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# Thermal characterization of submicron polyacrylonitrile fibers based on optical heating and electrical thermal sensing

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In this work, the thermal diffusivity of single submicron (~800 nm) polyacrylonitrile (PAN) fibers is characterized using the recently developed optical heating and electrical thermal sensing technique. In the experiment, a thin Au film (approximately in the nanometer range) is coated on the surface of nonconductive PAN fibers. A periodically modulated laser beam is used to irradiate suspended individual fibers to achieve noncontact periodical heating. The periodical temperature response of the sample is monitored by measuring the electrical resistance variation of the thin Au coating. The experimental results for three different synthesized PAN fibers with varying Au coating thickness are presented and discussed. © *2006 American Institute of Physics*.

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In recent years, the rapid advancement in microelectromechanical and nanoelectromechanical systems places great demand for advanced, reliable, and accurate techniques to characterize the thermophysical properties of different materials at micro-nanoscales. To measure the thermophysical properties of one-dimensional micro-nanostructures, the $3\omega$ technique,[1,2] microfabricated devices method,[3–8] and photothermal technique[9] have been developed and employed in the past few years.

For the techniques mentioned above, the $3\omega$ method provides a compelling means to characterize the thermal conductivity of conductive materials with sound accuracy. On the other hand, this technique cannot be directly applied to nonconductive nanowires. Theoretically, a thin metallic film can be coated on the outside of nonconductive nanowires to make the $3\omega$ technique applicable. However, our extensive experimental work has found substantial difficulty with this technique modification, especially for submicron/nanoscale nonconductive wires. In the experiment, the required electrical heating could result in coating-wire separation and experimental failure. In the microfabricated devices method, one membrane is heated to cause heat conduction through the sample to the other membrane.[3–8] This method is good for characterizing one-dimensional micro-nanoscale structures with short length and sound thermal conductivity, no matter if the sample is conductive or not. For low thermal conductivity nanowires/tubes, the heat transfer by direct radiation between the two membranes could be comparable to the heat conducted by the sample, leading to poor experimental accuracy. The photothermal technique[9] requires the tubes/wires to be well aligned in the direction normal to the substrate.

Motivated to overcome the challenge of characterizing the thermal diffusivity of nonconductive submicron/nanoscale wires/tubes, in our recent work,[10] a technique based on optical heating and electrical thermal sensing (OHETS) has been developed for measuring the thermophysical properties of one-dimensional micro-nanostructures. In this letter, this technique is applied to investigate the thermophysical properties of polyacrylonitrile (PAN) fibers at the submicron scale. Due to their high surface area and porosity, submicron/nanoscale fibers have found potential applications in many fields as composites, filter medium, tissue scaffolds, and adsorption layers in protection clothing.[11] Little information about the thermophysical properties of submicron/nanoscale PAN fibers has been reported.

The physical principle of the OHETS method is detailed in our previous work.[10] Figure 1 shows the experimental principle for measuring the thermophysical properties of nonconductive wires. The to-be-measured wire is suspended between two copper electrodes. A thin Au film is coated on the outside of the wire for electrical thermal sensing. The wire is irradiated with a periodically modulated laser beam as shown in Fig. 1. The periodical laser heating results in a periodical temperature change, leading to a periodic resistance change of the wire. A dc is constantly fed through the coating and its periodical resistance variation will produce a periodical voltage variation across the wire. The thermophysical properties of the wire and the coating will strongly influence the temperature change, which will be reflected by the periodical voltage variation. The phase shift of the voltage variation with respect to the modulated laser beam can be used to determine the thermophysical properties of the sample. The modulation frequency of the laser will be care-

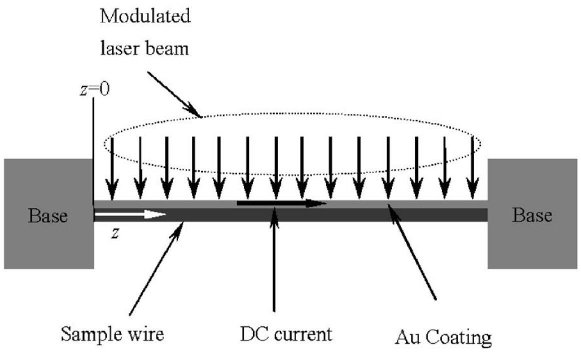

FIG. 1. Schematic of the experimental principle for OHETS method (not to scale).

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fully selected to ensure that the thermal diffusion length within each heating period is 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. Detailed derivation and mathematic expression of the temperature variation of the wire can be found in our recent work.[10] In the experiment, a series of frequencies is chosen to measure the phase shift and data fitting is conducted to determine the thermal diffusivity of the wire.

In our previous work,[10,12] the detailed numerical study showed that the nonuniformity of the laser beam distribution in the OHETS technique has negligible effect on the measured phase shift. In addition, our study[2] also indicated that, based on the experimental conditions in this experiment, the radiation heat loss from the wire surface has negligible effect on the measured phase shift. The real phase shift between the temperature variation and the modulated laser beam is calculated as $\phi_{\text{mea}}-\phi_{\text{calc}}$, where $\phi_{\text{mea}}$ and $\phi_{\text{calc}}$ are the raw measurement data for the voltage variation over the wire and system time delay. This system time delay is calibrated by measuring the phase shift between the modulated laser beam and the synchronizing signal of the function generator.[12]

As the diameter of the wire is reduced in the OHETS method, the thin Au coating will have a considerable contribution to the heat conduction. The reason is that the to-be-measured wire is a low thermal conductivity material while the Au film has a relatively high thermal conductivity. In fact, the measured thermal diffusivity $\alpha_m$ is an effective value that includes the effect of the thin metallic coating. The effect of the thin metallic coating on the measured $\alpha_m$ can be ruled out using the concept of thermal conductance. The thermal conductance $(G_f)$ of the thin film coating is defined as $G_f=A_f k_f/L$, where $k_f$, $A_f$, and $L$ are the thermal conductivity of the film in the axial direction of the wire, cross-sectional area of the thin film, and the wire length, respectively. In this work, $G_f$ is determined by using the Wiedemann-Franz law, which relates the thermal conductivity $(k)$ of metal to its electrical conductivity $(\sigma)$ as $L_{\text{Lorenz}}=k/(\sigma T)$.[13] The Lorenz number $L_{\text{Lorenz}}$ for Au has weak dependence on temperature: $2.35\times10^{-8}\ \mathrm{W\,\Omega/K^2}$ at 0 °C and $2.40\times10^{-8}\ \mathrm{W\,\Omega/K^2}$ at 100 C.[13] Based on the Wiedemann-Franz law, the thermal conductance of the thin film coating can be readily calculated from the measured electrical resistance $(R)$ of the wire as $G_f=L_{\text{Lorenz}}T_0/R$.

In our experiment, the measured thermal diffusivity is a combined contribution from the wire and Au coating, and can be expressed as

$$\alpha_m=\frac{k(1-\beta)+k_f\beta}{\rho c_p(1-\beta)+\rho_f c_{p,f}\beta}, \tag{1}$$

where $\rho_f$ and $c_{p,f}$ are the density and specific heat of the Au coating. $\beta=A_f/A_e$ is the cross-sectional area ratio of Au coating over the coated wire. Since $\beta\ll1$, $\rho_f c_{p,f}\beta\ll\rho c_p(1-\beta)$ and $1-\beta\cong1$ the real thermal diffusivity of the wire $(\alpha)$ can be obtained as

$$\alpha=\alpha_m-\left(\frac{L_{\text{Lorenz}}T}{R}\frac{L}{A_w}\right)/(\rho c_p). \tag{2}$$

In this work, the measured submicron PAN fibers are synthesized using the electrospinning technique. In the electrospinning process, the polymer (polyacrylonitrile) is dissolved into dimethylformamide solvent. A high voltage (15–20 kV) is applied to a copper wire inserted into the polymer solution in order to generate an electrical field between the solution and a collector.[14,15] When the electrostatic force overcomes the surface tension, the jetting from the liquid droplet can become a stable cone referred to as the Taylor cone by applying an appropriate electrical potential between the pipette and the collector.[16] The stable conical shape of the jetting provides a way to catch the fibers directly under the pipette using a base with two electrodes.

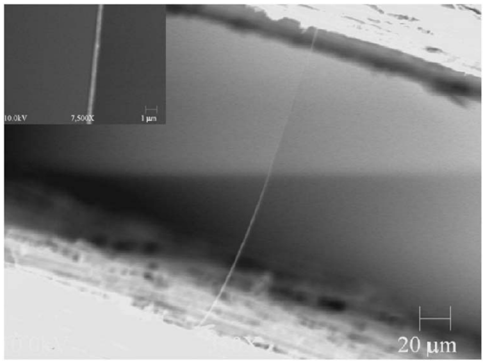

FIG. 2. SEM pictures of a coated PAN fiber (sample 3) studied in this work.

Three PAN fibers are measured using the OHETS technique. The thickness/diameter of the PAN fiber is around 800 nm and the typical length is around 200 $\mu$m. Figure 2 shows the scanning electron microscopy (SEM) image of sample 3 measured in our experiment. The density $(1.15\times10^3\ \mathrm{kg/m^3})$ and specific heat $(1.285\times10^3\ \mathrm{J/kg\,K})$ needed in Ea. (2) take the values of bulk PAN.[17,18] Table I gives details of the experimental conditions and properties of the PAN fibers characterized in the experiment. Since the connected fiber is not straight, it is divided into several relatively straight sections to measure its length. For each section, we use a caliper to measure the fiber's image length and calculate the real length based on the scale bar in the picture. After experimental data are obtained, theoretical fitting is conducted to obtain the effective thermal diffusivity $(\alpha_m)$. Then Ea. (2) is employed to determine the real thermal diffusivity $(\alpha)$ of the PAN fiber. The phase shift fitting results for the three submicron PAN fibers are shown in Fig. 3. Sound agreement is obtained between the fitting result and the experimental data. The standard deviation between the fitting result and the experimental data $(\phi_{\text{diff}})$ is shown in Table I. The determined real thermal diffusivities of the submicron PAN fibers are summarized in Table I. Based on the thermal

TABLE I. Details of experimental conditions and properties for the PAN fibers characterized in this work.

| | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|
| Length ($\mu$m) | 200 | 200 | 227 |
| Resistance of sample ($k\Omega$) | 14.73 | 44.6 | 37.3 |
| dc voltage (V) | 0.4 | 0.4 | 2.0 |
| Laser power (W) | 4.0 | 4.0 | 4.0 |
| Resistance of the resistor serially connected with the sample ($k\Omega$) | 11.3 | 10.6 | 10.0 |
| $\phi_{\text{diff}}$ (deg) | 3.1 | 3.0 | 3.1 |
| $\alpha_m$ $(10^{-7}\ \mathrm{m^2/s})$ | 1.46 | 1.69 | 1.61 |
| $L_{\text{Lorenz}}TL/(RA_w\rho c_p)$ $(10^{-7}\ \mathrm{m^2/s})$ | 0.32 | 0.42 | 0.56 |
| $\alpha$ $(10^{-7}\ \mathrm{m^2/s})$ | 1.14 | 1.27 | 1.05 |

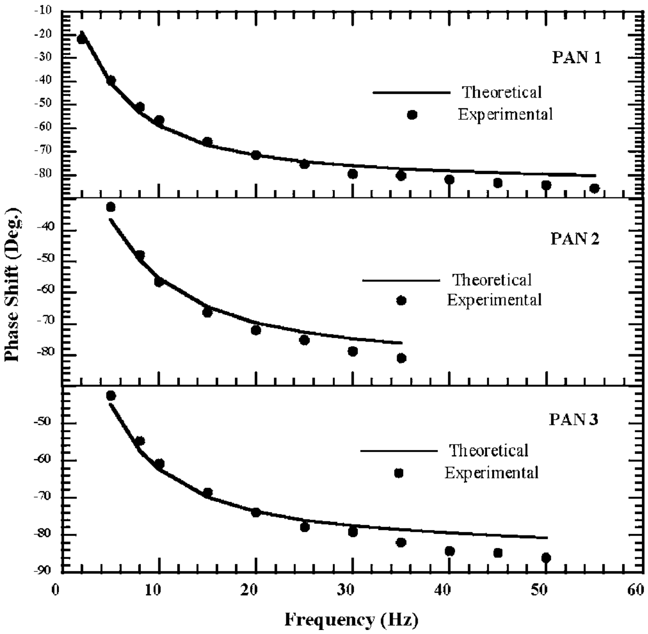

FIG. 3. Measured phase shift vs the fitting results for the PAN fibers.

conductivity (0.26 W/$m$ K) of bulk PAN, its thermal diffusivity is calculated as $1.75 \times 10^{-7}$ m$^2$/s. The average of our measured thermal diffusivity for submicron PAN fibers is $1.15 \times 10^{-7}$ m$^2$/s, a little smaller than the bulk value. This difference is probably due to structural defects in the PAN fibers. The mean free path of phonons in PAN is estimated to be less than 1 nm based on its bulk property. This scale is much smaller than the thickness (~800 nm) of the PAN fibers measured in this work. It is expected that the size of the measured PAN fibers will not affect their thermal conductivity. The electrospining technique used to make submicron PAN fibers may induce some structural defects such as nanopores in PAN fibers, which can enhance phonon scattering and reduce the thermal conductivity to a certain extent.

In summary, the OHETS technique was applied to characterize the thermal diffusivity of individual submicron PAN fibers. This represents an early attempt to characterize the thermophysical properties of nonconductive submicron/nanoscale wires. Our study showed that if the Au film coating is controlled at a reasonable (approximately in the nanometer range) thickness, the OHETS method can be applied to measure the thermal diffusivity of low thermal conductivity and nonconductive wires of submicron thickness. The measured thermal diffusivity of submicron PAN fibers was a little less than that of bulk PAN, probably due to the structure defects induced during the electrospinning process.

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[1] L. Lu, W. Yi, and D. L. Zhang, Rev. Sci. Instrum. **72**, 2996 (2001).
[2] X. Wang, P. Vellelacheruvu, J. Hou, C. Liu, and H. Cheng, *The 9th AIAA/ASME Joint Thermophysics and Heat Transfer Conference Poceedings*, San Francisco, CA (American Institute of Aeronautics and Astronautics, Reston, VA, 2006), Paper No. 3122.
[3] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, Phys. Rev. Lett. **87**, 215502 (2001).
[4] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, Physica B **323**, 67 (2002).
[5] L. Shi, D. Li, C. Yu, W. Jang, D. Kim, Z. Yao, P. Kim, and A. Majumdar, J. Heat Transfer **125**, 881 (2003).
[6] D. Li, Y. Wu, P. Kim, L. Shi, P. Yang, and A. Majumdar, Appl. Phys. Lett. **83**, 2934 (2003).
[7] L. Shi, Q. Hao, C. Yu, N. Mingo, X. Kong, and Z. L. Wang, Appl. Phys. Lett. **84**, 2638 (2004).
[8] M. Fujii, X. Zhang, H. Xie, H. Ago, K. Takahashi, T. Ikuta, H. Abe, and T. Shimizu, Phys. Rev. Lett. **95**, 065502 (2005).
[9] X. Wang, Z. Zhong, and J. Xu, J. Appl. Phys. **97**, 064302 (2005).
[10] J. Hou, X. Wang, and J. Guo, J. Phys. D **39**, 3362 (2006).
[11] T. Subbiah, G. S. Bhat, R. W. Tock, S. Parameswaran, and S. S. Ramkumar, J. Appl. Polym. Sci. **96**, 557 (2005).
[12] J. Hou, X. Wang, C. Liu, and H. Chen, Appl. Phys. Lett. **88**, 181910 (2006).
[13] C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), p. 178.
[14] Y. Yang, M. Aponte, N. Leon, I. Ramos, R. Furlan, and N. Pinto, J. Am. Ceram. Soc., **88**, 2059 (2005).
[15] Y. Wen, Ph.D. thesis, University of Nebraska-Lincoln, 2004.
[16] G. I. Taylor, Proc. R. Soc. London, Ser. A **313**, 453 (1969).
[17] C. Harper, *Handbook of Plastics, Elastomers, and Composites*, 2nd ed. (McGraw-Hill, New York, 1992), p. C.6.
[18] J. Kroschwitz, *Encyclopedia of Polymer Science and Engineering* (Wiley-Interscience, New York, 1985), Vol. 16, pp. 711–737.