THERMAL BOUNDARY CONDUCTANCE BETWEEN THIN METAL FILMS AND GRAPHITE SUBSTRATES

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ABSTRACT

Due to the high intrinsic thermal conductivity of graphitic structures, much interest has developed in incorporating these materials into modern nano-devices for improved thermal abatement. In order to be integrated successfully, thermal energy must be able to transport efficiently through the graphitic materials and into the surrounding structure, most commonly a metal. However, thermal boundary conductance at metal-graphite interfaces is traditionally poor in comparison to non-graphitic substrates, due in large part to the weak van der Waals adhesion force between the metal and underlying carbon structure. To be applicable as thermal abatement materials, an enhanced understanding of the role of the metal-carbon interface is required. This paper reports the changes to phononic thermal transport across the interface between metallic thin films and highly oriented pyrolytic graphite (HOPG) substrates due to changes in interface structure and chemistry. The temperature dependent thermal boundary conductance is measured using transient thermoreflectance from 100 K to 400 K. It is found that the differences in metal-carbon bonding and structure at the interface have a significant impact on the thermal conductance between the metallic thin films and the HOPG substrates.

INTRODUCTION

With increasing power densities in modern micro- and nano-devices, thermal abatement has moved to the forefront as the major limiting factor in the continued development of smaller devices and is ultimately inhibiting device performance. Due to their intrinsically high thermal conductivity, allotropes of carbon, i.e. carbon nanotubes (CNTs) and graphite, have become of great interest for thermal management solutions. In-plane thermal conductivity in highly oriented pyrolytic graphite (HOPG) is $\sim 2,100 \text{ W/m-K}$ at room temperature [1], and the room temperature thermal conductivity of single walled and multiwalled CNTs has been measured between 1,750-5,800 W/m-K [2–4]. Incorporation of these allotropes into thermal abatement solutions has already shown promising results, specifically with CNT-based thermal interface materials (TIMs) [5, 6], and carbon reinforced metallic heat spreaders [7, 8].

While there is currently very little literature on experimental measurements of thermal boundary conductance, $(h_{BD})$, between metallic films and HOPG [9, 10], current results show generally low $h_{BD}$ compared to typical metal-semiconductor systems [11]. The low $h_{BD}$ of the metal-HOPG system can be attributed to many contributing factors including the large
vibrational spectrum mismatch between the metallic thin film and the underlying $sp^2$ carbon bonded HOPG substrate [12], and the weak adhesion forces between the metal and carbon structure [13]. It has been shown that increased vibrational mismatch between two materials comprising an interface, often summarized by a difference in Debye temperature, results in decreased $h_{BD}$ [11]. The $sp^2$ bonding between carbon atoms is responsible for high elastic stiffness, and thus, high phonon group velocities and vibrational cutoff frequencies in the basal plane when compared to metals. Thus, it can be expected that the large vibrational mismatch between metals and CNT’s or HOPG will create a situation for rather low $h_{BD}$. Additionally, the adhesion between metals and graphite has been shown to be very weak due to a lack of chemical bonding between metals and pristine HOPG [14, 15]. Instead, the bonding can be described as a van der Waals type interaction [16]. However, the presence of oxygen or defects on the surface can lead to the formation of carbides at the metal-graphite interface. These defects can be induced through ion bombardment of the HOPG surface prior to metal deposition [14, 15]. There have been attempts to quantify the reduction in $sp^2$ bonds during ion bombardment of the pristine HOPG surface, which is approximately a 2% reduction after a 230 s dose of ions (2 keV, $\sim$ 10 $\mu$A/cm$^2$) [17]. This bonding is of direct importance to thermal transport, as molecular dynamics simulations have been used to show that the addition of a single covalent bond at the interface between a CNT and Si substrate increased the $h_{BD}$ nearly two orders of magnitude [18].

Traditional theoretical models for predicting $h_{BD}$ at the interface between two dissimilar materials such as the diffuse mismatch model (DMM) generally only consider the phonon spectrum mismatch in the consideration of thermal transport [19]. Several groups have made modifications to the DMM in order to better describe certain physical conditions: interface mixing [20, 21], contributions of inelastic scattering [22, 23], and anisotropy [24, 25]. In order to better quantify the effect of poor adhesion on thermal transport across interfaces, Prasher developed an acoustic mismatch model for van der Waals interactions, v-AMM [13]. In his work, Prasher shows a significant reduction in $h_{BD}$ for low adhesion energies. Specifically, the v-AMM predicts for a reduction in adhesion energy from 500 mJ/m$^2$ to 100 mJ/m$^2$, a nearly 80% reduction in $h_{BD}$. However, several studies have shown that comparison of experimental results and predictions of the DMM can vary by up to an order of magnitude [11, 26]. One significant possibility for the discrepancy between theoretical calculations and the experimental results is the lack of consideration of the interface structure and chemistry. Even for the same material system, the conditions at the material interface can vary significantly due to deposition conditions and post deposition annealing [27]. This work begins to investigate the role that interface chemistry and structure have on the measured value of $h_{BD}$ for a system which is traditionally believed to have the same phononic properties, i.e. all samples tested are Au-HOPG. However in each sample, the HOPG is subjected to a different surface pre-treatment prior to deposition of the metallic film. In this way, the role of the interface in thermal transport is studied. Different surface treatments should have a significant impact on the condition of the Au-HOPG interface, as it has been demonstrated that contaminants and defects can lead to increased interaction between metals and HOPG [14, 15].

**EXPERIMENT**

In order to investigate the effect of interfacial structure and chemistry on $h_{BD}$, three metal-on-graphite samples were prepared for experimental thermal characterization. The three samples consisted of thin Au films on 12 mm x 12 mm x 1 mm grade 1 highly-ordered pyrolytic graphite substrates (HOPG) from Structure Probe Incorporated. Gold was chosen over other possible metals in order to reduce the number of variables affecting thermal transport across the interface. Previous work has shown that Au does not wet HOPG or other carbon-based substrates. As a result, the Au-HOPG surface interaction is characterized by weak van der Waals adhesion [16, 28, 29].

Prior to metal deposition, each substrate underwent a different surface pretreatment to influence the interfacial structure and chemistry. The first substrate was cleaved using the “scotch tape method” to remove the first few layers of graphene, and no other pretreatment or cleaning method was used. The second substrate was cleaved in the same manner and subsequently ion cleaned. A 3 cm ion source, located 14 cm from the substrate, with a beam voltage of 300 V was used to surface etch the substrate, for a total exposure time of 7 minutes. As a means of comparison, exposing a SiO$_2$ wafer to these conditions removes approximately 5-10 nm of material from the surface and creates a disordered surface. The third substrate was again cleaved in the same manner and was subsequently electron cleaned. The conditions of the electron cleaning were the same as the ion cleaning, however, the beam voltage was turned off. It is presumed the electron heating from both the cathode filament and the neutralizer filament (which sits outside/at the end of the ion source) helps to remove surface water from the substrate. After all surface pretreatments, 50 nm of Au was deposited on the HOPG surfaces by DC sputtering.

Measurements of the thermal boundary conductance of the prepared samples were conducted using a transient thermoreflectance, TTR, method. Transient thermoreflectance reflectance techniques [30–32] and similar variations [33, 34] are optical pump-probe thermometry techniques that allow for simultaneous heating and measurement of the thermal decay of thin film metallic systems. From the characteristic thermal decay measured as a function of time and the appropriate thermal models, the thermophysical properties of the material system, including
the $h_{\text{BD}}$ across the system interface, can be determined.

The TTR setup used in this experiment consists of a Coherent RegA 9000 regenerative amplifier seeded by a Mira 900 oscillator (see Fig. 1). Both the oscillator and the amplifier are optically pumped by a Coherent Verdi V18 with the output power split 5W:13W to the oscillator and amplifier, respectively. The total output of the system produces a laser pulse train at 800 nm with pulse energy on the order of $\mu$J/pulse, a FWHM pulse width of $\tau_p = 177 \text{ fs} \pm 7 \text{ fs}$, all at a rep rate of 250 kHz. The pump beam is modulated by a Conoptics Electro-Optical Modulator (EOM) at a frequency of 125 kHz, setting up a one-pulse-on/one-pulse-off heating scheme. The pump pulses are then passed through an Inrad 5-035C frequency doubling system to improve filtering of scattered pump light off the sample surface before reaching the signal photodetector, and improving the signal to noise ratio. The pump beam is focused down onto the sample with a final spot size of $236 \mu\text{m} \pm 2 \mu\text{m}$. The temporal resolution of the probe beam is provided by a Newport 600 mm linear delay stage, with a total delay of 4 ns, and producing less than 2 $\mu\text{m}$ drift along the vertical and horizontal direction along the length of the stage. The probe beam is focused at the center of the pump spot down to a spot size of $26 \mu\text{m} \pm 0.6 \mu\text{m}$. All data was taken with a pump fluence of $\sim 2 \text{ J/m}^2$.

In order to determine the measured $h_{\text{BD}}$, a thermal model is iteratively fit to the decay of the measured thermoreflectance signal. In this work the model used was Carslaw and Jaeger’s solution for surface temperature of a multilayered system, assuming 1D thermal flow due to periodic steady heating [35], as implemented by Feldman [36], and detailed for thermoreflectance experiments by Hopkins et al. [37]. The model is scaled to the measured data starting at 1,000 ps to ensure that electron-phonon non-equilibrium processes have ceased and diffusive transport dominates. In the thermal model the $h_{\text{BD}}$ is treated as a single free parameter and iteratively incremented to minimize the square of the difference between the experimental data and the thermal model. An inverse parabolic interpolation scheme is used to reduce the number of subsequent iterations needed for the model and data to converge.

The anisotropic nature of the thermophysical properties of the HOPG substrates, namely the thermal conductivity, requires additional consideration when fitting the thermal model to the data as compared to more traditional isotropic systems. The in-plane vs. cross-plane thermal conductivity of HOPG can differ by 3 orders of magnitude, 2,096 W/m-K vs. 5.59 W/m-K at room temperature, respectively [1]. Due to the low rep rate of our TTR system, (250 kHz), produced by using the regenerative amplifier, our heating scheme is transient rather than modulated as in most systems. Traditional high rep rate systems (76-80 MHz) using an oscillator alone deal with modulated heating, and therefore the primary direction of heat flow and the sensitivity to directional thermal conductivity is dependent on the ratio of pump-to-probe spot sizes and the pump modulation rate [37, 38]. However, in the transient system, an individual heat pulse is allowed to fully dissipate before the arrival of a subsequent pulse. Therefore the thermal energy is not “driven” as in a modulated system, but rather follows the path of least resistance (see Fig. 2). In the case of the anisotropic nature of the HOPG, this would be the high thermal conductivity in-plane direction. Therefore, for the application of the thermal model in this study, the in-plane thermal conductivity is used for the thermophysical properties of the substrate.
RESULTS

The temperature-dependent $h_{BD}$ for each of the three different Au-HOPG samples is presented in Fig. 3. Each data point shown represents the average over 10 scans, taken successively at a single location, of the best fit $h_{BD}$ values at the given temperature. The error bars represent the standard deviation of the best fit values of $h_{BD}$ over the 10 scans. Also represented in Fig. 3 are elastic and elastic + inelastic models for thermal transport between isotropic solids and anisotropic substrates presented by Duda et al. [24, 25].

It is clearly shown in Fig. 3 that the different surface preparations drastically change the phonon thermal transport across the Au-HOPG interface. The as-cleaved sample exhibited the highest $h_{BD}$ across the temperature range, followed by the electron cleaned and finally the ion cleaned. The difference in $h_{BD}$ between the as-cleaved and ion cleaned samples is over 300%, demonstrating how significantly the surface structure and chemistry of the HOPG surface prior to metal deposition effects thermal transport.

In addition to the experimental data, Fig. 3 also includes the results from theoretical models predicting the elastic and inelastic contributions to phononic thermal transport across the Au-HOPG interface. Comparing the theoretical models to the experimental data, a few important features should be noted. First, note that the data for the electron-cleaned sample best fits the prediction considering both the elastic and inelastic phonon transport. This can be explained as follows: considering that electron cleaning effectively removed surface water and hydrocarbon contaminants from the HOPG surface without changing the surface structure, the Au-electron-cleaned-HOPG interface most closely mimics the ideal interface assumed by most theoretical models, such as the diffuse mismatch model mentioned previously. It has been shown that freshly cleaved graphite (cleaved in air) has an RMS surface roughness less that 1 nm [39] and the choice of Au film (deposited on a clean surface) will only interact with the surface through weak van der Waals interaction [16]. For the as-cleaved sample, having been cleaved in air, the presence of impurities should lead to increased reactivity between the Au and the HOPG [14], suggesting increased bonding strength, and hence and increased $h_{BD}$ [13]. Lastly, for the ion-cleaned sample, the ion bombardment during cleaning should have resulted in increased disorder and roughness of the HOPG surface prior to deposition of the metal. As shown by Hopkins et al. [27], increased atomic mixing and inter-diffusion of the constituent materials at the interface can have a detrimental effect of the $h_{BD}$. While the trends between the experimental data and the literature can be inferred with confidence, in order to have a full understanding of the effect of surface structure and chemistry on $h_{BD}$ further interfacial and surface characterization is still required.
To solidify the comparison between the experimental results and the expected interface structure induced by the deposition conductions and pre-deposition surface treatments, cross sectional transmission electron microscopy, TEM, images were taken of each sample. The TEM images were collected by Evans Analytical Group and bright field TEM images from each of the three samples are shown in Fig. 4. A comparison of the TEM images of the electron cleaned and as-cleaved samples, Figs. 4a and 4b, shows that both interfaces have similar surface structures, with very little interface roughness. Therefore, again, the difference in $h_{BD}$ between the two samples is attributed to the presence of surface impurities and changes to the chemical structure of the interface. The TEM image for the ion cleaned sample, Fig. 4c, shows a significant increase in surface roughness as compared to the other two samples. It is assumed that the decreased $h_{BD}$ in the ion cleaned samples is due to increased phonon scattering at the rough interface.

In order to ensure that the data collected for each sample was generally representative of the $h_{BD}$ across the surface of the sample surface, a secondary data set was collected at 300 K across the sample surface. A total of 7 scans were taken across the sample surface in a grid pattern detailed in Fig. 5. At each of the 7 locations a total of 5 scans were taken and the collected data averaged. A comparison of the data collected and reported in Fig. 3 and the standard deviation of measurements across the sample surface is shown in Table 1.

As the table shows, the standard deviation of the 10 scans at a single location is within or on the order of the standard deviation of measurement across the sample surface. Therefore, we have taken the data collected for each sample to be representative of the $h_{BD}$ of the entire sample.

Table 1: Comparison of the standard deviation of the 10-scans taken at a single location and the standard deviation of the scans at 7-locations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$h_{BD}$ (W/m$^2$·K)</th>
<th>SD$_{10}$--Scans</th>
<th>SD$_{7}$--Locations</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Cleaved</td>
<td>$3.07 \times 10^7$</td>
<td>$1.42 \times 10^6$</td>
<td>$1.06 \times 10^6$</td>
</tr>
<tr>
<td>Electron Cleaned</td>
<td>$2.33 \times 10^7$</td>
<td>$2.47 \times 10^6$</td>
<td>$3.84 \times 10^6$</td>
</tr>
</tbody>
</table>

**SUMMARY**

While graphite and other carbon allotropes exhibit high intrinsic thermal conductivity, the thermal bottleneck for their integration into thermal abatement solutions is the interface between the graphitic structure and surrounding metal. The results of this study have shown that besides the vibrational and crystallographic properties of the constitutive materials normally considered in thermal modeling, an in-depth understanding of the surface structure and chemistry is required for effective thermal engineering. In order to tune and manage the thermal transport properties in nano-devices utilizing graphitic thermal abatement systems, an enhanced understanding of the effects of surface structure and metal-HOPG bonding on $h_{BD}$ will be key.

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