

Diameter-dependent thermal conductivity of carbon nanotubes

Hai-Bo Zhao^{a,b}, Dai-Ming Tang^{c,d,*}, Lili Zhang^a, Meng-Ke Zou^{a,b}, Rui-Hong Xie^{a,b}, Chang Liu^{a,b,*}, Hui-Ming Cheng^{a,e}

^a Shenyang National Laboratory for Materials Science, Institute of Metal Research (IMR), Chinese Academy of Sciences, 72 Wenhua Road, Shenyang, 110016, PR China

^b School of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, PR China

^c Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, 305-0044, Japan

^d Department of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8573, Japan

^e Faculty of Materials Science and Energy Engineering/Institute of Technology for Carbon Neutrality, Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, PR China

*Corresponding author. E-mail: tang.daiming@nims.go.jp; cliu@imr.ac.cn

Abstract

Carbon nanotubes are uniquely featured by the nanoscale tubular structure with a highly-curved surface and defined chirality. The diameter and chirality fundamentally determine their stability, electrical and thermal properties. Up to now, the relationship between the intrinsic thermal conductivity and the atomic features of CNTs has not been established, due to the challenges in precise measurements and characterizations. In this work, we develop a micro electro-thermal device enabling simultaneous thermal measurements by Raman spectroscopy and atomic structural characterization by transmission electron microscopy for individual CNTs. The influence of diameter and chirality is systematically investigated. In addition, the temperature dependence of the thermal conductivity was extracted from parameter optimization of finite-element modeling. It is found that the thermal transport of CNTs depends mainly on the diameter, while the chiral angle has no significant influence. Along with increasing diameter, the room temperature thermal conductivity increases and eventually approaches the limit of flat graphene.

Keywords: Carbon nanotubes; Thermal conductivity; Diameter; Chirality; Raman spectroscopy

1. Introduction

Carbon nanotubes (CNTs) are one-dimensional tubular structures that are conceptually formed by rolling a graphene sheet along a chiral vector, defined as the “chirality”. The chirality can be described by the chiral indices of n and m , or by the diameter (d) and chiral angle (θ) of the CNT. Fundamentally, the chirality determines the structural stability, mechanical, electrical, and thermal properties of CNTs. For the electrical properties, it is well known that the chirality plays a dominating role, so that even for the CNTs with the same diameters, they can be a metal or a semiconductor, depending on the chiral angle [1]. On the other, for the thermal properties, there is still no consensus regarding the relationship between thermal conductivity and atomic structures of CNTs.

Thermal transport of CNTs has been intensively investigated, both theoretically and experimentally. There have been many experimental measurements on the thermal conductivity, including steady-state heat flow methods [2–5], the 3ω method [6–8], self-heating methods [9], and the Raman shift method [10–12]. Unusually high thermal conductivity ($6600 \text{ W m}^{-1} \text{ K}^{-1}$) was reported, and attributed to the large phonon mean free paths [13].

Regarding the influence of diameter and chiral angle on thermal conductivity, there have been mainly theoretical works. Several theoretical calculations predicted that the thermal conductivity increases with decreasing diameter due to the lower occurrence of Umklapp processes in smaller CNTs [14–16]. Other simulations showed that the thermal conductivity is enhanced with increasing diameter due to the longer phonon relaxation time [17,18] and increased low-frequency modes in the radial direction [19]. For the effect of chiral angle, it has been reported that chiral angle should not have a major effect on the thermal conductivity, since the density of states of phonons shows no significant difference [15,20,21], while in other theoretical works the thermal conductivity can change as much as 20%, depending on the chiral angle [22–24].

There are mainly two obstacles to precisely measure the thermal conductivity of individual CNTs and to establish the relationship with the microstructures. First, it is challenging to combine the measurement of intrinsic thermal conductivity and structural characterization with atomic resolution. For example, the Raman shift method provides a non-contact way of measuring the local temperature and has been used to obtain the intrinsic thermal conductivity of CNTs independent of contact resistance [25], but the atomic structures of the CNTs cannot be characterized directly, except for the nanotubes resonate with the laser energy. Second, thermal conductivity is a function of temperature. The extrinsic factors of temperature dependence of the thermal conductivity must be considered to reveal the thermal conductivity determined by the intrinsic structures.

In this work, we developed a micro electro-thermal device that is compatible with both measurement of thermal conductivity and atomic structural characterization of individual CNTs. Temperature distributions of Joule-heated suspended CNTs are measured by the Raman frequency shift method, and their diameters and chiralities are characterized by transmission electron microscope (TEM) imaging and electron diffraction (ED) patterns. The temperature dependence of thermal conductivity has been extracted by parameter optimization of finite-element modeling (FEM), considering the heating effect of the laser. By statistical analysis on the thermal conductivity of CNTs with different diameters and chiral angles, it was found that the diameter plays a dominating role while the chiral angle does not have a significant influence on the thermal conductivity of CNTs.

2. Experimental

2.1. Suspended CNT microdevice preparation

The microdevice was composed of four electrodes and a set of slits. The fabrication of the microchips started from a Si wafer with a silicon nitride coating (thickness 100 nm). The substrate was etched from the backside to form an approximately 10 μm thick film in the center using wet etching procedures. 100 nm-thick W electrodes were patterned on the top surface of

the SiNx using standard photolithography. A series of through-substrate slits and number marks were etched by deep silicon etching after the reactive ion etching of SiNx. The narrow slits (width 2–4 μm , length 300 μm , with protruding marks along both edges) were designed for TEM characterization. A wide slit (width 30–40 μm , length 300 μm) was used for thermal measurements of the CNTs.

Ultralong CNTs were grown by a fast-heating chemical vapor deposition (CVD) method similar to previous work [26]. A Fe thin film with a nominal thickness of 0.05 nm was deposited on a silicon wafer with a 300 nm thick thermally oxidized layer as the catalyst substrates. The microdevices were placed downstream of the catalyst substrate to receive the CNTs. The catalyst substrate was calcined in air at 750°C for 5 min and then treated at 750°C in Ar/H₂ (100 sccm/100 sccm) for 10 min to reduce the catalyst before CNT growth. A mixture of 15 sccm CH₄ and 40 sccm H₂ was fed into the quartz tube, and the growth of CNTs was initiated by fast heating the substrates to 975°C. After 10 min CNT growth, the substrates were cooled in Ar to room temperature. As a result, suspended nanotubes directly grown on the microdevices were obtained.

2.2. CNT structure and chirality characterization

The morphology of the synthesized CNTs was observed using a FEI Verios G4 SEM. The diameter and chirality of the CNTs were characterized by HRTEM and ED patterns. A nanofocused electron beam was used in a Titan Cubed Themis G2 60-300 and JEM-ARM200F TEM to obtain the ED patterns. The microscopes were operated at 80 kV accelerating voltage to minimize the electron irradiation damage. It was easy to locate the CNTs in the TEM by the through-substrate number marks.

2.3. Raman shift for temperature calibration

A heating stage with a temperature controller was used to change the sample temperature from room temperature to 613 K. The Raman spectra of CNTs were collected after the stage temperature remained stable for at least 5 min. Raman signals were collected with a Witec con-

focus Raman (alpha 300R) equipped with 532 nm and 633 nm lasers. The chamber was pumped to a vacuum of 4×10^{-4} Torr during the measurements. The collected Raman spectra were fitted with Lorentzian curves to obtain the peak frequency. The temperature-dependent Raman shift was obtained for each CNT.

2.4. Thermal measurements of Joule-heated CNTs

The thermal measurements were made using the 4-terminal circuit and Raman spectroscopy. To electrically heat the suspended CNTs and to monitor the precise heating power, a dual-channel source-measuring unit (Keithley 2634B) was used to connect the four electrodes on the device. The temperature increases in the middle of an electrically heated CNT at different bias voltages were measured by the Raman shift. The temperature distributions of some CNT samples were also measured at certain voltages to elucidate the effect of temperature on the thermal conductivity. The measurements were also performed in a vacuum to reduce the heat dissipated by convection.

2.5. FEM modelling

FEM simulations were performed to extract the temperature-dependent thermal conductivity from the measured temperature distributions. All FEM simulations were done using the Mecway commercial package. The models used for CNTs were three-dimensional shell structures as shown in Fig. S1. And the validation of the mesh independence for the FEM was conducted using different mesh density, including 3000, 6000, 7500, and 9000 elements. As shown in Table S1, the results of the temperature are almost the same when the number of elements is more than 7500. The electrical conductivity of the CNTs was determined from the four-wire electrical tests. To do thermal analysis with Joule heating, the models were first solved as DC current flow. Then the temperature distribution was obtained by solving the thermal models, with the power density obtained from DC analysis.

The boundary conditions were applied by fixing the temperatures at the two ends of the CNT models to be the experimentally measured temperatures. Extensive FEM calculations

were carried out to determine the temperature-dependent thermal conductivity. The initial values of the unknown parameters in the thermal conductivity-temperature relationship were set according to the previous study [9]. Then, the optimum values were determined by an iterative approach to minimize the error between temperature distributions from the simulation and experiments, as shown in Fig. S2. The physical parameters used for the FEM of different CNT samples are summarized in Table S2.

3. Results and Discussion

3.1. Thermal measurements of CNTs with defined structures

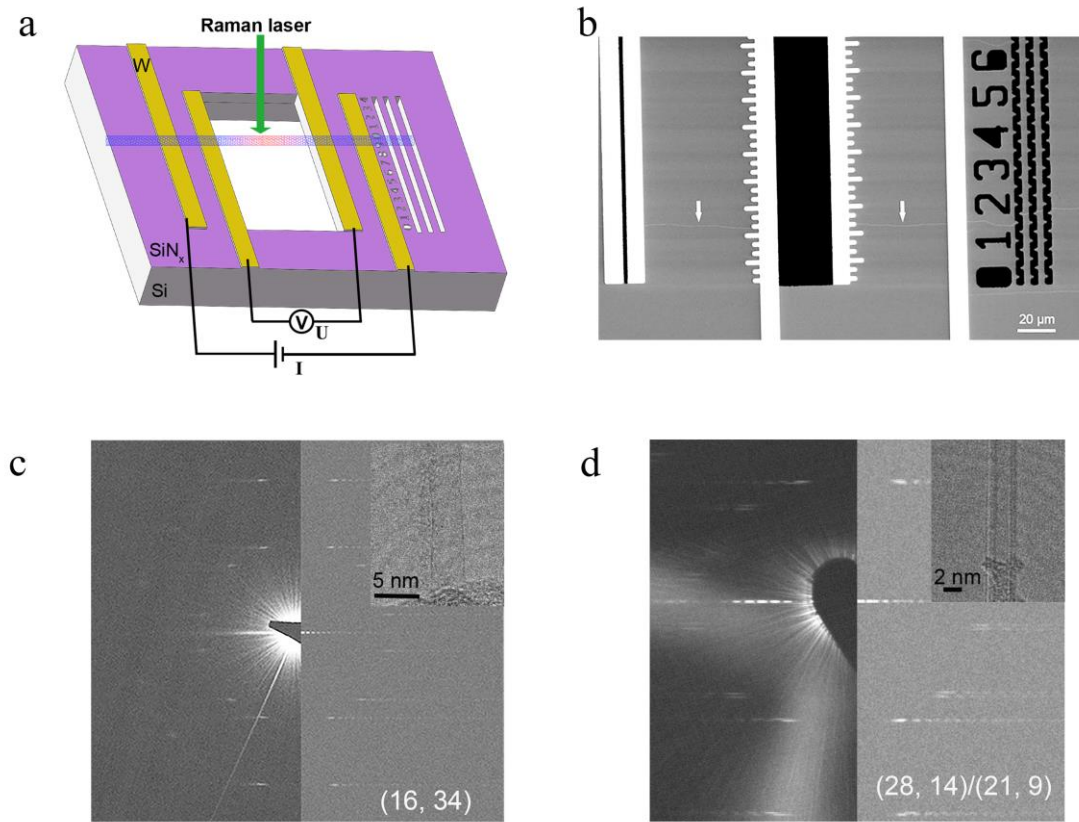


Fig. 1. The microdevice for the thermal measurements and atomic structure characterizations of CNTs. (a) Schematic of the electro-thermal microdevice. A suspended CNT connected to four tungsten electrodes was electrically heated, where the current (I) was applied between the outer electrodes and the voltage (U) was measured between the inner electrodes. The section of the CNT suspended over the narrow slit is used for TEM characterization. (b) SEM image of

the suspended CNT microdevice. The white arrows indicate the position of the CNT. (c, d) Experimental and simulated ED patterns of (c) a (16, 34) SWCNT and (d) a (28, 14)/(21, 9) DWCNT (left: experimental; right: simulated). Insets are HRTEM images of the CNTs.

Figure 1(a, b) show a schematic and scanning electron microscope (SEM) image of our designed electro-thermal microdevice. A suspended CNT connected to four tungsten electrodes was electrically heated, where the current (I) was applied between the outer electrodes and the voltage (U) measured between the inner electrodes. The temperature in the middle of the suspended CNT was higher than at the ends, and the temperature rise reflects the thermal conductivity of the CNT. The Raman shift method was used to measure the temperature. Since the microdevice is compatible with conventional TEM specimen holders, the atomic structure of the CNT can be characterized by HRTEM and ED as shown in Fig. 1(c, d). The precise chiral (n, m) indices of single-wall (SWCNT) and double-wall CNTs (DWCNT) were determined from their ED patterns.

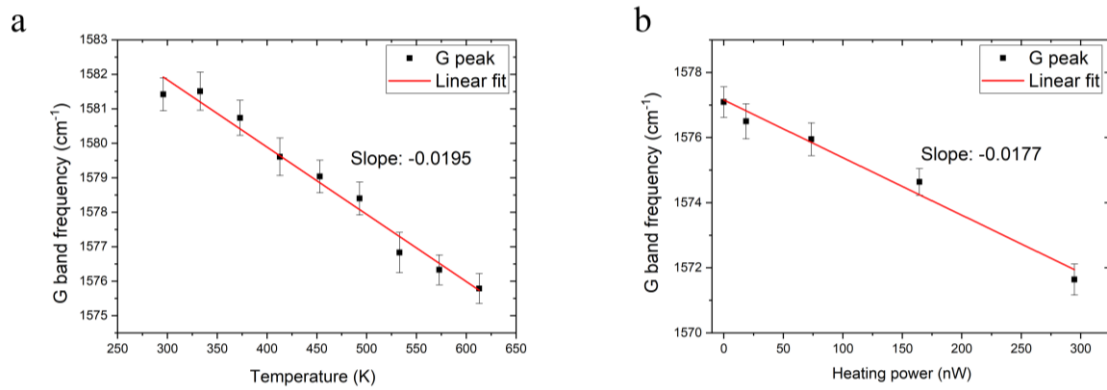


Fig. 2. (a) G band frequency shift with temperature and (b) G band frequency at different heating powers in the middle of a (16, 34) SWCNT.

The Raman shift with temperature was calibrated at a series of temperatures as shown in Fig. 2(a). The collected Raman spectra were fitted with Lorentzian shapes to obtain the peak frequency. The plot in Fig. 2(a) was fitted by a linear function to obtain the temperature coefficient, which was determined to be $0.0195 \text{ cm}^{-1} \text{ K}^{-1}$ for the (16, 34) SWCNT, which is comparable to previously reported values [25,27,28]. The temperature coefficient was

measured for each CNT sample to ensure accurate temperature measurement. The heat transfer along the CNTs can be described by the Fourier heat conduction law for one-dimensional systems as:

$$\dot{Q} = -k \times \frac{dT}{dx} \quad (1)$$

where $\dot{Q}$, k , T are the heat flux density, thermal conductivity and local temperature, respectively. When a CNT is electrically heated and reaches thermal equilibrium, the whole heating power is equal to the heat conducted along the CNT to the substrate.

$$P = \oint_S \dot{Q} \cdot d\vec{S} = \int_V (\nabla \cdot \dot{Q}) dV \quad (2)$$

where $P = UI$ is the heating power. The close surface integral on the heat flux density can be transformed to the volume integral according to Gauss's theorem. And the heating power is equal to the integral of the power density over the entire volume. Thus we can get the heat conduction differential equation as:

$$\rho = -k \times \frac{d^2T}{dx^2} \quad (3)$$

where ρ is the heat power density. ρ is equal to P/AL , where A is the cross-section of the CNT calculated as an annular ring, and L is the length of the suspended CNT. We assumed that the temperatures at the two ends of the CNT were the same, and the temperature in the middle of the CNT was the highest. When the thermal conductivity k is a constant, by integrating Eq. (3) and introducing the boundary conditions, we can obtain the thermal conductivity:

$$k = \frac{UIL}{8A\Delta T} \quad (4)$$

where ΔT is the temperature increase in the middle of the suspended CNT. Because the temperature rises were measured at different heating powers, the thermal conductivity k can be calculated as:

$$k = \frac{\alpha_G L}{8A\alpha_{\text{heat}}} \quad (5)$$

where α_G is the temperature coefficient of the G band frequency, and α_{heat} the heating power coefficient. The G band frequency shift with heating power of a (16, 34) SWCNT is shown in Fig. 2(b). The heating power was determined exactly from four-wire electrical tests. The G band shifts to lower frequencies with increasing heating power, due to the higher temperature rises. The plot in Fig. 2(b) is fitted with a linear function and the absolute value of the slope is the heating power coefficient α_{heat} , which is $0.0177 \text{ cm}^{-1} \text{ nW}^{-1}$ for this SWCNT. The measurements were performed in a vacuum ($\sim 0.04 \text{ Pa}$), hence the heat transferred to surrounding gas molecules can be ignored. The thermal conductivity of this (16, 34) SWCNT is calculated to be $1512.4 \text{ W m}^{-1} \text{ K}^{-1}$ using Eq. (5), which is of the same order of magnitude as previous results [2–4,9,10,12]. Note that this value of thermal conductivity is an apparent value due to the inhomogeneous temperature distribution along the CNT. The apparent thermal conductivity is the calculated thermal conductivity of CNT without considering the temperature dependence. It can be considered as the average thermal conductivity of the CNT over the temperature range.

Using the same method, the apparent thermal conductivities of 15 CNT samples with defined structures were measured. Their chiralities, corresponding temperature coefficients and heating power coefficients, and apparent thermal conductivities are summarized in Table 1. We can see that the apparent k values of individual CNTs range from $331.7 \text{ W m}^{-1} \text{ K}^{-1}$ to $1512.4 \text{ W m}^{-1} \text{ K}^{-1}$ with an average of $928.7 \text{ W m}^{-1} \text{ K}^{-1}$, while the k values of CNT bundles are in the range $390.0\text{--}1257.3 \text{ W m}^{-1} \text{ K}^{-1}$ with an average value of $691.9 \text{ W m}^{-1} \text{ K}^{-1}$. The average apparent thermal conductivity obtained for individual CNTs is relatively lower than those in some previous reports [9,10,12], which may be due to the higher temperature increase induced by the Raman laser and the electrical heating in our system. The temperature dependence of thermal conductivity and the thermal conductivities at 350 K in Table 1 will be discussed in the following discussion.

Table 1. Summary of the chiralities, temperature coefficients, heating power coefficients, and thermal conductivities of 15 CNT samples.

Chirality	Type	Diameter (nm)	α_G ($\text{cm}^{-1} \text{ K}^{-1}$)	α_{heat} ($\text{cm}^{-1} \text{ nW}^{-1}$)	Apparent k ($\text{W m}^{-1} \text{ K}^{-1}$)	$k-T$	$k_{T=350 \text{ K}}$ ($\text{W m}^{-1} \text{ K}^{-1}$)
(16,34)	SWCNT	3.46	0.0195	0.0177	1512.4	None	2581.2
(11,23)	SWCNT	2.35	0.0141	0.0298	737.8	$(6.97 \times 10^{-7} T + 2.55 \times 10^{-9} T^2)^{-1}$	1797.5
(16,22)	SWCNT	2.59	0.0219	0.0402	738.8	None	1981.2
(14,20)/(9,15)	DWCNT	2.32/1.64	0.0167	0.0454	331.7	$(2.59 \times 10^{-6} T + 4.19 \times 10^{-10} T^2)^{-1}$	1042.2
(11,26)/(9,17)	DWCNT	2.58/1.79	0.0163	0.0147	916.2	None	1334.7
(21,10)/(13,7)	DWCNT	2.15/1.38	0.0389	0.0314	1261.0	$(2.40 \times 10^{-6} T + 9.83 \times 10^{-10} T^2)^{-1}$	1040.8
(28,14)/(21,9)	DWCNT	2.90/2.09	0.0270	0.0224	896.2	None	1578.3
(31,22)/(25,18)	DWCNT	3.61/2.93	0.0225	0.0146	845.1	None	1511.0
None	TWCNT	2.8/2.1/1.3	0.0220	0.0114	1119.4	$(2.04 \times 10^{-6} T + 2.50 \times 10^{-9} T^2)^{-1}$	1024.5
None	2 CNT bundle (DW; DW)	2.4/1.6; 3.6/2.9	0.0232	0.0107	743.4	None	1253.2
None	2 CNT Bundle (DW; SW)	2.4/1.8; 2.0	0.0181	0.0222	475.2	None	654.2
None	2 CNT Bundle (DW; SW)	2.1/1.4; 2.8	0.0224	0.0332	390.0	None	768.8
None	2 CNT Bundle (DW; DW)	2.7/1.9; 2.8/2.1	0.0207	0.0111	712.5	None	1349.8
None	2 CNT Bundle (DW; DW)	4.0/2.2; 3.8/3.0	0.0317	0.0085	1257.3	None	1204.8
None	3 CNT Bundle (DW; SW; SW)	2.3/1.5; 3.3; 3.0	0.0236	0.0148	573.3	$(2.35 \times 10^{-6} T + 1.66 \times 10^{-9} T^2)^{-1}$	975.6

The measurement uncertainty may come from the fitting errors of temperature and heating power coefficients, stress, local non-equilibrium of phonons, and absorption of Raman laser. Errors of temperature coefficient and heating power coefficient were determined from linear fitting processes of the G-band frequency with temperature and heating power. The fitting errors of the two coefficients and the corresponding thermal conductivity error of each CNT sample are shown in Table S3. The stress in CNTs could induce a shift of Raman peak. The suspended CNTs were initially subjected to bending deformation as a result of high-temperature growth. The deformation would be increased once the CNT was electrically heated. According to the

previous report [29], we have estimated the G-band shift arising from the bending deformation to be less than 0.01 cm^{-1} . In addition, it has been reported that the temperature coefficient does not change with the variation of the residual stress [30,31]. Thus, the effect of stress is negligible to our thermal measurements. The different phonon modes can be driven out of local equilibrium under laser excitation [32]. The degree of local phonon nonequilibrium depends on the laser spot size and the laser power. It was predicted that the effect is negligible when the spot radius is greater than 5 times the average phonon mean free path [33]. In our experiments, the radius of laser spot is about 590 nm, while the average phonon mean free path is less than 100 nm [6,21]. In addition, a relatively low laser power (0.6 mW) was used in our measurements. Therefore, the effect of local non-equilibrium of phonons could also be neglected in our measurements. Even though the laser would inevitably heat the CNTs, this effect could be counteracted by changing the electrical heating power. According to the above discussions, the errors of temperature coefficient and heating power coefficient are the dominant error sources.

3.2. Temperature dependence of the thermal conductivity

The temperature dependence of the thermal conductivity must be considered to elucidate the effect of structures. We found that when the heating power was high enough, the relationship between G band frequency and heating power deviated from a linear relationship as shown in Fig. 3(a). In this case, the thermal conductivity cannot be assumed to be a constant according to Eq. (5), suggesting that the effect of temperature on the thermal conductivity is obvious. We measured the spatial temperature distributions of a CNT at 0 nW (without electrical heating) and 252 nW (Fig. 3(b)) by converting the changes in G band frequency to temperature changes using the temperature coefficient α_G . The temperature profile fitted a parabola without electrical heating, however, when the heating power was 252 nW, it was not parabolic as shown by the black squares in Fig. 3(b). This also indicates that the effect of temperature on the thermal conductivity is significant at high heating powers.

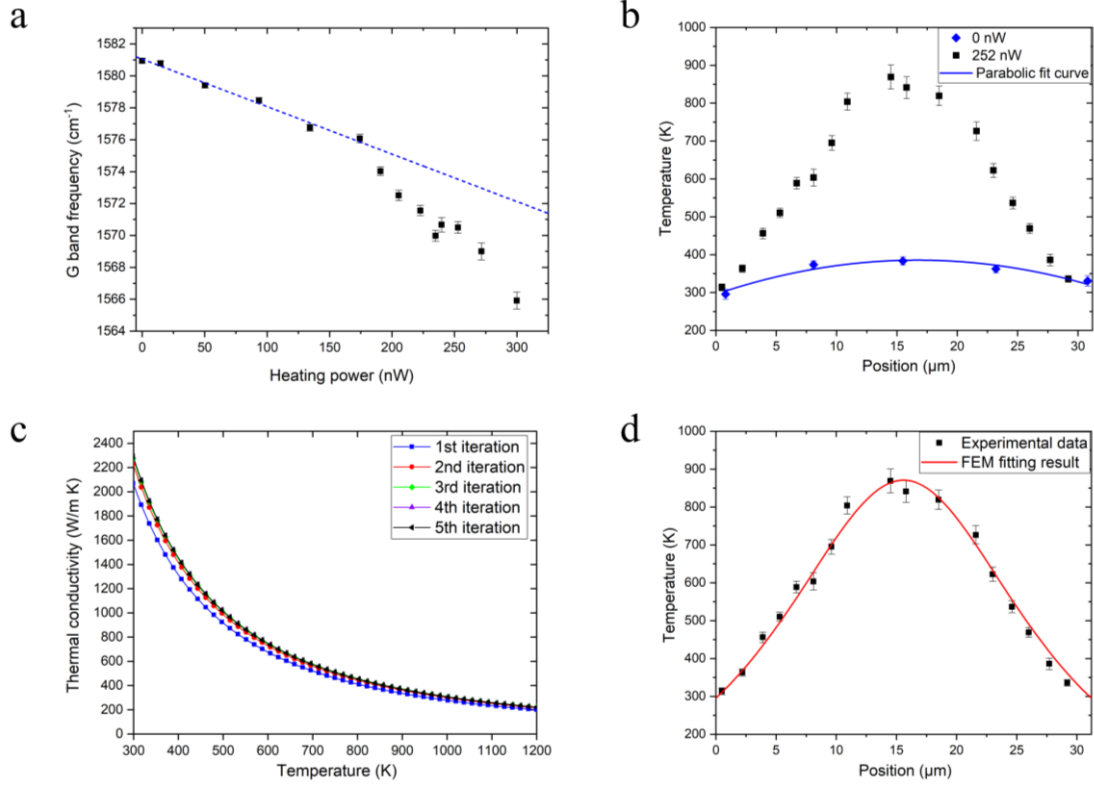


Fig. 3. Effect of temperature on the thermal conductivity of the SWCNT. (a) G band frequencies of a (11, 23) SWCNT at different heating powers. (b) Temperature distributions of the SWCNT measured at 0 nW (without Joule heating) and 252 nW. The blue solid line is a parabola fitting the temperature profile without electrical heating. (c) Iterative calculations of the temperature dependence of thermal conductivity considering the heating effect of the Raman laser. (d) Temperature distribution along the SWCNT at 252 nW obtained by FEM calculation using the optimized temperature dependence of thermal conductivity.

We proposed a new strategy to extract the temperature dependence of thermal conductivity from the resulting temperature distribution using reverse estimation using FEM. According to previous reports, phonon scattering processes dominate the thermal transport of CNTs above room temperature [14,15,24,34]. The temperature dependence of thermal conductivity can be described as [9,35,36]:

$$k = \frac{1}{aT + bT^2} \quad (6)$$

where a and b are unknown constants. The term of T^{-1} corresponds to the first-order Umklapp scattering processes, and the term of T^{-2} corresponds to the second-order three-phonon Umklapp scattering processes [37]. The values of a and b were optimized to make the simulation results closest match with the experimental results. The physical parameters used for the FEM and the process of optimization are given in Table S2 and Fig. S2. The FEM simulation is a part of our experimental data analysis, to extract the temperature dependence of thermal conductivity as a fitting parameter. Detailed atomic structure of CNTs were not involved in the calculation processes. To precisely evaluate the temperature dependence of the thermal conductivity, the heating effect of the Raman laser has to be taken into account. Since the laser power absorbed by a CNT is difficult to estimate accurately, we used a strategy of iterative calculations. Specifically, the effective laser heating power was calculated by $P' = 8A\Delta T_0 k/L$, where ΔT_0 was the temperature rise in the middle of the CNT without electrical heating. We used the apparent thermal conductivity k to calculate the initial effective laser heating power. The total heating power, including the electrical and effective laser heating power, was then input into the FEM model. We obtained the initial temperature dependence of thermal conductivity by this method. The effective laser heating power was then reevaluated using the relationship between temperature and thermal conductivity. The procedure was repeated until the obtained thermal conductivity remained almost unchanged. The iteration results are shown in Fig. 3(c). It was found that the results converge to nearly the same value after five iterations. More details can be found in Fig. S3 and Table S4. The FEM result of the temperature profile obtained with the optimized temperature dependence of thermal conductivity fits the experimental data well, as shown in Fig. 3(d). We also simulated the temperature rise in the middle of suspended CNT at different heating powers using the optimized temperature-dependent k as shown in Fig. S4, and this is consistent with the experimental results.

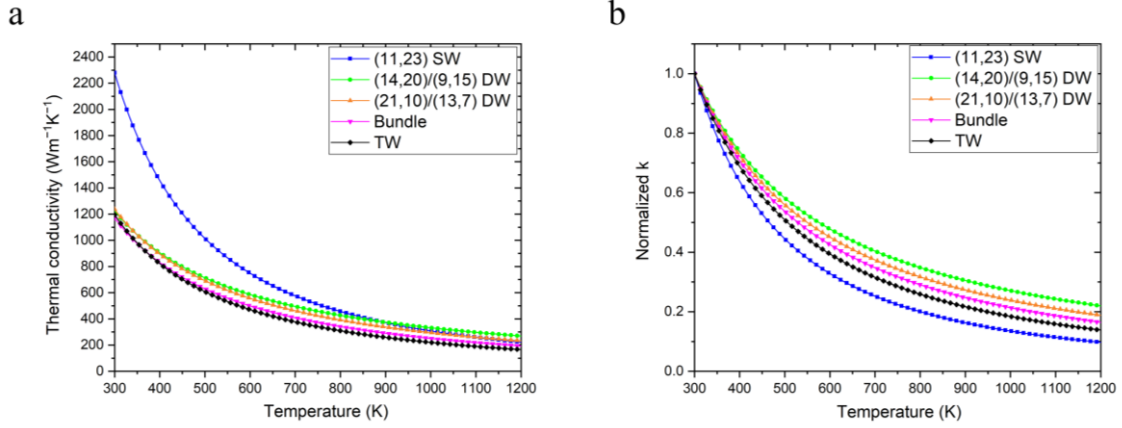


Fig. 4. (a) Temperature dependence of the thermal conductivities of five CNT samples, with defined structures, including one SWCNT, two DWCNTs, one TWCNT, and one CNT bundle. (b) Normalized thermal conductivities of these five as a function of temperature. The thermal conductivities were normalized by the value at 300 K.

Using this method, the temperature dependence of the thermal conductivities of five samples with defined structures, four individual CNTs and a CNT bundle, were obtained (Fig. 4(a)). The results show that the temperature dependence of k can be described by $k = 1/(aT + bT^2)$, where a is in the range $6.97 \times 10^{-7} - 2.59 \times 10^{-6}$, and b is in the range $4.19 \times 10^{-10} - 2.55 \times 10^{-9}$. It was found that the thermal conductivity of an (11, 23) SWCNT is higher than that of other CNTs below 1000 K. The thermal conductivities of the different CNTs normalized by the value at 300 K are shown in Fig. 4(b). The temperature dependence of thermal conductivity is similar to those in some earlier reports [9,35]. Compared with previous studies, we don't need to measure the thermal conductivity at a series of temperatures, when the temperature-induced change of thermal conductivity along the CNT and heating effect of the Raman laser are considered.

3.3. Diameter and chirality dependence of the thermal conductivity

The dependence of the thermal conductivity of the CNTs on diameter is shown in Fig. 5(a). It was normalized to that at 350 K, to make the results comparable with that of graphene previously reported [38,39]. We measured the thermal conductivities of 15 CNT samples,

including three SWCNTs, five DWCNTs, one triple-wall CNT (TWCNT), and six CNT bundles as listed in Table 1. The diameters given for the bundles in Fig. 5(a) are the average diameters of the outer walls of the CNTs in the bundle. For the CNT samples without measuring the temperature dependence of thermal conductivity, we used the average normalized thermal conductivity to calculate the thermal conductivity at 350 K. We can see that the thermal conductivity of individual CNTs is higher than that of CNT bundles, and SWCNTs have a higher thermal conductivity than DWCNTs and the TWCNT. More importantly, it was found that the thermal conductivity of SWCNTs tends to increase with increasing tube diameter, and the thermal conductivity of the (16, 34) SWCNT with diameter of 3.46 nm is close to that of the monolayer graphene. And the thermal conductivities of DWCNTs and CNT bundles have the similar diameter dependence, in which thermal conductivity increases with increasing diameter and approaches that of bilayer graphene.

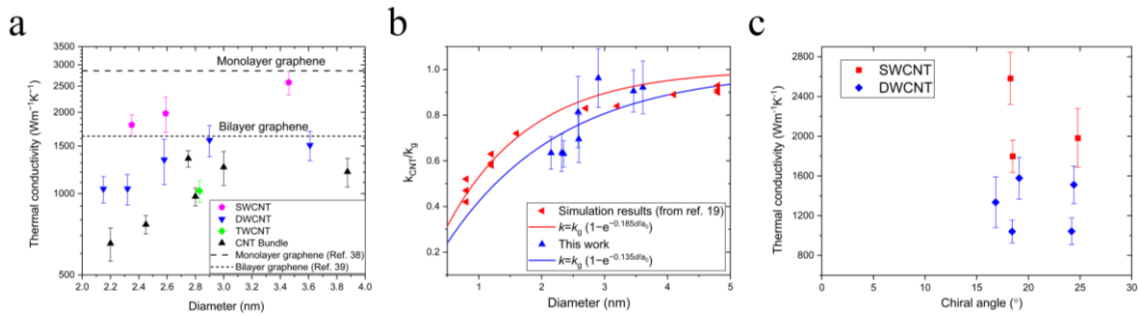


Fig. 5. Diameter and chirality dependence of the thermal conductivity. (a) Diameter dependence of the thermal conductivity of CNTs with different diameters at 350 K. The diameters of the DW/TWCNTs are the those of the outer walls, and those of CNT bundles are the average diameter of the outer walls of the CNTs in the bundle. The thermal conductivity of monolayer graphene and bilayer graphene are from Ref. 38 and Ref. 39, respectively. (b) The normalized thermal conductivity of CNTs as a function of the nanotube diameter, in which the thermal conductivity are normalized with that of graphene (k_g). The data are fitted with exponential functions. The simulation results (red triangle) are from Ref. 19. (c) The thermal conductivity of CNTs versus chiral angle at 350 K. The chiral angles of DWCNTs refer to the outer walls.

A theoretical study have predicted a similar tendency as shown in Fig. 5(b) [19]. The phonon density of state and the power spectrum of phonons were analyzed, from which they found smaller diameter nanotubes have relatively more high frequency radial breathing modes. However, these high frequency modes contribute little to the thermal conductivity due to their near-zero group velocities. Nanotubes with larger diameters possess more low frequency radial breathing modes which are more effective in heat conduction, exhibiting higher thermal conductivity. They also found that the thermal conductivity of SWCNTs can be described by $k(d) = k_g(1 - e^{-0.185/a_0})$, where d is the diameter, $a_0 = 0.246$ nm is the graphene lattice constant. When the diameter of a CNT is large enough, the thermal conductivity approaches that of graphene (k_g). We normalized the measured thermal conductivity of SWCNTs and DWCNTs with the value of monolayer graphene and bilayer graphene from Ref. 38 and Ref. 39, respectively. Our experimental data were fitted by $k(d) = k_g(1 - e^{-0.135/a_0})$. The deviation between our results and the molecular dynamics simulations may due to the difference of the CNTs length. The lengths of calculated CNTs are less than $2.4\ \mu\text{m}$ in the simulation work, while the lengths of our measured CNTs are larger than $30\ \mu\text{m}$. This result agrees with the theoretical work which shows that the diameter dependence of thermal conductivity becomes stronger with increasing nanotube length [40]. The underlying reason for the similar diameter dependence of DWCNTs and CNT bundles is the extremely high anisotropic thermal transport and the low interlayer thermal conductivity of CNTs [41,42]. For our microdevices, only the outer layers of the CNTs are in contact with the substrate, so that thermal transport through the outer walls is dominant. The thermal conductivity of DWCNTs/TWCNT is lower than SWCNTs because of the larger cross-sectional areas of the former. Phonon scattering produced by the inter-layer van der Waals interactions may also contribute to the reduced thermal conductivity [43].

Figure 5(c) shows the effect of chirality on the thermal conductivity of CNTs at 350 K. The chiral angles of the DWCNTs in Fig. 5(c) are those of the outer walls. A random distribution of thermal conductivity was revealed from the statistical analysis on chiral angles, indicating

that the chirality has no major effect on the thermal conductivity compared to the diameter. This finding is consistent with some theoretical studies [15,21], according to which the phonon density of states does not show a significant change for CNTs with different chiralities.

4. Conclusions

The structure-dependent intrinsic thermal conductivity of CNTs is investigated by using custom-made electro-thermal microchips, which enables both thermal measurements by Raman and atomic structure characterizations by electron diffraction of individual CNTs. After extracting the temperature dependence of thermal conductivity through finite element modelling, the relation between thermal conductivity and the intrinsic structures was established. It was found that the thermal conductivity of CNTs depends mainly on the tube diameter, while the chiral angle has no significant effect. The thermal conductivity increases along with the increase of diameter, and approaches that of flat graphene asymptotically.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

H.-B.Z.: Conceptualization, Data Curation, Investigation, Methodology, Validation, Visualization, Writing—original draft. **D.-M.T.:** Conceptualization, Investigation, Supervision, Funding acquisition, Writing—review & editing. **L.Z.:** Investigation, Supervision, Writing—review & editing. **M.-K.Z.:** Investigation. **R.-H.X.:** Investigation. **C.L.:** Conceptualization, Investigation, Supervision, Funding acquisition, Writing—review & editing. **H.-M.C.:** Supervision.

Acknowledgements

The authors thank Dr. Ovidiu Cretu, from Center for Basic Research On Materials, National Institute for Materials Science, for help with the FEM simulations. This work was supported by the National Key Research and development Program of China (Grant No. 2022YFA1203303),

National Natural Science Foundation of China (Grant Nos. 52130209, 52188101), JSPS Kakenhi (Grant Nos. JP25820336, JP20K05281, JP23H01796), JST-FOREST Program (Grant No. JPMJFR223T), WPI-MANA “Challenging Research Program (CRP)”, National Institute for Materials Science (NIMS) “Support system for curiosity-driven research”, and "Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM)" of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (Grant No. JPMXP1223NM5306).

References

- [1] R. Saito, M. Fujita, G. Dresselhaus, M.S. Dresselhaus, Appl. Phys. Lett. 60 (1992) 2204–2206.
- [2] P. Kim, L. Shi, A. Majumdar, P.L. McEuen, Phys. Rev. Lett. 87 (2001) 1–4.
- [3] M. Fujii, X. Zhang, H. Xie, H. Ago, K. Takahashi, T. Ikuta, H. Abe, T. Shimizu, Phys. Rev. Lett. 95 (2005) 1–4.
- [4] C. Yu, L. Shi, Z. Yao, D. Li, A. Majumdar, Nano Lett. 5 (2005) 1842–1846.
- [5] M.T. Pettes, L. Shi, Adv. Funct. Mater. 19 (2009) 3918–3925.
- [6] T.Y. Choi, D. Poulikakos, J. Tharian, U. Sennhauser, Nano Lett. 6 (2006) 1589–1593.
- [7] Z.L. Wang, D.W. Tang, X.B. Li, X.H. Zheng, W.G. Zhang, L.X. Zheng, Y.T. Zhu, A.Z. Jin, H.F. Yang, C.Z. Gu, Appl. Phys. Lett. 91 (2007).
- [8] T.Y. Choi, D. Poulikakos, J. Tharian, U. Sennhauser, Appl. Phys. Lett. 87 (2005) 93–96.
- [9] E. Pop, D. Mann, Q. Wang, K. Goodson, H. Dai, Nano Lett. 6 (2006) 96–100.
- [10] Q. Li, C. Liu, X. Wang, S. Fan, Nanotechnology 20 (2009) 1–5.
- [11] J.-H. Liu, H.-H. Xie, Y.-D. Hu, X. Zhang, Y.-Y. Zhang, Int. J. Heat Mass Transf. 108 (2017) 572–576.
- [12] P. Li, D. Feng, Y. Feng, X. Liu, M. Xiong, X. Zhang, J. Liu, J. Therm. Sci. (2022).
- [13] S. Berber, Y.-K. Kwon, D. Tománek, Phys. Rev. Lett. 84 (2000) 4613–4616.
- [14] J.X. Cao, X.H. Yan, Y. Xiao, J.W. Ding, Phys. Rev. B 69 (2004) 1–4.

- [15] G. Zhang, B. Li, J. Chem. Phys. 123 (2005).
- [16] X.H. Yan, Y. Xiao, Z.M. Li, J. Appl. Phys. 99 (2006) 124305.
- [17] L. Lindsay, D.A. Broido, N. Mingo, Phys. Rev. B 82 (2010) 161402.
- [18] B. Qiu, Y. Wang, Q. Zhao, X. Ruan, Appl. Phys. Lett. 100 (2012) 1–4.
- [19] A. Cao, J. Qu, J. Appl. Phys. 112 (2012) 1–9.
- [20] T. Yamamoto, S. Watanabe, K. Watanabe, Phys. Rev. Lett. 92 (2004) 1–4.
- [21] J. Wang, J.S. Wang, Appl. Phys. Lett. 88 (2006) 1–3.
- [22] M.A. Osman, D. Srivastava, Nanotechnology 12 (2001) 21–24.
- [23] W. Zhang, Z. Zhu, F. Wang, T. Wang, L. Sun, Z. Wang, Nanotechnology 15 (2004) 936–939.
- [24] M. Grujicic, G. Cao, W.N. Roy, J. Mater. Sci. 40 (2005) 1943–1952.
- [25] Y. Zhang, L. Xie, J. Zhang, Z. Wu, Z. Liu, J. Phys. Chem. C 111 (2007) 14031–14034.
- [26] S. Huang, M. Woodson, R. Smalley, J. Liu, Nano Lett. 4 (2004) 1025–1028.
- [27] N.R. Raravikar, P. Keblinski, A.M. Rao, M.S. Dresselhaus, L.S. Schadler, P.M. Ajayan, Phys. Rev. B 66 (2002) 1–9.
- [28] Z. Zhou, L. Ci, L. Song, X. Yan, D. Liu, H. Yuan, Y. Gao, J. Wang, L. Liu, W. Zhou, S. Xie, Y. Du, Y. Mo, Chem. Phys. Lett. 396 (2004) 372–376.
- [29] S. Malola, H. Häkkinen, P. Koskinen, Phys. Rev. B 78 (2008) 153409.
- [30] Y. Wang, X. Zhang, J. Appl. Phys. 136 (2024) 074302.
- [31] W. Cai, A.L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi, R.S. Ruoff, Nano Lett. 10 (2010) 1645–1651.
- [32] S. Sullivan, A. Vallabhaneni, I. Kholmanov, X. Ruan, J. Murthy, L. Shi, Nano Lett. 17 (2017) 2049–2056.
- [33] J. Xu, Y. Hu, H. Bao, Phys. Rev. Appl. 19 (2023) 014007.
- [34] A. Nasir Imtani, J. Phys. Chem. Solids 74 (2013) 1599–1603.

- [35] K. Yoshino, T. Kato, Y. Saito, J. Shitaba, T. Hanashima, K. Nagano, S. Chiashi, Y. Homma, ACS Omega 3 (2018) 4352–4356.
- [36] D.J. Ecsedy, P.G. Klemens, Phys. Rev. B 15 (1977) 5957–5962.
- [37] J.M. Ziman, Electrons and Phonons, Oxford University Press: Oxford, U.K., 1960.
- [38] S. Chen, A.L. Moore, W. Cai, J.W. Suk, J. An, C. Mishra, C. Amos, C.W. Magnuson, J. Kang, L. Shi, R.S. Ruoff, ACS Nano 5 (2011) 321–328.
- [39] H. Li, H. Ying, X. Chen, D.L. Nika, A.I. Cocemasov, W. Cai, A.A. Balandin, S. Chen, Nanoscale 6 (2014) 13402–13408.
- [40] Y. Feng, J. Zhu, D.-W. Tang, J. Nanosci. Nanotechnol. 15 (2015) 3092–3097.
- [41] Z. Ma, Z. Guo, H. Zhang, T. Chang, AIP Adv. 7 (2017) 1–8.
- [42] H. Hamasaki, S. Takimoto, K. Hirahara, Nano Lett. 21 (2021) 3134–3138.
- [43] X. Zhang, W.-X. Zhou, X.-K. Chen, Y.-Y. Liu, K.-Q. Chen, Phys. Lett. A 380 (2016) 1861–1864.