Thermal conductivity of individual multiwalled carbon nanotubes

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1. Introduction

Over the past decade rapid development on nanoscale electronic devices excites a great interest in its thermal management because by decreasing the size of the device to nanometres length scale, a significant amount of energy may be dissipated in the compact space. One of the thermal management techniques for removing the heat is using high thermal conductance component such as carbon nanotubes and graphene in nanodevices. On the other hand due to unique electrical properties of carbon based structures, they became great promising candidates as a component in nanoelectronic devices. In both case, understanding thermal properties of carbon nanotubes and graphene is an essential key to understanding their overall behaviour. So far, some experimental and molecular dynamic studies have been reported thermal conductivity of individual or bundle single walled and MWCNTs in the range of 20–6000 W/mK [1–13]. Although thermal properties of individual MWCNTs were measured, these measurements were either based on using optical method to measure thermal conductivity of a group of MWCNTs and then determine the effective thermal conductivity of individual MWCNT or using electrical method to determine thermal property of individual MWCNTs [2,6,11]. In this study, thermal conductivity of individual MWCNTs is measured by using pulsed photothermal reflectance (PPR) technique [14] at room temperature, which is based on pump and probe method. This technique is non-contact method and is applicable for measuring thermal properties of thin film. The advantage of this method is that there is not any boundary scattering due to reservoir junction that has been observed in electrical method.

2. Experimental details

2.1. Sample fabrication

In order to apply PPR method to measure thermal conductivity of individual MWCNTs the specific configuration of the sample, shown in Fig. 1(a) and (b), is designed and fabricated. In this configuration, single MWCNT of diameter 150 nm with length of 2 μm is anchored at the bottom of a trench created by etching of SiO2. The dimension of the trench is 100 μm × 100 μm × 2 μm. A gold layer of width 10 μm, length of 1 mm and thickness of 200 nm is deposited on top of the CNT for optical absorption of the excitation pulse. The fabrication process of the required sample began by deposition of a 40 nm thick SiO2 as a barrier layer on a standard Si wafer. 10 nm thick Ni was evaporated onto the substrate as the catalyst for the CNT growth. The patterning of catalyst layer was achieved through electron beam lithography and lift-off processes.
made. To avoid the unnecessary growth of CNT from the alignment marks, a photolithography process was done and the Ni marks were etched by immersing in FeCl₃ solution. New alignment marks made of Ti and then deposited. The wafer was diced into chips before the CNTs growth step. The CNTs were grown by plasma-enhanced chemical vapor deposition (PECVD). The growth gases were 40 sccm C₂H₂ and 160 sccm NH₃. A direct current (DC) plasma was applied at 500 °C to initialize the growth and the heater temperature was slowly ramping to 750 °C where the main growth happens. A 10 min growth process produces well aligned single CNTs about 4–5 μm long. A 2 μm SiO₂ layer was deposited by PECVD after the CNT growth. The CNTs were thus buried inside the SiO₂ layer. The chip surface was polished to planarize the structure. After that, a 200 nm thick Au layer was deposited on the CNT by standard photolithography, evaporation, and lift-off processes. Fig. 2(a) shows the SEM image of individual MWCNT and Fig. 2(b) is the SEM image of gold bridge on the sample.

2.2. PPR setup

PPR technique for the first time used by Kaeding et al. to measure the thermal conductivity of the thin SiO₂ films [14]. Following that several studies by using PPR method has been done to measure thermal properties of thin film [15–19] and also MWCNTs film [3]. The schematic diagram of PPR setup is shown in Fig. 3. In this technique, there are two lasers in which one acts as an excitation laser and another one acts as a probe laser. The excitation pulse laser provides momentarily heat pulse to the sample whereas the probe laser senses the temperature change at the surface of the sample. To facilitate heat absorption, a gold layer is deposited on top of the sample. After the gold layer absorbed the excitation pulse energy, heat is generated and conducts from the gold layer through the sample and into the substrate. The surface temperature of the sample is monitored by changes in refractive index of the gold layer. The signal is captured by a photoreceiver. Also, it is expected that the power of the probe beam decrease when the temperature rises and slowly return back to the original power level when the temperature returns to the room temperature. The temperature decay time is governed by thermal conduction properties of the film underneath the gold layer.

In our experimental setup the excitation laser is 2nd harmonic Nd:YAG laser (532 nm) operated at 10 Hz with a pulse width (FWHM) of 8 ns, spot size of 2 μm, pulse energy of 3 μJ. The probe laser is continuous HeNe laser (632 nm) with 0.5 mW power. These two lasers beams are combined by dichroic mirrors and focused through a microscope objective (100×, NA 0.7) onto the sample, which is mounted on a 3D stage and has a step size resolution of 5 nm.

3. Result and discussion

Since the reflectance of the probe beam and temperature excursion of the sample has an inverse linear relationship; therefore surface temperature profile can be obtained by inverting the intensity profile of the probe beam.

To extract thermal conductivity of the sample, the normalized surface temperature profile is fitted with the Laplace transform of surface temperature T(s), which is the analytical solution of heat diffusion equation in three-layer [15].
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le using three-layer heat conduction model. The fitting parameters are thermal conductivity of Au, thermal conductivity of the integrated MWCNT and SiO₂. The average of integrated thermal conductivity of integrated MWCNT and SiO₂ (K_{tube}) for several samples is obtained 27.3 W/mK. The volume filling fraction is considered to be 0.010. By substituting the average value of integrated thermal conductivity of integrated MWCNT and SiO₂ (K_{tube}) and K_{SiO₂} = 1.4 W/mK into equation (3), the intrinsic thermal conductivity of individual MWCNT (K_{tube}) is extracted to be 2586 W/mK. Kim et al. [6] have measured thermal conductivity of individual MWCNT by using microfabricated suspended device. They reported that the thermal conductivity of a single MWCNT with a diameter 14 nm is more than 3000 W/mK at room temperature. Also, Fujii et al. [4] have showed that the thermal conductivity of single MWCNT with a diameter 9.8 nm is 2069 W/mK by T-type nanosensor and reported thermal conductivity of MWCNT decreases with increasing the diameter of MWCNT. Our measurement for 150 nm diameter of single MWCNT is much higher than that obtained by Kim and Fujii. This discrepancy of results can be attributed to the difference in the experimental

![Fig. 3. Schematic diagram of pulsed photothermal reflectance experiment.](image)

![Fig. 4. Schematic diagram of parallel resistor model.](image)

where e₁ = \sqrt{\nu_i c_i K_i}, e₂ = e_1/e_j, \eta_i = d_i/\sqrt{\alpha_i}, i = 1, 2, 3. Subscript 1, 2, and 3 stand for Au layer, the integrated MWCNT and SiO₂ and the silicon substrate, respectively. d is the thickness of the layer; \rho is the density, c is the specific heat, K is the thermal conductivity, and \alpha is thermal diffusivity. Q(s) is the Laplace transformed Gaussian pulse (Nd:YAG) which can be described as:

\[
Q(s) = \frac{1}{\sqrt{2\pi}} \left[ 1 + \text{Erf} \left( \frac{b_{\text{Nd:YAG}} - c_{\text{Nd:YAG}}}{2} \right) \right] \times \exp \left[ -b_{\text{Nd:YAG}}^2 + 1 - \frac{1}{\alpha_s^2} \right]
\]  

(2)

where \(b_{\text{Nd:YAG}} = 2 \times 10^{-8} \text{s}\) and \(c_{\text{Nd:YAG}} = 3.37 \times 10^{-9} \text{s}\) are the fitted values to our Nd:YAG pulse laser.

The reason of considering the second layer as the integrated MWCNT and SiO₂ is that the focused spot size of the probe beam (1.5 \(\mu\)m) is much larger than the diameter of the MWCNT (150 nm). Thus the signal of the probe beam is not only dedicated to intrinsic thermal conductivity of individual MWCNT, but rather is related to the thermal properties of integrated MWCNT and SiO₂. After we curve fitted the detected signal, the extracted thermal conductivity would be an integrated value due to both SiO₂ and the individual MWCNT. In order to extract the thermal conductivity of individual MWCNT from the temperature profile, we apply the parallel resistor model [3] in which SiO₂ is treated as a conducting channel that transports heat in parallel with MWCNTs as shown in Fig. 4.

Using the relationship of thermal resistance \(R = d/K\), where d is the conduction length and K is the thermal conductivity, after applying the parallel resistor model, we obtain:

\[
\frac{K_{\text{tube}}}{d} = \frac{K_{\text{tube}}}{d} + K_{\text{SiO₂}} \left(1 - \frac{\delta}{d} \right)
\]

(3)

where \(K_{\text{tube}}\) is the integrated thermal conductivity due to both SiO₂ and MWCNT, \(K_{\text{tube}}^*\), and \(K_{\text{SiO₂}}\) is the intrinsic thermal conductivity of the MWCNT and SiO₂, respectively, and \(\delta\) is the volume filling fraction. Through curve fitting with the normalized temperature profile, \(K_{\text{tube}}\) can be obtained and using the experimental data of \(\delta\) and the literature value of \(K_{\text{SiO₂}}, K_{\text{tube}}^*\) can then be determined.

Fig. 5 shows the normalized values of surface temperature and fitted temperature profile using three-layer heat conduction model. The fitting parameters are thermal conductivity of Au, thermal conductivity of the integrated MWCNT and SiO₂. The average of integrated thermal conductivity of integrated MWCNT and SiO₂ (K_{tube}) for several samples is obtained 27.3 W/mK. The volume filling fraction is considered to be 0.010. By substituting the average value of integrated thermal conductivity of integrated MWCNT and SiO₂ (K_{tube}) and K_{SiO₂} = 1.4 W/mK into equation (3), the intrinsic thermal conductivity of individual MWCNT (K_{tube}) is extracted to be 2586 W/mK. Kim et al. [6] have measured thermal conductivity of individual MWCNT by using microfabricated suspended device. They reported that the thermal conductivity of a single MWCNT with a diameter 14 nm is more than 3000 W/mK at room temperature. Also, Fujii et al. [4] have showed that the thermal conductivity of single MWCNT with a diameter 9.8 nm is 2069 W/mK by T-type nanosensor and reported thermal conductivity of MWCNT decreases with increasing the diameter of MWCNT. Our measurement for 150 nm diameter of single MWCNT is much higher than that obtained by Kim and Fujii. This discrepancy of results can be attributed to the difference in the experimental
method and the sample geometry. In our measurement, individual MWCNT is vertically aligned and heat was applied on top of the MWCNT. In this method, all the walls including both the outer and inner walls are having the same contribution in thermal transport from top of the MWCNT to the heat sink. But in Kim’s and Fujii’s electrical methods, single MWCNT was suspended between the heater and heat sink. In their geometry, only the outer walls of the MWCNT have good thermal contacts to both the heater and heat sink. In our measurement, individual MWCNT was suspended between the heater and heat sink and thus higher contribution to the thermal transport than the inner walls [6]. Since in our sample geometry, all the walls are having equal contribution to thermal transport, a much higher thermal conductivity can be expected in our measurement result. The high thermal conductivity of individual MWCNT could be concluded from the existence of ballistic flux of long-wave acoustic phonon. Our measured value of thermal conductivity of individual MWCNT is an order of magnitude higher than the value that obtained for thermal conductivity of a bundle of MWCNTs [3], which consists of an array of MWCNTs surrounded by air. This difference could be attributed to the existence of thermal boundary resistance between the tubes in bundle of MWCNTs that causes more phonon scattering.

4. Conclusion

Thermal conductivity of individual MWCNT was measured using pulsed photothermal reflectance technique and parallel resistor method. Our simulation confirmed that despite the relatively large probing area (a few μm) individual MWCNT can be detected and thermal conductivity can be measured when the MWCNT is embedded inside SiO$_2$ volume. The average intrinsic thermal conductivity value of several samples is determined to be 2586 W/mK.

References