

Thermal Conductance and Thermopower of an Individual Single-Wall Carbon Nanotube

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ABSTRACT

We have observed experimentally that the thermal conductance of a 2.76- μm -long individual suspended single-wall carbon nanotube (SWCNT) was very close to the calculated ballistic thermal conductance of a 1-nm-diameter SWCNT without showing signatures of phonon–phonon Umklapp scattering for temperatures between 110 and 300 K. Although the observed thermopower of the SWCNT can be attributed to a linear diffusion contribution and a constant phonon drag effect, there could be an additional contact effect.

The thermal conductance (G) and thermoelectric power (or Seebeck coefficient, S) of single-wall (SW) carbon nanotubes (CNTs) have been topics of intense research. Because the phonon spectrum of a SWCNT is quantized¹ and only four acoustic phonon subbands are populated at temperatures (T) below 6 K, the maximum possible lattice thermal conductance (G_p) equals $4g_0$ at $T < 6$ K,² where $g_0 = \pi^2 k_B^2 T / 3h \approx (9.456 \times 10^{-13} \text{ W/K}^2)T$ is the universal quantum of thermal conductance and represents the maximum possible thermal conductance per phonon mode.³ As T increases, optical phonon subbands at energy levels above about 2.5 meV are populated and the contribution from additional phonon modes leads to a G_p larger than $4g_0$ at intermediate temperatures. The results from an equilibrium molecular dynamic (MD) simulation have suggested that the lattice thermal conductivity (κ_p) of a (10, 10) SWCNT reaches the maximum value of about 37 500 W/m K at $T \approx 100$ K, and decreases to about 6000 W/m K at $T = 300$ K.⁴ The decrease is due to anharmonic interactions that produce phonon–phonon Umklapp scattering. The high thermal conductivity near room temperature is very attractive for thermal management applications.⁵

The thermal conductivity of SWCNTs have been reported only for SWCNT mats and bundles.^{6–8} The reported κ values are 1 or 2 orders of magnitude lower than many theoretical results as well as the measurement results for an individual multiwall (MW) CNT.⁹

Similarly, the temperature-dependent thermoelectric power of SWCNTs has been measured only for SWCNT mats and bundles.^{8,10–13} Recently, thermoelectric power measurements have been made for individual SWCNTs deposited on an oxidized doped silicon substrate at different gate voltages applied to the silicon back gate,^{14,15} but S versus T curves were not reported. Although it was observed that pressure had a noticeable effect on only the electrical conductance but not on the thermoelectric power of a SWCNT mat,¹¹ one cannot rule out the possibility that the measured thermoelectric power of the mats and bundles is affected by catalysts and other impurities as well as electron tunneling and phonon coupling between adjacent tubes in the mats and bundles. In fact, it is unclear whether a recently reported measurement result of the thermoelectric power of a SWCNT strand was due to the intrinsic property of individual SWCNTs or the characteristic of electron tunneling processes at blockade sites.¹³

To investigate the intrinsic thermal properties of SWCNTs, we have measured the thermal conductance and thermoelectric power of an isolated suspended SWCNT in the temperature range between 110 and 300 K. The thermal conductance was found to be very close to the calculated ballistic thermal conductance of a 1-nm-diameter SWCNT, and

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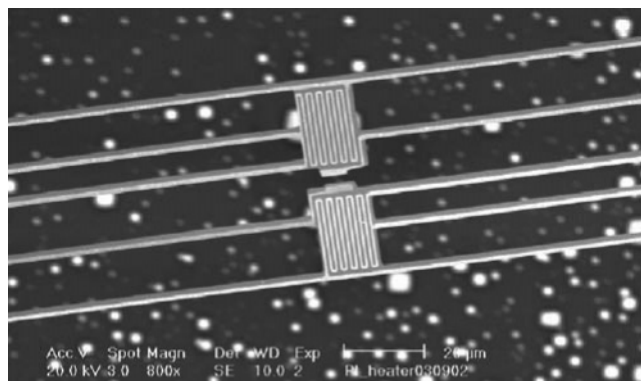


Figure 1. SEM image of the suspended microdevice used for measuring the thermal conductance and thermoelectric power of the SWCNT.

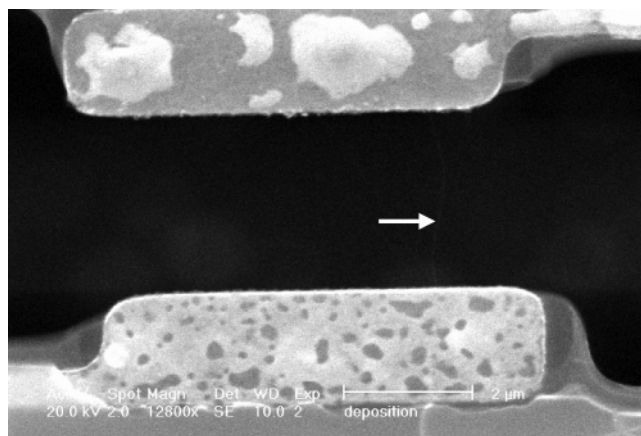


Figure 2. SEM image showing a suspended SWCNT (indicated by the arrow) grown between the two Pt electrodes of the measurement device.

signatures of the phonon–phonon Umklapp scattering are absent in the temperature range. The thermoelectric power measured in the same temperature range increases linearly with temperature and extrapolates to a nonzero value at temperature 0 K. Although the nonzero value can be attributed to a constant phonon-drag effect, the observed thermoelectric power could be influenced by a temperature drop at the contacts.

We employed a suspended microdevice⁸ to measure the G and S of the SWCNT. A similar method was used to obtain the thermal conductance of the individual MWCNT reported previously.⁹ To grow the SWCNT between the two membranes of the microdevice shown in Figure 1, we used a sharp probe to deliver catalysts containing Fe, Mo, and Al₂O₃ nanoparticles onto the two membranes. The microdevice was then loaded into a 900 °C tube furnace with flowing methane. The chemical vapor deposition (CVD) method¹⁶ produced an individual suspended SWCNT bridging the two platinum (Pt) electrodes patterned on the inner edges of the two membranes, as shown in the scanning electron microscopy (SEM) image of Figure 2. SWCNTs are visible in SEM because of electron charging. High-magnification SEM measurement indicates that the diameter (d) of the SWCNT should be less than 5 nm. However, an accurate diameter measurement was not feasible with the use of the SEM

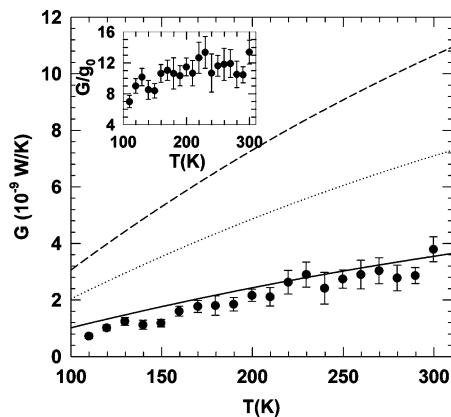


Figure 3. Thermal conductance (G) of the SWCNT as a function of temperature (T). Filled circles are the measurement results. The solid, dotted, and dashed lines are the ballistic thermal conductance of a 1-nm-, 2-nm-, and 3-nm-diameter SWCNT, respectively, from ref 17. The inset shows the G/g_0 ratio.

because of its accuracy of about 3 nm. The substrate of the suspended microdevice was not completely etched through so that transmission electron microscopy (TEM) measurement of the SWCNT diameter was not feasible. Instead, we have conducted atomic force microscopy (AFM) measurements of the diameter of a large number of SWCNTs grown using the same method on silicon substrates. The diameter was in the range of 1–2 nm for most of the SWCNTs, although a diameter of 2–3 nm was observed occasionally.

As shown in Figure 3, the measured thermal conductance of the SWCNT increases with temperature from 0.7×10^{-9} W/K or about $7g_0$ at 110 K to 3.8×10^{-9} W/K or about $14g_0$ at 300 K. The G/g_0 ratio in the inset of Figure 3 increases with temperature because more optical phonon subbands are populated at higher temperatures. The measurement result was very close to the calculated ballistic thermal conductance of a 1-nm-diameter SWCNT and was about 50% and 30% of the ballistic thermal conductance of a 2-nm- and 3-nm-diameter SWCNT, respectively. The diameter of the SWCNT should not be smaller than 1 nm because the measurement result was larger than the calculated ballistic thermal conductance of a SWCNT of $d < 1$ nm. The ballistic thermal conductance is the maximum possible value calculated by Mingo and Brodio¹⁷ for the case that phonon transport is ballistic in the SWCNT and phonons from the SWCNT enter the two contacts without suffering reflection. In the calculation, the temperature of the phonon flow entering the SWCNT from each contact equals that of the contact along the entire length of the SWCNT, as shown in Figure 4. Because of the absence of scattering, the two opposite phonon flows are at two different temperatures and are not at equilibrium with each other. The obtained ballistic thermal conductance is not infinite because the phonon flow is scattered after it exits the SWCNT and enters the opposite contact in order for the phonon flow to adopt the different temperature of the contact. Hence, the ballistic thermal conductance is essentially the maximum contact thermal conductance between the SWCNT and the two thermal reservoirs.

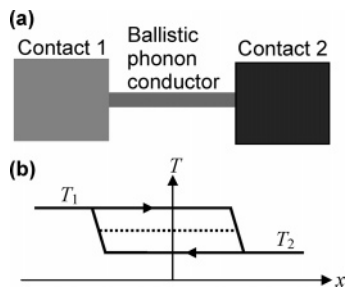


Figure 4. (a) Schematic diagram of a 1D ballistic phonon conductor connected to two side contacts at different temperatures (i.e., T_1 and T_2). (b) The temperature distribution of the two opposite phonon flows inside the ballistic phonon conductor. The dotted line is the average temperature of the two phonon flows.

The calculated ballistic thermal conductance consists of the contribution from phonons only. The electronic thermal conductance (G_e) of CNTs depends on whether the CNT is metallic or semiconducting. For semiconducting CNTs, G_e is negligible compared to the lattice thermal conductance or G_p . For metallic CNTs, the two electron subbands, each with two different spins, contribute to a maximum possible G_e value of $4g_0$. For a (10, 10) SWCNT, it has been calculated that G_e is negligible compared to G_p at moderate temperatures.² The calculation results show that the G_e/G_p ratio decreases with temperature from a value of 1 at $T < 6$ K to about 0.3 at 100 K and about 0.12 at 300 K. In the temperature range between 110 and 300 K, therefore, the measured thermal conductance of the SWCNT consists of mainly the lattice contribution.

Mingo and Brodio¹⁷ noted that the thermal conductance measurement results of the individual MWCNT reported previously was close to 40% of the ballistic thermal conductance of graphite for $T < 300$ K. Here, the measured G of the SWCNT is also proportional to the ballistic thermal conductance for SWCNTs in the temperature range between 100 and 300 K. Phonons can be reflected when entering the two contacts from the CNT, lowering the thermal conductance of the CNT to a fraction of the ballistic thermal conductance. Additionally, local defects in the suspended CNT can reduce the phonon transmission coefficient, lowering G to a fraction of the ballistic thermal conductance. The G reduction resulting from these two effects is approximately temperature-independent to the first order, and the resulting G versus T curve is proportional to the ballistic thermal conductance. However, the phonon–phonon Umklapp scattering process can reduce G from the ballistic thermal conductance, and a larger reduction is expected at higher temperatures, making the G versus T curve deviate from the trend of the ballistic thermal conductance. Because the measured G versus T curve is proportional to the ballistic thermal conductance at $T < 300$ K for both the SWCNT and the MWCNT, we conclude that Umklapp process is insignificant at $T < 300$ K. At $T > 300$ K, the G curve of the MWCNT increases to a maximum value at $T = 340$ K and decreases rather rapidly with temperature at $T > 340$ K. The rapid decrease deviates from the trend of the ballistic thermal conductance for graphite and is a signature of the Umklapp process at high temperatures.¹⁷

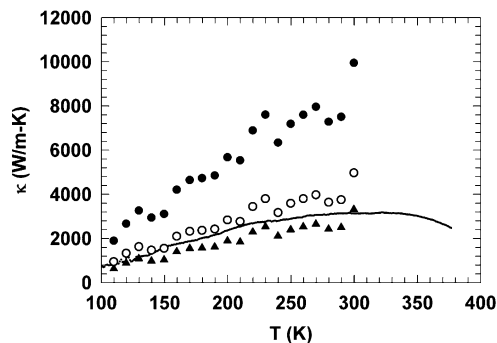


Figure 5. Thermal conductivity (κ) of the SWCNT if the diameter was 1 nm (filled circles), 2 nm (open circles), and 3 nm (filled triangles). The line is the measurement result of an individual MWCNT from ref 9.

The thermal conductivity of the SWCNT has been calculated for the case that the diameter was 1, 2, and 3 nm, according to $\kappa = GL/A$, where L is the length of the suspended segment of the SWCNT between the two membranes and A is the cross section, which is not a well-defined quantity for a SWCNT. We followed ref 17 to calculate $A = \pi d \delta$, where $\delta = 0.335$ nm is the layer separation in graphite. The obtained κ in Figure 5 is of the same order of magnitude as the measurement results of an individual MWCNT, which is also shown in the Figure.

We have calculated the phonon mean free path (l). For bulk materials, l can be calculated from the thermal conductivity formula $\kappa = Cv/3$, where C is the specific heat and v is the phonon group velocity. For one-dimension (1D) conductors, the factor of 1/3 should be dropped from the formula. We obtained C by converting the results obtained for SWCNT mats¹⁸ using the density of graphite. Using a typical v of about 10^4 m/s for the four acoustic modes of a (10, 10) SWCNT¹, we used the calculated κ values to obtain that l at 300 K was about 750, 375, and 250 nm for the SWCNT, respectively, if d was 1, 2, and 3 nm. Because the measurement result was very close to the ballistic thermal conductance of a 1-nm-diameter SWCNT, however, l should be close to the 2.76- μm length of the SWCNT and larger than 750 nm if d was 1 nm. The discrepancy is caused by errors in the C and v values as well as the inaccuracy of the thermal conductivity formula that was obtained with the phonon dispersion ignored and all phonon modes assumed to have the same v and l . It has been shown that this formula can underestimate l for silicon.¹⁹ For the cases of $d = 2$ or 3 nm, the measurement result was 50% or 30% of the ballistic thermal conductance, so that l could be a few times smaller than the length. Furthermore, for the case of $d = 1$ nm, the contact thermal conductance should be very close to the maximum possible value of the ballistic thermal conductance; whereas, for the case of $d = 2$ or 3 nm, the contact thermal conductance could be smaller than the maximum possible value because of phonon reflection while entering from the SWCNT into the thermal reservoirs.

The mean free path due to Umklapp phonon scattering (l_U) should be much longer than the calculated l . Without the presence of local defects and for temperatures below 300 K, phonon scattering at the two contacts limits l until the

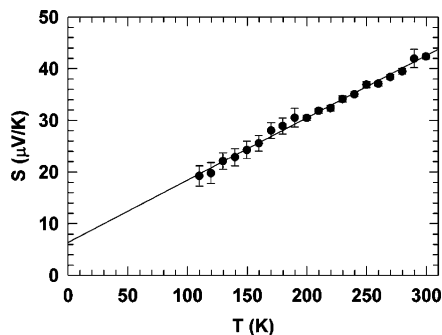


Figure 6. Thermoelectric power (S) of the SWCNT as a function of temperature. The circles are measurement data. The solid line is the least-squares linear fit of the measurement data and the fitting equation is $S = (6.373 + 0.1206 T) \mu\text{V/K}$.

length of the SWCNT is increased to be comparable to l_U . Hence, the thermal conductance is expected to remain constant as the length is increased to be comparable to l_U . This feature causes an increase of the thermal conductivity with increasing length, as suggested by the results of a nonequilibrium MD simulation,²⁰ which imposed phonon-boundary scattering at the two ends of the SWCNT and is thus analogue to the experimental condition for thermal conductance measurement. For a SWCNT shorter than the l_U value at $T = 300$ K, moreover, the maximum thermal conductivity should occur at $T > 300$ K, where l_U is reduced to be smaller than the length of the SWCNT. This behavior has been reported by another nonequilibrium MD simulation²¹ of short SWCNTs and should be the case for the SWCNT sample in our experiment. In the equilibrium MD simulation of Berber et al.,⁴ however, phonon-boundary scattering was not imposed at the two ends of the short SWCNT segment and the mean free path was limited by the Umklapp process instead of phonon-boundary scattering. In this case, the maximum κ was found to occur at $T \approx 100$ K. This result does not contradict with the monotonic increase of the ballistic thermal conductance of a SWCNT with temperature because the Umklapp process is ignored deliberately and phonon transport is taken to be ballistic for the calculation of the ballistic thermal conductance.

The thermoelectric power of the SWCNT was measured together with the thermal conductance and is shown in Figure 6, where the contribution from the small thermopower of the Pt electrodes has been ignored. At $T = 300$ K, the observed S was about $42 \mu\text{V/K}$, which is similar to those obtained for SWCNT mats and about 1 order of magnitude higher than that of graphite or a typical metal. The large S value suggests that electron transport was not ballistic in the sample.²² For the SWCNT mats, the large positive S values at $T = 300$ K were attributed to oxygen doping^{23,24} that lowers the Fermi level below the band crossing point for a metallic SWCNT. Oxygen doping should also be the origin for the large S of the isolated SWCNT sample in our experiment. For the suspended SWCNT sample, the S versus T curve in Figure 6 is linear between 110 and 300 K, similar to the behavior of the diffusion thermoelectric power of a metal, which is caused by the diffusion of charge carriers under a temperature gradient. For SWCNT mats and bundles, several

measurements^{8,10–13} obtained nonlinear S versus T curves for temperatures below 200 K. The origin of the nonlinearities has been the subject of much debate. Several effects that could lead to such behavior have been discussed in the literature. These include parallel transport through semiconducting tubes in the mats,¹⁰ Kondo effects due to magnetic catalytic impurities in the mats,²⁵ and the phonon drag effect.^{11,12,26} The phonon drag effect is a thermoelectric power caused by additional charge carriers dragged from the hot to the cold end by phonon flux via momentum transfer. Although our measurement data in Figure 6 shows a linear temperature dependence, a linear curve fit to the measurement data intercepts with the y axis at a nonzero value of about $6 \mu\text{V/K}$ at $T = 0$, as shown in Figure 6. Because the linear diffusion thermoelectric power extrapolates to zero at $T = 0$ K, the nonzero intercept in Figure 6 has to come from another effect. We found that this additional effect can be explained by a phonon drag contribution. Because phonon–phonon Umklapp scattering has been found to be insignificant in the isolated SWCNT, the phonon relaxation time should be approximately independent of temperature. For the case in which the phonon relaxation time is independent of temperature, the calculation results by Scarola and Mahan²⁶ show that the phonon drag contribution in a SWCNT increase rapidly with T at low temperatures and approach approximately a constant for $T > 100$ K. Hence, the thermoelectric power of the SWCNT can be attributed to a linear diffusion contribution of about $(0.12 T) \mu\text{V/K}$ as well as a phonon drag effect of about $6 \mu\text{V/K}$, which was approximately constant for temperatures between 110 and 300 K because of the absence of phonon–phonon Umklapp scattering.

However, the observed S could be influenced by a temperature drop at the contacts especially if the diameter of the SWCNT was 1 nm. For $d = 1$ nm, phonon transport would be quasiballistic in the SWCNT and the two opposite phonon flows inside the SWCNT would not be thermalized with each other. Consequently, the average phonon temperature would remain approximately the same along the SWCNT, resulting in a drop of the average phonon temperature at each contact, as shown in Figure 4. For this case, electron–phonon scattering in the SWCNT is still allowed because such scattering poses only very small resistance to the phonon flows. Consequently, electrons could be thermalized with the average phonon temperature, resulting in a drop of the electron temperature at each contact. Hence, the obtained S would be affected by the temperature drop at the contacts. The contact effect would be less a problem if the diameter was 2 or 3 nm, for which cases backscattering of phonons with local defects could effectively thermalize the phonons despite of a long l_U , leading to a temperature gradient along the SWCNT.

We show that phonon–phonon Umklapp scattering is weak in the $2.76\text{-}\mu\text{m}$ -long SWCNT for temperatures below 300 K, and the observed thermoelectric power could be influenced by a temperature drop at the contacts although the measurement result can be attributed to a linear diffusion contribution of about $(0.12 T) \mu\text{V/K}$ and an phonon drag

effect of about $6 \mu\text{V/K}$. Although the thermal conductance was found to be very close to the ballistic thermal conductance of a 1-nm-diameter SWCNT, the thermal conductivity of the SWCNT should be at least comparable to the previous measurement result of an individual MWCNT. More accurate measurement of the thermal conductivity can be obtained if a through-hole can be etched in the substrate of the microdevice to allow for accurate TEM measurement of the diameter of the SWCNT.

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$$I = \frac{4e}{h} \int_{-\infty}^{\infty} \left\{ \frac{1}{1 + \exp[(E - \mu_1)/k_B T_1]} - \frac{1}{1 + \exp[(E - \mu_2)/k_B T_2]} \right\} dE = \frac{4e}{h} (\mu_1 - \mu_2)$$
 where μ_1 and μ_2 are the electrochemical potentials of the two contacts. The open circuit thermoelectric voltage is $V = (\mu_1 - \mu_2)/e = 0$ because $I = 0$.
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