Control of electron- and phonon-derived thermal conductances in carbon nanotubes

Takahiro Yamamoto¹, Yoshiki Nakazawa and Kazuyuki Watanabe

Department of Physics, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
and
CREST, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan
E-mail: takahiro@rs.kagu.tus.ac.jp

New Journal of Physics 9 (2007) 245
Received 16 April 2007
Published 1 August 2007
Online at http://www.njp.org/
doi:10.1088/1367-2630/9/8/245

Abstract. We present a method for controlling the electron- and phonon-derived thermal conductances in carbon nanotubes with vacancy defects involving numerical analysis based on the nonequilibrium electron/phonon Green’s function method. The electron-derived thermal conductance can be controlled by tuning the external gate voltage because the resonant backscattering level (dangling σ-bond states around vacancies) can be shifted by the gate voltage. In contrast, thermal annealing is effective in increasing the phonon-derived thermal conductance because the quasi-bound phonon state localized around a vacancy disappears due to the annealing-induced vacancy rearrangement.

¹ Author to whom any correspondence should be addressed.
1. Introduction

Heating of elements in electronic devices is an unavoidable, but serious problem that presents an obstacle to realizing next-generation nanoscale devices. Carbon nanotubes (CNTs) have received significant attention as a potential candidate as a heat remover because of their high thermal conductivity [1]. In addition, thermal transport in CNTs exhibits quantum characteristics at low temperatures [2, 3], nonlinear behaviour with respect to the tube length at room temperature [4], and thermal conductivity decay due to strong phonon–phonon scattering at higher temperatures [5]. However, the intrinsic thermal transport properties of pure CNTs may be lost due to the presence of defects. Nevertheless, the influence of defects on heat transport in CNTs remains unclear. The objective of the present study is to elucidate the influence of such defects and establish a method by which to control the thermal conductance of defective CNTs.

Recent classical molecular-dynamics (MD) simulations have shown that various types of defects (e.g., vacancy defects, isotopes and Stone–Wales defects) reduce the phonon-derived thermal conductivity in CNTs [6, 7]. Among these defects, a vacancy defect with three dangling bonds (hereinafter monovacancy) decreases the thermal conductivity most markedly [7]. Monovacancies are generated during the synthesis process or by artificial procedures such as acid purification and ion/electron irradiation. Although classical MD simulations have been successfully applied to the study of phonon-derived thermal transport in CNTs at room temperature, they cannot address electron-derived thermal transport or low-temperature phonon-derived thermal transport, which exhibits quantum features.

In the present paper, we use a fully quantum mechanical theory based on the non-equilibrium Green’s function (NEGF) method to investigate the electron- and phonon-derived thermal transport in defective CNTs. For electron-derived thermal conductance, the NEGF method is used together with the density-functional theory (DFT) [8, 9]. To the best of our knowledge, the present study is the first to combine NEGF and DFT (hereinafter NEGF+DFT) in order to investigate electron-derived thermal transport in nanoscale objects. Meanwhile, phonon-derived thermal conductance is analysed by the NEGF method, which was developed in previous studies by the present authors [10] and others [11, 12].
2. Electron-derived thermal transport

CNTs can be either metallic or semiconducting, depending on the chirality. For semiconducting CNTs, the electron contribution to thermal transport is negligible for moderate temperatures because of the large electronic band gap. For metallic CNTs, on the other hand, heat is carried by conduction electrons as well as phonons. At low temperatures, electrons and phonons travel coherently through CNTs without scattering, and the total thermal conductance of metallic CNTs is given by the sum of the contributions of electron- and phonon-derived values: \( \kappa_{\text{tot}} = \kappa_{\text{el}} + \kappa_{\text{ph}} \). In this section, we discuss the electron contributions to thermal transport in CNTs.

2.1. Theory and numerical method

We describe a theory for thermal transport by coherent electrons. According to the Landauer formula, the thermal current or the energy flux is expressed as

\[
J_{\text{el}} = \frac{1}{\hbar} \int_{-\infty}^{\infty} \frac{d\epsilon}{2\pi} (\epsilon - \mu) \left[ f_{\text{F}}(\epsilon, T_L) - f_{\text{F}}(\epsilon, T_R) \right] \zeta_{\text{el}}(\epsilon).
\]

Here, \( f_{\text{F}}(\epsilon, T_{L/R}) \) is the Fermi–Dirac distribution function for an electron with energy \( \epsilon \) in the left/right heat reservoir with the temperature \( T_{L/R} \) (\( T_L > T_R \)), \( \mu \) is the averaged chemical potential between the hot and cold heat reservoirs. \( \zeta_{\text{el}}(\epsilon) \) is the transmission function for an incident electron with energy \( \epsilon \). Thus, the electron-derived thermal conductance \( \kappa_{\text{el}}(T) = J_{\text{el}}/(T_L - T_R) \) is given by

\[
\kappa_{\text{el}}(T) = \frac{k_B}{\pi} \int_{-\infty}^{\infty} d\epsilon \left( \frac{\epsilon - \mu}{k_B T} \right)^2 \frac{e^{(\epsilon-\mu)/k_B T}}{\left(e^{(\epsilon-\mu)/k_B T} + 1\right)^2} \zeta_{\text{el}}(\epsilon),
\]

as the temperature difference between the hot and cold heat reservoirs approaches zero. Here, the Planck constant \( \hbar \) is chosen to be unity (\( \hbar = 1 \)) in equation (2). \( k_B \) is the Boltzmann constant and \( T \equiv (T_L + T_R)/2 \) is the averaged temperature between the hot and cold heat reservoirs. At low temperatures, only transmission in the narrow energy range of around the Fermi level \( \epsilon_F \) contributes to the thermal conductance. Therefore, equation (2) can be approximated as

\[
\kappa_{\text{el}}(T) \approx 2\kappa_0(T)\zeta_{\text{el}}(\epsilon_F),
\]

where \( \kappa_0 = \pi k_B^2 T/6 \) is a universal value for thermal conductance, and the prefactor 2 is the spin degrees of freedom. Note that the following discussion on the electron-derived thermal conductance \( \kappa_{\text{el}} \) can be applied to the electrical conductance \( G \) because \( G \) is expressible via the well-known Landauer formula \( G = (2e^2/h)\zeta_{\text{el}} \).

To discuss the influence of thermal annealing on electron-derived thermal conductance, we calculate the \( \zeta_{\text{el}}(\epsilon) \) for a (8,8) CNT with a 5-1 db defect, which is given by the Fisher–Lee relation

\[
\zeta_{\text{el}}(\epsilon) = 4\text{Tr} \left[ (\text{Im } \Sigma_L(\epsilon)) G(\epsilon) (\text{Im } \Sigma_R(\epsilon)) G^\dagger(\epsilon) \right],
\]

where \( G(\epsilon) \) is the retarded Green’s function for the scattering region including the 5-1 db defect and \( \Sigma_{L,R}(\epsilon) \) is the self-energy due to the left/right lead region. The Green’s function is self-consistently obtained by numerical calculation based on the NEGF+DFT method \[7, 8\] and the self-energy is calculated by the mode matching method \[13\], which enable us to use the nonorthogonal atomic basis sets.
Figure 1. Zero-bias electron transmission function of (8,8) CNT with the 5-1 db defect. The solid and dash-dotted curves are the transmission functions calculated by our NEGF+DFT implementation and Atomistix ToolKit, respectively. The dotted curve represents the (8,8) CNT without defects. The inset shows the dangling $\sigma$-bond state around the 5-1 db defect, which is located at the transmission dip near the Fermi level.

In our numerical implementation of the NEGF+DFT method, we have used a very efficient electronic-structure package called SIESTA for the DFT part [14]. We have also chosen a single-zeta basis set, the Troullier–Martins norm-conserving pseudopotentials [15], and the Ceperley–Alder exchange-correlation potential [16]. We confirmed that the single-zeta basis set ensures high accuracy for present calculations by comparing the results obtained by the single-zeta and double-zeta basis sets. The computation procedure used in the NEGF portion is the same as that used in the conventional NEGF technique. The details of this procedure can be found in [8].

2.2. Results and discussions

According to equation (3), the ballistic electrons in metallic CNTs without defects contribute four quanta ($\kappa_{el} = 4\kappa_0$) to the thermal conductance at low temperature because $\zeta_{el}(\epsilon_F) = 2$ corresponding to two channels crossing the Fermi level [3]. With a monovacancy, the electron-derived thermal conductance is reduced because the conduction electrons are scattered by the dangling $\sigma$-bond states around the monovacancy, which has an energy close to the Fermi level [17]. Since the monovacancy in CNTs is energetically metastable, rebonding of two dangling-bond atoms occurs and only one dangling-bond atom remains (i.e. rearrangement of the monovacancy) upon thermal annealing [18, 19]. This stable structure, consisting of a single pentagon and one dangling bond (hereinafter 5-1 db), is shown in the inset of figure 1. We would thus expect the thermal conductance of CNTs with monovacancy to change as a result of the monovacancy rearrangement induced by thermal annealing.

Figure 1 shows the $\zeta_{el}(\epsilon)$ for the (8,8) CNT with a 5-1 db defect (solid and dash-dotted curves) and without defects (dotted curves). The solid and dash-dotted curves are the results
Figure 2. Electron-derived thermal conductance $\kappa_{el}$ of the (8,8) CNT with a 5-1 db defect as a function of the electrostatic potential $V_g$ induced by the applied gate voltage. The inset schematizes the CNT device, which has a cylindrical gate electrode. The separation between the hot and cold reservoirs is chosen to be 3.4 nm and the width of gate electrode is found to be 1.3 nm.

The electron-derived thermal conductance is estimated to be $\kappa_{el}/(2\kappa_0) = 1.52$ at low temperatures.

As mentioned in the introduction, our objective is to control the thermal conductance of CNTs. To this end, we consider a CNT device with three terminals (i.e. source, drain and gate terminals), as in the case of a CNT transistor. The source and drain terminals are used as the hot and cold heat reservoirs, respectively. The gate terminal controls the electron flow through the scattering region (see the inset of figure 2). In our NEGF+DFT scheme, the effect of the gate electrode is treated as a shift in potential: $H_g = V_gS$. Here, $V_g$ is the electrostatic potential induced by the gate electrode and $S$ is a matrix representing the overlap between atomic orbitals. The constant $V_g$ with respect to atom positions means a coaxial gate electrode wrapping a CNT. In our calculations, the gate voltages are applied to a local region of 1.3 nm around the 5-1 db defect, and the separation between the hot and cold reservoirs is chosen to be 3.4 nm, as shown in the inset of figure 2. Figure 2 shows the gate-voltage dependence of the electron-derived thermal conductance $\kappa_{el}$ of the (8,8) CNT with a 5-1 db defect in units of the universal value $2\kappa_0$. $\kappa_{el}$ is a sensitive function of the bias voltage. At $V_g = -0.12$ eV, $\kappa_{el}$ shows a minimum. With increasing gate voltage, $\kappa_{el}$ increases monotonically to $V_g = 0.15$ eV.
Figure 3. (a) Electron transmission functions $\zeta_{el}(\epsilon)$ and (b) LDOS near the Fermi energy ($\epsilon_F = 0$ eV) of the (8,8) CNT with a 5-1 db defect for $V_g = -0.12$ eV (dotted curve), 0.0 eV (solid curve) and 0.15 eV (dashed curve).

To establish the gate-voltage dependence of $\kappa_{el}$ in figure 2, we show the electron transmission function $\zeta_{el}(\epsilon)$ and the local density of states (LDOS) around the 5-1 db defect of the (8,8) CNT for $V_g = -0.12$ (dotted curve), 0.0 (solid curve) and 0.15 eV (dashed curve) in figures 3(a) and (b), respectively. The positions of both the transmission dip and LDOS peak shift to higher energies with increasing $V_g$. The LDOS peak corresponds to the position of the energy level of the dangling $\sigma$-bond state depicted in the inset of figure 1. Thus, figures 3(a) and (b) suggest that the position of the resonant backscattering level can be tuned by the gate voltage. Thus, $\kappa_{el}$ shows a minimum at $V_g = -0.12$ eV, in which case the LDOS peak is located at $\epsilon_F = 0$ eV and increases monotonically as the LDOS peak is shifted from the Fermi level, as shown in figure 2.

3. Phonon-derived thermal transport

In this section, we discuss the phonon contribution to thermal transport in a metallic (8,8) CNT. Below the room temperature, not only electrons but also phonons propagate through the CNTs coherently [22, 23].
3.1. Theory and numerical method

For the coherent phonon transport, the phonon-derived thermal current is expressed by a formula similar to equation (1):

\[ J_{\text{ph}} = \int_0^\infty \frac{d\omega}{2\pi} \hbar \omega \left[ f_B(\omega, T_L) - f_B(\omega, T_R) \right] \zeta_{\text{ph}}(\omega). \] (5)

Here, \( f_B(\omega, T_{L/R}) \) is the Bose–Einstein distribution function for phonons with energy \( \hbar \omega \) in the left/right heat reservoir. \( \zeta_{\text{ph}}(\omega) \) is the transmission function for phonons with energy \( \hbar \omega \). Thus, the phonon-derived thermal conductance is given by

\[ \kappa_{\text{ph}}(T) = \kappa_B \frac{k_B}{2\pi} \int_0^\infty d\omega \left( \frac{\omega}{k_B T} \right)^2 \frac{e^{\omega/k_B T}}{\left[ e^{\omega/k_B T} - 1 \right]^2} \zeta_{\text{ph}}(\omega), \] (6)

in the limit of the small temperature difference between the hot and cold heat reservoirs [24]. In equation (6), the Plank constant was chosen to be unity (\( \hbar = 1 \)), and the phonon angular frequency \( \omega \) is hereinafter regarded as the phonon energy. According to equation (6), the acoustic phonon mode contributes a universal quantum of \( \kappa_0 = \pi k_B^2 T / 6 \) to the phonon-derived thermal conductance of pure CNTs without defects.

The phonon transmission function \( \zeta_{\text{ph}}(\omega) \) in equation (6) is given by an expression similar to \( \zeta_{\text{el}}(\epsilon) \) in equation (4) by replacing the electron Green’s function and the electron self energy by the phonon Green’s function and the phonon self energy, respectively. The phonon Green’s function is calculated by numerical calculation based on the NEGF technique for phonon transport developed in our previous study [10]. The self energy is calculated using the mode matching method [13] applied for phonon systems. The force constants between carbon atoms in CNTs are numerically determined by the Brenner empirical potential [25], which is particularly suitable for potential functions of carbon materials.

3.2. Results and discussions

Figure 4 plots the phonon transmission \( \zeta_{\text{ph}}(\omega) \) for the (8,8) CNT with and without defects as a function of incident phonon energy \( \omega \). The dotted curve is the transmission function for the perfect (8,8) CNT without defects. The solid and dash-dotted curves represent \( \zeta_{\text{ph}}(\omega) \) for the (8,8) CNT with a monovacancy and a 5-1 db defect, respectively. Perfect transmission can be observed below \( \sim 10 \) meV, even in the presence of the monovacancy and the 5-1 db defect because the low-energy phonons are not scattered by local defects having dimensions that are much smaller than their phonon wavelengths. In contrast, the short-wavelength phonons excited above \( \sim 10 \) meV are scattered by the local defects, especially the monovacancy. In our previous paper [10], we discussed in detail the reduction of thermal conductance by the monovacancy in the (8,8) CNT. The reduction is caused by resonant backscattering due to the quasi-bound phonon states at \( \omega = 11.6 \) and 18.8 meV, corresponding to the transmission dips indicated by arrows in figure 4. This strong reflection is also confirmed by phonon wavepacket scattering simulations based on the MD method [26]. In the present paper, we discuss the influence of structural change from monovacancy to 5-1 db defect on the phonon-derived thermal conductance. As shown in figure 4, the transmission dips disappear for the dash-dotted curve for the 5-1 db defect. Thus, the thermal conductance of a defective CNT having a monovacancy increases by the structural change to the 5-1db defect. We next discuss the physical origin of the disappearance of transmission dips.
In order to fully understand the increase in thermal conductance from the microscopic point of view, we calculate the nonequilibrium phonon density distribution of defective CNTs using the relation $\rho_i(\omega) = -iG_{ii}^< (\omega)$, where $G_{ii}^< (\omega)$ is a diagonal element of the lesser Green’s function matrix. The upper panels in figures 5(a) and (b) show $\rho_i(\omega)$ around the monovacancy at (a) $\omega = 11.6 \text{ meV}$ and (b) $18.8 \text{ meV}$, which coincide to the transmission dip positions indicated by arrows in figure 3. The shading on the spheres representing atoms in figure 5 indicates the phonon density. As shown in the upper panels of figures 5(a) and (b), the phonon density is strongly localized around the monovacancy at both $\omega = 11.6 \text{ meV}$ and $18.8 \text{ meV}$. After the rearrangement of the monovacancy into a 5-1 db defect upon thermal annealing, the quasi-bound phonon states disappear, as shown in the bottom panels of figures 5(a) and (b). Thus, the rearrangement allows easy transmission of the incident phonons (see figure 4) and, consequently, the thermal conductance increases.

4. Total thermal conductances

Finally, we describe the total thermal conductance $\kappa_{\text{tot}} = \kappa_{\text{el}} + \kappa_{\text{ph}}$ of the (8,8) CNT, focusing in particular on the electron contribution to $\kappa_{\text{tot}}$. Without defects, the electron- and phonon-derived thermal conductances show the same universal value, $\kappa_{\text{el}} = \kappa_{\text{ph}} = 4\kappa_0$, at low temperatures below $\sim 4 \text{ K}$ [3]. However, as discussed previously, the electron-derived thermal conductance is significantly reduced by the 5-1 db defect ($\kappa_{\text{el}} = 3.04\kappa_0$), while the phonon-derived thermal conductance is not affected by the 5-1 db defect ($\kappa_{\text{ph}} = 4\kappa_0$). The electron contribution is found to be approximately 43% of the total thermal conductance at low temperatures below $T \sim 4 \text{ K}$. As shown in section 2, the electron contribution is controlled by changing the gate voltage. For example, the minimum and maximum values of the electron contribution are estimated...
Figure 5. Nonequilibrium phonon density in the scattering region of (8,8) CNT under the thermal current. The nonequilibrium phonon density around the monovacancy (top) and 5-1 db defect (bottom) at (a) 11.6 meV and (b) 18.8 meV. The shading on the atom spheres indicates the phonon density.

to be 37% for $V_g = -0.12$ eV and 49% for $V_g = 0.15$ eV. With increasing temperature, the ratio $\kappa_{el}/\kappa_{tot}$ decreases rapidly for the following reason. The excitation energy of the lowest electron transverse mode is of the order of electron volts, whereas the excitation energy of the lowest optical phonon is typically less than 0.01 eV. Consequently, the electron-derived thermal conductance increases very little from $\kappa_{el} = 3.04 \kappa_0$ up to room temperature, whereas the phonon-derived thermal conductance begins to increase rapidly from $\kappa_{ph} = 4 \kappa_0$ above $T \sim 4$ K for the (8,8) CNT with the 5-1 db defect. Thus, the electron contribution to the thermal transport becomes small with increasing temperature [3]. The reduction of the electron contribution to $\kappa_{tot}$ for typical gate voltages ($V_g = -0.12$, 0.00 and 0.15 eV) is shown in figure 6. In addition, figure 6 shows that the electron-derived thermal conductance $\kappa_{el}$ can be controlled, even at $T = 100$ K, by the gate voltage although the controllability decreases with increasing temperature.

5. Conclusions

In conclusion, we have investigated the thermal transport by electrons and phonons in defective CNTs with a vacancy-type defect (a monovacancy and a 5-1 db defect), focusing on the control of their thermal conductance. The phonon-derived thermal conductance can be increased clearly by the structural change of the monovacancy into a 5-1 db defect through thermal annealing. In contrast, the electron-derived thermal conductance of CNTs with the 5-1 db defect can be controlled by applying a gate voltage to the CNTs. Not only the thermal conductance but also the electrical conductance can be controlled by tuning the local gate potential. For example, the idea would be applied to a novel variable resistance that switches the current density in
Figure 6. Temperature dependence of electron contribution, $100 \times \kappa_{el}(T)/\kappa_{tot}(T)$, to the total thermal conductance of (8,8) CNT with the 5-1 db defect. The dotted, solid and dash-dotted curves are the electron contributions to the total thermal conductance for $V_g = -0.12$, 0.00 and 0.15 eV, respectively.

CNT-based elements. The present study is expected to pave the way for defect engineering of future nanodevices based on CNTs.

Acknowledgments

This study was supported in part by the ‘Academic Frontier’ Project and by the Ministry of Education, Culture, Sports, Science and Technology of Japan through Grants-in-Aid (nos 30408695 and 19540411). Some of the numerical calculations were performed on the Hitachi SR11000s at the ISSP at the University of Tokyo.

References

[1] Iwai T et al 2005 IEEE IEDM Tech. Digest 257
[2] Hone J, Whitney M, Piskoti C and Zettl A 1999 Phys. Rev. B 59 R2514
[3] Yamamoto T, Watanabe S and Watanabe K 2004 Phys. Rev. Lett. 92 075502
[4] Maruyama S 2002 Physica B 323 193
[5] Pop E, Mann D, Wang Q, Goodson K E and Dai H 2006 Nano Lett. 6 96
[6] Maruyama S, Igarashi Y, Taniguchi Y and Shiomi J 2006 J. Therm. Sci. Tech. 1 138
[7] Kondo N, Yamamoto T and Watanabe K 2006 e-J. Surf. Sci. Nanotech. 4 239
[8] Brandbyge M, Mozos J-L, Ordejon P, Taylor J and Stokbro K 2002 Phys. Rev. B 65 165401
[9] Taylor J, Guo H and Wang J 2001 Phys. Rev. B 63 245407
[10] Yamamoto T and Watanabe K 2006 Phys. Rev. Lett. 96 255503
[11] Mingo N 2006 Phys. Rev. B 74 125402
[12] Wang J-S, Wang J and Zeng N 2006 Phys. Rev. B 74 033408
[13] Ando T 1991 *Phys. Rev.* B **44** 8017
[14] Soler J M, Artacho E, Gale J D, Garcia A, Junquera J, Ordejon P and Sanchez-Portal D 2002 *J. Phys.: Condens. Matter* **14** 2745
[15] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[16] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[17] Choi H J, Ihm J, Louie S G and Cohen M L 2000 *Phys. Rev. Lett.* **84** 2917
[18] Miyamoto Y, Berber S, Yoon M, Rubio A and Tománek D 2002 *Physica* B **323** 78
[19] Krasheninnikov A V and Nordlund K 2002 *J. Vac. Sci. Technol.* B **20** 728
[20] Online at [http://www.atomistix.com](http://www.atomistix.com)
[21] Ke S-H, Baranger H U and Yang W 2005 *Phys. Rev.* B **71** 113401
[22] Mingo N and Broido D A 2005 *Phys. Rev. Lett.* **95** 096105
[23] Yu C, Shi L, Yao Z, Li D and Majumdar A 2005 *Nano Lett.* **5** 1842
[24] Rego L G C and Kirczenow G 1998 *Phys. Rev. Lett.* **81** 232
[25] Brenner D W 1990 *Phys. Rev.* B **42** 9458
Brenner D W 1992 *Phys. Rev.* B **46** 1948
[26] Kondo N, Yamamoto T and Watanabe K 2006 *Japan J. Appl. Phys.* **45** L963