $\rho_C$ as we observe with oxygenated contacts. On the other hand, the fluorinated contacts exhibit a decreasing trend in $\rho_C$ with increasing surface coverage, possibly due to the aforementioned doping of the graphene adjacent to the metal contacts. Reference [11] makes an important point that $\rho_C$ can change by a factor of 10 depending on the carrier type and concentration present in the region adjacent to the metal contact. In that work, they state that such an effect is normally observed for high-quality contacts and is attributed to the strong in-plane doping that extends well into the adjacent graphene. In our fluorinated contacts, the adsorbates at the edges of the contacts and not covered in the metallization step have strongly p-doped the graphene adjacent to the contacts, effectively increasing the number of conduction modes available to carriers between the contact and the channel. Therefore, if the decrease that we observe in $\rho_C$ with increasing fluorine coverage can be attributed to an affect similar to that presented in Ref. [11], it would suggest that it may be possible to decrease $\rho_C$ at a fluorinated Au-SLG contact to values comparable to the current state of the art. [8, 9] Clearly, additional experiments are necessary to validate these assertions, but the observed results have significant implications in the engineering of graphene and other two-dimensional material-based devices.

The presence of chemical moieties between graphene and gold contacts is shown to affect the thermal and electrical transport properties compared to unfunctionalized Au-graphene contacts. Concerning thermal transport across an Au/SLG interface, we have shown that functionalization with oxygen and nitrogen enhances the conductance by as much as 40% at coverages close to 15 at. %, which we attribute to the increased surface energy and subsequently enhanced reactivity of graphene functionalized with these adsorbates. Conversely, we find that functionalization with fluorine results in little to no change in the thermal conductance, potentially due to a decrease in surface energy following functionalization. Regarding electrical transport at similar interfaces, we have shown that functionalization with oxygen leads to a significant increase in $\rho_C$, while func-
tionalization with fluorine can actually decrease $\rho_C$ with increasing percent coverage. While the exact mechanism behind this observation is quite complex, the experimental results here suggest that it is due in large part to the presence of fluorinated graphene adjacent to the functionalized contacts that aids the injection and extraction of carriers between the contact and channel regions. This work demonstrates the ability to tune both the thermal and electrical transport properties in graphene-metal contacts, an important aspect in the development of graphene devices.

**Associated Content**

**Supporting Information**

Time-domain Thermoreflectance (TDTR) and Transfer Length Method (TLM) experimental methods and data analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Author Contributions**

P.E.H. and S.G.W. conceived the idea for this experiment and supervised all aspects. J.T.R. synthesized and transferred the graphene onto the SiO$_2$/Si substrates. S.C.H. functionalized and chemically patterned the graphene, metalized the samples, performed XPS and Raman characterization and their respective data analysis. B.M.F., J.C.D. and P.E.H performed the thermal and electrical measurements and analysis of the data.
Notes

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