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Physics Letters A 369 (2007) 120–123

PHYSICS LETTERS A

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Thermal diffusivity and conductivity of multiwalled carbon nanotube arrays

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Received 11 November 2006; accepted 15 February 2007

Available online 28 February 2007

Communicated by R. Wu

Abstract

A laser flash technique was applied to measure the thermal diffusivity along a multiwalled carbon nanotube (CNT) array in temperature range of −55–200 °C. In the measurements, a nanosecond pulsed laser was used to realize noncontact heating and the temperature variations were recorded by an infrared detector. The experimental results show that the thermal diffusivity of the CNT array increases slightly with temperature in the −55–70 °C temperature range and exhibits no obvious change in the 75–200 °C temperature range. The CNT array has much larger thermal diffusivity than several known excellent thermal conductors, reaching about 4.6 $cm^2 s^{-1}$ at room temperature. The mean thermal conductivity (λ) of individual CNTs was further estimated from the thermal diffusivity, specific heat (C_p), and density (ρ) by using the correlation of $\lambda = \alpha\rho C_p$. The thermal conductivity of individual CNTs increases smoothly with the temperature increase, reaching about 750 $W\,m^{-1}\,K^{-1}$ at room temperature.

PACS: 66.30.Xj; 65.80.+n; 81.07.De

Keywords: Carbon nanotubes; Thermal diffusivity; Thermal conductivity

1. Introduction

Because of their unique structure, novel properties and potential applications [1], carbon nanotubes (CNTs) have attracted significant attention since their discovery. Large quality of CNTs can be produced by either arc discharge [2–5] or thermal decomposition of hydrocarbon vapor [6,7], which provide the opportunity to utilize CNTs in large-scale production. It is fundamental to understand the physical and chemical behaviors of CNTs for the full utilization of their superior properties. The electrical and mechanical properties have been investigated extensively, even down to a scale of one single nanotube level [8]. The thermal properties of CNTs are also of interest for basic science as well as for technological applications.

Theoretical investigations have demonstrated that the thermal conductivity of this new class of one-dimensional materials could exceed that of diamond and graphite which have been well known in nature to have superior thermal performance. Berber et al. [9] conducted molecular dynamics (MD) simulation on single-walled CNTs (SWNTs) and obtained a value of 6600 $W\,m^{-1}\,K^{-1}$ for the thermal conductivity of SWNT at room temperature. Che et al. [10] reported a room temperature thermal conductivity of 2980 $W\,m^{-1}\,K^{-1}$ for SWNT. However, many experiments only revealed the thermal conductivity values from several tens to hundreds $W\,m^{-1}\,K^{-1}$ for CNT mats and bundles [11–14]. The direct, quantitative measurement of thermal transport properties of individual nanotubes has remained a paramount challenge to the scientific community. Two elegant experiments have been performed on the measurement of a single CNT [15,16]. Kim et al. [15] developed a microfabricated suspended device and measured the thermal conductance of a single CNT in a temperature range of 8–370 K. Fujii et al. [16] investigated the dependence of thermal con-

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0375-9601/$ – see front matter
doi:10.1016/j.physleta.2007.02.079

ductivity of a single CNT on measurement temperature and nanotube diameter by a novel T-type short-hot-wire probe technique. However, it is very difficult to estimate accurately the contact thermal resistance in these two measurements. Also the remarkable technical difficulty in device fabrication and CNT manipulation makes it arduous to employ these two techniques routinely.

In this Letter, we report on the measurement of the thermal diffusivity along a multiwalled CNT array which is deposited on a glass. We further estimate the mean thermal conductivity of one single CNT from the thermal diffusivity value. The possible heat transport mechanism in the CNT array is discussed.

2. Experimental details

The multiwalled CNT array used in these measurements was obtained from Nano-lab, Inc., USA. This sample was prepared using plasma enhanced hot filament chemical vapor deposition (PECVD). The detailed preparation procedure has been described by Ren et al. [17,18]. The CNT array is vertical to the glass substrate (Fig. 1). The low inset in Fig. 1 represents the higher magnification of the CNT array. A layer of chromium (Cr) with thickness of 70 nm is deposited on the glass substrate. The thickness of the CNT array is about 20 μm. The diameter of the CNTs is around 60–150 nm from the scanning electron microscope (SEM) picture.

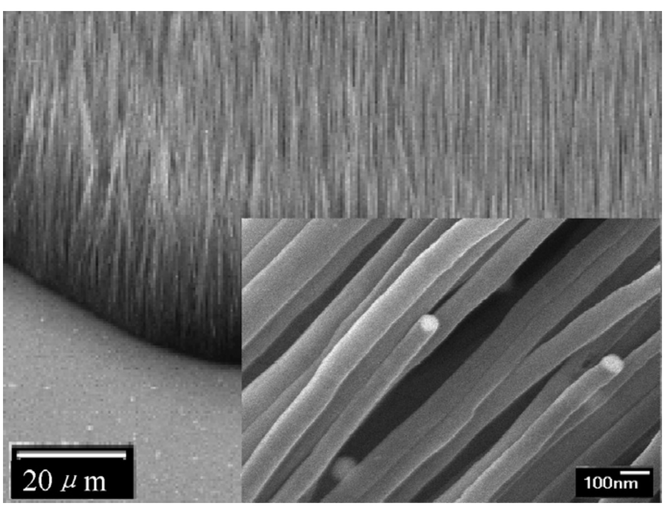

Fig. 1. SEM micrograph of the CNT array. Low inset: magnification of the CNT array. The CNT array is vertical to the glass substrate.

A laser flash (LF) technique was used to measure the thermal diffusivity of the CNT array. We show schematically the experimental setup in Fig. 2. A nano-second laser pulse with a pulse width of 6 ns from a Q-switched Nd:YAG laser (Continuum Surelite I-10) at a wavelength of 1064 nm is used to irradiate the backside of the glass substrate. Because the glass substrate is transparent to the laser pulse at this wavelength, the Cr layer is directly irradiated by the laser pulse. A fraction of the pulse energy is absorbed to heat the Cr layer. Heat diffuses through the Cr layer and transports along CNTs and cause temperature increase at the rear tips (rear face) of CNT arrays. The thermal diffusion time ($\delta^2/\alpha_{\mathrm{Cr}}$, where δ is the thickness of Cr layer and α_{Cr} is the thermal diffusivity of Cr) in the Cr layer is $\sim 10^{-10}$ s, much smaller than the laser pulse duration. The temperature in Cr layer reaches at equilibrium immediately after laser irradiation. Furthermore, the CNT array has a thermal diffusivity larger than 4.0 $\mathrm{cm^2\,s^{-1}}$, whereas the glass substrate has a value of about 0.006 $\mathrm{cm^2\,s^{-1}}$. In our experiments, heat transfer through the glass substrate is negligible. The tested sample was settled on a holder in a vacuum chamber with two windows. The front window through which the heating laser beam passes is made of Cr glass with a thickness of 4 mm. The rear window is made of germanium glass with a thickness of 4 mm. The infrared (IR) emission from the CNT tip can pass through this window and is detected by an IR detector. The heat loss due to convection is suppressed because the vacuum chamber is kept at about 0.1 Pa (10^{-3} torr) during all the measurements. Since the experimental temperatures are relatively low (not higher than 200 °C), the heat loss caused by radiation is not significant. Therefore the temperature rise at the rear tips of the CNT array can be described as [19]:

$$T(t) = \frac{Q}{\rho C_p L}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(\frac{-n^2\pi^2}{L^2}\alpha t\right)\right] \tag{1}$$

where Q is the absorbed energy per unit area, ρ is the density, C_p is the specific heat, L is the thickness. $Q/(\rho C_p L)$ means the

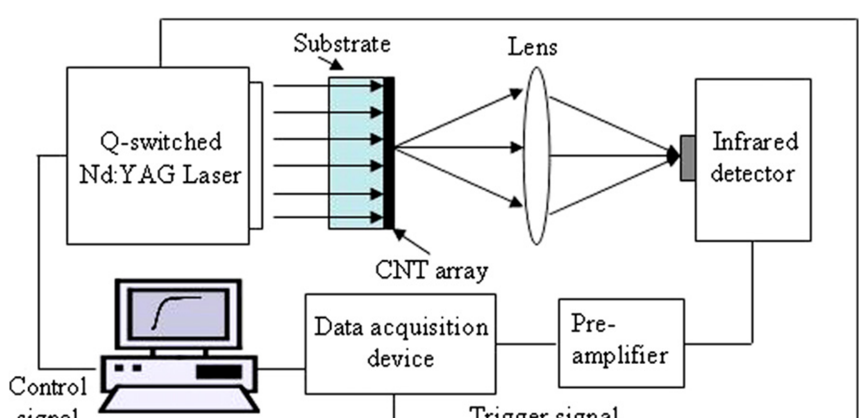

Fig. 2. Schematic diagram of the experimental setup.

maximum temperature rise $T_{\max}$. Eq. (1) is further normalized by dividing two sides with $T_{\max}$, which gives:

$$\theta = 1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(\frac{-n^2\pi^2}{L^2}\alpha t\right). \tag{2}$$

The temperature rise leads to infrared (IR) emission variation of the CNT tips. This variation is detected by using a liquid-nitrogen-cooled photovoltaic (PV) type of mercury cadmium telluride (MCT) detector of 1.0 mm in diameter (Infrared Corp.). In small temperature range, the IR emission variation is linear to the temperature change. The time-dependent temperature rises after heating by the laser flash are extracted from the time-dependent voltage variations collected by a digital oscilloscope (TDS 3032B).

3. Results and discussion

Fig. 3 shows the normalized temperature rise of the rear tips of the CNT array as a function of time after laser pulse heats the front surface in a typical measurement. After laser pulse heating, the temperature of the CNT array tip increases and follows Eq. (2). It is shown in Fig. 3 that the temperature rise reaches maximum value in very short time (about 300 ns). The thermal diffusivity is determined from the following formula [19]

$$\alpha = \frac{0.138L^2}{t_{1/2}}, \tag{3}$$

where $t_{1/2}$ is the time when the temperature rise arrives at the half value of the maximum temperature rise. We measured α of the CNT array in the temperature range of −55–200 °C and showed the dependence of α on the temperature in Fig. 4. Two observations can be made from Fig. 4. First, α of the CNT array increases slightly with temperature in the −55–70 °C temperature range and exhibits no obvious change in the 75–200 °C temperature range. This tendency is similar to the previous measurements of CNT bundles by using 3ω method [20]. However, our results show one-order-of-magnitude larger thermal diffusivity than that in Ref. [20]. The second observation is that the tested CNT has very large room-temperature thermal diffusivity which is about 4.6 $cm^2\,s^{-1}$, much greater than that of copper which is well known as a very good thermal conductor. Copper has a thermal diffusivity of about 1.2 $cm^2\,s^{-1}$ at room temperature. This result indicates CNTs possess excellent thermal transport properties. Borca-Tasciuc et al. used a photothermoelectric technique and a self-heating 3ω technique to measure the thermal diffusivity along multiwalled CNT array and obtained a value of about 0.52 $cm^2\,s^{-1}$ for it at room temperature [21]. Hou et al. developed a photothermal–resistance technique and apply it to investigated thermal transport properties of single-walled CNT array. They measured three samples and got their thermal diffusivity values of 0.30, 0.44 and 0.66 $cm^2\,s^{-1}$, respectively [22]. All the data reported in the above mentioned literatures are about one-order-of-magnitude smaller than the present measurements. Two reasons might account for this difference. First, the CNTs used in these two previous studies have lengths at scales of mm or cm. Both are

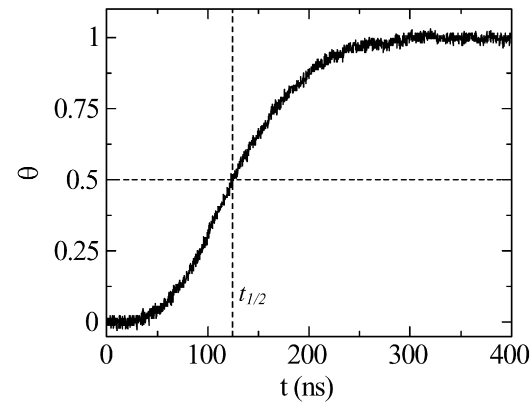

Fig. 3. Normalized temperature rise of the rear surface of the CNT array as a function of time after laser pulse heats the front surface. The thermal diffusivity is determined from the time when the temperature rise arrives at the half value of the maximum temperature rise.

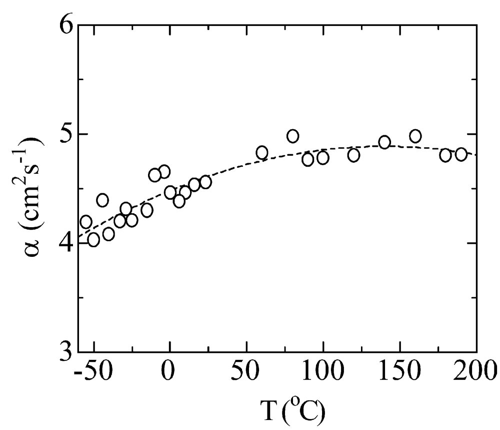

Fig. 4. Thermal diffusivity vs temperature of the CNT array.

much longer than the presently used CNTs. It can be expected much more defects in those longer CNTs, which would enhance phonon scattering and reduce the thermal transport capability. Secondly, the CNT bundles used by Borca-Tasciuc et al. are not perfectly aligned. Although no micrographs for the CNT bundles are given in Ref. [22], it is reasonable to image that the alignment will not be good for cm-long single-walled CNT bundles. For the in-plane transport, heat transfer mechanism would involve junctions formed between neighboring bundles, with heat following a tortuous path along the bundles and across the junctions [21]. By contraries, the CNTs used in our experiment display an overall better alignment (Fig. 1) since they are much shorter. Therefore, heat would transfer more effectively.

The mean thermal conductivity (λ) of individual CNTs was estimated from the thermal diffusivity, specific heat (C_p), and density (ρ) by using the correlation of $\lambda = \alpha \times \rho \times C_p$. Two following assumptions are made in this consideration: (1) heat conduction takes place along every CNT separately; (2) all CNTs have same sizes. It has been reported that the C_p of CNT are close to graphite at temperatures lower than room temperature [13,23]. Our previous measurement of specific heats from room temperature to 700 °C shows similar results [24]. Therefore, in the calculations, specific heats of graphite at cor-

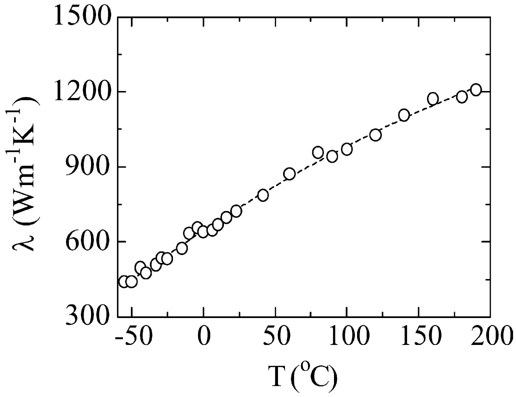

Fig. 5. Dependence of the estimated thermal conductivity of individual CNTs on the temperature.

responding temperatures were taken for CNT. The density of CNT was taken as 1.65 $\mathrm{g\,cm^{-3}}$ [25]. Fig. 5 represents the calculated thermal conductivity of individual CNTs. Although α only varies moderately with the temperature, it is clearly seen from Fig. 5 that λ of individual CNTs increases smoothly with the temperature increase, reaching about 750 $\mathrm{W\,m^{-1}\,K^{-1}}$ at room temperature. Fujii et al. [16] reported a room-temperature thermal conductivity of about 500 $\mathrm{W\,m^{-1}\,K^{-1}}$ for one single CNT with a diameter of 28.2 nm. It is worthy noting that the measurement in Ref. [16] only gives the lowest bound of intrinsic thermal conductivity of the tested CNT.

Several previous studies investigated the effective thermal conductivity (λ_{eff}) of CNT arrays [11,13,20]. In the present work, λ_{eff} is estimated by the mean thermal conductivity of one single CNT (λ), CNT number in unit area (N), and average area of one single CNT (A_{CNT}) from the correlation of $\lambda_{\mathrm{eff}} = \lambda \times N \times A_{\mathrm{CNT}}$. To the as-measured CNT array, $N \sim 10^9/\mathrm{cm}^2$ and the average diameter (d_{CNT}) is about 100 nm. $A_{\mathrm{CNT}} = \pi d_{\mathrm{CNT}}^2/4 \sim 0.8 \times 10^{-14}$. Therefore, $\lambda_{\mathrm{eff}} \sim 0.08\lambda$. At room temperature, λ_{eff} is about 60 $\mathrm{W\,m^{-1}\,K^{-1}}$, whereas that is about 100 $\mathrm{W\,m^{-1}\,K^{-1}}$ at 200 °C. These values are at the same order of magnitude to the previous results [11,20].

4. Conclusions

We investigated the thermal transport properties of carbon nanotube arrays. The observed thermal diffusivity is much larger than those of copper and silver that are known as excellent thermal conductors. Its thermal diffusivity increases slightly with temperature in the −55–70 °C temperature range and exhibits no obvious change in the 75–200 °C temperature range. We further estimated the mean thermal conductivity of individual CNTs from the correlation between the thermal conductivity, thermal diffusivity, specific heat, and density. It was found that the thermal conductivity of individual CNTs increases smoothly with the temperature increase, reaching about 750 $\mathrm{W\,m^{-1}\,K^{-1}}$ at room temperature.

Acknowledgements

This work was partly supported by the project of Shanghai Pujiang Program (No. 06PJ14045).

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