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Transient thermal characterization of micro/submicroscale polyacrylonitrile wires

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ABSTRACT In this work, the thermal diffusivity of single polyacrylonitrile (PAN) wires with diameters from 4.62 μm down to 324 nm is measured by using our recently developed transient electro-thermal technique. The wires span from 23 μm to 126.2 μm in our measurement. Since PAN wires are dielectric, a thin Au film is coated on the surface of the wires to make them conductive. In the experiment, a step current (with ∼ 2 μs rising time) is fed to the sample. The sample is heated and takes a certain time to reach its steady thermal state. The temperature rising response of the sample is sensed by measuring the resistance change of the thin Au coating. From the average temperature evolution of the sample, the thermal diffusivity can be extracted. Three PAN wires with different diameters are synthesized using the electro-spinning technique and are measured to obtain their thermal diffusivities (around 1.53×10^{-7} m^2/s), which are slightly smaller than the bulk value.

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1 Introduction

Development of micro- and nanostructures/devices pushes researchers to design accurate and reliable techniques to characterize their thermophysical properties at micro/nanoscales for improved system functionality and dependability. The single wire $3-\omega$ method [1–3], the microfabricated device method [4–8], and optical heating and electrical thermal sensing (OHETS) technique [9–11] have been developed to measure the thermal properties of one dimensional structures at micro- and nanoscales. For the 3ω method, a linear I–V relationship is required for the sample itself, which significantly limits the measurement scope to conductive materials. In addition, separate measurement of the temperature coefficient of resistance for the sample is needed. The micro-fabricated device method, which involves heating one membrane and measuring the heat flux to the other one, has been developed to measure the thermal conductivity of multiwalled carbon nanotubes (MWCNTS) [4, 5] and silicon nanowires [7]. However, when measuring low thermal conductivity materials, the microfabricated method encounters difficulty in accurately estimating the heat flow through the suspended samples between the membranes. The OHETS technique provides a compelling means of measuring the thermal diffusivity of one-dimensional structures. With irradiating a periodically modulated laser over the sample, the periodical temperature variation of the sample is recorded and the phase shift difference between the temperature and the laser beam is used to extract the thermal diffusivity. Using the OHETS technique, we have measured successfully a large number of one-dimensional samples from micron to sub-micron scales [9–11].

Due to the large surface area, high porosity, and significantly improved mechanical strength, nanoscale organic and ceramic wires have found many applications, such as nanocomposites, filter medium, tissue scaffolds, and adsorption layers in protection clothing. However, very little research has been done to understand the thermophysical properties of nanoscale wires, probably due to the great difficulty in accurately characterizing the heat flux through them and the temperature gradient in them. To predict, evaluate, and improve the thermal performance of nanoscale wires during their fabrication and engineering applications, solid experimental data about their thermophysical properties, as well as knowledge about the structure-thermophysical property relationship, becomes extremely important. Such information is needed as the feedback in manufacturing of nanowires to significantly improve their structural properties, functions, and thermal stability. To overcome the challenge in thermal characterization of nanoscale fibers/wires, a transient electro-thermal (TET) technique has been developed in our lab [12]. This work reports the very early measurement of non-conductive nanoscale wires by using the TET technique.

2 Experiment details

In this work, PAN wires are synthesized using the electrospinning technique. In a typical electrospinning process, the polymer (polyacrylonitrile) is dissolved into dimethylformamide (DMF) solvent. The mixture solution is loaded into a glass tube, and a copper wire is inserted in the solution. A high voltage (15 ∼ 20 kV) is applied between the copper wire and the collector plate [13, 14]. When the electrostatic force overcomes the surface tension, the jet from the liquid droplet (which comes from the glass tube) becomes

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a continuous ultrathin nanoscale wire which is collected on an aluminum foil or directly captured under the pipette. To make the TET technique applicable, the wire needs to be coated with a very thin (a few nm) Au film to make it conductive. The wire is placed in a gold plating system (used for coating SEM samples) for Au coating. During coating, the Au vapor is mainly accumulated on one side of the wire. However, the nonuniform coating will not affect the one dimensional heat transfer model because heat will quickly transfer to the other side of the wire to make the temperature uniform over the wire cross section. Before doing wire coating, the coating time-film thickness relation is calibrated using a glass substrate. It is estimated that the thickness of the Au coating on the wire is less than 5 nm. During thermal characterization experiment, the coated wire is suspended over a groove in a quartz substrate, which is fabricated using femtosecond laser ablation. The groove is about 20 μm wide and 100 μm deep. For micrometer thick PAN wires, they are placed over a groove between two razor blades. The spacing between the two blades is about 100 μm. After suspending the sample over the groove, silver paste is applied to the wire-quartz/blade contact region to enhance the contact. The silver paste contacts also work as electrodes for connecting the sample to the measurement circuit as shown in Fig. 1. When feeding a step dc current to the sample, its temperature will increase and take a certain time to reach its steady state. The time taken to reach the steady thermal state is directly related to the thermal diffusivity of the sample [12]. From the temperature evolution, the thermal diffusivity of the sample can be determined. When the sample has a small temperature rise, its electrical resistance will have a small change proportional to its temperature rise. Considering this resistance change and the dc current through the sample, we find that a voltage variation over the sample will arise and can be recorded to represent its temperature evolution. The physical model and principles about the TET technique are detailed in our recent work [12]. Using this technique, we have measured micro-thick Pt wires to check its the accuracy. The measured thermal diffusivity agrees with the reference value with a difference less than 5%.

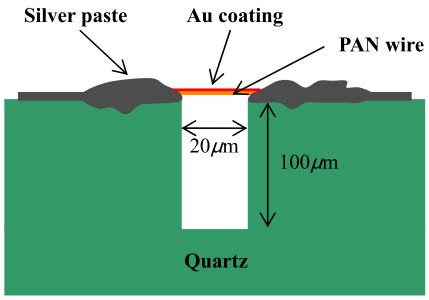

FIGURE 1 Schematic of the experiment principle. Silver paste is used to enhance the wire-base contact

In this work, a constant current source (KEITHLEY 6221) operated at a periodically modulated mode (square waves) is used to provide the constant step dc current through the sample. The current source itself has an internal modulator that can be configured to output square-wave current. The rising time of the square wave is about 2 μs, which is much shorter than the typical time taken to reach the steady state for the sample. The voltage variation over the sample is measured using a digital oscilloscope. As the diameter of the PAN wire is reduced to micro/nanoscales, the radiation between the wire and environment is becoming more important. In order to reduce the radiation effect and make it much less than the heat conduction along the wire, the length of the PAN wire used in this paper is only about 20 μm for the nanowire, and around 100 μm for the microwire. Numerical simulations have been conducted about the radiation effect for the measured samples. The results confirm that for the samples measured in this work, the radiation heat transfer from the wire surface has negligible effect compared with the heat conduction along the wire. The normalized average temperature change in the sample can be described as [12]

$$T^* = \frac{96}{\pi^4}\sum_{m=1}^{\infty}\frac{1-\exp[-(2m-1)^2\pi^2\alpha t/L^2]}{(2m-1)^4}, \quad (1)$$

where α and L are the thermal diffusivity and length of the sample, respectively.

Because of the reduced diameter, the thin Au coating on the wire will have a considerable contribution to heat conduction, for the reason that the Au film has a relatively higher thermal conductivity than PAN wires. Consequently, the measured thermal diffusivity α_m is a combined effect of PAN wire and thin Au coating, and is expressed as

$$\alpha_m = \frac{k(1-\beta)+k_f\beta}{\varrho c_p(1-\beta)+\varrho_f c_{p,f}\beta}, \quad (2)$$

where ϱ and c_p are the density and specific heat of the PAN wire, ϱ_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 wire. Using the Wiedemann–Franz law and concept of thermal conductance (G_f) of the thin film coating ($G_f = A_f k_f/L$, where k_f, A_f, and L are the thermal conductivity of the film in the axial direction, cross-sectional area of the thin film and the wire length, respectively), one can substract the effect of the thin Au coating on the measured α_m as

$$\alpha = \alpha_m - \left(\frac{L_{Lorenz}T}{R}\frac{L}{A_w}\right)/(\varrho c_p), \quad (3)$$

where A_w is the cross-sectional area of the wire and R is the resistance of the Au coating. The density ϱ and specific heat c_p used here are $1.15\times10^3\,\mathrm{kg\,m^{-3}}$ and $1.285\times10^3\,\mathrm{J\,kg^{-1}K^{-1}}$ for polyacrylonitrile [15, 16]. The Lorenz number L_{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 [17]. The temperature used in this work is generally taken as 300 K. Derivations of (3) are detailed in work by Guo et al. [12]. When using the resistance R to calculate the real thermal diffusivity in (3), the calculated thermal diffusivity is over-evaluated than the real value for the reason that the resistance R inevitably includes some contact resistance. However, the effect of the contact resistance could be insignificant since the Au coating is very thin and features large electrical resistance. In addition, the silver paste at the wire-base contact point will reduce the contact resistance significantly, which is confirmed by our extensive experiments using other samples. For the very thin Au coating used in this work, its small thickness and internal nanostructures will significantly enhance the scattering of free electrons and reduce their mean

free path. It is expected the electrical conductivity and electron thermal conductivity will be reduced with the same ratio by this mean free path reduction. Furthermore, the small dimension and nanostructure of the Au film will significantly enhance phonon scattering and reduce the lattice thermal conductivity. Therefore, similar to bulk Au, the lattice thermal conductivity will be much smaller than the electron thermal conductivity in the Au coating. As a result, the Wiedemann–Franz law can still be used to evaluate the effect of the Au film on heat transfer in the measurement result.

3 Results and discussion

In this work, three PAN wires with different diameters are measured to obtain their thermal diffusivities. Figure 2 shows the SEM images of the three samples measured in our experiment. Table I lists all the parameters and properties of three PAN wires characterized in the experiment. The least square fitting method is used to determine the thermal diffusivity of the sample. In this method, trial values of the thermal diffusivity are used to calculate the normalized temperature evolution of the sample. The value giving the best fit (least square) of the experimental data is taken as the property of the sample. Since the experiment data are very limited in the small range of time, the two other methods developed in our work [12] – characteristic point and initial linear fitting are not suitable to characterize the thermal diffusivity. After measuring the effective thermal diffusivity of the sample, (3) is employed to determine the real thermal diffusivity (α) of the PAN wires. The normalized temperature rise by experiment versus the fitting results is shown in Fig. 3. The deviation between the experimental results and the theoretical fitting is 1.0% for PAN 1, and 3.5% for PAN 2 and 3 based on the normalized scale for temperature rise. The real thermal diffusivities obtained are 1.77×10^{-7}, 1.35×10^{-7} and $1.47 \times 10^{-7}\,\mathrm{m^2/s}$. The detailed fitting results are listed in Table 1. Compared with the bulk value $1.76 \times 10^{-7}\,\mathrm{m^2/s}$, the measured thermal diffusivity is a little smaller. Since the size of the measured PAN wire ($\sim 300\,\mathrm{nm}$) is much larger than the estimated mean free path

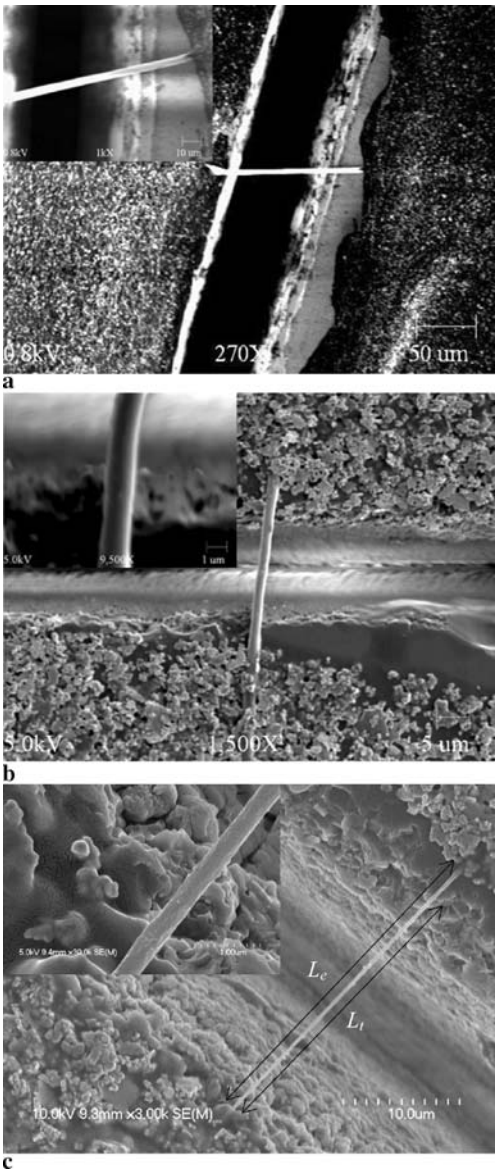

FIGURE 2 SEM images of three PAN wires measured in this work. (**a**) is for the thick sample (PAN 1) suspended over two electrodes 126.2 μm apart, (**b**) and (**c**) are for PAN 2 and 3. It is observed the thinnest PAN wire (**c**) has a diameter around 300 nm

($\sim 1.5\,\mathrm{nm}$) of phonons in bulk PAN, it is expected that the difference is probably caused by structure defects in PAN wires, such as nanopores, which can enhance phonon scattering and reduce the sample density and thermal conductivity, thereby reducing the thermal diffusivity to a certain extent.

For each of the three samples, experiments are conducted for several times to check the repeatability. Less than 15% deviation among experiments is achieved. When measuring the length of PAN wires for data processing, the length (denoted as thermal length: L_t) between the wire-quartz/blade contact

	Sample 1	Sample 2	Sample 3
Diameter (μm)	4.620	1.436	0.324
Length (μm)	126.2	23.0	24.9
Sample resistance (Ω)	44.9	273.5	1503.0
Current (μA)	1000	420	60
Voltage rise ΔV (mV)	0.867	1.221	2.296
α_m ($10^{-7}\,\mathrm{m^2/s}$)	9.85	3.85	11.12
$L_{\mathrm{Lorenz}}TL/(RA_w\varrho c_p)$ ($10^{-7}\,\mathrm{m^2/s}$)	8.08	2.50	9.65
α ($10^{-7}\,\mathrm{m^2/s}$)	1.77	1.35	1.47

TABLE 1 Details of experimental parameters and results for the PAN wires characterized in this work

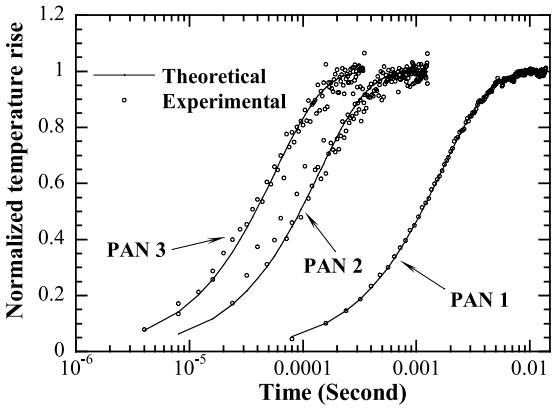

FIGURE 3 The normalized temperature rise by experiment versus the fitting result for the three PAN wires

points is used (as shown in Fig. 2c). This is because when the wire is in contact with the quartz/blade, the heat transfer from the wire will quickly go to the substrate and dissipate. Thus, the small part of the wire (denoted as $L_e - L_t$) between the edge of the substrate and the silver paste will have much reduced effect on heat transfer. In (3), the resistance of the wire is used to subtract the coating effect on heat transfer. If the silver paste does not have the same edge as the groove, the thermal length used for heat transfer analysis will be shorter than that (denoted as electrical length: L_e) between the wire-silver paste contacts. Under this situation, the resistance used in (3) will be calculated as $R = R_m L_t / L_e$, where R_m is the measured electrical resistance of the sample. It needs to be pointed out that use of thermal length in data processing could slightly underevaluate the thermal diffusivity of the sample since the part of wire immediately on the substrate can still have some contribution to heat transfer. This technical problem can be readily solved by using focused ion beam to deposit Pd pads precisely on the sample-electrode contact.

To evaluate the temperature rise of the sample, the steady state average temperature increase $\Delta T = q_0 L^2 / 12 k_{\text{eff}}$ is used. q_0 is the heating power per unit volume calculated from $4I^2R/\pi D^2 L$, k_{eff} is the effective thermal conductivity, which can be calculated from $k_{\text{eff}} = \alpha_m \varrho c_p$. Taking sample 3 as an example, the heating power q_0 is 2.64×10^{12} W/m^3 and the effective thermal conductivity is 1.64 W/m K. The average temperature rise is calculated to be 83.2°. When calculating the heating power, the resistance used inevitably includes contact resistance, which will make the estimated temperature higher than the real value. For an average temperature rise of 83.2°, the absolute temperature at the middle point of the wire will be 422.8 K (124.8° temperature rise at middle under 25 °C room temperature), which is higher than the glass transition temperature of PAN wire 363 K [18] and will break the sample. The very thin (< 5 nm) Au coating on one side of the PAN wire is not strong enough to hold the wire if it breaks since it is about 100 ∼ 1000 times thicker than the Au coating. However, our SEM observation confirms that the sample is not broken after experiment. Therefore, it is conclusive that the average temperature increase of the wire will be much lower than 83.2°. If considering the glass transition of PAN, it is estimated that the average temperature rise cannot exceed 43.3 °C. When feeding a current to the sample, based on the measured voltage rise ΔV over the sample, the average temperature increase can be estimated using the equation $\Delta V/(IR) = \varepsilon \Delta T$, where ε is the temperature coefficient of resistance for the Au film. Since the Au film is about few nanometers thick, we cannot use the bulk material value to calculate the temperature rise. Nevertheless, first order estimation can still be made to evaluate the temperature rise. Taking the bulk value for temperature coefficient of resistance ε for Au film 3.4×10^{-3} /°C [17], we estimated the average temperature rise to be about 7.5 °C only. Once again, the resistance used to calculate the voltage over the sample includes contact resistance, which will make the estimated temperature smaller than the real value. The real average temperature rise for sample 3 should be between 7.5 to 43.3 °C.

4 Conclusion

In conclusion, the TET technique was applied to characterize the thermal diffusivity of PAN nanowires as thin as 324 nm. This technique provides a novel way to achieve heating of the sample and observe its fast thermal response. The thermal diffusivity of nanoscale PAN wire is measured to be around 1.53×10^{-7} m^2/s, which is slightly smaller than the bulk value. This work demonstrated that the TET method can be used to characterize the thermal diffusivity of nonconductive wires at submicron and nanoscales.

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