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Thermal conductivity measurement of few layer graphene film by a micropipette sensor with laser point heating source

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Abstract
We report a thermal characterization method for a large-scale free-standing chemical vapor deposited few layer graphene (FLG), in which a micropipette temperature sensor with an inbuilt laser point heating source was used. The technique is unique as it exhibits in general the characteristic features of high accuracy measurement of thermal conductivity of free-standing ultrathin films. Using the micropipette sensor we successfully implemented the characterization technique to show high thermal transport behavior in free-standing graphene. For accurate and successful measurement of thermal conductivity, FLG grown on Ni was transferred to a polycarbonate (PC) membrane with holes (average diameter of 100 μm) in order to isolate the graphene film from heat spreading through the bottom of the film by the laser point heating. The thermal conductivity of FLG by this method was measured at 2868 ± 932 W/m°C. The large uncertainty of 32% in thermal conductivity measurement is mainly due to the non-uniform (∼30% deviation) thickness of the film.

1. Introduction

Graphene and other 2D layered materials have attracted considerable attention due to their noteworthy electronic, thermal, mechanical and optical properties [1–4]. These remarkable properties result in potential applications in photonic and electronic devices [5, 6], solar cells [7, 8], sensors [9], and thermal management [10]. From the previous reports [11, 12], graphene has been shown to exhibit highly anisotropic thermal properties because of its anisotropic structure, which means the covalent sp2 bonds between adjacent carbon atoms on the intralayer are stronger than the weak interlayer van der Waals interactions between adjacent graphene planes. Recently, the thermal conductivity of free standing single layer graphene was measured by a Raman-based technique, the results of which have been reported up to 5300 W m−1 K−1 near room temperature [4]. With increasing the number of layers from 2 to 4, the thermal conductivity decreased from 2800 to 1300 W m−1 K−1 [13]. Nonetheless, few layer graphene (FLG) was studied for a candidate heat spreading material because of its high in-plane thermal conductivity [13]. It can be integrated with electronic devices and chips as a heat spreader.

The thermal conductivity of graphene was experimentally measured by different techniques such as Raman optothermal method [13, 14], electrical self heating [15, 16], and modified T-bridge [17]. The advantages of Raman method are simple measurement and sample preparation, while it has some limitations related to uncertainty in the measurements of optical absorption, laser spot size, and location of laser heat source [13, 14]. Electrical techniques have also some advantages in terms of the cover of a large range of temperatures. However, there remains still an issue related with polymer residues on the sample after vacuum annealing process [15]. We suggest herein a novel method of determining the thermal conductivity of suspended FLG; this method can be applied to other 2D materials. In this study, micropipette thermal sensors (MTS) [18–22] with a few micron-sized tips (less than 3 μm) were used to measure the temperature on the film which had a spatial resolution of less than 3 μm. Accurate measurements of the temperature distribution on the surface of graphene film were made...
through temperature resolution of 0.01 °C provided by the pipette sensor. Even though there have been many attempts to measure thermal conductivity using thermal sensor based techniques, a fabrication process of thermal sensor was intricate and required many sequential processes [9, 11]. The MTS proposed here can be a promising way to reduce overall fabrication process as well as aforementioned limitations on measurement uncertainties.

2. Experimental method and characterization

2.1. Preparation of FLG

A FLG sample was prepared by the chemical vapor deposition (CVD) method. To this end, E-beam evaporated thin film of Ni with a thickness of 300 nm was coated on a SiO2/Si substrate on which graphene is grown. Then the substrate was placed inside a low pressure thermal CVD (Atomate, USA) system and the graphene was deposited via catalytic thermal dissociation of methane (CH4) gas under reducing atmosphere at 1000 °C. The ambient pressure of the chamber was kept at ~0.8 atm during the entire growth process.

2.2. Transfer of graphene on to a holed polymer substrate

The graphene on Ni film was transferred to a pre-holed thin poly carbonate (PC) membrane to measure the thermal conductivity of suspended free-standing FLG. The transfer was performed using a chemical process. To this end, PMMA (poly methyl methacrylate) was coated on the FLG film grown on Ni. Ni was etched by Ni etchant (FeCl3) and PMMA with FLG films was transferred on the PC membrane. Finally, the PMMA was removed using acetone, which was followed by rinsing with deionized water. Once the FLG film was successfully transferred onto the PC membrane, the characterization of the number of layer on the suspended FLG film was made through Raman spectroscopy.

2.3. Raman analysis of FLG

Raman spectra were measured in a system with a spectral resolution of 4 cm\(^{-1}\) with an argon ion (Ar+) laser (Spectra Physics, model 177G02) at a wavelength of 514.5 nm. The Raman spectra were collected using a high-throughput holographic imaging spectrograph (model HoloSpec f/1.8i, Kaiser Optical Systems) inbuilt with a volume transmission grating, holographic notch filter, and thermoelectrically cooled charged coupled device (CCD) detector (Andor Technology). Figure 1 shows Raman spectrum of the characteristic G-band and 2-D of graphene and the optical image of suspended FLG. The intensity ratio of G-band and 2D band (IG/2D) in figure 1(a)–(c) reflects successful growth of graphene on Ni thin film. The number of FLG was estimated by the Raman analysis. The ImageJ (version 1.48v, National Institutes of Health, USA) [23] was used to estimate the average number of layers on FLG by analyzing the area percentage of different number of layers on different spots of the FLG sample.

The apparent contrast in the optical image in figure 1(d) may have been caused by precipitation of Ni atom into the graphene layer [24]. However, the different contrast is believed to be due to the different thickness of graphene because the number of layers revealed by Raman spectroscopy coincides with the optical contrast map.

2.4. Measurement of surface temperatures

Figure 2 shows the measurement setup for thermal conductivity of FLG film consisting of a laser source, optical device, a CCD camera, and a MTS. The laser was aligned on the surface of the samples with the guide of optical devices.

Heat was produced by the laser absorption and was diffused from the center of the sample in the radial direction while the convective heat loss to the environmental air is neglected. All experiment procedures such as the landing of the micropipette sensor and the illumination of the laser source were monitored using CCD. In every temperature measurement, consistent mechanical contact between the probe and graphene was ensured by motorized z-stage and voltage measured by nanovoltmeter. When the probe contacted with the heated suspended graphene, the measured voltage was significantly changed. Once the probe touched the graphene surface, the probe was pushed vertically by 1 μm to have a consistent contact force between the probe and the graphene. The thermal sensor was fabricated by using the microscale thermocouple principle, which was explained in previously published work [19]. The prototype thermal sensor was composed of a borosilicate glass, Tin (Sn) alloy, and Nickel (Ni) coating layer as shown in figure 2(b). The fabricated thermal sensor was calibrated in a thermally insulated chamber that was filled with water, and the chamber temperature varied from 22 °C (room temperature) to 40 °C.

The Seebeck coefficients of the micropipette sensor to measure the FLG membrane temperature were determined from the calibration results using the method described in the previous study [19]. Figure 3 presents a linear relation between voltages provided by the sensor and temperatures measured by a digital thermometer.
The Seebeck coefficients of the sensor was obtained from the slope in figure 3. This Seebeck coefficient of the micropipette sensor was used to determine temperature difference in between two positions.

2.5. Measurement of laser power

In this study, green laser at wavelength of 532 nm (Opto Engine- MGL-III with maximum of power 200 mW at stability of <1% power fluctuation) was used as a heat source. The initial power from the laser was different from the absorbed power by FLG because of reflection and transmission of the incident laser light as well as instrumental loss from the optics. A power meter (THORLABS PM100D) was used to measure the laser power at different positions from 1 to 4 in figure 2. Transmitted power and total incident power were measured at positions 1 and 2, respectively. The power loss in the objective lens was determined by measuring power at position 3, while reflected power was measured at position 4. With these powers measured, the absorbed power was determined by the relationship

\[ P_{\text{absorbed}} = P_{\text{incident}} - P_{\text{Reflected}} - P_{\text{Transmitted}}. \]  

(1)

From radial position and temperature difference between the two positions, the thermal conductivity of the FLG film was calculated by the Fourier’s equation (equation (2))

\[ \dot{Q} = \frac{2\pi kl(T_1 - T_2)}{\ln(r_2/r_1)}, \]  

(2)

where \( \dot{Q} \), \( k \), \( L \), \( r_1 \) and \( r_2 \), \( T_1 \) and \( T_2 \) are power absorbed, thermal conductivity of FLG film, thickness of FLG film, radius of two measurement positions and temperature at two measurement positions respectively. When the absorbed power was spread out through the FLG film in the radial direction, the power loss due to convection, radiation, and finite tip size can be ignored [19]. The experiment has been conducted in a controlled environment where the room temperature is maintained at a constant level and air current is minimized, i.e., in an enclosure. Therefore, the convection heat transfer is mainly due to natural convection. When the laser was
fixed at 134 $\mu$W for example, the sensor detected that the laser would produce a temperature of 27 °C at the center of the film as is revealed after extrapolation of the radial temperature measurements. Since the experiment was conducted at a room temperature of 22 °C, the mean film temperature to calculate the convection heat transfer was estimated at 24.5 °C. At this mean film temperature Rayleigh number was determined at $2.79 \times 10^{-4}$ which confirmed that there will be natural convection only. Using the Lienhard [25] assumption, we determined the convective heat transfer coefficient at the mean film temperature of 24.5 °C for air to be
22.9 W m\(^{-2}\) K\(^{-1}\). Then using Newton’s law of cooling the heat loss due to the natural convection was determined to be 0.26 \(\mu\)W which is only 0.2% of the absorbed power 134 \(\mu\)W.

In order to justify one dimensional heat conduction in equation (2), we have estimated heat loss through the probe tip, which can be estimated by temperature difference along the tip (\(\Delta T\)) and theoretical thermal resistance. By assuming that the heat transfer mainly occurs through Sn alloy in the probe, the theoretical thermal resistance can be expressed as follows

\[ R_{\text{pipette}} = -\int_{x_{\text{pipette}}}^{T_{\text{pipette}}} \frac{dT}{dx} dx = \int_{0}^{L_{\text{pipette}}} \frac{dx}{kA_c}, \]  

where \(L_{\text{pipette}}\) is the length (~1 mm) along the tapered section of the probe, \(k\) is thermal conductivity of Sn alloy, \(A_c\) is cross sectional area. \(A_i\) is expressed as \(\pi D_x^2/4\) in \(\mu m^2\) with a half cone angle of 5\(^{\circ}\), where \(D_x\) is 0.5 + 2tan5\(^{\circ}\) x. The thermal resistance is then calculated at \(-10^6\) K W\(^{-1}\). The heat loss (\(\Delta T/R_{\text{pipette}}\)) is estimated at 1 \(\mu\)W, assuming \(\Delta T = 0.1\) K. This small heat loss may be negligible as compared to the absorbed power (134 \(\mu\)W) of graphene film so that one dimensional heat flow assumption could be valid. Nonetheless, the heat loss through the probe will have negligible effect on the measurement accuracy because the temperature gradient between the two points (\(T_1 - T_2\) in equation (2)) does not change regardless of existence of heat loss, assuming that the thermal contact resistance between the tip and the sample remains the same.

3. Results and discussion

3.1. Average number of FLG layers

After being transferred to the holed PC substrate, the suspended FLG is characterized to measure the average number of layers by Raman spectroscopy. Figure 1 shows the Raman spectrum and an optical image of the FLG sample. The transferred graphene sample had not only a single layer but also few layers of graphene which is indicated in figure 1. It is well known that the thickness and quality of graphene grown on Ni catalyst are affected by cooling rate, annealing time and Ni microstructure [24, 26, 27]. The crystallinity of Ni strongly affects the thickness uniformity of graphene [24]. The non-uniform thickness in the sample was resulted from the aforementioned factors during growth. The number of graphene layers was estimated at 1–10 layers which was revealed from the intensity ratio of G-band to 2D band and full width at half maximum of 2D band in figures 1(a)–(c). The percentage of each layer in the suspended FLG sample was processed by ImageJ. This result was used for calculation of the average number of graphene layer. This non-uniform thickness of FLG adversely affected the measurement accuracy of thermal conductivity of the graphene film, resulting in hindering heat transport through its single layer of basal plane whose thermal conductivity was reported to be 2000–4000 W m\(^{-1}\) K\(^{-1}\) [28–30]. As is well known, the thermal conductivity of graphene is significantly influenced by the number of layers [13, 31]. Thus, the average thickness of the suspended FLG should be calculated to properly estimate its thermal conductivity by the following equation

\[
\text{Average thickness} = \frac{1}{\sum_i A_i} \sum_i x_i A_i,
\]

where \(x_i\) and \(A_i\) are the number of layers and the fractional ratio of each region, respectively. The average thickness of FLG film was estimated at 7.4 layers using equation (4).

3.2. Thermal conductivity of FLG

The thermal conductivity measurement of the transferred FLG film was conducted by the MTS. Figure 4 shows three positions on the suspended FLG film where MTS is contacted to measure its surface temperature.

The radial position from the center of the laser heating source was determined by pixel counts of the digital image from a CCD camera, for which an imaging system has been calibrated as 0.505 \(\mu m\) per pixel. The measured radial distances from position 1 to position 3 were 18.8 \(\mu m\), 32.3 \(\mu m\), and 44.8 \(\mu m\) respectively. Voltage generated by MTS at each position was converted to temperature in order to calculate the thermal conductivity of the suspended FLG film. The temperature measured by MTS at each position and the curve fit are shown in figure 5(a). It should be noted that the boundary condition (i.e., ambient temperature of 22 °C at the edge of the suspended membrane) for one-dimensional heat transport could be satisfied as the measured temperature at \(r = 44 \mu m\) is 22.3 °C, which is already close to ambient temperature. The curve fit of temperatures was calculated by equation (5) from rewriting equation (2)

\[
T = T_0 + \frac{Q}{2\pi kL} \ln \left( \frac{r}{r_0} \right)
\]

The deviation in the curve fit in figure 5(a) may be due to the uncertainty during temperature measurement. From the measured temperature at each position, temperature differences between positions 1 and 2 and
between positions 1 and 3 were obtained to be 1.68 °C and 2.43 °C, respectively. With the laser power measurements using a power meter (THORLABS PM100D) and equation (1), the absorbed laser power was determined to be $1.34 \times 10^{-4}$ W. With these measured data, the thermal conductivity of the suspended FLG on PC was calculated by using equation (2).

Figure 5(b) shows the thermal conductivity of the FLG film at different radial positions. Thermal conductivity in each position turned out to be different. In addition, the thermal conductivity measured by temperatures 1 and 2 was shown lower than that by temperatures 2 and 3, even though the radial distances between positions 1 and 2 and between positions 2 and 3 were measured 13.1 μm and 13.12 μm, respectively. Such different results of thermal conductivity may be resulted from different number of layers within the measured region as shown by Raman analysis in figure 1. This implies that the thermal conductivity of the suspended FLG which was grown by CVD on Ni substrate was strongly influenced by non-uniform thickness of FLG sample. Thermal conductivity of FLG also differs by the uncertainty in temperature measurement which is related to finite temperature difference between the micropipette sensor tip and the sample surface. Due to the effective tip size of a sensor, the error in temperature measurement for 1 and 2 positions and 1 and 3 positions were determined to be 0.06 °C and 0.05 °C respectively. Then this error would affect the calculation of thermal conductivity of FLG. The average thermal conductivity was calculated to be 2868 \pm 932 W/m °C (averaged from three sequential measurements indicated in figure 4(b)).

Figure 4. Temperature measurement of FLG film with micropipette thermal sensor at different positions; (a) pipette sensor and laser heating on suspended FLG film, (b) radial position at each position.

Figure 5. Temperature and thermal conductivity.
with respect to measurement power absorbed, radial position, temperature difference and thickness of FLG. The uncertainties of them were calculated by the root-sum-squared (RSS) method [32] which is expressed by

$$u_k = \left[ \left( \frac{\partial k}{\partial Q} u_Q \right)^2 + \left( \frac{\partial k}{\partial R} u_R \right)^2 + \left( \frac{\partial k}{\partial L} u_L \right)^2 + \left( \frac{\partial k}{\partial \Delta T} u_{\Delta T} \right)^2 \right]^{1/2},$$  \hspace{1cm} (6)

where $u_Q$, $u_R$, $u_L$, and $u_{\Delta T}$ mean the uncertainty of power measurement, radial position, thickness, and temperature measurement respectively. The uncertainty in temperature measurement was calculated by

$$\Delta T = \Delta V / S,$$

where $\Delta T$, $\Delta V$, and $S$ are temperature uncertainty, voltage uncertainty and Seebeck coefficient, respectively. This relationship was applied to a RSS equation in order to calculate the uncertainty in temperature measurement. Similarly, the uncertainty in radial position measurement was calculated by RSS equation with $R = \ln (r_2 / r_1)$. In addition, the uncertainty in thickness measurement was considered the standard deviation during measuring the area of different thicknesses and Raman shifts. Power at each position in figure 3 was measured by power meter and the standard deviations were used for uncertainty calculation. The power measurement uncertainty is relatively low because the laser specifies inherent power fluctuation less than 1%. We found that the measurement uncertainty was 4.19% in power absorbed, 10.49% in radial position, 2.85% in temperature difference and 30.33% in thickness of graphene. While the calibration of CCD image and pipette sensor resulted in the uncertainty associated with radial position and temperature, instruments errors were related to the uncertainty of power and thickness measurement. Finally, overall uncertainty in the measurement of thermal conductivity was calculated to be 32.5%. As noticed, the main error in thermal conductivity of FLG film was caused by the thickness measurement of FLG.

4. Conclusion

In summary, the thermal conductivity of suspended FLG which was grown by CVD method on Ni catalyst was measured by a MTS at room temperature. The measured thermal conductivity of FLG was 2868.98 ± 932 W/m °C. From the error analysis, the uncertainty in the measured values for thermal conductivity of FLG was determined to be 32.5% which was strongly influenced by the nonuniform thickness of FLG; this relatively high uncertainty is not originated from the measurement technique. With a uniform thickness of graphene, this MTS technique suggested in this study would enable high accuracy temperature, thus high accuracy thermal conductivity measurements in a localized region of a few microns such as the surface of 2D materials.

References