Toward Enhancing Thermal Conductivity of Polymer-based Thin Films for Microelectronics Cooling

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ABSTRACT

Thermal interface materials with high thermal conductivity can remove heat efficiently from electronic devices. Carbon nanotube/polymer composite is a good candidate for thermal interface materials. We calculated the thermal conductivity of vertically aligned carbon nanotube/polyethylene (CNT/PE) composite and compared it with vertically aligned CNT and PE based on equilibrium molecular dynamics. We found that the thermal conductivity of CNT/PE composite along the alignment direction can be as high as 470.1±45.1 W/(mK), which is about 40% of that of CNT and about 16 times larger than that of PE. This can be well explained by vibrational density of states. The ultrahigh thermal conductivity of aligned CNT/PE composite may open up exciting opportunities towards enhancing the cross-plane thermal conductivity of polymer-based thermal interface materials for efficient microelectronics cooling.

KEY WORDS: Thermal Interface Materials, Thermal Conductivity, CNT/PE Composite, Equilibrium Molecular Dynamics, Vibrational Density of States

NOMENCLATURE

D	vibrational density of states
J	heat flux, W
k	thermal conductivity, W/(mK)
N	number of atoms
t	time, s
T	temperature, K
V	volume, m^3
k_B	Boltzmann constant

Greek symbols

ρ	mass density, g/cm^3
τ	the delay time, s
ω	vibrational frequency, THz
ν	velocity, m/s

Subscripts

z	direction in coordinate system
ij	direction component

INTRODUCTION

One of the most critical problems with current electronic devices is thermal management- removing heat from nanoscale regions. The heat intensities increase steeply, created by an exponential increase in power densities and a significant decrease in device sizes. Thermal interface materials are essential for efficient heat removal from thermoelectric power generators and electronic systems[1, 2]. However, polymer-based thermal interface materials usually have very low thermal conductivity resulting in low-efficient heat removal. Therefore, improving the thermal conductivity of thermal interface materials is crucial. Significant attention has been paid to vertically oriented carbon nanotubes (CNT) arrays as promising thermal interface materials due to their unique structural feature and ultrahigh thermal conductivity. CNTs alone, however, have been demonstrated to possess large contact resistances due to the non-uniform heights across the CNTs.[3, 4]

CNT/polymer composites have been studied to take advantages of the high thermal conductivity of CNTs and the conformity of polymers to reduce contact resistance. Unfortunately, due to the large thermal resistance between CNT and polymer matrix, the thermal conductivity of CNT/polymer composites with randomly dispersed CNTs in a polymer matrix only shows a modest enhancement of 2~3 times larger thermal conductivity than that of amorphous polymers (~0.2 W/(mK)).[5-9] On one hand, it has thus been proposed to vertically align CNTs in a polymer matrix to enhance the thermal conductivity. Kim *et al.*[10] found that alignment of 5 wt% CNTs in amorphous ethylene propylene diene rubber matrix (0.28 W/(mK)) resulted in larger improvements in thermal conductivities (0.7 W/(mK)). Marconnet *et al.* demonstrated that nanocomposites with a 17 vol% aligned CNTs in amorphous epoxy could enhance the thermal conductivity up to ~4.9 W/(mK). On the other hand, it has been proposed to enhance the thermal conductivity by increasing the thermal conductivity of the polymer matrix. Haggenmueller *et al.* [9] showed that thermal conductivity of CNT/PE composite with a 20 vol % randomly oriented CNT and high-density PE (78% crystalline) increases to 3.5 W/(mK). If one could combine vertically aligned CNT with vertically aligned crystalline polymer chains, it should significantly boost the thermal conductivity. By non-equilibrium molecular dynamics, Liao *et al.*[11] showed that aligned CNT-PE composites can have a thermal conductivity ~99.5 W/(mK) with a length of 320 nm although the cross section of CNT is heavily distorted. Further enhancement of the thermal conductivity of CNT/polymer composites is still in great demand as it can translate to huge energy saving on cooling. In this paper, we studied thermal conductivity of vertically-aligned CNTs and polymer chains while well maintaining the CNT shapes. In addition, our polymers chains were located outside of CNT, which is different from Ref. 11 and should be more practical to synthesize. We found that thermal conductivity of CNT/PE composite along the alignment direction can be as high as 470.1±45.1 W/(mK) based on equilibrium molecular dynamics (EMD) simulation. This remarkable enhancement can be well explained by calculating vibrational density of states.

METHOD

We built all the vertically aligned structures in BIOVIA Materials Studio[12] as shown in Figure 1. We put 4 CNTs (3, 3) in a triclinic box (Figure 1(a)) and 8 polyethylene chains (PE) in an orthogonal box (Figure 1(b)). For aligned carbon nanotubes and aligned polyethylene (CNT/PE) composite, we combine 4 CNTs (3, 3) and 4 polyethylene chains in an orthogonal box (Figure 1(c)). The length of all the structures is about 50 Å. We first performed geometry optimization using Polymer Consistent Force-Field (PCFF) within Materials Studio. PCFF, a class II potential which includes anharmonic bonding terms [13, 14], is intended for applications in polymers and organic materials. We used LAMMPS package[15] to perform EMD simulations with PCFF. EMD simulations have been widely used and have shown good agreements with experiments [16-20]. In EMD simulations, the temperature is kept uniform throughout the system and thermal conductivity is determined from the autocorrelation of instantaneous heat flux through the Green-Kubo formula based on linear response theory[21, 22]. The thermal conductivity is given by

$$k_{ij}(T) = \frac{1}{V k_B T^2} \int_0^{\infty} \langle \vec{J}_i(t) \cdot \vec{J}_j(t+\tau) \rangle \, d\tau \qquad (1)$$

where k_{ij} is the thermal conductivity tensor, V is the volume of the simulation system, k_B is Boltzmann constant, T is the absolute temperature, J is the heat flux, ij are the directional components, and τ is the delay time. We chose 0.5 fs as the timestep and 10.0 Å as a cutoff distance for the Lennard-Jones interaction. Since all the CNT or PE chains are along z direction, we only calculated thermal conductivity in the z direction (k_z). All the k_z values were averaged over 5 different ensembles. For all the structures, periodic boundary conditions were applied in x, y and z direction. We relaxed the systems in an NPT, an NVT, and an NVE ensemble consecutively for 500 ps in each ensemble to make sure the systems had been equilibrated before we collected heat flux data in an NVE ensemble for another 500 ps.

The vibrational density of states (VDOS), $D(\omega)$, is determined by the Fourier transform of the velocity autocorrelation[23].

$$D(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\sum_{i=1}^{N} \langle v_i(t) \cdot v_i(0) \rangle}{\sum_{i=1}^{N} \langle v_i(0) \cdot v_i(0) \rangle} e^{i\omega t} dt \qquad (2)$$

where N is number of atoms, and v_i denotes the velocity of the *i*-th atom.

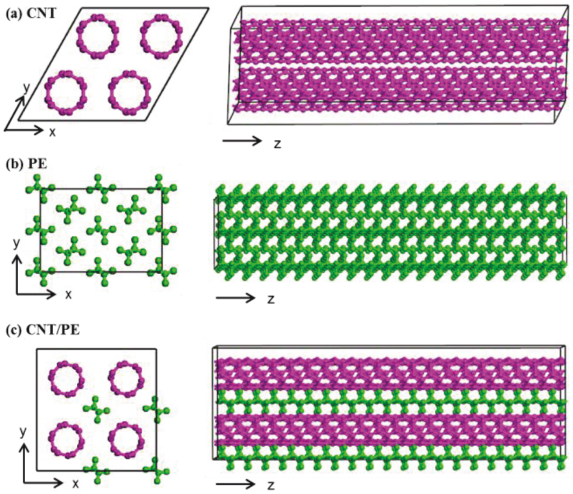

Fig. 1 Simulation supercells: (a) vertically aligned CNT (3, 3); (b) vertically aligned PE; (c) vertically aligned CNT/PE composite; All the structures have been applied periodic boundary conditions. The structures on left side show the top view of the cross section in x-y plane and structures on right side show side view along z direction.

RESULTS AND DISCUSSION

First of all, we calculated the k_z of all structures as summarized in Table 1. The k_z of vertically aligned CNT (3,3) is 1250.1±84.7 W/(mK), which falls into the typical range of reported values for individual single-wall CNTs based on MD simulation and experiments[24]. Vertically aligned PE has a k_z of 29.9±1.2 W/(mK), which agrees with the reported MD values for 3D crystalline PE from Henry *et al.*[25]. Note that this value is about two orders of magnitude higher than that of amorphous polymers, which reiterates the importance of polymer morphology on thermal transport. Remarkably, we found the k_z of vertically aligned CNT/PE composite is as high as 470.1±45.1 W/(mK), which is a record-high value for CNT/PE composites. This value is two orders of magnitude higher than the highest experimental value on CNT/PE composites (~3.5 W/(mK))[9]. This highlights the incredible potential of enhancing k_z by well-aligning both components in the composites.

Table 1. Thermal conductivities of three different structures

	CNT	PE	CNT/PE
k_z	1250.1±84.7	29.9±1.2	470.1±45.1
ρ	2.29	1.00	2.04

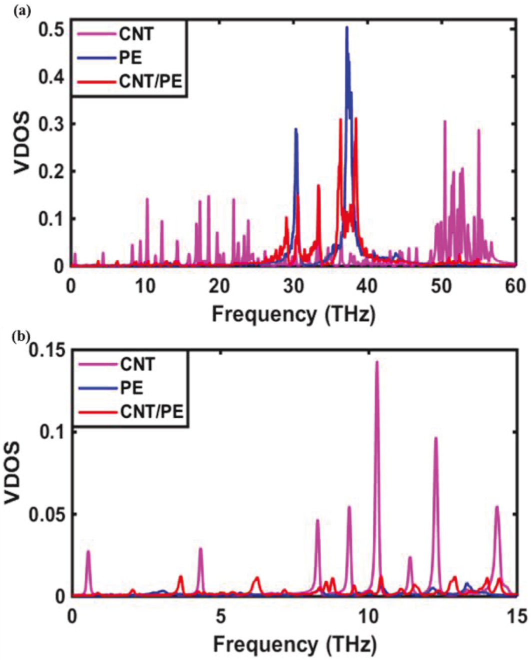

Fig. 2 (a) VDOS along z-direction of different structures: vertically aligned CNT (3, 3), vertically aligned PE, and vertically aligned CNT/PE composite; (b) Zoom-in VDOS of 0-15 THz.

In order to look into the details of phonon modes which lead to the k_z in Table 1, we calculated their VDOS as shown in Figure 2(a). Obviously, CNT has many high peaks in low-frequency range (0~15THz) (Figure 2(b)). Because low-frequency phonon modes are dominant heat carriers, this can explain why vertically aligned CNT has the highest k_z among these three structures. Vertically aligned CNT/PE composite has much higher peaks in frequency (0~15 THz) than vertically aligned PE, which can well explain about 16 times enhancement in k_z of CNT/PE compared to PE.

SUMMARY & CONCLUSIONS

In summary, we applied equilibrium molecular dynamics simulations to study vertically aligned CNT/PE composite and compared it to vertically aligned CNT and PE. We observed about 16 times enhancement in thermal conductivity in comparison to that of vertically aligned PE, which can be attributed to the difference in VDOS. Vertically aligned CNT/PE composite has higher VDOS peaks in frequency (0~15 THz) than vertically aligned PE. Remarkably, there is at least 130 times enhancement in k_z of CNT/PE composite compared to isotropic CNT/PE composite containing 20 vol% randomly oriented CNT and high-density PE (78% crystalline) (~3.5 W/(mK))[9]. This highlights the potential to enhance the thermal conductivity by well-aligning both components in CNT/polymer composites. Although bulk samples were studied, we expect this trend to hold for thin-films. We will work on experimental demonstration as the next step. This study may open up an innovative way to engineer thermal interface materials with ultrahigh thermal conductivity for efficient microelectronics cooling.

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