Thermal interface conductance across a graphene/hexagonal boron nitride heterojunction

Chun-Chung Chen,1 Zhen Li,1 Li Shi,2 and Stephen B. Cronin1
1Department of Electrical Engineering, University of Southern California, Los Angeles, California 90089, USA
2Department of Mechanical Engineering and Texas Materials Institute, University of Texas at Austin, Austin, Texas 78712, USA

(Received 25 November 2013; accepted 7 February 2014; published online 25 February 2014)

We measure thermal transport across a graphene/hexagonal boron nitride (h-BN) interface by electrically heating the graphene and measuring the temperature difference between the graphene and BN using Raman spectroscopy. Because the temperature of the graphene and BN are measured optically, this approach enables nanometer resolution in the cross-plane direction. A temperature drop of 60 K can be achieved across this junction at high electrical powers (14 mW). Based on the temperature difference and the applied power data, we determine the thermal interface conductance of this junction to be $7.4 \times 10^6 \text{W m}^{-2}\text{K}^{-1}$, which is below the $10^7$–$10^8 \text{W m}^{-2}\text{K}^{-1}$ values previously reported for graphene/SiO$_2$ interface. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4866335]

During the past two years, a number of 2 dimensional (2D) heterostructure devices have emerged, such as graphene/hexagonal boron nitride (h-BN), graphene/MoS$_2$, and InAs/WSe$_2$. For in-plane electron transport in graphene, much higher electron mobility is observed in graphene/h-BN devices than graphene/SiO$_2$ devices. Moreover, vertical 2D heterostructure devices have achieved much larger on/off ratios than lateral graphene devices and show interesting transport phenomena, such as rectification and negative differential resistance. In these types of devices, a large cross-plane electric field exists across a thin 2D stack and can result in localized heating. Despite the large in-plane thermal conductivity of graphene even when supported on an amorphous substrate, heat dissipation from 2D devices has been found to be limited by vertical heat transfer. Consequently, the operating temperature of 2D devices is strongly influenced by the interface thermal conductance between the 2D materials and the materials in contact.

There have been several measurements of graphene/SiO$_2$, graphene/metal, graphene/Si, and graphene/SiC interfaces, as well as theoretical calculations of thermal interface transport across such interfaces. It has been predicted that high interface conductance can be achieved in graphene/h-BN interfaces because of the similar crystal structure. However, experimental measurement of interface thermal conductance across such an interface is still lacking.

Here, we measure the thermal interface conductance across the graphene/h-BN interface by depositing graphene on h-BN substrates and passing electric current through the graphene to electrically heat the graphene. The temperature variation of the graphene and the underlying h-BN substrate during the electrical heating is monitored by Raman spectroscopy. Because of the optical transparency of graphene, Raman spectroscopy of both the graphene and h-BN can be monitored at the same time. The most prominent features in the Raman spectra of graphene are the $G$ (1580 cm$^{-1}$) and 2D (2680 cm$^{-1}$) bands, which downshift with increasing temperature. The Raman frequency of the optical phonon mode in h-BN can be observed at 1370 cm$^{-1}$. This mode also downshifts significantly with increasing temperature, enabling the lattice temperature to be determined from the Raman spectra. From these Raman frequencies, the temperature of the graphene and the h-BN can be obtained during the electrical heating process to obtain the temperature drop across the graphene/h-BN interface and, thus, the interfacial thermal conductance.

Figure 1(a) shows an optical microscope image of the graphene/h-BN device. Here, the h-BN flake is exfoliated from bulk BN by the “Scotch tape” method and deposited on a Si/SiO$_2$ substrate. graphene is grown on a copper substrate at 1000 ºC by chemical vapor deposition (CVD) using CH$_4$ as the carbon feedstock. The graphene is then transferred to the BN flake using a polymethyl methacrylate (PMMA) transfer layer and wet chemical etching. Electron beam lithography (EBL) and oxygen plasma etching are then used to pattern a 3 µm by 10 µm graphene strip on the h-BN surface, as shown in Figure 1(a). This procedure patterns a PMMA mask that protects the active graphene device area during the etch process. Raman spectroscopy confirms that this graphene is monolayer with a single 2D peak. The Ti/Au electrodes are patterned and deposited using another EBL step and metal evaporation. The device is baked under vacuum at 150 ºC for 5 h to anneal the graphene/h-BN interface. Once annealed, the device is more robust against any further substrate-induced doping and strain associated with the elevated temperatures reached during the electrical heating process. The device is then subsequently mounted in a vacuum cryostat. Figure 1(b) shows the schematic diagram of the device and the experiment setup. Electric current is passed through the graphene strip ranging from 0 to 1.5 mA. Raman spectra are collected with a Renishaw inVia spectrometer using a 40x/0.6 NA objective lens to focus a 532 nm excitation laser at the center of the graphene strip. Raman spectra are also collected every 0.25 mA increment in current to monitor the temperature changes in the graphene and underlying h-BN.

Figures 2(a) and 2(b) show the Raman frequencies of the $G$ and 2D bands of the graphene monolayer plotted as a function of the applied electric power. Both modes show a...
significant downshift with increasing applied power, indicating heating in the graphene. The Raman frequency of the h-BN optical phonon mode is also monitored, as shown in Figure 2(c). This mode also downshifts indicating a temperature rise in the h-BN flake. The Joule heating-induced peak shifts of these Raman modes downshift linearly with the applied power, as one would expect from increasing lattice anharmonicity with temperature. The experiment was then repeated to ensure that no irreversible changes occur in this structure during the measurement, such as strain or compression caused by the mismatch of the thermal expansion between graphene and h-BN due to the electrical heating.44,47 We observe consistent results in the Raman frequency shifts during the first and second electrical heating measurements and the Raman spectra taken before and after the measurement, which is provided in the supplementary material,48 show no significant changes, indicating that no oxidation or irreversible damage occur during this procedure.

Electrostatic doping by an applied voltage can also result in changes in the Raman peak positions and linewidths, however, the full width at half maximum (FWHM) of the 2D and G bands are FWHM_{2D}(0 A) = 35.8 cm⁻¹, FWHM_G(0 A) = 20.5 cm⁻¹, and FWHM_{2D}(1.5 mA) = 35.6 cm⁻¹, FWHM_G(1.5 mA) = 20.2 cm⁻¹. These variations with applied voltage/current are less than 1 cm⁻¹, indicating that electrostatic doping effects are negligible in these measurements.49

The temperature-induced downshifts of the Raman modes of the graphene and h-BN are calibrated in a temperature-controlled stage from 300 K to 400 K, as shown in Figure 3. These downshifts show a linear dependence on temperature with coefficients of −0.0102 and −0.0215 cm⁻¹/K for the graphene G and 2D bands, respectively, and −0.0246 cm⁻¹/K for the h-BN. Based on these coefficients, we can convert the Raman downshifts observed in Figure 2 to temperature, and plot the temperature as the function of the applied power, as shown in Figure 4. Figure 4(b) shows the temperature data from a second subsequent data run, showing excellent agreement with the first, as shown in Figure 4(a), indicating that no irreversible changes took place during initial electrical heating measurement.

The measured temperature drop across the graphene-BN interface, (ΔT = T_{Graphene} − T_{BN}), shown in Figure 5, increases with the electrical heating power, Q = I²R. The slope of the curve normalized by the interface area (A = 30 µm²) is the interface thermal conductance (G_{th}) of the graphene/h-BN interface, G_{th} = Q(A × ΔT), where A is the graphene-BN contact area.50 Based on the G band and 2D band temperatures, respectively, the G_{th} values are 6.88 MWm⁻²K⁻¹ and 7.73 MWm⁻²K⁻¹ during the first electrical heating (Figure 5(a)), and 7.57 MWm⁻²K⁻¹ and 7.47 MWm⁻²K⁻¹ from the second electrical heating (Figure 5(b)). These values are averaged to obtain G_{th} of 7.41 ± 0.43 MWm⁻²K⁻¹, which is substantially

![FIG. 1. (a) Optical image and (b) schematic diagram of the graphene/h-BN device and experiment setup.](image1)

![FIG. 2. Raman frequency shifts of the (a) G and (b) 2D bands of the graphene, and (c) h-BN optical phonon mode plotted as a function of the electrical heating power.](image2)
lower than the theoretically calculated value of $1.87 \times 10^8$ Wm$^{-2}$K$^{-1}$ \cite{Ref.24} and previously reported values of $10^7$–$10^8$ Wm$^{-2}$K$^{-1}$ for graphene/SiO$_2$, graphene/Ti/Au, and graphene/Au interfaces, but higher than the value of $1.89 \times 10^4$ Wm$^{-2}$K$^{-1}$ reported for graphene/SiC interfaces.\cite{17–20,23}

We expect the thermal interface conductance of these randomly stacked heterostructures obtained by mechanical exfoliation and PMMA transfer to be significantly lower than that of lattice-matched graphene grown on BN, which more closely resembles theoretical calculations.\cite{24} This is a current limitation of our experimental approach that may be resolved technically in the future. However, lower thermal interface conductance is advantageous for applications in thermoelectric energy conversion. Moreover, it is likely that contaminations of the interface by liquid or organic residues have resulted in further discrepancies between the measured and theoretical results, as well as, variations between different experimental results.

Motivated by a recent Raman measurement of thermal interface conductance between graphene and the SiC substrate,\cite{23} this experiment shows that the thermal interface conductance of a graphene/h-BN interface can be obtained by
electrical heating of the graphene sheet while monitoring the temperatures of the graphene and BN using Raman spectroscopy. While the depth resolution of the measured SiC temperature was set by the optical penetration depth in the SiC substrate in the earlier measurement, the current measurements can achieve atomic scale depth resolutions in the measured temperatures in both graphene and h-BN. As such, the current experiments are able to resolve the temperature drop over atomic distance between the graphene and underlying h-BN, which allows for direct probing of the graphene/h-BN thermal interface conductance. In contrast to theoretical predictions of high thermal interface conductance across a clean graphene/h-BN interface, the results show that the thermal interface conductance for the graphene/h-BN device prepared by the PMMA transfer method is 7.41 ± 0.43 MWm⁻²K⁻¹, which is lower than those reported for graphene/SiO₂, graphene/Ti/Au, and graphene/Au interfaces and higher than that reported for graphene/SiC interface. The results suggest the importance in improving the interface quality in order to increase the interface conductance.

This research was supported by DOE Award Nos. DE-FG02-07ER46376 and DE-FG02-07ER46377.


