Development of photothermal-resistance technique and its application to thermal diffusivity measurement of single-wall carbon nanotube bundles

J. Hou and X. Wang[a)]
Department of Mechanical Engineering, N104 Walter Scott Engineering Center, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0656

C. Liu and H. Cheng
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

(Received 8 February 2006; accepted 31 March 2006; published online 3 May 2006)

In this work, a photothermal-resistance technique is developed to characterize the thermophysical properties of one-dimensional micro/nanostructures. In this technique, a periodically modulated laser beam is used to achieve noncontact heating of suspended individual wires. The temperature response of the sample is monitored by measuring its electrical resistance variation. A 25.4 μm thick platinum wire is used as the reference sample to verify the technique. Applying the photothermal-resistance technique, the thermal diffusivity of single-wall carbon nanotube bundles is measured. The measured thermal diffusivities for three different single-wall carbon nanotube bundles are 2.98×10^{-5}, 4.41×10^{-5}, and 6.64×10^{-5} m^2/s, respectively. These values are much less than the thermal diffusivity of graphite.
[DOI: 10.1063/1.2199614]

In recent years, due to the demand of developing reliable microelectromechanical systems (MEMSs) and nanoelectromechanical systems (NEMSs), characterizing the thermophysical properties of different materials at micro/nanoscales has received considerable attention. In the past, transient thermoreflectance (TTR),[1] 3ω,[2] photothermal deflection (PTD),[3] and photoacoustic[4] (PA) methods have been well developed to measure the thermal properties of thin films. For investigation of the thermophysical properties of one-dimensional micro/nanostructures, limited experimental approaches have been developed. At present, the 3ω method[5,6] and microfabricated devices method[7,8] represent the main measurement techniques to obtain thermophysical properties of materials in such low dimensions and small scales.

Because the thermophysical properties of carbon nanotubes (CNTs) are of fundamental interest and play a critical role in controlling the performance and stability of CNT devices,[9] a large number of theoretical and experimental investigations have been conducted to understand the thermophysical properties of CNTs. For single-wall carbon nanotubes (SWCNTs), Hone *et al.*,[10,11] by using a comparative method, conducted a series of experiments to measure the thermal conductivity. Later, comparative steady state method was used to study SWCNTs filled with C_{60} by Vavro *et al.*[12] Recently, one-dimensional SWCNT bundles and individual SWCNTs were investigated by Shi *et al.*[8] and Yu *et al.*[13] For multiwall carbon nanotube (MWCNT), Xie *et al.*,[14] Yi *et al.*,[15] and Lu *et al.*[5] studied the thermal conductivity of MWCNT bundles by employing the 3ω method. Conventional laser-flash method was used by Zhang *et al.*[16] to measure the thermal conductivity of MWCNT bulk material. Recently, thermal conductivity of individual MWCNTs was investigated by a microfabricated suspended device (Kim *et al.*),[7] noncontact photothermal experiment (Wang *et al.*),[17] 3ω method (Choi *et al.*,[18] and a temperature sensing scanned microscope probe (Brown *et al.*).[19]

For the techniques reviewed above, the 3ω method provides a compelling means to characterize the thermal conductivity of CNTs with sound accuracy. On the other hand, this technique requires that the sample is conductive and endowed with linear *I-V* behavior in the applied ac voltage range. Meanwhile, CNTs have both metallic and semiconducting properties, depending on their chirality indices (n, m). A layer in the MWCNT will have metallic conduction when the difference between the two indices (n and m) is divisible by 3 (Dresselhaus *et al.*).[9] Otherwise, the layer will be semiconducting, leading to a nonlinear *I-V* relationship. As a result, the 3ω technique can only be applied to metallic CNTs.

In this work, a technique, photothermal-resistance technique, and the associated analytical solution for investigating the thermophysical properties of one-dimensional micro/nanostructures are developed. This technique is applicable to both metallic and semiconducting materials. In the photothermal-resistance experiment, the to-be-measured wire is suspended between two copper electrodes. The wire is irradiated with a periodically modulated laser beam as shown in Fig. 1. Upon the periodical laser heating, the wire will experience a periodical temperature change with time. As a result, the resistance of the wire will change with time periodically. In order to detect the resistance variation of the wire, a dc (I) is passed through the wire. The dc and the periodical resistance variation of the wire will produce a periodical voltage variation over the wire with the same frequency of the modulated laser beam. The heat conduction along the thin wire strongly affects the temperature variation along the wire which will be probed by measuring the voltage variation. The phase shift of the voltage variation relative to the laser beam can be used to determine the thermophysical properties of the sample. The modulation frequency of the laser irradiating the wire will be carefully selected to

[a)]Author to whom correspondence should be addressed; electronic mail: xwang3@uni.edu

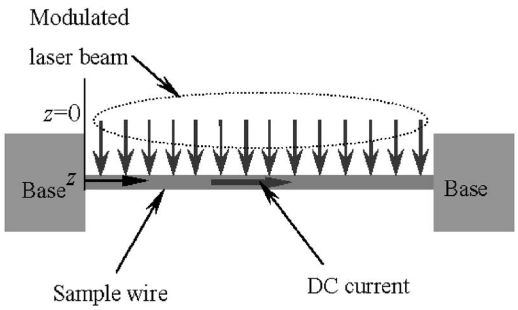

FIG. 1. Schematic of the experimental principle for the photothermal-resistance technique.

make the thermal diffusion length $\mu=\sqrt{2\alpha/f}$ (α: thermal diffusivity of the wire; f: modulation frequency) much larger than the wire diameter D. As a result, it is physically reasonable to assume that the wire has a uniform temperature distribution in its cross section. Consequently, only the heat transfer along the axial direction of the wire needs to be considered. A physical model was developed to relate the temperature variation of the sample to its thermophysical properties. Our physical model gives the periodic voltage across the wire as

$$V_\omega = \bar{\theta}_m \frac{dR}{dT} I \cos(\omega t + \phi), \tag{1}$$

where dR/dT, ω, $\bar{\theta}_m$, and ϕ are the temperature coefficient of resistance, laser modulation frequency, amplitude of temperature variation, and its phase shift. The phase shift ϕ strongly depends on the length of the wire, frequency ω, and thermal diffusivity of the wire. In the experiment, a series of frequencies is chosen to measure the phase shift and conduct the fitting to determine the thermophysical properties of the wire.

Our model assumes that the laser is uniformly distributed over the wire while the laser in practical situations has a nonuniform distribution. Calculation of extreme nonuniform energy distribution is conducted for a Pt wire that has the same dimension as that used in our experiment for calibration and validation purposes. Our study shows that the nonuniformity of the laser beam distribution in the photothermal-resistance experiment has a negligible effect on the measured phase shift. Our study also indicates that based on the experimental conditions in this experiment, the radiation effect is negligible. The experimental results using Pt wires also confirm these two points.

Figure 2 shows the diagram of the photothermal-resistance experimental setup. An infrared diode laser (λ $=809$ nm) is modulated by a function generator. The laser beam passes through a collimator and is directed by a focal lens to the to-be-measured wire. A dc voltage is applied to the thin wire. A large resistor is connected in the circuit to control the current and to satisfy the impedance requirement (over 50 Ω) of the dc power supply. A digital lock-in amplifier is used to pick up the ω signal over the thin wire, and a synchronizing signal from the same function generator is used as lock-in amplifier's reference. In order to minimize the influence from air convection, the thin wire is housed in a vacuum chamber where the pressure is maintained at a level of 1×10^{-3} Torr. A computer is used to control the experiment for automatic data acquisition.

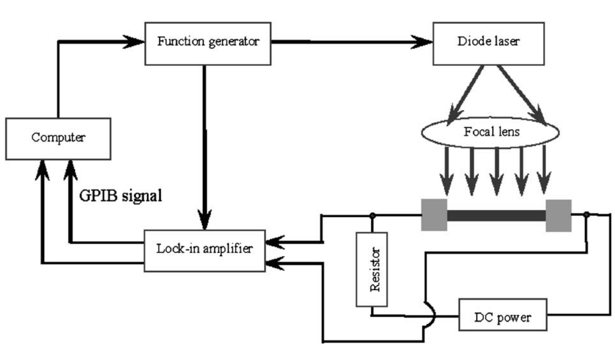

FIG. 2. Schematic setup for the photothermal-resistance experiment.

TABLE I. Details of experimental conditions for the Pt wire and three SWCNT samples characterized in the experiment.

	Pt wire	Sample 1	Sample 2	Sample 3
Length (mm)	6.35	6.35	6.35	6.35
Resistance of sample (Ω)	1.35	90.0	443.0	392.0
dc voltage (V)	1.80	0.3	0.3	0.3
Laser power (W)	1.60	4.0	0.8	0.8
Resistance of the resistor (Ω)	99.52	99.48	99.48	99.48
ϕ_{diff} (deg)	0.5	1.0	2.3	1.5

In this photothermal-resistance experiment, the measurement result will inevitably include some time delay induced by the equipment used in the experiment. The real phase shift between the thermal variation and the modulated laser beam is calculated as $\phi_{\mathrm{mea}}-\phi_{\mathrm{calc}}$, where ϕ_{mea} and ϕ_{calc} are the raw measurement data for the voltage variation over the wire and system time delay, respectively. The system time delay is characterized by replacing the sample in the experiment with a photodiode, whose time response is less than 1 ns.

In order to verify this characterization technique and the theoretical model, a 25.4 μm thick and 6.35 mm long platinum wire is measured. The experimental conditions are listed in Table I. By using least squares data fitting, the thermal conductivity of the platinum wire is found to be 71.4 W/m K, close to the literature value of 71.6 W/m K.[20] Figure 3 shows the fitting result in comparison with the experimental data. In the experiment, the uncertainty of the measured phase shift is less than 0.5 deg. Based on this criterion, the thermal conductivity k is found to be

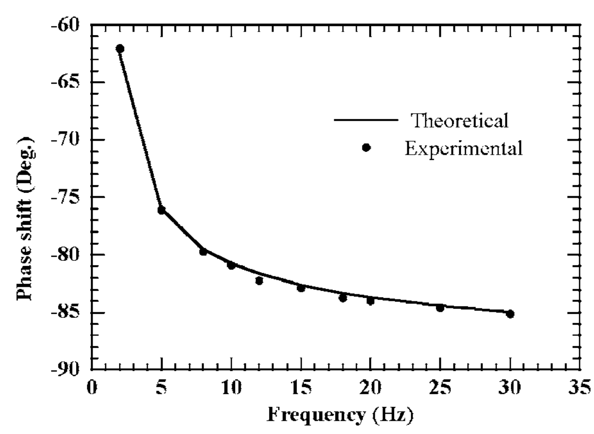

FIG. 3. Phase shift as a function of the modulation frequency for the platinum wire.

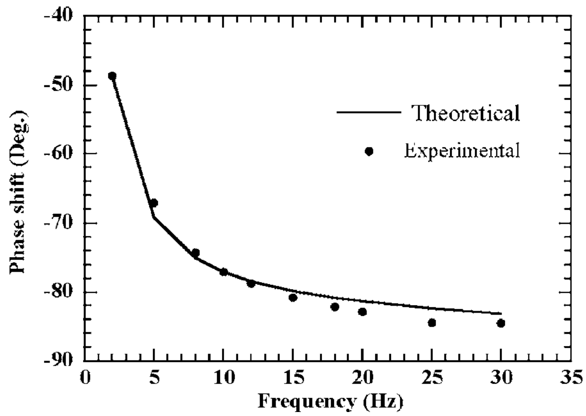

FIG. 4. The measured phase shift vs the fitting results for one of the SWCNT bundles.

$71.4^{+3.67}_{-3.44}$ W/m K, showing the uncertainty of the final measurement result is around ±5%.

Bundles consisting of SWCNTs are measured using the established photothermal-resistance technique and the developed solution. Centimeters long ropes of well-aligned SWCNTs were fabricated using a H_2/Ar arc discharge method (Liu *et al.*).[21] The SWCNT bundle is connected between two copper electrodes using silver paste. Table I shows the length and resistance of the three SWCNT bundles measured in the experiment. The typical thickness/diameter of the SWCNT bundles is measured to be around 100 μm. The thermal conductivity of the SWCNT bundle becomes difficult to determine based on the experimental data due to the lack of knowledge about their density and specific heat. Instead, the thermal diffusivity of the sample is characterized based on the phase shift of the ω signal.

Figure 4 shows the fitted phase shift versus the experimental data for one of the samples in which the SWCNTs have sound alignment along the wire axis. For the three samples measured in the experiment, different values of ρc_p are used to fit the thermal conductivity. Although a large number of thermal conductivity and ρc_p combinations can fit the experimental data well, their ratio-thermal diffusivity remains at a certain value for each sample. Their thermal diffusivities are fitted to be $(2.98^{+0.33}_{-0.16}) \times 10^{-5}$, $(4.41^{+0.42}_{-0.32}) \times 10^{-5}$, and $(6.64^{+0.35}_{-0.22}) \times 10^{-5}$ m^2/s, respectively. For different samples, ϕ_{diff} is fixed at different values shown in Table I, which can both guarantee best agreement between experiment and theoretical model and a large number of thermal conductivity and ρc_p combinations. Based on the obtained experimental results, the thermal diffusivity of the three samples is in the same order. The difference among them is probably attributed to different alignments of the tubes in the bundle and tube-tube interaction. The average thermal diffusivity of the above stated three different SWCNT samples is around 4.68×10^{-5}m^2/s.

In summary, a photothermal-resistance technique was developed to characterize the thermal transport in one-dimensional micro/nanostructures. Applying this technique, the thermal conductivity of a platinum wire was measured to be 71.4 W/m K, agreeing well with the reference value. Our uncertainty analysis showed that the experiment has an uncertainty less than 10%. We have measured the thermal diffusivity of SWCNT bundles of different thicknesses and the average measurement value was 4.68×10^{-5} m^2/s, which is much smaller than that of graphite in the layer direction.

Support for this work from NSF (CTS: 0400458), Nebraska Research Initiative, the MURI grant from ONR, and Layman Award of the University of Nebraska-Lincoln (UNL) are gratefully acknowledged. Support from Dr. Dennis Alexander and Haifeng Zhang of Electrical Engineering at UNL for characterizing the laser beam energy distribution is very much appreciated.

[1] C. Paddock and G. Eesiey, J. Appl. Phys. **60**, 285 (1986).
[2] D. Cahill and R. Pohl, Phys. Rev. B **35**, 4067 (1987).
[3] W. McGahan and K. Cole, J. Appl. Phys. **72**, 1362 (1992).
[4] H. Hu, X. Wang, and X. Xu, J. Appl. Phys. **86**, 3953 (1999).
[5] L. Lu, W. Yi, and D. L. Zhang, Rev. Sci. Instrum. **72**, 2996 (2001).
[6] X. Wang, P. Vellelacheruvu, J. Hou, C. Liu, and H. Cheng, to be presented at the Ninth AIAA/ASME Joint Thermophysics and Heat Transfer Conference, San Francisco, CA, 5–8 June 2006 (unpublished).
[7] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, Phys. Rev. Lett. **87**, 215502 (2001).
[8] L. Shi, D. Li, C. Yu, W. Jang, D. Kim, Z. Yao, P. Kim, and A. Majumdar, J. Heat Transfer **125**, 881 (2003).
[9] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996).
[10] J. Hone, M. Whitney, C. Piskoti, and A. Zettl, Phys. Rev. B **59**, R2514 (1999).
[11] J. Hone, M. C. Llaguno, N. M. Nemes, A. T. Johnson, J. E. Fischer, D. A. Walters, M. J. Casavant, J. Schmidt, and R. E. Smalley, Appl. Phys. Lett. **77**, 666 (2000).
[12] J. Vavro, M. C. Llaguno, B. C. Satishkumar, D. E. Luzzi, and J. E. Fischer, Appl. Phys. Lett. **80**, 1450 (2002).
[13] C. Yu, L. Shi, Z. Yao, D. Li, and A. Majumdar, Nano Lett. **5**, 1842 (2005).
[14] S. Xie, W. Li, Z. Pan, B. Chang, and L. Sun, J. Phys. Chem. Solids **61**, 1153 (2000).
[15] W. Yi, L. Lu, D. Zhang, Z. Pan, and S. Xie, Phys. Rev. B **59**, R9015 (1999).
[16] H. L. Zhang, J.-F. Lia, K. F. Yao, and L. D. Chen, J. Appl. Phys. **97**, 114310 (2005).
[17] X. Wang, Z. Zhong, and J. Xu, J. Appl. Phys. **97**, 064302 (2005).
[18] T. Y. Choi, D. Poulikakos, J. Tharian, and U. Sennhauser, Appl. Phys. Lett. **87**, 013108 (2005).
[19] E. Brown, L. Hao, J. C. Gallop, J. C. Macfarlane, Appl. Phys. Lett. **87**, 023107 (2005).
[20] F. Incropera and D. Dewitt, *Heat and Mass Transfer*, 5th ed. (Wiley, New York, 2002).
[21] C. Liu, H. M. Cheng, H. T. Cong, F. Li, G. Su, B. L. Zhou, and M. S. Dresselhaus, Adv. Mater. (Weinheim, Ger.) **12**, 1190 (2000).