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Titanium contacts to graphene: process-induced variability in electronic and thermal transport

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Abstract
Contact resistance ($R_C$) is a major limiting factor in the performance of graphene devices. $R_C$ is sensitive to the quality of the interface and the composition of the contact, which are affected by the graphene transfer process and contact deposition conditions. In this work, a linear correlation is observed between the composition of Ti contacts, characterized by x-ray photoelectron spectroscopy, and the Ti/graphene contact resistance measured by the transfer length method. We find that contact composition is tunable via deposition rate and base pressure. Reactor base pressure is found to effect the resultant contact resistance. The effect of contact deposition conditions on thermal transport measured by time-domain thermoreflectance is also reported. Interfaces with higher oxide composition appear to result in a lower thermal boundary conductance. Possible origins of this thermal boundary conductance change with oxide composition are discussed.

Supplementary material for this article is available online

Keywords: graphene, vacuum deposition, contact resistance, thermal boundary conductance, x-ray photoelectron spectroscopy, thermal transport, interface chemistry

(Some figures may appear in colour only in the online journal)

Introduction

One of the major challenges associated with the design of two-dimensional (2D) devices is the large contact resistance ($R_C$) at the interface between the 2D material and the metal [1, 2]. The contribution of $R_C$ to the total device resistance increases as the channel length is scaled down, meaning that $R_C$ can ultimately be the limiting factor in the performance of 2D devices. Graphene has excellent electrical and thermal transport properties, making it particularly important to understand the mechanisms of losses across the metal/Gr interface. A large volume of recent experimental [3–9] and theoretical [10–12] work is focused on understanding the chemistry and electronic properties of the metal/Gr interface. Many assume ideal interfaces in which $R_C$ is explained by intrinsic interactions between graphene and the metal, such as effects of orbital hybridization, electrochemical equalization, and other mechanisms, which cause changes in the electronic structure of graphene due to the presence of a metal overlayer [10]. The effects of processing conditions on the chemistry and properties of the contact are often overlooked. The details of graphene processing procedures and contact deposition conditions, such as base pressure and deposition rate, are rarely reported in device studies, even in those which focus specifically on characterization of contacts. Several works demonstrate that $R_C$ is independent of the gate voltage and the number of graphene layers, indicating that it is dominated by the properties of the metal/Gr interface [5, 8, 13].
warrants more thorough interface characterization. Titanium was selected for this work as it is commonly used as a contact or adhesion layer for graphene due to its low work function and low electron Schottky barrier.

**Experimental details**

To fabricate samples for this experiment, commercial graphene grown by chemical vapor deposition (CVD) on Cu foil (from Graphene Supermarket) was transferred to SiO₂ by a polymethyl methacrylate (PMMA) carrier film followed by a ultra high vacuum (UHV) anneal to remove PMMA residues [14]. Following the transfer, a 5 nm film of titanium was deposited onto Gr/SiO₂ in a high vacuum (HV) electron beam evaporator at pressures of 10⁻⁷ or 10⁻⁹ Torr and deposition rates ranging from 0.01 to 0.5 nm s⁻¹, indicated by a quartz crystal monitor. Samples for TLM measurements were fixed with a shadow mask described elsewhere [9] prior to metal evaporation. The samples were not exposed to atmosphere following the deposition of Ti. Au was deposited to cap the samples prior to removal from UHV, in order to prevent further oxidation of the Ti layer upon air exposure. Au films of 500 nm, 80 nm, and 2 nm were deposited on samples for TLM, thermal measurements, and XPS, respectively. X-ray photoelectron spectroscopy data was collected with a monochromated x-ray source at a pass energy of 50 eV in a UHV system described previously [15]. Spectra were deconvoluted using kolXPD software [16] to extract relative compositions of Ti metal and Ti oxide. The samples were then characterized by the transfer length method and time-domain thermoreflectance to determine $R_C$ and thermal boundary conductance, respectively. More detailed descriptions of these measurements are included in the supporting information available online at stacks.iop.org/NANO/29/145201/mmedia.

**Results**

We have found that oxide composition is largely dependent on the contact deposition conditions. Titanium is highly reactive and will readily oxidize under high-vacuum deposition conditions. As others have suggested [17–19], the adsorption of oxidizing species onto the substrate surface during deposition will affect the chemistry of the contact, which is expected to manifest in the electrical and thermal properties of the interface. Figure 1 shows oxide composition versus deposition rate for samples fabricated from three individually transferred pieces of graphene.

Each color represents a single piece of graphene transferred to SiO₂ and subsequently split into three (or four) samples to receive metal deposition at three (or four) different deposition rates. Sample-to-sample variability is observed, but there appears to be a trend of decreasing oxide composition with increasing deposition rate. The deposition rate determines the impingement rate of Ti atoms on the surface of the substrate relative to the impingement rate of the oxidizing species from residual gases. It is therefore expected that higher deposition rates result in lower oxide composition, since at higher deposition rates Ti atoms arrive at the sample surface at faster rates than oxidizing species in the chamber. The anomalous data point can be explained by the presence of additional oxidizing species from PMMA residues which will be addressed in the discussion section.

Base pressure also has a substantial effect, which can dominate over deposition rate. A sizable partial pressure of residual H₂O or OH is typically detected in elastomer-sealed vacuum chambers and the base pressure is a measure of the quantity of residual gases in the chamber. During deposition, these residual H₂O and OH molecules are impinging on the sample surface, along with the Ti. Depositing at higher pressures increases the amount of oxidizing species available for reaction with Ti, and depositing at lower deposition rates increases the fraction of Ti atoms that will react with oxidizing species upon reaching the surface. This is observed in figure 2. To overcome any issue of sample-to-sample variability, each sample represented in figure 2 was cut from a single piece Gr/SiO₂ produced in a single transfer. Two out of the three samples were deposited on at the same base rate but different base pressures, and two out of three were deposited on at the same base pressure but different rates. In figure 2(a), (i) corresponds to a deposition 1 × 10⁻⁷ Torr and a rate of 0.01 nm s⁻¹, (ii) corresponds to a deposition at 1 × 10⁻⁷ Torr and a rate of 0.1 nm s⁻¹ and (iii) corresponds to a pressure of 1 × 10⁻⁶ Torr at a rate of 0.1 nm s⁻¹. The corresponding TLM data for each are shown in figure 2(b). Comparison of (i) and (ii) illustrates the effect of deposition rate alone at the same base pressure. As previously discussed, a lower oxide composition results at a faster deposition rate. In (ii) and (iii), we observe the effects of varying base pressure at the same deposition rate. Depositing at 1 × 10⁻⁷ Torr yields 25% oxide whereas 1 × 10⁻⁶ Torr results in 78% oxide. This indicates that base pressure has a substantial effect on oxide composition. The TLM results corresponding to (i) and (iii)
indicate that two samples of similar oxide composition can exhibit markedly different $R_C$ if deposited under different base pressures. This suggests that while composition can be controlled by either deposition or base pressure, it is base pressure that has the greater impact on contact resistance. It is known that UHV depositions result in cleaner interfaces and improved $R_C$ for unreactive metals like Au [20]. Our comparison of samples processed under lower and higher base pressures show that $R_C$ might be dominated by the composition of the interface, rather than the composition of the contact itself. The larger error bars and confidence interval in the TLM data in (iii) are also indicative of greater variability in measured $R_C$ throughout different regions of the sample.

We have observed an overall correlation between the oxide compositions of the contacts shown in figure 3. While large sample-to-sample variability is observed, the data has a linear correlation coefficient of 0.7. The linear correlation coefficient describes the extent to which two variables support a linear relation [21]. Thus, a value of this linear correlation coefficient approaching unity indicates a linear relationship likely exists where the probability of correlation depends on the number of data points acquired. For the 13 values reported in this work, the probability of a linear correlation is 99.2%. Thus, we conclude there exists a linear relationship between oxide composition and $R_C$. Differences in the cleanliness of the interface observed in figure 2 might also explain why contacts of similar oxide composition show large variations in $R_C$ as seen in figure 3.

The effects of contact processing conditions manifest in thermal transport properties. Figure 4(a) shows XPS spectra acquired for four samples fabricated with four different deposition rates and figure 4(b) shows the corresponding TDTR data as a function of oxide composition. XPS shows significant oxide composition at the slowest deposition rate of 0.01 nm s$^{-1}$. The oxide composition decreases between 0.01 and 0.1 nm s$^{-1}$. The thermal data indicates that thermal boundary conductance $h_K$ is inversely related to the oxide composition. For the deposition rate of 0.1 nm s$^{-1}$, which resulted in the lowest oxide composition, $h_K = 65 \pm 7$ MW m$^{-2}$ K$^{-1}$, whereas for the slowest deposition rate, which resulted in the highest oxide composition, $h_K = 32 \pm 3$ MW m$^{-2}$ K$^{-1}$. The values of $h_K$ correspond to Au/SiO$_2$ interface where the effective interfacial regions between Au and SiO$_2$ for this analysis is the Ti/Gr layers, as mentioned previously.

The measured value of $h_K$ for the slower deposition rates matches very well with those measured for a similar Au/Ti/Gr/SiO$_2$ interface deposited at 0.05 nm s$^{-1}$ and reported by Koh et al [22]. The twofold increase in $h_K$ with the faster deposition rate corresponds to the relative decrease in the oxide composition between the different deposition rates.
corresponds to samples that were cut from the same piece of oxide composition showing a linear trend with a correlation coefficient of 0.7. Each set of identical markers on the plot corresponds to samples that were cut from the same piece of transferred graphene but processed under different conditions.

Figure 3. Plot of width-normalized contact resistivity as a function of oxide composition showing a linear trend with a correlation coefficient of 0.7. Each set of identical markers on the plot corresponds to samples that were cut from the same piece of transferred graphene but processed under different conditions.

dedicatedly, our results suggest that to minimize the thermal resistance at the Au/Ti/Gr/SiO₂ contact, the Ti should be as metallic as possible. In contrast to thermal transport, electrical transport does not appear to be as sensitive to the composition of the contact for this particular sample; however, the results shown in figure 3 indicate that the reactor base pressure does have an impact on \( R_C \).

Discussion

It is apparent in figure 1 that samples processed identically might result in different oxide compositions. A major source of variability in the Gr/metal interface chemistry is related to PMMA residue from the transfer process. PMMA is typically removed by dissolution in acetone followed by an anneal in UHV at a temperature high enough to dissociate the various hydrocarbon species [23]. The thermal decomposition of PMMA is inherently a random process, and generated radicals can react with defects in the graphene or form longer polymer chains that cannot be removed [24]. Therefore, samples which undergo the same PMMA removal process can be left with different quantities of PMMA residue, and the quantity of PMMA residue is unlikely to be uniform across a single sample. Lee et al. have shown that a PMMA-free transfer process results in lower contact resistance than that which uses PMMA [25]. PMMA residues are known to dope graphene and alter its electronic properties [23]. Furthermore, transport across the Ti/Gr interface will be inhibited by the presence of contaminants, which scatter charge carriers and obstruct hybridization between the graphene \( \pi \)-orbitals and Ti metal d-orbitals [10, 26]. Orbital hybridization will be inhibited both by the presence of polymer residues at the interface and by the presence of an oxidized contact rather than a metallic one. It has been shown that PMMA residues react with Ti overlayers [27]. Other sources of variability, in both the interface and contact chemistry, could be related to intrinsic defects in the CVD-grown graphene film or due to other extrinsic effects of transfer process including residual Cu, incomplete removal of graphene from the back of the Cu foil, wrinkles and tears in the film, or adsorbates. While measures can be taken to assess the quality and uniformity of the transferred graphene prior to device fabrication, such as characterization with Raman spectroscopy, these defects are inherent to the transfer process and are fundamentally uncontrollable.

Despite the inevitable sample-to-sample variability, our results suggest that some degree of control over contact composition is achievable during the deposition process, particularly via deposition rate and base pressure. The overall linear correlation between oxide composition and \( R_C \) summarized in figure 3 is not surprising given that the electrical resistivity of TiO₂ is orders of magnitude higher than that of metallic Ti [28]. The results presented in figure 2 indicate that the cleanliness of the graphene/TiO₂ interface, which is affected by the base pressure of the deposition, likely dominates \( R_C \) to a greater extent than the oxide composition. While we observe a relationship between deposition rate and oxide composition in figure 1, and a correlation between \( R_C \) and oxide composition in figure 3, it is important to note that deposition rate does not have a substantial effect on \( R_C \). It then follows that oxide composition is not the prevailing factor determining \( R_C \).

The possible origins of the change in thermal boundary conductance with change in oxygen content of the Ti layer between the Au and graphene could manifest from various changes in electronic and vibrational scattering and interfacial transport in each layer of the Au/Ti/Gr/SiO₂ boundary.
region. The major contributors to this change in thermal resistance, \( \Delta R = 1/\hbar_k \sim 15.9 \text{ m}^2 \text{ K GW}^{-1} \), could be the change in \( \hbar_k \) at the Au/Ti interface, the change in thermal conductivity of the Ti, and the change in \( \hbar_k \) across the Ti/Gr/SiO\(_2\) interface that would occur with a change in oxygen content in the Ti layer. For exemplary purposes, we pose the extreme cases in which one would expect the Ti layer to either be fully TiO\(_2\), with a thermal conductivity of \( \sim 1.2 \text{ W m}^{-1} \text{ K}^{-1} \) [29] or fully metallic Ti, with a thermal conductivity of \( \sim 21.9 \text{ W m}^{-1} \text{ K}^{-1} \) [30]. These cases lead to a change in resistance of this layer as \( \Delta R = 5 \times 10^{-9}/1.2 - 5 \times 10^{-9}/21.9 \sim 4 \text{ m}^2 \text{ K GW}^{-1} \). We note this example calculation considers the extreme case to calculate the maximum hypothetical resistance change of this layer. As is evident, the above calculation for \( \Delta R \) cannot explain the entire observed change in thermal boundary resistance with different oxygen content in the Ti layer (as previously mentioned, \( \Delta R \sim 15.9 \text{ m}^2 \text{ K GW}^{-1} \)). We note also that size effects were not considered in this \( \Delta R \) calculation [31]. Thus, the change in thermal resistance of the Ti layer cannot solely explain the measured changes in thermal boundary conductance.

Another possibility for the observed change in thermal conductance across the Au/Ti/Gr/SiO\(_2\) region is the change in the Ti/Gr/SiO\(_2\) thermal boundary conductance. Our previous work has demonstrated that changes in graphene surface chemistry induced from plasma functionalization (including oxygen functionalization) can lead to appreciable changes in thermal boundary conductance [9]. Thus, one could hypothesize that the change in oxygen stoichiometry in the Ti layer would also lead to changes in how the Ti reacts with residues and thereby lead to changes in the chemistry at the Ti/Gr interface; thus impacting thermal boundary conductance. We note that residual PMMA residue is present on all samples. Therefore it is presumed that all Gr/Ti interfaces will actually be TiO\(_2\)/Gr with some variation in the amount of hydrocarbon incorporated [27]. At this time, the impact of the variations in hydrocarbon incorporation at the interface on the thermal boundary conductance is unknown. Therefore, we cannot rule this out as a potential mechanism, and thus leave an intricate study of the chemistry effects on Ti/Gr thermal boundary conductance to future work.

Finally, we consider the change in thermal boundary conductance at the Au/Ti interface as a possible contributor to the measured change in \( \Delta R \) of the Au/Ti/Gr/SiO\(_2\) interfacial region. At pure metal/non-metal interfaces, the thermal boundary conductance is driven by the electron density of states at the Fermi energies of the metals [32], and this corresponding thermal boundary conductance can be more than an order of magnitude greater than those at metal/non-metal interfaces [33]. While the thermal boundary conductances across Au/metal Ti and Au/TiO\(_2\) interfaces have not been explicitly and reliably measured previously due to the exceptionally high \( \hbar_k \) affiliated with metal/metal interfaces, we can assume that the resistance associated with the metallic phase of Ti in contact with the Au will offer negligible resistance as compared to the non-metal oxide phases in the Ti layer. Indeed, typical values for thermal boundary conductances across Au/non-metal interfaces range from \( \sim 50 \) to \( 100 \text{ MW m}^{-2} \text{ K}^{-1} \) [34–37], limited by the relatively narrow spectral phonon bandwidth in the Au. This corresponds to a \( \Delta R \) of \( \sim 10–20 \text{ m}^2 \text{ K GW}^{-1} \), on the order of our measured change in thermal boundary conductance with changes in oxygen content in the Ti (\( \Delta R \sim 15.9 \text{ m}^2 \text{ K GW}^{-1} \)).

We estimate these various electron-electron and phonon-phonon resistances at the Au/Ti layer interface in more quantitative detail through the use of diffuse mismatch models (DMM). As mentioned previously, the electron DMM (eDMM) predicts the thermal boundary conductance between two materials with large electron density of states compared to phonon density of states (e.g., at metal/metal interfaces) [35]. Assuming values for the electron density of states at the Fermi energy and calculated Fermi velocities for Au and Ti [38, 39], we predict a thermal boundary resistance of \( R_{e\text{Au/Ti}} = 0.17 \text{ m}^2 \text{ K GW}^{-1} \) (thermal boundary conductance of \( 5970 \text{ mW m}^{-2} \text{ K}^{-1} \) between the electronic systems in Au and Ti, assuming both are pure metals). This eDMM calculation thus predicts the thermal transport across the Au/Ti interface in the case when Ti is fully metallic. When the Ti layer is oxidized, this electron-electron interfacial thermal transport pathway will be reduced, and thus the Au phonon/Ti phonon interfacial thermal transport pathway can become a dominant conductance, since the electronic densities of states of the TiO\(_2\) regions of the adhesion layer will be greatly reduced compared to the metallic Ti regions. Thus, we quantify this phonon-phonon thermal boundary resistance using the traditionally implemented phonon DMM (pDMM) [40]. We calculate the phonon-phonon thermal boundary resistance of two cases: Au/Ti and Au/TiO\(_2\) (rutile). In our pDMM calculations, we assume sine-type phonon dispersions of the longitudinal and two degenerate transverse acoustic modes in each material with zone edge phonon frequencies taken from [41] for Au (\( \Gamma \rightarrow X \) direction), [42] for Ti (\( \Gamma \rightarrow A \) direction), and [43] for rutile (\( \Gamma \rightarrow A \) direction). From this, we predict phonon-phonon thermal boundary resistances of \( R_{p\text{Au/Ti}} = 6.17 \text{ m}^2 \text{ K GW}^{-1} \) (\( h_k,_{pp,\text{Au/Ti}} = 162 \text{ MW m}^{-2} \text{ K}^{-1} \)) and \( R_{p\text{pp,\text{Au/TiO}_2}} = 6.76 \text{ m}^2 \text{ K GW}^{-1} \) (\( h_k,_{pp,\text{Au/TiO}_2} = 148 \text{ MW m}^{-2} \text{ K}^{-1} \)) for the Au/Ti and Au/TiO\(_2\), respectively. Based on these eDMM and pDMM calculations, the predicted change in thermal boundary resistance associated with the change from a metal/metal Au/Ti interface (electron–electron) to a metal/non-metal Au/Ti (Au/TiO\(_2\)) interface (phonon–phonon) as \( \Delta R = 6.0 \text{ m}^2 \text{ K GW}^{-1} \) (6.6 m\(^2\) K GW\(^{-1}\)). While this calculation of \( \Delta R \) is slightly lower than our observed change in thermal boundary resistance across the Au/Ti/Gr/SiO\(_2\) interfaces (\( \Delta R \sim 15.9 \text{ m}^2 \text{ K GW}^{-1} \)), we caution that the assumptions required for DMM predictions could lead to uncertainties in these predicted values. Regardless, a clear change in Au/Ti thermal boundary conductance will occur when the interfacial transport transitions from an electron to phonon dominated process.

These simple qualitative and quantitative analyses suggest that the changes in thermal boundary conductance across the Au/Ti/Gr/SiO\(_2\) boundary originate from changes in resistance at the Au/Ti interface and possible additional changes in thermal conductivity in the Ti layer. However, much more work needs to be pursued to study this precise interface in more detail and to understand the fundamental electron and phonon scattering mechanisms driving this
thermal transport process with respect to changes in oxygen chemistry. This points to the future promise of manipulating metal/metal contacts through metal type and chemistry to impact the thermal resistances of graphene devices.

Conclusion

This work sheds light on the inherent variability in graphene devices. By attempting to correlate deposition conditions with the contact composition and contact resistance, we have found that contact resistance is sensitive to the partial pressure during contact deposition, and that the oxide of a Ti contact can strongly impact the thermal boundary conductance. It should be noted that reactor pressure and deposition rate are not parameters that are typically reported when describing device fabrication and yet this work demonstrates that both clearly affect device properties. The relationship between interface chemistry and contact resistance as well as thermal transport opens doors for interface engineering. The data indicates that conditions which minimize the adsorption of oxidizing species on the substrate, low base pressure and fast deposition rate, result in lower electrical and thermal contact resistance, respectively. This also suggests that UHV deposition might be optimal for improved device performance; however, this requires further study. While the role of interface morphology has not been explored in this study, we intend to examine it in future work.

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