Molecular-dynamics simulations of thermal transport in carbon nanotubes with structural defects *

Naoaki Kondo, Takahiro Yamamoto,† 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.

(Received 14 October 2005; Accepted 3 February 2006; Published 17 February 2006)

Effects of structural defects on thermal transport in carbon nanotubes are revealed through nonequilibrium molecular-dynamics simulations with the Tersoff-Brenner bond-order potential. The thermal conductivity of carbon nanotubes decreases rapidly down to 25 % with only 1 % vacancy defects. By performing thermal annealing, the vacancy defects are mainly transformed into 5-6 defects consisting of pentagon-hexagon pairs, and the reduced thermal conductivity due to vacancy defects is increased by 4-7 %. This improvement in thermal conductivity can be understood from the result that the thermal resistance of the 5-6 defects is smaller than that of the vacancy defects. [DOI: 10.1380/ejssnt.2006.239]

Keywords: Carbon nanotube; Surface defects; Molecular dynamics; Phonons

I. INTRODUCTION

Since the discovery of carbon nanotubes (CNTs) in 1991 [1], continuous efforts have been devoted toward the realization of CNT-based nanodevices utilizing their excellent physical properties [2]. However, there is concern that the excellent properties diminish owing to defects generated during the synthesis process or by artificial operations such as acid purification and ion/electron irradiation [3, 4]. The stable existence of atomic-scale defects in CNTs such as pentagon-heptagon pairs (Stone-Wales defects), adatoms and vacancies has been predicted by tight-binding and first-principles calculations [5–7]. These defects have been directly observed using high-resolution transmission electron microscopy [8].

Recently, among the excellent physical properties of CNTs, a high thermal conductivity has received significant attention because heat dissipation is one of the key issues to be resolved in the development of nanoscale devices [9–13]. According to theoretical predictions via molecular-dynamics (MD) simulations, the thermal conductivity of CNTs along the tube axis at room temperatures is as high as that of diamond or graphite due to intermolecular strong covalent bonding [14–22]. In contrast, the thermal conductivity of CNTs perpendicular to the tube axis is very low because of the tube-tube weak coupling due to van der Waals interactions. This anisotropic thermal conductivity is potentially helpful for thermal management of nanodevices [23]. From a fundamental scientific point of view, it is also interesting that the thermal conductance of CNTs exhibits universal quantization at low temperatures [24, 25]. On the other hand, the MD studies suggest that the thermal conductivity of CNTs at moderate temperatures diverges algebraically with tube length [17, 18].

A few attempts have been made to clarify the effects of defects of various types on the thermal conductivity of CNTs within the framework of MD methods thus far [14–17]. The defects are responsible for the drop in the thermal conductivity at room temperatures. For example, the thermal conductivity decreases by approximately 60 % with 40-50 % 14C isotope impurity [17]. However, the physical origin of reduced thermal conductivity due to various types of defect in CNTs has not yet been understood sufficiently.

In this paper, we perform nonequilibrium molecular-dynamics (NEMD) simulations [26] with the Tersoff-Brenner bond-order potential [27] to investigate thermal transport through defective CNTs. Moreover, we give an interpretation of influences of defects on the thermal transport through CNTs in terms of thermal resistance associated with defects.

This paper is organized as follows. In Sec. II, we explain the NEMD method for thermal transport phenomena. The system treated in this paper and the calculation procedure of thermal conductivity are briefly summarized. In Sec. III, our NEMD results (thermal currents, temperature profiles, thermal conductivities, and thermal resistances) are presented. We find that the vacancy defects markedly suppress the thermal conductivity more than the case of isotope impurities. Thermal annealings are attempted to improve the reduced thermal conductivity caused by the vacancy defects. The paper is finally summarized in Sec. IV.

II. NUMERICAL METHOD

Recent experiments [9, 10] and theories [24] have concluded that heat in CNTs is dominantly transported by phonons at room temperature, independent of whether CNTs are metallic or semiconducting. To understand thermal transport by phonons in CNTs, we perform NEMD simulations with the Tersoff-Brenner bond-order potential that accurately reproduces several physical properties (e.g., structural, mechanical, and thermal properties) of carbon materials such as diamond, graphite, and CNTs. In our NEMD simulations, we assign different temperatures, \( T_L \) and \( T_R (> T_L) \), to the left- and right-end layers of CNTs to generate a thermal current through the CNTs (see Fig. 1). Here, the temperature \( T \) is defined by...
FIG. 1: Schematic diagram of (8,0) carbon nanotube. The carbon atoms indicated by black spheres in each end layer are fixed. The temperatures of the blue and red layers are controlled as \( T_L \) and \( T_R (> T_L) \), respectively. The thermal current \( J_{th} \) flows through the CNTs from right to left.

The thermal conductivity \( \lambda \) is calculated from the Fourier law,

\[
J_{th} = -\lambda \frac{dT}{dz},
\]

where \( J_{th} \) is the steady-state thermal current and \( dT/dz \) is the temperature gradient along the tube axis (\( z \)-axis). In order to estimate \( J_{th} \), we calculate the time development of thermal current defined by

\[
J_{th}(n) = \frac{1}{S} \sum_{j=1}^{n} \left[ \Delta Q_R(j) - \Delta Q_L(j) \right],
\]

where \( \Delta t \) is the MD time step, \( \Delta Q_R(j) \) and \( \Delta Q_L(j) \) are additional kinetic energies at \( j \)th time step by the Gaussian thermostat to maintain the temperatures of the right- and left-end layers, respectively. The factor 2 in the denominator comes from the arithmetic average of the incoming current toward the hot layer and the outgoing current from the cold layer. The cross-sectional area \( S \) of CNT is taken to be an annular ring with a thickness of 3.4 Å, which is the interlayer distance of graphite.

III. RESULTS AND DISCUSSION

We first focus on the effect of vacancy defects on the thermal conductivity of CNTs at room temperature. Figure 2 shows the time development of thermal current for the (8,0)-semiconductor CNT with the vacancy concentrations of 0.0 (red), 0.5 (green), 1.0 (blue), and 1.75 % (black). Here, the tube length is assumed to be 108 Å including 25 unit cells (800 carbon atoms), and the temperatures at the left- and right-end layers of the CNT are assigned as \( T_L = 250 \) K and \( T_R = 350 \) K, respectively. The thermal currents for all vacancy concentrations attain steady states in approximately 200 ps and consequently become constant. Steady-state thermal current decreases monotonically with increasing vacancy concentration \( \rho \). For \( \rho = 0.0, 0.5, 1.0, \) and 1.75 %, \( J_{th} = 2.43, 1.74, 1.40, \) and 1.17 nW/Å², respectively.

Figure 3 shows the temperature profiles of the CNTs with \( \rho = 0.0 \) (red solid curve) and 1.0 % (blue solid curve) as typical examples. The temperature profiles for \( \rho = 0.0 \) and 1.0 % exhibit linear behavior with finite gradients of \( dT/dz \) = 0.276 (red dashed curve) and 0.662 K/Å (blue dashed curve) in the central region of the CNTs, respectively. The finite gradient behavior for \( \rho = 0.0 \) means
that the thermal transport in CNTs is diffusive at room temperature even for perfect CNTs without any defects. This is in contrast with ballistic thermal transport in perfect CNTs with flat temperature profiles at low temperatures. It is known that the phonon transport in perfect CNTs shows a crossover from the ballistic to the diffusive regime as temperature increases. On the other hand, the temperature gradient for defective CNTs is steeper than that for perfect ones because incident phonons from the temperature-controlled left- and right-layers are scattered by vacancy defects. Thermal resistances due to vacancy defects will be estimated below.

In the vicinity of the left- and right-end layers of the CNT, the temperature profiles in Fig. 3 exhibit a strong nonlinear behavior, which is attributed to the strong scattering by the temperature-controlled layers. Similar behaviors were also reported in previous NEMD simulations [17, 18, 26]. To argue this point would deviate us from the main subject of this paper.

Figure 4 shows the dependence of thermal conductivity on defect concentration. The thermal conductivity $\lambda$ is calculated from Eq. (1). As seen in Fig. 4, thermal conductivity decreases significantly as defect concentration increases. Surprisingly, it decreases by approximately 75% with only 1.0% vacancy defects. This result is in qualitatively good agreement with previous results from the equilibrium molecular dynamics simulations by Che et al. [14]. On the other hand, it is known that the isotope (¹³C and ¹⁴C) impurity does not reduce thermal conductivity rapidly compared with the case of vacancy defects [16, 17]. As mentioned in Sec. I, the 40-50% ¹⁴C impurity reduces the thermal conductivity to approximately 60% [17]. This is because the isotope impurity does not disrupt the hexagonal network of CNTs in contrast to vacancy defects.

Next, we discuss the relation between the thermal conductivity $\lambda$ and vacancy concentration $\rho$. The total phonon mean free path $l_{\text{tot}}$ of the CNT with vacancy defects consists of $l_{\text{pure}}$ being the phonon mean free path in pure CNT and of $l_{\text{vac}}$ being that induced by vacancy defects, that is $l_{\text{tot}}^{-1} \approx l_{\text{pure}}^{-1} + l_{\text{vac}}^{-1}$. If the phonon group velocity $v$ and heat capacity $C$ are not affected by the vacancy defects, we obtain the relation,

$$\lambda(\rho) = \frac{\lambda_{\text{pure}}}{1 + \lambda_{\text{pure}}/\lambda_{\text{vac}}},$$

using the kinetic relation $\lambda = Cv l_{\text{tot}}$. We also assume that the contribution of vacancy to thermal conductivity $\lambda_{\text{vac}}$ is related with the vacancy concentration $\rho$ via a scaling law $\lambda_{\text{vac}} \propto \rho^{-\alpha}$. Thus, we can obtain the relation between the thermal conductivity and vacancy concentration:

$$\lambda(\rho) = \frac{\lambda_{\text{pure}}}{1 + A\rho^{\alpha}}.$$  \hspace{1cm} (4)

Our numerical data in Fig. 4 can be well fitted with this relation by choosing the fitting parameters, $A = 2.94$ and $\alpha = 0.694$. The fitting curve is shown by the dashed curve in Fig. 4.

We attempt to improve the reduced thermal conductivity due to vacancy defects by heat treatment. In our simulations, the defective CNTs are heated at 1400 K for 0.5 ns and quenched at 0 K in 0.1 ns. We observed that vacancy defects in CNTs before annealing are transformed into two other types of defect, one consisting of single pentagon-one dangling bond atomic configurations.
FIG. 6: Temperature profiles of CNTs with (a) a vacancy defect and (b) a 5-6 defect. Dashed lines represent the linear fitting of the temperature profiles in the regions far from the defect at $z = 0$.

(1) From the detailed observations of the structure of annealed CNTs, it turns out that approximately 80% of vacancy defects changed into 5-6 defects and the rest into 5-1db defects. The stabilization energies of the 5-1db and 5-6 defects are $E_{stabilize} = -1.52$ eV and $E_{stabilize} = -1.80$ eV, respectively. This result is consistent with the dominant existence of 5-6 defects after annealing.

We estimate the thermal resistances associated with the 5-6 and vacancy defects in the (8,0) CNT, to clarify the dependences of the different types of defect on thermal conductivity. The temperature profiles around a vacancy defect and a 5-6 defect are shown in Figs. 6 (a) and (b), respectively. As clearly seen in the figures, a large step appears at the point of the defect in both temperature profiles. We estimated the thermal resistance [30] per defect, which is defined as

$$R_{th} = \frac{\Delta T}{J_{th}},$$

where $\Delta T$ is the magnitude of the temperature step. The magnitudes for the vacancy and 5-6 defects are $\Delta T = 12.5$ and $10.2$ K, respectively. Therefore, the thermal resistance $R_{th}$ for the 5-6 defect is estimated as $4.58$ KÅ$^2$/nW, which is smaller than that for the vacancy defect of $5.53$ KÅ$^2$/nW. Thus, we expect that the dominant existence of 5-6 defects accounts for the improvement in thermal conductivity.

Keeping the above in mind, we repeat a series of NEMD simulations using the obtained structures by the simulated annealing as initial conditions. The thermal conductivities increase by $\sim 7\%$ compared with those before annealing. This recovery by the aid of thermal treatment is much smaller than the reduction due to vacancy defects. Considering this fact, defect-repair methods other than thermal annealing are required to restore thermal conductivity more. High-quality CNTs are desirable to induce the intrinsic high thermal conductivity of CNTs.

IV. SUMMARY

In this study, we elucidated the role of structural defects on thermal transport in CNTs within the framework of the NEMD method employing the Tersoff-Brenner potential. Vacancy defects decrease thermal conductivity markedly in comparison with isotope impurities, because the vacancy defects disrupt the hexagonal network of CNTs locally in contrast with the isotope impurities. Furthermore, thermal annealing was performed to improve the reduced thermal conductivity due to vacancy defects. After the thermal annealing, the thermal conductivity is improved because the vacancy defects are transformed into other structural defects (called 5-6 and 5-1db defects) with small thermal resistances by annealing.

Acknowledgments

We would like to thank Prof. Yoshikazu Homma for valuable discussions about defects in carbon nanotubes. This work was supported in part by the “Academic Frontier” Project of MEXT (2005-2010). Part of the numerical calculations was performed on the Hitachi SR11000s at ISSP, The University of Tokyo.

[1] S. Iijima, Nature (London) 354, 56 (1991).
[2] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998).
[3] J. Han, M. P. Anantram, R. L. Faffe, J. Kong and H. Dai, Phys. Rev. B 57, 14983 (1998).
[4] P.M. Ajayan, V. Ravikumar and J.-C. Charlier, Phys. Rev. Lett. 81, 1437 (1998).
[5] K. Nordlund, J. Keinonen and T. Mattila, Phys. Rev. Lett. 77, 699 (1996).
[6] A. V. Karashennikov, K. Nordlund, M. Sirviö, E. Salonen and J. Keinonen, Phys. Rev. B 63, 245405 (2001).
[7] M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor and K. Stokbro, Phys. Rev. B 65, 165401 (2002).
[8] A. Hashimoto, K. Suenaga, A. Gloter, K. Urita and S. Iijima, Nature (London) 430, 870 (2004).
[9] J. Hone, M. Whitney, C. Piskoti and A. Zettl, Phys. Rev. B 59, R2514 (1999).
[10] J. Hone, M. C. Liaguno, N. M. Nemes, A. T. Johnson, J. E. Fischer, M. J. Casavant, J. Schmidt and R. E. Smalley, Appl. Phys. Lett. 77, 666 (2000).
[11] P. Kim, L. Shi, A. Majumdar and P.L. McEuen, Phys. Rev. Lett. 87, 215502 (2001).
[12] D. J. Yang, Q. Zhang, G. Chen, S. F. Yoon, J. Ahn, S. G. Wang, Q. Zhou, Q. Wang and J. Q. Li, Phys. Rev. B 66, 165440 (2002).
[13] M. Fujii, X. Zhang, H. Xie, H. Ago, K. Takahashi, T. Ikuta, H. Abe and T. Shimizu, Phys. Rev. Lett. 95, 065502 (2005).
[14] J. Che, T. Çağin and W. A. Goddard III, Nanotechnology 11, 65 (2000).
[15] A. Cummings, M. Osman, D. Srivastava and M. Menon, Phys. Rev. B 70, 115405 (2004).
[16] S. Maruyama, Y. Taniguchi and Y. Shibuta, Eurotherm 75, Champagne (2003).
[17] G. Zhang and B. Li, J. Chem. Phys. 123, 114714 (2005).
[18] S. Maruyama, Physica B 323, 193 (2002).
[19] S. Berber, Y.-K. Kwon and D. Tománek, Phys. Rev. Lett. 84, 4613 (2000).
[20] M. A. Osman and D. Srivastava, Nanotechnology 12, 21 (2001).
[21] A. Cummings, M. Osman, D. Srivastava and M. Menon, Phys. Rev. B 70, 115405 (2004).
[22] W. Zhang, Z. Zhu, F. Wang, T. Wang, L. Sun and Z. Wang, Nanotechnology 15, 936 (2004).
[23] P. K. Schelling, L. Shi, and K. E. Goodson, Materials Today 8, 30 (June 2005).
[24] T. Yamamoto, S. Watanabe and K. Watanabe, Phys. Rev. Lett. 92, 075502 (2004).
[25] H.-Y. Chiu, V. V. Deshpande, H. W. Ch. Postma, C. N. Lau, C. Mikó, L. Forró and M. Bockrath, Phys. Rev. Lett. 95, 226101 (2005).
[26] P. K. Schelling, S. R. Phillpot and P. Keblinski, Phys. Rev. B 65, 144306 (2002).
[27] D. W. Brenner, Phys. Rev. B 42, 9458 (1990).
[28] F. Zhang, J. Chem. Phys. 106, 6102 (1997).
[29] M. Tuckerman, B.J. Berne and G.J. Martyna, J. Chem. Phys. 97, 1990 (1992).
[30] A. Maiti, G.D. Mahan and S.T. Pantelides, Solid State Commun. 102, 517 (1997).