Temperature Distribution and Thermal Conductivity Measurements of Chirality-Assigned Single-Walled Carbon Nanotubes by Photoluminescence Imaging Spectroscopy

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ABSTRACT: It is expected that single-walled carbon nanotubes (SWCNTs) have high thermal conductivity along the tube axis and that the thermal conductivities depend on their structure, such as length, diameter, chirality \((n, m)\), and so forth. Although many experimental measurements of the thermal conductivity have been reported, the SWCNT structure was not characterized sufficiently. In particular, the chirality was not assigned, and it was not confirmed whether SWCNT was isolated or not (bundled with multiple SWCNTs). Therefore, measured values widely vary (10¹ to 10⁴ \(\text{W/(m·K)}\)) so far. Here, we measured the thermal conductivity of chirality-assigned SWCNTs, which were individually suspended, by using photoluminescence (PL) imaging spectroscopy. The temperature distribution along the tube axis was obtained, and the temperature dependence of the thermal conductivity was measured in a wide-temperature range (from 350 to 1000 K). For \((9, 8)\) SWCNTs with 10⁻¹² \(\mu\text{m}\) in length, the thermal conductivity was 1166 ± 243 \(\text{W/(m·K)}\) at 400 K. The proposed PL imaging spectroscopy enables to measure the thermal conductivity of SWCNTs with high precision and without any contacts, and it is an effective method in the temperature distribution measurements of nanomaterials.

1. INTRODUCTION

Because of the recent development of integration technologies, the heat-generation density in electric devices rapidly increases, and the management of thermal transport becomes an urgent issue. To improve and control the thermal transport, new materials that possess novel thermal properties are needed and nanomaterials are an excellent candidate. Their properties generally depend on crystal structure, size in nanoscale, and morphology, and the desired thermal properties can be realized by the combination of structure-designed nanomaterials.

In particular, single-walled carbon nanotubes (SWCNTs) are the nanomaterials that attract attention. It is known that SWCNT has high thermal conductivity along the tube axis, and the high thermal conductivity is anticipated for thermal management of devices. The dependence of thermal properties on the tube diameter, length, and chirality is theoretically discussed. By contrast, experimental measurements for individual SWCNTs are extremely difficult, and their thermal properties are unclear. The thermal conductivity measurement of suspended SWCNTs has been performed by Joule-heating method, steady-state method, and the temperature dependence of the G-band. That of SWCNTs on substrates has been also performed by 3ω method. The obtained values of the thermal conductivity diverge because they are affected by the assumed temperatures distribution, contact thermal resistance, the temperature dependence of the electric resistance, and so on. In addition, the characterization of SWCNTs for the thermal property measurement is not sufficient, and only one measurement of chirality-assigned SWCNT is reported. Because the physical properties of SWCNTs strongly depend on their chirality, the thermal properties have to be measured from SWCNTs that are fully characterized. Because SWCNTs are chemically stable and they can be applied to devices at high temperatures, the thermal properties and their temperature dependence in a high-temperature range are also important.

In this study, we used a long suspended SWCNT that was fully characterized by optical spectroscopic methods and measured the temperature distribution and thermal conductivity along the tube axis by photoluminescence (PL) imaging.
spectroscopies. The PL imaging spectroscopy made it possible to measure the local temperature of SWCNTs in a wide temperature range without contacts or destruction. PL and Raman scattering spectroscopy determined the chirality, diameter, and crystallinity of the measured SWCNTs and confirmed that they were singly isolated (not bundled).

2. METHODS

PL cannot be observed from SWCNTs on a substrate. Therefore, we performed PL measurements using individual SWCNTs suspended between silica micropillars. The distance between the pillars was 10—12 μm, and the height of the pillar was 18 μm. The surface of the silica substrate, except for the top area of the pillars, was covered with a thin silicon layer of 40 nm thickness. Catalytic metals were alloyed with silicon and lost their catalysis. Thus, the SWCNTs were grown from only the top pillar area, and we could obtain the information from the top area of the pillars. The power of the excitation laser was 50 μW, and the spot size was 1.6 μm in diameter. The low-power density avoided additional heating of SWCNTs. The temperature distribution of suspended SWCNT along the axis was ignorable because of the short length (1.2—2.4 μm) and low thermal resistance between the SWCNT and silicon substrate. Therefore, it was ensured that the temperature of suspended SWCNTs was equal to that of the silicon substrate.

3. RESULTS AND DISCUSSION

Because of high thermal conductivity of silicon even at high temperature, the temperature of silicon substrate was uniform. The power of the excitation laser was 50 μW, and the spot size was 1.6 μm in diameter. The low-power density avoided additional heating of SWCNTs. The temperature distribution of suspended SWCNT along the axis was ignorable because of the short length (1.2—2.4 μm) and low thermal resistance between the SWCNT and silicon substrate. Therefore, it was ensured that the temperature of suspended SWCNTs was equal to that of the silicon substrate.

Figure 1a shows the scanning electron microscope (SEM) image of a suspended SWCNT. The suspended SWCNT was supported at both ends, which were connected with the pillar tops. Therefore, the SWCNT length (L) was determined by the spacing between two pillars. Figure 1b shows the PL map of the suspended SWCNT in air. The PL map was composed of PL spectra. The wavelength (full width at maximum, fwhm) of the excitation light was 10.87 μm, which was larger enough for the irradiation of whole-suspended SWCNTs. The total absorption energy of the whole-suspended SWCNT (I₀) is

\[ I_0 = L_0 \int_{-L/2}^{L/2} dx \int_{-d_{tube}/2}^{d_{tube}/2} dy \frac{1}{2\sigma_{laser}} \exp \left( -\frac{(x-x_0)^2 + (y-y_0)^2}{2\sigma_{laser}^2} \right) \]

where \((x_0, y_0)\) is the center position of laser, and \(L_0\) is the total power of the laser. L and \(d_{tube}\) are the length and tube diameter of the SWCNT, respectively. x- and y-axes are parallel and perpendicular to the tube axis, respectively. The PL images from the SWCNTs were acquired with an InGaAs two-dimensional (2D) photodetector, when the bandpass wavelength of an acousto-optical tunable filter was changed at every 5 nm from 1300 to 1400 nm. The pixel size of the 2D photodetector was 600 × 600 nm².

The temperature dependence of PL emission wavelength was measured from suspended SWCNTs between a trench (the width was 1.2—2.4 μm) on a thermally oxidized silicon substrate. The suspended SWCNTs were directly grown over the trenches by the same CVD method as that for the silica micropillars. PL spectra were measured with changing the temperature in vacuum. The silicon substrate was directly heated by Joule-heating method with ac voltage, whereas the substrate temperature was monitored with a thermocouple.
emitted PL signals between the pillars, the emission intensity changed along the tube axis depending on the band-pass wavelength. The nonuniformity of PL emission wavelength will be discussed later. Figure 2b shows the relationship between the intensity and the band-pass wavelength of PL images at the edge and the center of SWCNT. PL colored image of suspended SWCNT which was constituted from PL images in (a).

The emission wavelength depends on stress,14 temperature,15 and the dielectric constant around the SWCNTs.16,17 As shown in Figure 2c, the emission wavelength was not uniform along the tube axis. The nonuniformity was investigated focusing on the temperature distribution. Figure 3a shows the PL emission spectra measured from suspended SWCNTs over Si trenches at different temperatures in vacuum. PL emission energy decreased and the peak width increased. Figure 3b shows the temperature dependence of emission energy shift measured for six different chiralities of SWCNTs from 300 to 760 K. The temperature of the silicon substrate was measured with the thermocouple, and the temperature is considered to be uniform because of high thermal conductivity of silicon. It is assumed that the SWCNT temperature is equal to that of the silicon substrate.

The peak position of all chirality continuously shifted to lower energy as the temperature increases. The amount of energy shift $\Delta E$ follows the empirical formula of Varshni,18

$$\Delta E = - \frac{aT^2}{T + T_0}$$

(2)

where $a$ is the constant and $T_0$ corresponds to the Debye temperature. The black dotted line in Figure 3b is the result of fitting with the parameters $a = 0.177$ meV/K and $T_0 = 1800$ K, which is the Debye temperature of graphite at 600 K.19 All of the data from different chiralities are fitted well with a single line. These data do not exhibit type-dependence,14 which means that the stress effect can be ignored. Note that the temperature dependence has been measured in the lower temperature range, and the value of $a$ is reported to be 0.075 meV/K.15 Water molecules adsorb on the surface of suspended SWCNTs below the room temperature, and they increase the dielectric constant and change $E_{\text{ii}}$.20 On the other hand, the temperature range of our measurements is above the room temperature, and it was confirmed that water did not adsorb on SWCNTs by PL spectroscopy. It is possible that the adsorption and desorption of water make a difference in the temperature dependence of PL emission wavelength in the low temperature range.

PL colored images were measured from (9, 8) SWCNT with different laser powers, as shown in Figure 4. The excitation laser wavelength was 720 nm. The sharpening process was performed to correct the optical images. The details of the sharpening processing can be found in the Supporting Information.
at about 10 Pa, where the heat transfers between air molecules and the SWCNT could be ignored. The heat loss of the thermal radiation from the SWCNT is also ignored because of the small surface area and low temperature.

When \( I_0 = 2.03 \, \mu W \), the PL emission energy was almost uniform along the whole SWCNT, and it was about 1330 nm (930 meV). As \( I_0 \) increased, the emission energy at the center part shifted to a lower energy, whereas the edge part did not change. At \( I_0 = 4.15 \, \mu W \), the emission energy of the center part reached about 1371 nm (905 meV), which is 25 meV lower than that at \( I_0 = 2.03 \, \mu W \). The emission energy down shifts at higher temperature. Therefore, the nonuniformity of emission wavelength and its laser-power dependence can be understood by the temperature distribution along the tube axis.

As mentioned, SWCNTs are heated by laser irradiation. The exciton generated by the incident photon gradually relaxes with the scanning of optical phonons in a few femtosecond and acoustic phonons in a few picosecond, and then it reaches thermal equilibrium. On the other hand, the group velocity of acoustic phonons is \(~10^3\) m/s, and the thermal energy travels \(~10^1\) nm in a few picosecond. Therefore, it is not necessary to consider the nonthermal equilibrium state nor thermals transports under laser irradiation.

We converted the distribution of emission energy into the temperature distribution along the tube axis on the basis of the temperature dependence of emission energy by using eq 2. Figure 5a shows the temperature distribution of SWCNT with different laser powers. The x-axis is parallel to the tube axis, and the center of SWCNT was at \( x = 0 \). The SWCNTs touched the pillars at \( x = -6 \) and 6 \( \mu m \) because the suspended length was 12 \( \mu m \). The temperature difference between the center and edge of SWCNT was about 80 K at \( I_0 = 2.03 \, \mu W \), and it increased to about 500 K at \( I_0 = 4.15 \, \mu W \).

If the laser power density is uniform along the tube axis and the temperature dependence of the thermal conductivity \( \kappa \), is negligible, the temperature distribution is exactly parabolic. However, the temperature distribution, as shown in Figure 5, was not parabolic. Therefore, the power density distribution of the excitation laser and the temperature dependence of \( \kappa \) were considered. The power distribution of the excitation laser is Gaussian, and the power density for SWCNTs, \( P_{laser}^{1D}(x) \), is expressed by

\[
P_{laser}^{1D}(x) = \frac{L_0}{2\pi \sigma_{laser}^2} \exp\left(-\frac{(x-x_c)^2 + (y-y_c)^2}{2\sigma_{laser}^2}\right)dx
\]

The \( \kappa \) of SWCNT was calculated on the basis of the heat equation

\[
A \frac{d}{dx}\left[\kappa(T(x)) \frac{dT(x)}{dx}\right] + \alpha P_{laser}^{1D}(x) = 0
\]

where \( T(x) \) is the temperature distribution and \( A \) is the cross-sectional area of SWCNT, \( A = \pi d_{tube} b \) with the van der Waals distance, \( b (3.4 \, \AA) \). \( \alpha \) is the absorption coefficient. In the case of \((9,8)\) SWCNT, \( \alpha \) at 720 nm was calculated to be 0.0560.\(^{21}\) In the calculation of \( \alpha \), \( E_{11} = 0.9270 \, eV \) and \( E_{22} = 1.590 \, eV \) which are the optical transition energies of \((9,8)\) in vacuum,\(^{17}\) were used. Note that when the \( E_o \) changes with temperature, \( \alpha \) also changes. If the excitation energy is near the \( E_o \), the \( \alpha \) drastically changes with temperature. However, because the energy of the excitation laser (1.72 \, eV) used here is far from the \( E_{22} \) of \((9,8)\) SWCNT, the temperature dependence of \( \alpha \) is negligible. The second derivative of \( T \) with respect to \( x \) was calculated from the temperature distribution, and \( \kappa \) was calculated based on eq 4.

Figure 5b shows the temperature dependence of \( \kappa \) obtained for the temperature distribution caused by the excitation laser irradiation. The \( \kappa \) clearly depends on the local temperature along the tube axis. Four \((9,8)\) SWCNTs with different length (10 or 12 \( \mu m \)) were measured. They showed the similar temperature dependence of \( \kappa \), as shown in Figure 5b, and the thermal conductivity continuously decreases as the temperature increases. The black circle plots were calculated from the temperature distribution shown in Figure 5a. The details of the other plots (green diamonds, blue squares, and red triangles) can be found in the Supporting Information. The length dependence of the thermal conductivity was theoretically predicted\(^{23}\) and it was expressed by \( \kappa \propto L^\gamma \), where \( L \) is the SWCNT length and \( \gamma = 1/3 \) in one dimension. Recent experimental paper reported that \( p = 0.48 \) at most in the case of SWCNTs.\(^{24}\) Therefore, the length difference (10 and 12 \( \mu m \)) is ignored, and there was no clear length dependence of \( \kappa \) in Figure 5b.

In general, Umklapp phonon–phonon scattering is a dominant factor on the thermal conductivity at high temperatures. As the temperature increases, in addition to that of 3-phonon scattering, the contribution of higher order phonon scattering processes to the thermal conductivity appears. The temperature dependence of thermal conductivity at high temperatures follows a simple Matthiessen’s rule as

\[
\kappa(T) = \frac{1}{c_1T + c_2T^2}
\]

and the terms of \( T^{-1} \) and \( T^{-2} \) correspond to 3-phonon and higher order phonon scattering processes, respectively. The experimental data in Figure 5b were well-fitted to this equation with \( c_1 = (1.90 \pm 0.10) \times 10^{-6} \) and \( c_2 = (6.11 \pm 2.10) \times 10^{-10} \). Taking into account the accuracy of \( \alpha (20\%) \), the thermal conductivity of \((9,8)\) SWCNTs was obtained to be 1166 ± 243 W/(m·K) at 400 K. We can see that the term of \( T^{-1} \) is dominant in the measurement temperature range, and the feature of the temperature dependence of \( \kappa \) is similar to the
previous research for an SWCNT with 1.7 nm diameter. Note that the thermal conductivity obtained here is relatively lower than some of the previously reported ones. However, our measurement was performed for the fully characterized and multiplicate (9, 8) SWCNTs with high precision (the measurement error was 2%). Therefore, we believe that our measurement and results are reliable.

4. CONCLUSIONS
We obtained the temperature distribution of (9, 8) SWCNTs along the tube axis by PL imaging spectroscopy. The chirality, diameter, and length were perfectly characterized by PL and Raman spectroscopies. Moreover, we derived the temperature dependence of thermal conductivity for 350–1000 K by solving the heat equation. The temperature dependence can be formulated by the combination of 3- and higher order phonon scattering processes, and the 3-phonon scattering is dominant in the present temperature range.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00607. Method of image processing and the experimental data of the temperature distribution of the different (9, 8) SWCNTs (PDF)

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Notes
The authors declare no competing financial interest.

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