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THE VACANCY DEFECTS AND NITROGEN DOPING EFFECTS ON THE THERMAL CONDUCTIVITY OF CARBON NANOTUBES: MOLECULAR DYNAMICS SIMULATION

Shih-Kai Chien*
*Author for correspondence
Department of Mechanical Engineering,
University of National Cheng Kung University
No.1, University Road, Tainan City,
Taiwan,
E-mail: n1896101@mail.ncku.edu.tw

ABSTRACT

The influence of vacancy defects and nitrogen doping on the thermal conductivity of typical armchair (10,10) single-walled carbon nanotubes is investigated using a molecular dynamics (MD) simulation. The second generation reactive empirical bond order potential and Tersoff potential are used to describe the interatomic interactions and the thermal conductivities are calculated using the Müller-Plathe approach (also called non-equilibrium MD simulation). Vacancy defects decrease the thermal conductivity whereas the substitution of nitrogen at vacancy sites improves the thermal conductivity. These results are useful for designs of thermal management networks, thermal rectifiers, and phonon devices which require extremely high thermal conductivity and structural stability.

INTRODUCTION

The work of Iijima [1] revealed the unique properties of carbon nanotubes (CNTs). Their remarkable electronic, mechanical properties, and extremely high thermal conductivity have attracted a lot of attention [2-4]. These properties are likely related to their graphitic lattice and low-dimensional structure. Due to the high cost of CNT experiments, molecular dynamics (MD) simulation is commonly used for investigating the mechanical properties of CNTs. Several MD simulations have shown ultrahigh thermal conductivities for CNTs of $300 \sim 6600\ Wm^{-1}K^{-1}$ [5, 6], which is mainly contributed by phonons rather than electrons at room temperature or below [7]. Zhang et al. [8] suggested that a nanoscale device with various heat conductivities can be made using nanotubes of different chirality. A single atomic layer, either in aligned or nonaligned form, provided them with great advantages for making composite materials. These features give CNTs great potential in thermal management applications [9, 10].

However, it is virtually impossible to obtain perfect CNTs. Defects which influence the physical and mechanical properties, inevitably occur during the growth of CNTs. Lu and Pan [11] studied the structural configuration and formation energy of point defects which depend on the radius and chirality, as well as the electric properties of a tube. Sammalkorpi et al. [12] studied the influence of various numbers of vacancy defects on the Young's modulus and final tensile strength of carbon nanotubes. Defects can also fundamentally change the thermal conductivity. The thermal conductivity of CNTs with topological defects has been studied [5], but the effect of the reconstruction of vacancy defects on the thermal properties of CNTs has not been investigated. Several studies have suggested doping CNTs with boron (B) and/or nitrogen (N) atoms [13-15]. Boron and nitrogen atoms are the natural choices for dopants, since B/N have roughly the same atomic sizes as that of carbon (C). Another way to reconstruct the defects of CNTs is to increase the temperature to higher than 2600 K [16].

In this paper, a model for typical armchair (10,10) single-walled carbon nanotubes (SWCNTs) that has various numbers of vacancy defects at various locations is developed to investigate the effects of vacancy defects and nitrogen doping on the thermal conductivity. MD simulation with analytical potentials is used to simulate the heat transfer mechanism. The reconstructed CNTs show identical phonon spectra to the perfect structure.

MODEL AND METHODS

Armchair (10,10) SWCNTs with a length of $L_{cnt} = 20$ nm and a periodic boundary condition in the axial direction are considered. The interactions between two atoms (C-C) are described using the second-generation reactive empirical bond order (REBO) potential [17], whereas those between different atoms (C-N) are described using the Tersoff potential [18]. Table 1 shows the Tersoff potential parameters for C and N, as proposed by Tersoff [18] and Kroll [19]. The thermal conductivities are calculated by introducing the Müller-Plathe

approach [20], which is a straightforward way of calculating the thermal conductivity in a non-equilibrium steady state. The method imposes the heat flux and then obtains the temperature gradient from simulations. Simulations were performed using the LAMMPS MD package [21]. As the vacancy concentration increased, the thermal conductivity smoothly decreased at an unexpected rate [5]. The various numbers of vacancy defects and nitrogen doping investigated in this study are illustrated in Fig. 1. The present study focuses on the effects of vacancy defects and nitrogen doping on thermal conductivity without considering chirality and length.

Table 1. Parameters for C and N used for Tersoff potential.

Parameter	N [19]	C [18]
A (eV)	1.1000×10^{4}	1.3936×10^{3}
B (eV)	2.1945×10^{2}	3.467×10^{2}
λ (1/Å)	5.7708	3.4879
μ (1/Å)	2.5115	2.2119
β	1.0562×10^{-1}	1.5724×10^{-7}
n	12.4498	0.72751
c	7.9934×10^{4}	3.8049×10^{4}
d	1.3432×10^{2}	4.384×10^{0}
h	–0.9973	–0.57058
R (Å)	2.0	1.8
S (Å)	2.3	2.1
Interactions (i-j)	$C-N$ [19]	
χ_{i-j}	0.9685	
ω_{i-j}	0.6381	

In the MD simulations, a 0.5 fs time step was used and a 200 ps Nosé-Hoover thermostat coupling (T=300 K) was used to equilibrate the systems. After equilibration, 500 ps was used for the Müller-Plathe approach and NVE ensemble. Two separated slabs were located at half of the nanotube length L/2. Fig. 2 shows the model of the heat source and heat sink. A heat flux J was created by switching the momentum between the hottest atom velocity in the cold (sink) region and the coldest atom velocity in the hot (source) region. During $N_{transfer}$ exchange were performed, the heat flux can thus be expressed as following equation:

$$J=\frac{\sum_{N_{transfer}}\frac{1}{2}m(v_h^2-v_c^2)}{2At_{transfer}} \quad (1)$$

where m is the mass of the atoms, t is the time period of the simulation, A is the cross-sectional area obtained by considering the CNTs as thin shells with a thickness of a single C-C bond length, and v_h and v_c are the velocities chosen from the cold and hot regions, respectively. After the system reaches equilibrium, the thermal conductivity λ of CNTs is evaluated as:

$$\lambda=-\frac{\langle J(t)\rangle}{\langle \partial T/\partial z\rangle} \quad (2)$$

where $\partial T/\partial z$ is the temperature gradient along the CNT axis and the brackets denote a statistical time average. The thermal conductivity of carbon materials is dominated by atomic vibrations or phonons. A detailed analysis of the phonon spectra under various nitrogen doping numbers was conducted to elucidate the physical basis for the change of thermal properties. The phonon power spectrum $D(\omega)$ was calculated from the Fourier transform of the velocity auto-correlation function [22]:

$$\gamma(t)=\left\langle\sum v(t)\cdot v(0)\right\rangle\Big/\left\langle\sum v^2(0)\right\rangle \quad (3)$$

where t is the simulation time, $v(t)$ is the atomic velocity, and brackets indicate that the summation is averaged over a suitable ensemble of CNTs.

RESULTS AND DISCUSSION

The influences of vacancy defects and nitrogen doping on the thermal conductivity were predicted using the proposed structural model. First, simulations were performed on perfect CNTs and on CNTs with various numbers of vacancy defects. Second, vacancy defects were reconstructed using nitrogen doping and combine the REBO with Tersoff potentials to simulate its phenomena. This reconstruction method can be easily implemented using current experimental techniques.

Fig. 3 plots the temperature profile as a function of position of half CNTs. The temperature profile of the other half is symmetrical. This figure only shows the perfect CNTs, double vacancy defects, double N doping, and three double vacancy defects (see right inset) types of CNT at 300 K. For perfect CNTs, the temperature curves decrease smoothly. However, the temperature suddenly drops at the positions of vacancy defects or nitrogen doping, resulting in interfacial (or Kapitza) thermal conductivities of approximately $\lambda_{interface}=69.147\ GWm^{-2}K^{-1}$ (double vacancy defects), $84.528\ GWm^{-2}K^{-1}$ (double N doping), and $55.674\ GWm^{-2}K^{-1}$ (three double vacancy defects). The interfacial thermal conductivity is defined as $\lambda_{interface}=J/2A\Delta T$ [23], where J is the thermal flux, A is the cross-sectional area, and ΔT is the temperature drop at the interface. To analyze the significance of the interfacial thermal resistance in terms of the equivalent length of perfect CNTs that provide the same thermal resistance, the Kapitza length is defined as $L=\lambda_0/\lambda_{interface}$, where $\lambda_0=65.53\ Wm^{-1}K^{-1}$ is the thermal conductivity of perfect CNTs. Thus, the defects or nitrogen doping are equivalent to a segment of CNTs with Kapitza lengths of 0.9476 nm (double vacancy defects), 0.7752 nm (double N doping), and 1.177 nm (three double vacancy defects). The numbers of vacancy defects increases with increasing interfacial thermal resistance. Therefore, a large Kapitza length limits the heat transfer performance of CNTs.

The dependence of the thermal conductivity on the CNT vacancy defects or nitrogen doping at 300 K is summarized in Fig. 4. The figure shows that the thermal conductivities of CNTs with vacancy defects or nitrogen doping are lower than their reference value λ_0 of perfect CNTs. The parameter λ_0 is the thermal conductivity of CNTs without any vacancy defects and nitrogen doping, where $\lambda_0=65.53\ Wm^{-1}K^{-1}$. This value is lower than the experimental value and that obtained in several MD simulations ($\approx 6600\ Wm^{-1}K^{-1}$) [3]. Because the system size here is shorter than the phonon scattering length (a

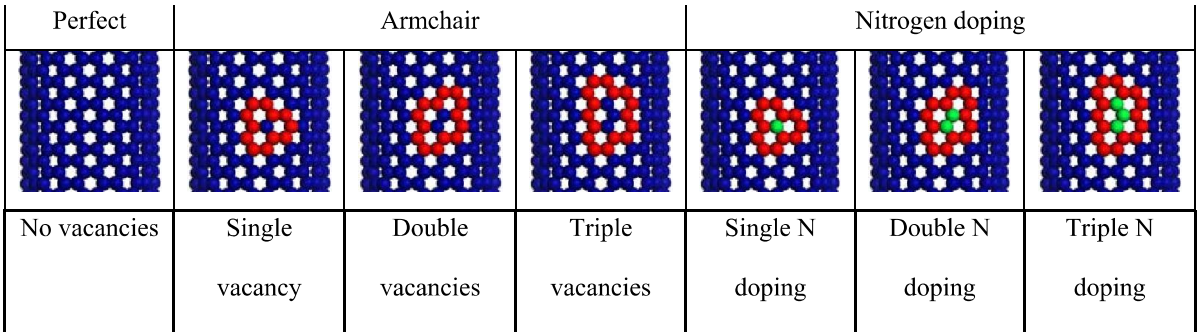

Fig. 1 Atomic structures of (10,10) SWCNTs with various numbers of vacancy defects (red) and nitrogen doping (green).

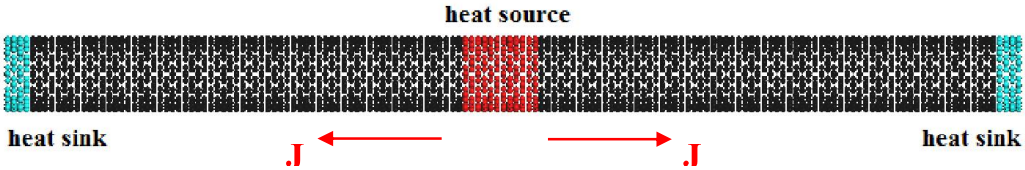

Fig. 2 Simulation model for thermal conductivity calculation: heat flux J moves from the heat source (red) region to the heat sink (blue) region.

few μm). Another reason for the divergence of the thermal conductivities is the potential used. The differences may be partially caused by the slightly different forms of the REBO, Tersoff-Brenner, and harmonic potentials. The results obtained in our work are in agreement with those obtained in a prior simulation report [24]. When vacancy defects occur, the thermal conductivity decreases with increasing number of vacancies. When the first vacancy defect forms, the thermal conductivity suddenly falls. In addition, the three double vacancy defects show the peak of the thermal conductivity which can be clearly elucidated by the lower Kapitza length. In CNTs with defects, the nitrogen doping reconstruction of vacancy defects enhances the thermal conductivity. This can improve the thermal conductivity by about 4% (for double N doping). When a vacancy defect forms, it leads to form hanging bonds around the vacancy. Nitrogen doping re-bonds the hanging bond, improving the stability of the structure.

Fig. 5 shows the phonon power spectrum for carbon atoms in perfect CNTs and in CNTs with nitrogen doping at 300 K. For single N, double N, and triple N doping, the positions of the peaks and the overall shape of the spectra do not change much, whereas the thermal conductivities decrease by about 6.1%, 7.2%, and 7.9%, respectively. This is due to the interfacial resistance increasing at the nitrogen doping position. This result suggests that the nitrogen doping reconstructs vacancy defects. In addition the nitrogen doping of CNTs is a possible way for thermal rectifiers, which is significant for an up-to-data electronic devices.

CONCLUSION

REBO (for CNTs) and Tersoff potentials (for nitrogen doping) along with the Müller-Plathe approach were used to calculate the thermal conductivity. It was found that vacancy defects and nitrogen doping affect the thermal transfer properties of CNTs at 300 K. Vacancy defects decrease thermal conductivity. For single, double, and triple vacancy defects, the thermal conductivity decreased by 8.1%, 10.9%, and 11.7%, respectively. Nitrogen re-bonds dangling bonds and improves the stability of CNTs. The thermal conductivities of single N, double N, and triple N doping, compared to those for vacancy defects, increased by about 2.1%, 4.2%, and 4.2%. It was found that nitrogen doping reconstructs the CNTs and improves thermal conductivity. The effects of temperature on the thermal conductance of CNTs were investigated. At the nanoscale, quantum effects influence the accuracy of the thermal conductance at lower temperatures and should thus be corrected. The numerical results of the thermal conductance agree with the experimentally observed values. These results can be used for designs of thermal management networks, thermal rectifiers, and phonon devices that require extremely high thermal conductivity and structural stability.

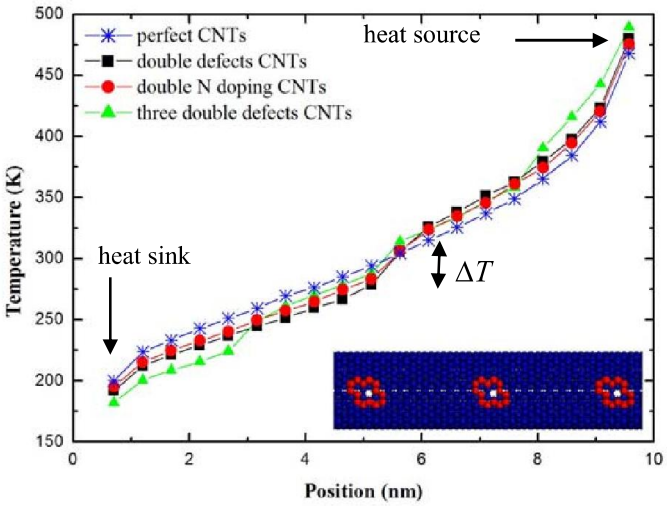

Fig. 3 Temperature profile along the axial position of half CNTs at 300 K.

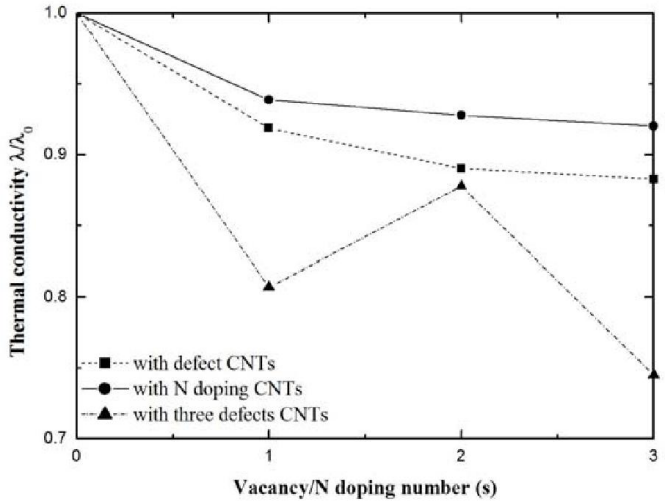

Fig. 4 Effect of various vacancy defects or nitrogen doping on thermal conductivity of CNTs at 300 K.

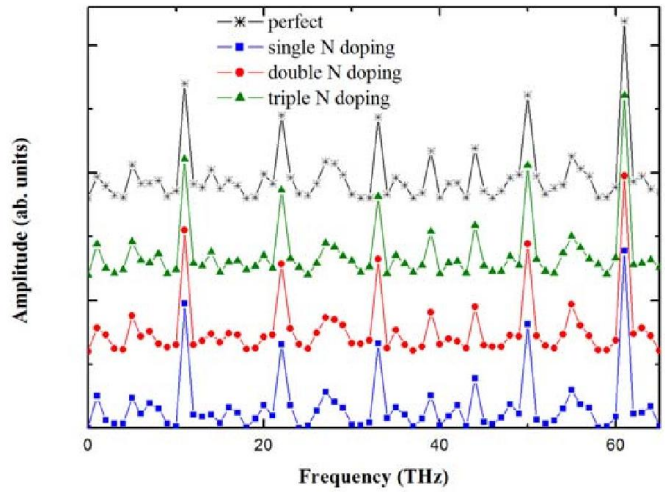

Fig. 5 Phonon spectra for CNTs with nitrogen doping at 300 K.

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