Thermal conductivity of B-C-N and BN nanotubes

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We have measured the temperature-dependent thermal conductivity $\kappa(T)$ of boron-carbon-nitride (B-C-N) and boron nitride (BN) nanotube mats. The thermal conductivity of B-C-N nanotubes is phonon dominated and reflects dimensional effect below 70 K. We employ a new analysis method to estimate the intrinsic $\kappa(T)$ of BN nanotubes converted from B-C-N nanotubes, and find that at room temperature $\kappa(T)$ of a multiwalled BN nanotube is within 0.04–0.32 times that of a multiwalled carbon nanotube. The lower $\kappa(T)$ of BN nanotubes than that of carbon nanotubes may be due to the enhanced isotope disorder effect in one dimension. © *2005 American Vacuum Society.* [DOI: 10.1116/1.2008266]

I. INTRODUCTION

As the feature sizes of microelectronic devices and circuits continue to be scaled down, the problem of thermal management becomes ever more important. For some photonic devices, the heat generation density has reached 10^6 W/cm^3. Unfortunately, very few materials are known to exhibit high thermal conductivity at reduced dimensions. Traditional semiconductors like Si show a dramatic suppression of thermal conductivity at the nano-scale.[1] Insulators used in microelectronic manufacture like Si_3N_4, SiO_2, and Al_2O_3 are all poor thermal conductors in traditional polycrystalline forms.

Boron nitride (BN) nanotubes have been shown to exhibit many interesting properties.[2,3] BN tubes can be viewed as geometrically derived by rolling a hexagonal BN sheet into a cylinder much like carbon nanotubes can be viewed as rolling a graphene sheet into a cylinder. Both single-walled and multiwalled BN nanotubes have been synthesized in recent years.[4] Because of low-dimensional effects, carbon and BN nanotubes have been predicted to exhibit unusual thermal properties.[5,6] The temperature-dependent thermal conductivity $\kappa(T)$ of an isolated multiwalled carbon nanotube has been measured by using a microfabricated device and its room temperature value exceeds 3000 W/m K.[7] Molecular dynamics simulations suggest an even higher value ($\sim$6600 W/m K) at room temperature for a (10,10) carbon nanotube.[8] Comparison with the κ(290 K)–400 W/m K of graphite indicates a large enhancement of phonon mean free path in carbon nanotubes. Similarly, the κ(290 K) of hexagonal BN crystal has been reported to be comparable to that of graphite.[9] Hence it is interesting to ask whether BN nanotubes also exhibit high thermal conductivity like carbon nanotubes.

Here we report $\kappa(T)$ measurements on B-C-N and BN nanotubes. The low temperature behavior of $\kappa(T)$ shows dimensional effects expected for large diameter nanotubes. And $\kappa(T)$ is dominated by phonons. Based on a substitution reaction that converts B-C-N nanotubes to pure BN nanotubes, we bracket the ratio of κ(290 K) of a single BN nanotube to that of a single carbon nanotube to be 0.04–0.32.

II. EXPERIMENT

B-C-N nanotubes were synthesized by a substitution reaction using multiwalled carbon nanotubes as a template.[10] B_2O_3 powder was placed in a crucible covered with carbon nanotubes. The crucible was held in a flowing nitrogen atmosphere at 1600 °C for 30 min. The mats of B-C-N nanotubes were made by first pressing the samples, followed by annealing at 150 °C in air. B-C-N nanotubes were transformed into BN nanotubes by a subsequent oxidation treatment at 650 °C.[11] The microstructure of the nanotubes was characterized by high-resolution transmission electron microscopy. B-C-N or BN nanotubes made by this method are predominantly multiwalled with an average diameter 6–8 nm and length $\sim$2 μm. Recent Raman and electron energy loss spectroscopy studies indicate that B-C-N nanotubes have strong phase separation between BN layers and carbon layers along the radial direction.[10,12]

Thermal conductivity was measured by a comparative method. A constantan rod whose $\kappa(T)$ had been measured was mounted in series with the sample using GE varnish. A chip resistor (vendor: VISHAY) was attached to the end of the constantan rod to provide heat. Type E thermocouples were used for determining the temperature difference, typically 0.8–1.2 K across the sample. In some measurements we employed two constantan rods, one before, one after the sample to estimate the heat loss through radiation and the thermocouples. The whole measurement process was as follows. First, we measured $\kappa(T)$ of mats of B-C-N nanotubes. Next, to estimate the carbon concentration in each sample, we used thermogravimetric analysis (TGA) to monitor the weight loss while heating the sample in oxygen at 650 °C for

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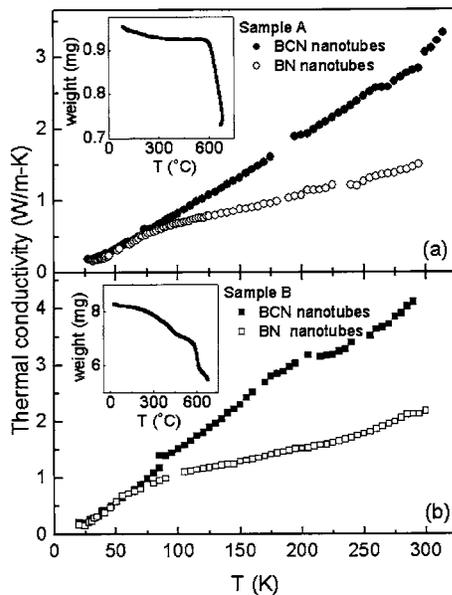[a)]Electronic mail: chihwei@berkeley.edu

FIG. 1. Thermal conductivity vs temperature for two different samples of nanotubes (a) before (closed symbols, B-C-N) and (b) after (open symbols, BN) the oxidation treatment. Insets show the corresponding weight vs temperature for each sample during the oxidation treatment. The weight ratio of carbon to BN is 0.30 and 0.50 in (a) and (b), respectively.

~30 min. This process had been demonstrated to completely remove the carbon nanotubes and transform the B-C-N nanotubes to pure BN nanotubes.[11] Macroscopic measurement showed that the heating/burning process did not alter the overall sample geometry. Finally, converted samples were mounted back to the thermal conductivity probe with the same thermocouple locations to minimize the geometrical uncertainties. $\kappa(T)$ of the mats of BN nanotubes was then measured.

III. RESULTS AND DISCUSSIONS

Figures 1(a) and 1(b) show $\kappa(T)$ of two samples before (B-C-N) and after (BN) the oxidation treatment. Both $\kappa(T)$'s of B-C-N and BN nanotubes show increasing thermal conductivity with increasing temperature. Note that the value $\kappa(T)$ shown here is the measured thermal conductivity without any density correction adapted in Refs. 13 and 14. A small slope change can be seen at ~100 K for BN nanotubes. The umklapp processes for hexagonal BN occurs at $T_U \sim 100$ K,[13] which indicates that the slope change of $\kappa(T)$ of BN nanotubes may be due to the umklapp processes in the mats. Since each nanotube has different chirality, the nonuniformity of the unit cell from one nanotube to another is expected to lead to a wide distribution of T_U in the mats. This would result in a somewhat smeared umklapp signature in the $\kappa(T)$ data. Similar observations have been reported for $\kappa(T)$ of mats of carbon nanotubes.[14,15]

The insets of Figs. 1(a) and 1(b) show the weight versus temperature monitored by TGA. Samples of Figs. 1(a) and 1(b) have a carbon to BN weight ratio 0.30 and 0.50, respectively. The difference of the two insets is due to the fact that sample B is more compact than sample A. Thus sample B
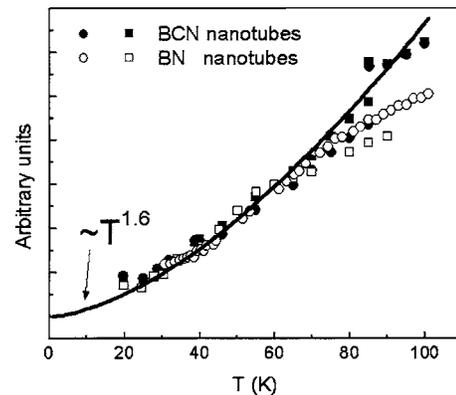
FIG. 2. Low temperature behavior of $\kappa(T)$ for B-C-N and BN nanotubes shown in Fig. 1. All the curves are normalized and can be fitted to a $T^{1.6}$ curve (solid line) below 70 K.

oxidizes slowly. Since the difference between the molecular weight of C_2 and BN is small, the weight ratio can be approximated to the number ratio of carbon layers to BN layers in each B-C-N nanotube.

Figure 2 shows the low temperature behavior of $\kappa(T)$ of B-C-N and BN nanotubes. All the curves are normalized and can be fitted to a $T^{1.6}$-dependent curve for T < 70 K. Since at low temperature $\kappa(T)$ is dominated by the heat capacity, the fact that the $\kappa(T)$ deviates from a linear temperature-dependent behavior reflects the intrinsic dimensionality of most large diameter nanotubes. Similar dimensionality effects on the low temperature $\kappa(T)$ have been observed for single-walled and multiwalled carbon nanotubes.[14,15]

Figure 3 shows the temperature-dependent electrical resistivity of sample A and its corresponding Lorenz number $L = \kappa\sigma/T$. The Lorenz number gives a good estimation of the electronic contribution to the total thermal conductivity. Comparing with the value derived from the free election gas ($L_0 = 2.45 \times 10^{-8}$ W Ω/K^2), the measured L is three orders of magnitude larger than L_0. Therefore, the thermal conductivity of B-C-N nanotubes is dominated by phonons for temperature below 300 K. This result is also consistent with the experiment on single-wall carbon nanotube mats.[15]

Of prime interest is the magnitude of the intrinsic thermal conductivity of BN nanotubes. Although previous experi-
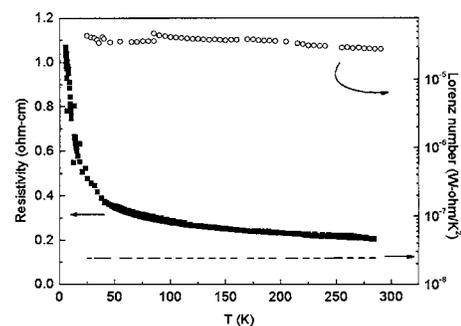

FIG. 3. Temperature-dependent resistivity of sample A (closed squares) and its corresponding Lorenz number (open circles). The Lorenz number derived from the free electron gas is also shown for comparison (dash lines).

mental results on $\kappa(T)$ of mats of carbon nanotubes reflect the intrinsic dimensionality of nanotubes at low temperature, the traditional experimental methods only give a lower limit of the magnitude of the intrinsic $\kappa(T)$ of a single nanotube. For example, the uncorrected $\kappa(290\ \mathrm{K})$ of single-walled carbon nanotube mats is only 0.7 W/m K which is believed to be lower than the intrinsic value by a factor of 2500–8300.[15] Besides, even if the measured $\kappa(T)$'s are corrected for the theoretical density of a close-packed bundle, the density correction factor in the reported $\kappa(T)$'s of mats are highly uncertain due to the difficulty in determining the actual microscopic sample geometry. For example, the corrected $\kappa(290\ \mathrm{K})$ of multiwalled carbon nanotube mats is only 25 W/m K,[14] while that of magnetically aligned single-wall carbon nanotubes films is 250 W/m K.[16] However, these values are still one to two orders of magnitudes smaller than that of an isolated multiwalled carbon nanotube measured by a microfabricated device (3000 W/m K).[7] Moreover, the electrical conductivity assumption used in Ref. 14 does not apply for insulating BN nanotubes. In the following paragraphs, we will use a novel analysis method to bracket the value of $\kappa(T)$ of an individual, multiwalled BN nanotube.

To estimate $\kappa(T)$ of a single BN nanotube, we employ an analysis method that necessitates the following justifiable assumptions:

1. For a single B-C-N nanotube, the BN layers and carbon layers have parallel contributions to the total thermal conductance.
2. Except for the carbon layers being removed from each B-C-N nanotube, the microscopic sample geometry does not change after the oxidation treatment.

The first assumption can be justified by the highly anisotropic thermal conductivity of graphite or hexagonal BN (c axis versus a-b plane). The weak van der Waals force implies that the intratube or intertube interactions have negligible contribution to the total thermal conductivity of B-C-N nanotubes in the axial direction. The second assumption relies on the structure of the outermost layer of B-C-N nanotubes. If the outermost layer is a BN layer, we expect that the microscopic geometry will not change after the oxidation treatment. If the outermost layer contains a carbon layer, the intertube interaction becomes weaker after the oxidation treatment (in which case the following analysis will underestimate the thermal conductivity of a BN nanotube).

The following analysis is based on the inequality:

$$\frac{A+m}{B+m} < \frac{A}{B} \quad \text{if } A > B,\ m > 0. \tag{1}$$

Since the measured thermal conductivity not only has contributions from nanotubes in the axial direction but also is limited by junctions across nanotubes, we adapt Matthiessen's rule for thermal conductance:

$$\frac{1}{\lambda_{\mathrm{mats}}} = \frac{1}{K_{\mathrm{tube}}} + \frac{1}{K_{\mathrm{jun}}}, \tag{2}$$

where λ_{mats} is the measured thermal conductance from the mats, K_{tube} and K_{jun} represent the sum of the thermal conductance from a single nanotube in the axial direction and across the nanotube junctions, respectively. Because the thermal conductance of a B-C-N nanotube is larger than that of its BN layers, Eqs. (1) and (2) give an upper limit of the thermal conductivity of BN nanotubes:

$$r \equiv \frac{\lambda_{\mathrm{BCN}}}{\lambda_{\mathrm{BN}}} = \frac{1/\lambda_{\mathrm{BN}}}{1/\lambda_{\mathrm{BCN}}} = \frac{1/K_{\mathrm{BN}} + 1/K_{\mathrm{jun}}}{1/K_{\mathrm{BCN}} + 1/K_{\mathrm{jun}}} < \frac{1/K_{\mathrm{BN}}}{1/K_{\mathrm{BCN}}}$$

$$= \frac{K_{\mathrm{BCN}}}{K_{\mathrm{BN}}} = \frac{K_{\mathrm{BN}} + K_{\mathrm{C}}}{K_{\mathrm{BN}}} = \frac{\kappa_{\mathrm{BN}} + x\kappa_{\mathrm{C}}}{\kappa_{\mathrm{BN}}} \quad \text{so,} \quad \kappa_{\mathrm{BN}} < \frac{x\kappa_{\mathrm{C}}}{r-1}, \tag{3}$$

where the subscripts of λ's and K's denote the thermal conductance contribution from B-C-N, BN, and carbon nanotubes, respectively. The subscripts of κ's are the thermal conductivity of BN and carbon nanotubes. x denotes the number ratio of carbon layers to BN layers in each B-C-N nanotube. Since our nanotubes have large diameters, the ratio of the cross-sectional area of carbon to BN layers in each B-C-N nanotube is approximately x. Similarly, Eqs. (1) and (2) also constrain the lower limit of κ_{BN}:

$$\frac{\lambda_{\mathrm{BCN}}}{\lambda_{\mathrm{C}}} = \frac{\lambda_{\mathrm{BCN}}}{\lambda_{\mathrm{BCN}} - \lambda_{\mathrm{BN}}} \equiv \frac{r}{r-1} = \frac{1/\lambda_{\mathrm{C}}}{1/\lambda_{\mathrm{BCN}}}$$

$$= \frac{1/K_{\mathrm{C}} + 1/K_{\mathrm{jun}}}{1/K_{\mathrm{BCN}} + 1/K_{\mathrm{jun}}} < \frac{1/K_{\mathrm{C}}}{1/K_{\mathrm{BCN}}} = \frac{K_{\mathrm{BCN}}}{K_{\mathrm{C}}}$$

$$= \frac{\kappa_{\mathrm{BN}} + x\kappa_{\mathrm{C}}}{x\kappa_{\mathrm{C}}} \quad \text{so,} \quad \kappa_{\mathrm{BN}} > \left(\frac{rx}{r-1} - 1\right)\kappa_{\mathrm{C}}. \tag{4}$$

We emphasize that κ_{BN} and κ_{C} represent the ensemble-averaged thermal conductivity of an individual multiwalled nanotube, not the mats of the BN and carbon nanotube, respectively.

From Eqs. (3) and (4), we determine κ_{BN} at 290 K to be $0 < \kappa_{\mathrm{BN}} < 0.32\kappa_{\mathrm{C}}$ and $0.04\kappa_{\mathrm{C}} < \kappa_{\mathrm{BN}} < 0.54\kappa_{\mathrm{C}}$ for samples A and B, respectively. A self-consistent constraint further narrows the window down to $0.04\kappa_{\mathrm{C}} < \kappa_{\mathrm{BN}} < 0.32\kappa_{\mathrm{C}}$. Since multiwalled carbon nanotubes have been shown to exhibit very high thermal conductivity ($\sim$3000 W/m K at 290 K),[7] our result suggests that $\kappa(290\ \mathrm{K})$ of an individual nanotube also lies in the range of 120 to 960 W/m K. Thus $\kappa(T)$ of an individual BN nanotube is one to two orders of magnitudes larger than that of the mat samples.

The total thermal conductivity of a nanotube can be written as $\kappa(T) = \Sigma Cvl$, where C, v, and l are, respectively, the specific heat, group velocity, and phonon mean-free-path, and the sum is over all phonon states. Since currently there are no available data for heat capacity of BN nanotubes, we assume the ratio of heat capacity of hexagonal BN to graphite to be the same as that of BN nanotubes to carbon nanotubes.[6] Choosing $v = 10$ km/s estimated by theory,[17,18] we have $l = 40$–320 nm for BN nanotubes, which is compa-

rable to $l \sim 500$ nm for an isolated multiwalled carbon nanotube, and is only a fraction of the average length (~ 2 μm) of our BN nanotubes.

Our results suggest that although κ(290 K) of BN nanotubes is lower than that of carbon nanotubes, it is still higher than that of most other nanoscaled structures. For example, Si or Si/Ge nanowires exhibit lower thermal conductivity than their bulk values.[19,20] In these nanowires, suppressions of the phonon transport from boundary scattering, or alloy scattering overwhelm the enhancement due to reduced dimensionality. Our results suggest that the tubular structure is the crucial factor for enhancing thermal conductivity of nanoscaled structures.

There are several reasons why BN nanotubes exhibit lower thermal conductivity than carbon nanotubes. First, theoretical calculations suggest a softer phonon mode in all branches of phonon dispersion curves for BN nanotubes than for carbon nanotubes.[17] Second, calculations also suggest the bulk modulus to be lower for BN nanotubes than for carbon nanotubes.[21] Third, since the natural abundance of boron is 19.9% ^{10}B and 80.1% ^{11}B, in contrast with that of carbon (98.9% ^{12}C, 1.1% ^{13}C), the effect of isotope disorder is much more severe for BN nanotubes than for carbon nanotubes. Theoretical calculations have suggested a larger enhancement factor of thermal conductivity [κ(isotopically pure)/κ(natural abundance)] for cubic BN (125%) than that of diamond (23%).[22] Because the disorder-induced localization effect is more pronounced in one dimension, we would expect that isotope disorder will highly reduce the thermal conductivity for the natural abundant BN nanotubes. On the other hand, BN nanotubes might be better thermal conductors than carbon nanotubes if made isotopically pure.

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