Low Temperature Electronic Properties of Electrospun PAN-Derived Carbon Nanofiber

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ABSTRACT

This paper reports the low temperature electronic transport properties of electrospun PAN-based carbon nanofiber, with diameters around 100nm. The resistance/conductance of carbon fibers was measured using the four-point probe method from 295K down to 15K. The semiconducting nature of the fiber is revealed by the thermal coefficient of resistance, i.e. the increase in conductivity, with the increase of the temperature. The correlation between conductivity (sigma) and temperature T can be fitted to a power law as: $\sigma=5768T^{0.338}\exp(-2\times10^{-6}eV/kT)$, suggesting an almost zero band gap and a strong temperature dependence of carriers mobility.

Keywords: carbon nanofibers, conductivity, electrospinning, low temperature, STB model

1 INTRODUCTION

Carbon fibers have wide applications in structural materials such as composites, and potentially in a multiplicity of non-structural applications such as sensors [1]. So far, the diameter of as fabricated carbon fibers has been in a scale of microns. 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 pyrolyzed into carbon fibers with diameter in the nano-scale 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 fiber electronic characterization becomes increasingly difficult with the decrease of the temperature to 0K and the reduction of diameter into the nano-scale. With the simple two band model (STB) [5, 6], weak electrons localization, electron-electron interaction, and Kondo effect are known to contribute to different temperature-dependent conductivity components for micron size diameter carbon fibers [7]. It is interesting to evaluate the scaling of such effects, that is, if similar effects exist after the diameter is reduced into the nano scale. This paper reports the electronic properties of electrospun PAN-based carbon nanofibers from between 15 and 295K, and plausible interpretations using the STB model.

2 EXPERIMENT

Using a homemade electrospinning setup shown in Fig. 1 and described in details elsewhere [4], Single Polyacrylonitrile (PAN) fibers were electrostatically deposited from 8wt% PAN/ N, N-Dimethyl Formamide (DMF) precursor solution onto a single crystal silicon wafer substrate with a patterned gold contact array of 1mm x 1mm. The samples were pyrolyzed at 1000°C for a half hour in a vacuum of 10^{-5} Torr. The vacuum-pyrolyzed fibers were characterized using Raman microscattering. Their cross section dimensions and area (S) were evaluated using scanning electron microscope (SEM) and scanning probe microscopes (SPM) [4]. Its resistance (R) was measured using the four point probe method from 295K down to 15K. The constant DC current passing trough the fibber was 1μA 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].

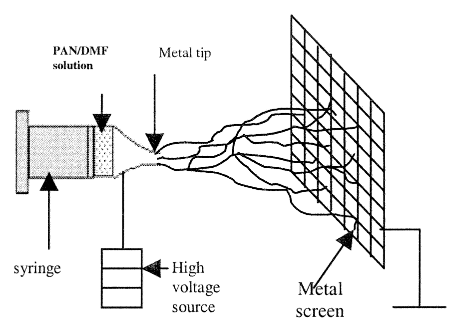


Fig. 1 Schematic of the homemade electrospinning setup

3 RESULTS AND DISCUSSIONS

Figure 2 show a SEM image of the pyrolyzed carbon fiber. Its horizontal diameter was measured to be around 120 nm. SPM height image analysis revealed an elliptical cross section profile, with approximately the same horizontal diameter of 120nm, a vertical diameter of only 75nm [8], and its area S = 7000±200nm^2. The Raman micro-scattering spectrum (Figure 3) shows strong peaks centered on 1371 and 1588 cm^{-1}, indicating disordered and graphitic carbons in the nanofiber. The in-plane graphitic crystallite size L_a was estimated to be around 2.5nm [9].

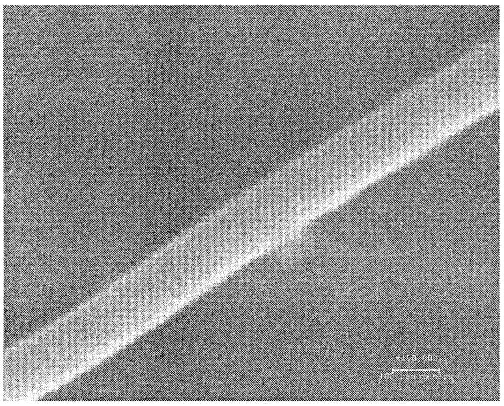


Fig. 2 SEM micrograph of carbon nanofibers

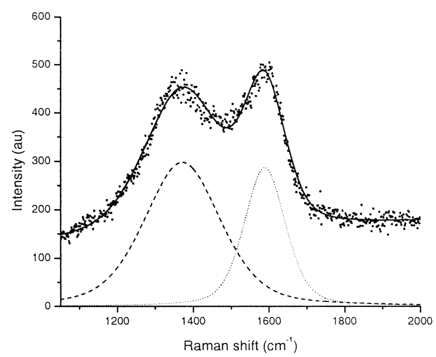


Fig. 3 Typical Raman spectrum

Figure 4 shows a plot of R and σ versus temperature (T) in the range from 15 to 295K in. Note that σ decreases monotonically and smoothly from 1.0×10^4 S/m at 15K to 2.75×10^4 S/m at 295K, indicating the semiconducting nature of the fiber. One may quickly suspect that the conductivity is thermally activated following an Arrhenius relation:

$$\sigma \propto \exp(-E_g/kT) \tag{1}$$

where E_g is the energy band gap and k is Boltzmann constant. When the data is plotted as shown in Figure 5a, the relation between lnσ and 1/T is nonlinear, indicating the temperature dependence of E_g in such a model. From the tangential slope of the ln σ vs 1/T curve in Fig 5a, we found that E_g decrease from 0.06eV around 295K to 0.0007eV at 15K, i.e. E_g/kT varies between 0.6 around 295K and 2.4 around 15K. Such a low E_g/kT value indicates that Eq. (1) is not valid because the latter holds only for $E_g/kT>>1$. This

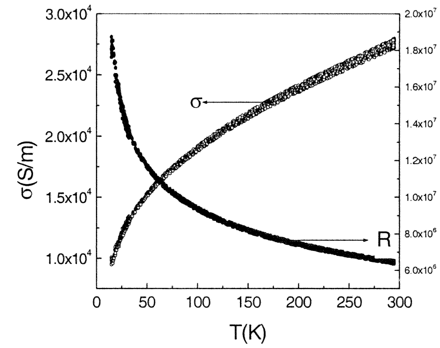


Fig. 4 Temperature dependence of R and σ

may indicate the need to manipulate the expression for conductivity, 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 mobility of electron and hole, respectively. Because of the intrinsic nature of our carbon nanofiber, $n_e=n_h=n$. If $\mu_e=\mu_h=\mu$ is assumed, $\sigma = 2en\mu$, where

$$n \propto kT\,\ln(1+e^{Eg/2kT}) \tag{2}$$

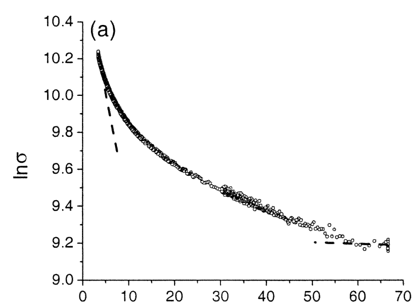
according to the STB model [5, 6], and $\mu\propto T^{-d}$, with 0<d<1 [10]. Consequently,

$$\sigma = c\,T^{1-d}\ln(1+e^{Eg/2kT}), \tag{3}$$

where c is a constant.
Since the variation in E_g is small, Eq. (3) can be approximated as

$$\sigma \propto T^{1-d} \tag{4}$$

which is verified in Figure 5b with d=0.661.



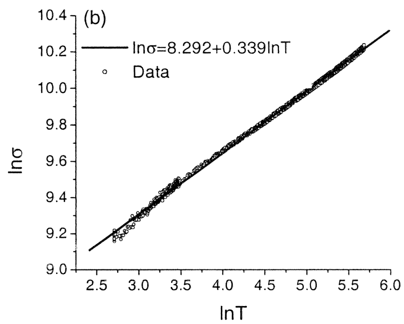


Fig. 5 Two possible fittings, using Eqs. (1) and (4) (a, b)

Finally, we used Eq. (3) to fit our results, and obtain c=5768±37, d=0.662±0.001 and $E_g=(2.0\pm9.7)\times10^{-6}$eV (Figure 6). The small value of E_g, consistent with Fig 4. Note that the large fitting error implies almost zero band gap. Consequently, the carriers' concentration is controlled predominately by the T in Eq. (3) pre-exponential factor. Also noteworthy is that the temperature dependence of mobility goes as $T^{-0.662}$. So the conductivity is controlled not only by the carrier concentration n(T), but also by their mobility μ(T), both of which contribute to the power law temperature dependence for σ.

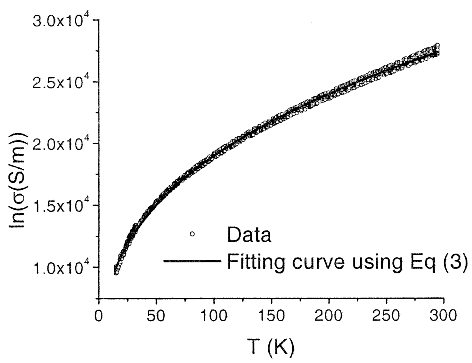


Fig. 6 The fitting results using Eq. (2)

4 CONCLUSION

The conductivity of electrospun PAN-based carbon nanofiber, pyrolyzed at 1000° C for half an hour was found to increase with temperature in the range from 15 to 295K. The relation can be best fitted as

$$\sigma = (5768\pm37)T^{0.3382\pm0.001} \exp[-(2.0\pm9.7)\times10^{-6}\mathrm{eV}/kT],$$

indicating very small band gap and a $T^{-2/3}$ carriers mobility temperature dependence.

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