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Yu Wang
University of California

Jorge J. Santiago-Aviles
University of Pennsylvania, santiago@seas.upenn.edu

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Low-Temperature Electronic Properties of Electrospun PAN-Derived Carbon Nanofiber

Abstract
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Keywords
Carbon nanofiber, electrospinning, hopping, low-temperature electronic properties, simple two-band model (STB)

Comments
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Low-Temperature Electronic Properties of Electrospun PAN-Derived Carbon Nanofiber

Yu Wang and Jorge J. Santiago-Avilés

***Abstract*—Although carbon nanofibers might have wide potentials in applications, most of their physical properties have yet to be investigated. This paper reports on the low-temperature electronic transport properties of an electrospun polyacrylonitrile-based carbon nanofiber, with its mean diameters around 120 nm. The resistance of the carbon fiber was measured using the four-point probe method from 295 down to 15 K. The semiconducting nature of the fiber is revealed by its positive temperature coefficient of conductance, i.e., an increase in conductivity with the temperature. The conductivity (σ) depends on temperature according to the relation, $\sigma = 5768\, T^{0.338} \exp(-2 \times 10^{-6}\ \mathrm{eV/kT})$, suggesting an almost zero bandgap and a strong temperature dependence of carriers mobility. Such temperature dependence of conductivity is very similar to that found in carbon microfibers, and can be explained using a simple two-band model with temperature-dependent mobility.**

***Index Terms*—Carbon nanofiber, electrospinning, hopping, low-temperature electronic properties, simple two-band model (STB) model.**

I. Introduction

CARBON fibers have wide applications in structural materials such as composites, and potentially in a multiplicity of nonstructural applications such as sensors [1]. The recent "rediscovery" of electrostatistic deposition has enabled one to spin a variety of ultra-fine polymer fibers in a simple way, which can be heat treated into carbon fibers with diameter in the nanoscale range [2]–[4]. The application of carbon nanofibers as sensing elements relies on their electronic transport properties being modulated by the sensing element physico–chemical interaction with the analyte. The authors recently evaluated the size of single electrospun polyacrylonitrile (PAN)-derived carbon nanofibers using a scanning probe microscope for measuring their conductivity at room temperature, and found that the conductivity depends on annealing temperature and time [5]. It has been known for a long time that the conductivity of carbon fibers decreases with temperature either monotonically or with an additional peak at very low temperature [6]. Such temperature dependence is not predicted by the usual analysis using the simple two-band model (STB) if the carrier mobility is assumed temperature independent [7], [8]. Thus far, weak electrons localization [6], electron–electron interaction [6], the Kondo effect [6], and the hopping mechanism [9] have been used to account for different temperature-dependent conductivity components for micrometer-size diameter carbon fibers. On the other hand, size effect has been found in carbon microfibers: conductivity increases with the increase of diameter from 1 to 7 μm [10]. It is interesting to investigate whether such temperature dependence of the conductivity trend continues in carbon fiber after the diameter is reduced into the nanoscale. Following a previous room-temperature conductivity investigation [5], this paper reports on the electronic properties of electrospun PAN-based carbon nanofibers between 15–295 K, and presents a plausible interpretation using the STB and hopping model.

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Y. Wang was with the Department of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, PA 19104 USA. He is now with the Department of Electrical and Computer Engineering, University of California at Davis, Davis, CA 95616 USA.

J. J. Santiago-Avilés is with the Department of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, PA 19104 USA.

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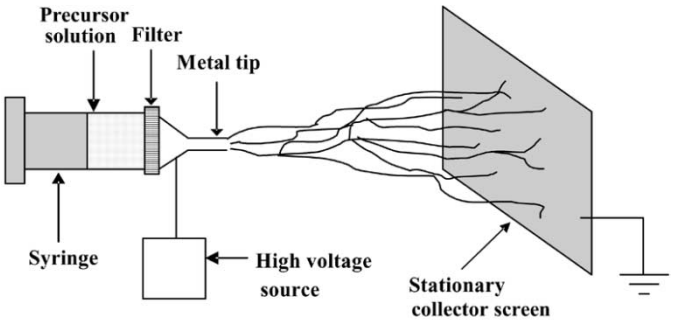

Fig. 1. Schematic of the homemade electrospinning setup.

II. Experiment

Using a homemade electrospinning setup, shown in Fig. 1 and described in detail elsewhere [4], single PAN fibers were electrostatically deposited from an 8 wt% PAN/N N-dimethyl formamide (DMF) precursor solution onto a single crystal silicon wafer substrate with a patterned gold contact array of 1 mm $\times$ 1 mm. The samples were heat treated at 1000 °C for 1/2 h in a vacuum of 10^{-5} torr. The vacuum heat-treated fibers were characterized using Raman microscattering. Their cross-sectional dimensions and area (S) were evaluated using a scanning electron microscope (SEM) and a scanning probe microscope (SPM) [4], [5]. Its resistance (R) was measured using the four-probe method from 295 down to 15 K with a sampling interval around 0.02 K. To suppress the possible heating effect during the measurement, the constant dc current passing through the fiber was kept at 1 μA or below, and the temperature was controlled automatically. Conductivity was $\sigma = L/RS$, where L, the length of the single fiber, was measured by an optical microscope [4], [5].

III. Results and Discussions

Fig. 2 shows an SEM image of the heat-treated carbon fiber. Its horizontal diameter was measured to be approximately

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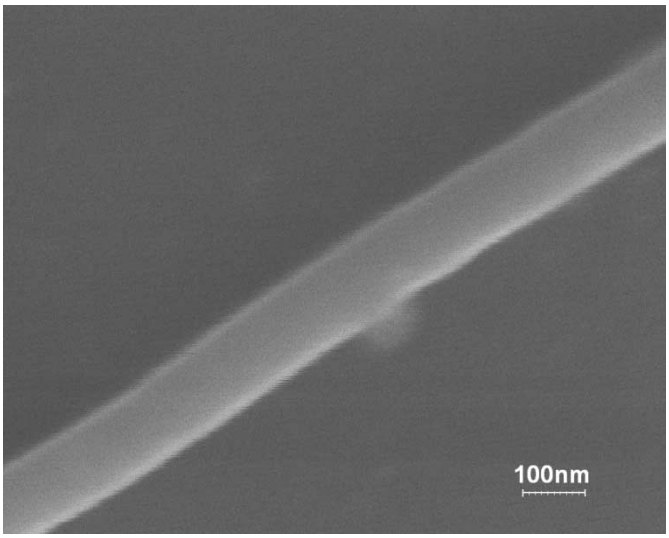

Fig. 2. SEM micrograph of carbon nanofiber.

120 nm. Scanning probe microscopy height image analysis revealed an elliptical cross-sectional profile with approximately the same horizontal diameter of 120 nm, a vertical diameter of only 75 nm [5], and its area $S = 7068 \pm 200$ nm^2. The Raman microscattering spectrum shows two strong peaks centered on 1371 and 1588 cm^{-1}, respectively, indicating disordered and graphitic carbons in the nanofiber. The in-plane graphitic crystallite size L_a was estimated to be around 2.5 nm [11].

Fig. 3 shows a plot of R and σ versus temperature (T) in the range from 15 to 295 K. Note that σ increases monotonically and smoothly from 1.0×10^4 S/m at 15 K to 2.75×10^4 S/m at 295 K, indicating the semiconducting nature of the fiber. Similar temperature dependence of conductivity was also found in carbon microfibers [8].

Since the fiber was heat treated at a relatively low temperature of 1000 °C, it is highly disordered with nanoscopic crystalline domains, and the conducting mechanism may be of the hopping type. For the hopping mechanism, the conductivity shows a T dependence such as

$$\sigma(T) = \sigma_0 \exp\left[-\frac{A}{T^{1/(d+1)}}\right] \tag{1a}$$

or

$$\ln\sigma = \ln\sigma_0 - AT^{-1/(d+1)} \tag{1b}$$

where d is the dimensionality and T and A are two other constants [9]. There is controversy about the dimensionality of carbon fiber [6], [12]. For inclusive purposes, $\ln\sigma$ was plotted against $T^{-1/4}, T^{-1/3}$, and $T^{-1/2}$ in Fig. 4 and, as expected, the three curves are linear for low-temperature values. Their deviation from a linear relation at higher temperature may be due to the increase in carrier concentration or mobility, as will be discussed later. From a comparison, it seems that $d = 3$ has the best fit to a linear form.

Although the investigated fiber is highly disordered, with small crystallite size, the binder or grain boundary material is deemed a minor part of the phase. Therefore, we may have small crystalline domains very near each other forming a quasi-continuous crystalline phase. In other words, the material

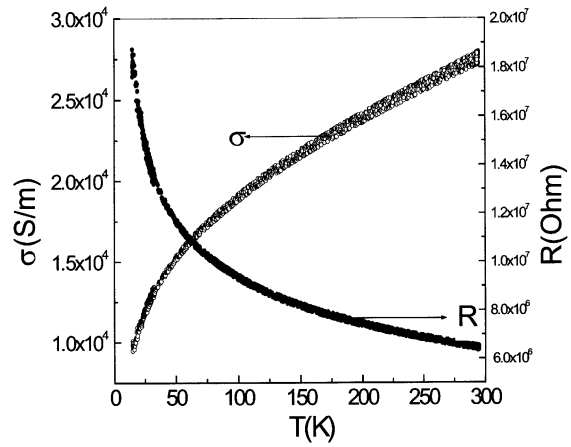

Fig. 3. Temperature dependence of R and σ.

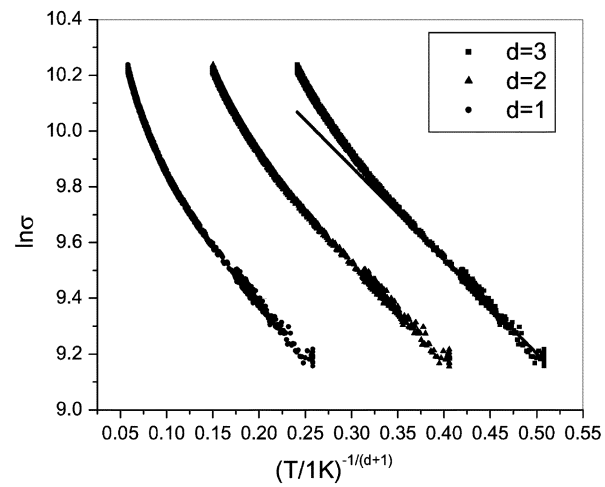

Fig. 4. $\ln\sigma$ versus $T^{-1/(d+1)}$ curves for different dimensionalities.

is seen as a continuum of turbostratic domains with defective areas as grain boundaries. Under such an assumption, one may quickly suspect that the conductivity is thermally activated following an Arrhenius relation

$$\sigma \propto \exp(-E_g/\mathrm{kT}) \tag{2}$$

where E_g is the energy bandgap and k is Boltzmann constant. When the data is plotted as shown in Fig. 5(a), the relation between $\ln\sigma$ and $1/T$ is nonlinear, indicating the temperature dependence of E_g in such a model. From the tangential slope of the $\ln\sigma$ versus $1/T$ curve in Fig. 5(a), we found that E_g decreases from 2.5×10^{-2} eV around 295 K to 2.8×10^{-4} eV at 15 K, i.e., E_g/kT varies between 0.987 around 295 K and 0.221 around 15 K. Such a low E_g/kT value indicates that (2) is not valid because the latter holds only for $E_g/\mathrm{kT} \gg 1$. The conductivity needs to be expressed as

$$\sigma = e(n_e\mu_e + n_h\mu_h)$$

where e is the charge of a single electron or hole, n_e, μ_e, n_h, and μ_h are concentration and mobility of electrons and holes, respectively. Considering the intrinsic nature of the investigated nanofiber, we assume $n_e = n_h = n$. If $\mu_e = \mu_h = \mu$ is assumed additionally, then

$$\sigma = 2en\mu$$

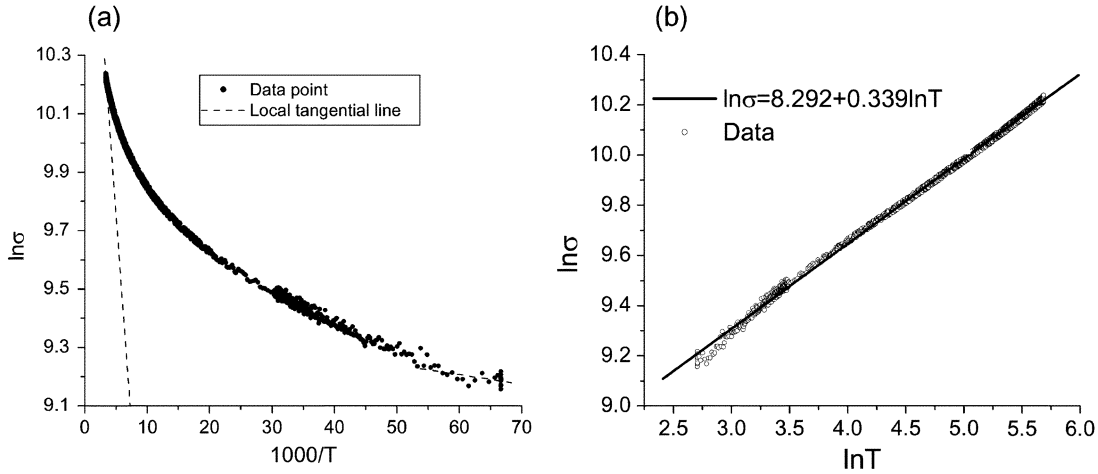

Fig. 5. Two possible fittings, using: (a) (2) and (b) (5).

where

$$n \propto \mathrm{kT} \ln\left(1 + e^{-Eg/2\mathrm{kT}}\right) \tag{3}$$

according to the STB model [7], [8]. In carbon fibers, carriers are scattered by lattice vibration and impurity, which limit μ in such a way as follows:

$$1/\mu = 1/\mu_0 + 1/\mu_i$$

where μ_0 and μ_i are the mobility determined by impurity scattering and lattice vibration scattering, respectively. Since impurity scattering is temperature insensitive and lattice vibration scattering is strongly temperature dependent, we assume μ_0 is independent of T and

$$\mu_i = \lambda T^{-\nu}$$

with constant coefficient λ and index ν ($0 < \nu < 1$) [12]. Therefore,

$$\sigma(T) = c\left[T/(T_c^{\nu} + T^{\nu})\right] \ln\left(1 + e^{-Eg/2\mathrm{kT}}\right) \tag{4}$$

where c is a constant, $T_c = (\lambda\mu_0)^{-1/\nu}$ is a characteristic temperature below which impurity scattering predominates lattice vibration scattering in determining carrier mobility.

Since the variation in E_g is small, for $T \gg T_c$, (4) can be approximated as

$$\sigma \propto T^{1-\nu} \tag{5}$$

which is verified in Fig. 5(b) with $\nu = 0.661$.

Fitting the results to (4), we obtained $c = 5771 \pm 249, \nu = 0.662 \pm 0.001$ and $E_g = (2.0 \pm 9.7) \times 10^{-6}$ eV, $T_c = 10^{-6}$ K (Fig. 6). The small value of E_g is consistent with Fig. 2. Consequently, the carriers' concentration is controlled predominately by the T in (4) pre-exponential factor. Meanwhile, the low T_c value implies a power law $T^{-0.662}$ dependence of mobility in the investigated temperature range. Thus, the conductivity is controlled not only by the carrier concentration $n(T)$, but also by their mobility $\mu(T)$, both of which depend on the temperature and contribute to the power law temperature dependence for $\sigma(T)$.

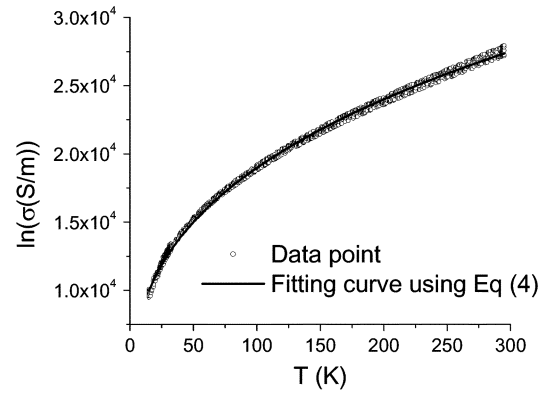

Fig. 6. Fitting the results to (4).

IV. Conclusion

The conductivity of electrospun PAN-based carbon nanofiber, annealed at 1000 °C for 1/2 h was found to increase with temperature in the range from 15 to 295 K. The relation can be best fitted as

$$\sigma = (5768 \pm 37) T^{0.3382 \pm 0.001} \exp\left[-(2.0 \pm 9.7) \times 10^{-6}\,\mathrm{eV/kT}\right]$$

indicating a very small bandgap and a $T^{-2/3}$ carrier's mobility temperature dependence. The conducting mechanism may be three-dimensional (3-D) hopping in the lower range of the investigated temperature.

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Yu Wang received the B.S. degree in materials science and engineering from Shanghai Jiaotong University, Shanghai, China, in 1988, and the M.S. and Ph.D. degrees in electrical engineering from the University of Pennsylvania, Philadelphia, in 2001 and 2003, respectively.

He is currently a Post-Doctoral Fellow with the Department of Electrical and Computer Engineering, University of California at Davis. He has performed research in the areas of diamond thin film, intermetallic alloys, nanotechnology (lead zirconate titanate, carbon nanofibers, and their electronic properties). His current research interest is field-emission vacuum microelectronics for flat-panel display.

Jorge J. Santiago-Avilés is currently an Associate Professor of electrical and system engineering at the University of Pennsylvania, Philadelphia. His research interests span the interface between electronic devices and materials science. He has performed research in II–VI semiconducting compounds for LEDs, carbon and graphite composites, silicon sensors and actuators, electroceramic devices, and low-temperature co-fired ceramic (LTCC) tape-based sensing and actuating devices. His current interests are focused on the field of nanostructures and nanomaterials.