Correlation of properties with preferred orientation in coagulated and stretch-aligned single-wall carbon nanotubes

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We report structure-property correlations in single-wall carbon nanotube (SWNT) fibers, among electrical, thermal, and chemical parameters with respect to stretch-induced preferential SWNT alignment along the fiber axis. Purified HiPco (high-pressure CO) conversion tubes are dispersed with the aid of an anionic surfactant and coagulated in the co-flowing stream of an adsorbing polymer. The fibers are then dried, rewetted under tensile load, and redried to improve the alignment. Complete removal of the polymer was assured by annealing in hydrogen at 1000 °C. The degree of alignment was determined by x-ray scattering from individual fibers using a two-dimensional detector. The half width at half maximum describing the axially symmetric distribution of SWNT axes decreases linearly from 27.5° in the initial extruded fiber to 14.5° after stretching by 80%. The electrical resistivity \( \rho \) at 300 K decreases overall by a factor \( \frac{4}{3} \) with stretching, for both as-spun composite and polymer-free annealed fibers. However, the temperature dependence \( \rho(T) \) is markedly different for the two, implying different electron-transport mechanisms with and without the polymer. Thermal conductivity also improves with increasing alignment, while the absolute values are limited by the disordered network of finite length tubes and bundles. Comparisons are made with results from similar fibers spun from oleum and with magnetically aligned buckypapers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1810640]

I. INTRODUCTION

Macroscopic oriented assemblies of single-wall carbon nanotubes (SWNT) are far more attractive for practical applications than the random tangles of bundled tubes typically found in as-grown or purified bulk samples. Fiber forms could be the starting point for the construction of useful structures which retain to some degree the excellent axial properties expected from perfect infinitely long tubes. Nanotube fibers can be spun by injection of a SWNT suspension through an orifice into a co-flowing stream of a coagulating solution.1,2 This general principle can be simply achieved by mixing an aqueous surfactant-stabilized SWNT dispersion into an aqueous solution that contains a polymer such as polyvinyl alcohol (PVA) as coagulating agent. The resultant fibers offer a promise for high strength, light weight, and thermally and electrically conducting structural elements at a lower cost than other nanotube forms. Industrial-scale continuous processing appears feasible. Mechanical,3 electrical, and thermal4 properties will depend on the degree of SWNT alignment induced by fiber synthesis and postprocessing. Similar fibers can also be spun from strong acid suspensions.5

In this paper we study the preferred orientation of PVA/SWNT fibers which are stretch-aligned after spinning6–9 and correlate their structural features with electrical resistivity and thermal conductivity. The degree of nanotube orientation with respect to the fiber axis is characterized by x-ray scattering.6–9 The angular distribution of the scattered intensity can be modeled by a Gaussian function, the half width at half maximum (HWHM) of which decreases overall by a factor \( \sim 4 \) with stretching, for both as-spun composite and polymer-free annealed fibers. However, the temperature dependence \( \rho(T) \) is markedly different for the two, implying different electron-transport mechanisms with and without the polymer. Thermal conductivity also improves with increasing alignment, while the absolute values are limited by the disordered network of finite length tubes and bundles. Comparisons are made with results from similar fibers spun from oleum and with magnetically aligned buckypapers. © 2004 American Institute of Physics.
lating PVA, allows the resistivity to be significantly reduced, by almost four orders of magnitude. Resistivity measurements from 1.4 to 300 K reveal more information on these structurally disordered conductors. Neat fibers contain up to 50 wt % PVA and thus can be considered composites of conducting fillers in an insulating matrix. The resistivity is thus very high and strongly temperature-dependent. We find ρ(4 K)/ρ(297 K) ≈ 10^6. The temperature dependence ρ(T) fits very well to the Mott-type phonon-assisted variable range hopping (VRH) but with unphysical parameters. For stretch-aligned fibers after annealing, excellent fits to three-dimensional (3D) weak localization (3DWL) and Coulomb gap variable range hopping (CG-VRH) above and below 25 K, respectively, are obtained. Both are consequences of disorder. The low-T CG-VRH regime indicates the opening of a small gap Δc in the density of states when Δc ≈ kT, signifying a metal-insulator transition.10 In contrast, the thermal conductivity is insensitive to the presence of PVA, the T dependence being dominated by the heat capacity as is generally observed.11 The present results show the critical importance of understanding the correlation between the chemical and structural nature of nanotube fibers and their electrical properties.

II. EXPERIMENT

The details of the principle of the spinning method has been described elsewhere.1 The present fibers are spun from purified HiPco (high-pressure CO) conversion tubes purchased from Carbon Nanotechnologies Inc. (batch CM26). The tubes were purified by a single pass of thermal oxidation followed by stirring in warm HCl, which typically reduces residual Fe catalyst from 6 to 10 to <1 at. %.12 Dispersions consisting of 0.3 wt % carbon nanotubes and 1.2 wt % sodium dodecyl sulfate ionic surfactant were prepared. The dispersion is sonicated to achieve a good homogenization. The coagulating medium is an aqueous solution that contains 5 wt % PVA. The nanotube dispersion is injected at 50 ml/h through a conical tip into the polymer solution contained in a rotating bath (100 rpm). The obtained fibers are then washed three times in pure water, dried in air at room temperature, and finally stretched, as follows.7,8

Dried fibers are reswollen in a 50/50 wt mixture of water and acetone and then loaded with a given weight and dried under tensile load. The corresponding elongation was determined for each given weight. This method allows the nanotube alignment within the fibers to be improved.6,8 Finally, a portion of each fiber stretched at different draw ratios is annealed at 1000 °C in hydrogen to remove the organic polymer. Annealed and nonannealed fibers have been investigated.

Electrical properties were measured and correlated to the fiber texture, which in turn was determined by the analysis of synchrotron x-ray fiber diagrams.7,9 Resistivity was measured by a four-probe dc technique. Voltage probes were about 2−3 mm apart. Samples were immersed in He, which could be pumped to ~1.5 K. Thermal conductivity κ was measured in the range 10−300 K using a comparator method.4 In brief, a known heat flow Q passes through a constantan rod, then the sample, and finally a second constantan rod, to a heat sink. Three differential type E thermodouples using 0.00025-in. diameter wires are employed to measure the temperature drops across the sample and the constantan standards, with small sapphire chips to electrically isolate the differential thermocouple from the electrically conducting fiber. Thermal conductance is obtained by averaging the two ratios of temperature drops across the sample and either constantan, then scaled by a dimensional factor. Averaging the two ratios accounts approximately for radiation losses since one of the two constantans is hotter or colder than the sample. The accuracy of both the ρ and κ data, estimated as ±30%, is limited by the errors in sample dimensions. Sample densities were not determined so no corrections for voids and porosity were made.

III. RESULTS AND DISCUSSION

The x-ray scattering experiments were performed on single fibers using synchrotron radiation at LURE, France (beam line D43). To avoid background due to the fluorescence from iron catalyst remaining even after purification, experiments were performed at an energy below the K absorption edge of iron, corresponding to a wavelength of 1.795 Å. We study the azimuthal intensity distribution at wave vectors corresponding to the (1,0) peak of the nanotube bundles as detailed in Ref. 6. The scattering maxima are perpendicular to the fiber axis, which shows that the nanotube bundles are preferentially aligned along this axis. The HWHM, deduced from a Gaussian fit, characterizes the distribution of nanotube bundle orientations in the fiber (together with their possible curvatures).

As shown in Fig. 1 and as expected, stretching neat or as-extruded PVA/SWNT fibers decrease the width of Gaussian fits to x-ray fiber diagrams, essentially monotonically with increasing elongation. The neat fiber (0% stretch) is already partially aligned due to the elongational shear flow accompanying the spinning process. The degree of alignment, as measured by the HWHM is slightly better than the best fibers spun from oleum11 but not as good as is found in

FIG. 1. Gaussian half width at half maximum (HWHM) vs stretch ratio for PVA/SWNT composite nanotube fibers. The initial alignment (stretch % =0) results from the extrusional flow during spinning. This improves due to extensional flow under tension.
The removal of the PV A leads to a reduction in resistivity, but the absolute value is intermediate between all SWNT fibers and polymer composites. The dashed line is a guide to the eye.

Resistivity at room temperature $\rho(297 \, \text{K})$ versus stretch ratio is plotted in Fig. 2 for unannealed fibers. A trend is evident; a decrease is found as the fibers are stretched, indicating that an improvement of nanotube alignment yields better conductivity. In detail, $\rho$ decreases rapidly at first, then saturates at $\sim 35\%$ stretch. Surprisingly, this behavior is not reflected in the alignment HWHM versus stretch % (Fig. 1), suggesting that above an intermediate degree of alignment, $\rho(297 \, \text{K})$ is limited by some other factor which does not improve with further stretching. For this set of experiments, the cross-sectional areas were determined fairly accurately from the image analysis of scanning electron microscopy (SEM) data, so we can safely conclude that improving the HWHM from 27.5° to 14.5° reduces $\rho(297 \, \text{K})$ by about a factor of 4.

Selected fibers were annealed in H$_2$ at 1000 °C after stretching to remove the insulating PV A and thereby obtain more highly conducting fibers. We showed previously that PV A is indeed entirely removed by such a procedure, while the nanotube alignment is unchanged.$^{12}$ In Fig. 3 we plot the 297 K resistivity versus stretch % after annealing. The data are more scattered than in Fig. 2 because the cross sections are less accurately known. Despite the scatter, it is unambiguous that the removal of the PV A leads to a reduction in $\rho(297 \, \text{K})$ by almost four orders of magnitude. This strong variation suggests that the conductivity in neat fibers is limited by the presence of PV A, possibly by reducing the density of contacts between nanotube bundles and/or creating strong tunneling barriers between conducting regions.

To gain more insight into the conduction mechanisms, we performed $\rho(T)$ measurements on a composite fiber stretched 53% and an annealed one stretched 76%. The data are shown in Fig. 4; note log-log scale. At 300 K $\rho$ for the composite fiber exceeds that of the annealed one by 4–5 decades, as noted above. At low temperature the difference is more dramatic. The composite fiber resistance became too high to measure at the lowest temperature. Extrapolating to 2 K, we deduce a ratio of at least 11 decades, strongly suggesting totally different conduction mechanisms in the two morphologies.

It is obvious from the data that disorder dominates the charge transport in both states. Furthermore, the disorder is most likely to encompass all three dimensions since the fibers consist of coupled and intertwined objects. In particular, we expect that the disorder is not limited to a one-dimensional (1D) carrier localization on individual tubes or bundles, nor to defect scattering/trapping on single tubes. The huge effect of PV A, which permeates the interbundle volumes in the composite fibers, cannot possibly be 1D.

First we discuss the model fits to $\rho(T)$ of annealed fibers. Figure 5 shows the data and fit to a log($\rho$) versus 1/$\sqrt{T}$ law in the range 1.4–300 K, characteristic of a strong localization. The fit is perfect below 25 K but deviates significantly.
at a higher $T$. It is tempting to assign this behavior to phonon-assisted (Mott) VRH between electron states localized in one dimension. As noted above, we believe this is inconsistent with the morphology of these materials. A second phenomenon with the same functional dependence is Coulomb gap VRH, wherein strong electron–electron correlations open a gap at the Fermi energy in the otherwise continuous density of states. This model also predicts $\rho(T) \propto \rho_0 \exp[ (T_0/T)^{1/2} ]$, with $1/T_0$ a measure of the spatial extent of the localized wave function; above $T_0$, the thermal energy is sufficient to thermally excite carriers across the Coulomb gap. [In the case of phonon-assisted (Mott) VRH, $kT_0$ is the average energy spacing between the localized states.] Above 25 K, the data fit well to a model of weak localization in 3D, $\rho(T) = \rho_0 \exp[ (T_0/T)^{1/2} ]$, with $\sigma(T)_{3DWL} = \sigma_0 (1 + (T/T_0)^{0.5})$ (not shown). The exponent $1/2$ depends on the details of the phase scattering, typical values ranging from 0.8 to > 2. We note from Fig. 5 that CG-VRH accounts for 3 decades of resistivity variation while the 3DWL regime covers less than a decade of $\rho(T)$.

Identifying the transport mechanism in composite fibers is less evident. Figure 6 shows the data for an 80% stretched composite fiber, along with an excellent fit to the generic strong localization formula $\rho \propto \exp(A/T)^s$ covering ~5 decades in resistivity. Unfortunately neither $A$ nor $s$ makes physical sense, for either Mott or CG strong localization. Fitted exponents $s$ are $0.20 \pm 0.03$ for five samples with different stretch ratios, whereas for CG, $s = 0.5$ and for the Mott-type VRH $s = 1/s_{VRH}$, if the dimensionality is 3, 2, or 1, respectively. One might argue that the fitted $s$ is sufficiently close to the 3D value of $1/s_{VRH}$ to be physically acceptable. Unfortunately, the corresponding $kT_0$ values would imply average localized state energy separations ranging from 260 to 2200 eV for different stretch ratios, clearly nonsensical. As an alternative, we offer an interesting and testable speculation at ~50 wt % insulating PVA, the composite system is barely above a percolation threshold at high $T$, and differential thermal expansion of PVA and SWNT conspire to bring the system below percolation at low $T$, for example, by reducing the number of intertube contacts. One test would be to study the effect of variable PVA content by controlling the coagulation bath composition and/or annealing at low temperatures.

Thermal conductivity $\kappa$ of the annealed fiber was measured from 10 to 300 K in a closed-cycle cryostat. The comparator method requires that the thermal conductance $G$ of the sample be comparable in magnitude to that of the constantan standards. Sufficient fiber length to achieve this criterion was only available for two stretch ratios, namely, 21% and 58%, for which 20 and 24 ~2-mm lengths, respectively, were assembled in parallel to achieve a sufficient $G$ (sample). The results are shown in Fig. 7. $\kappa$ is dominated by phonons so it increases smoothly with temperature as more vibrational modes become occupied. We did not attempt to measure the composite fibers.

Room-temperature values are approximately 4 and 10 W/mK for low and high stretch ratios, respectively, indi-
cating that $\kappa$ is improved by SWNT alignment, in common with electrical conductivity. Absolute values are about half of those measured for similar fibers spun from oleum,\textsuperscript{4} which is surprising since both fiber series involve HiPco SWNT and similar acid purification schemes. A trivial explanation would be different for effective sample dimensions due to gross voids and/or microporosity, since in both cases, the raw data were not corrected for density. A second possibility is that interparticle contacts are more favorable in the oleum-based fibers.\textsuperscript{14} In any event, all the fiber $\kappa$ values are very low compared to the $\kappa$ of graphite parallel to the layers. Density corrections account for a factor of only 2–5 from our previous experience. Also the tubes/bundles in the fiber are not perfectly aligned. The largest $\kappa$ measured to date, 19 W/mK, was obtained from a fiber with a mosaic HWHM of $21^\circ$,\textsuperscript{4} about half the value for the best magnetic-field-aligned buckypaper: 48 W/mK uncorrected for density, HWHM = $16^\circ$.\textsuperscript{15}

The SWNT in buckypaper sample were grown by pulsed laser vaporization, which generally produces longer tubes than the HiPco process. The most important reason for the rather low fiber $\kappa$’s achieved thus far is probably the aforementioned thermal barriers between bundles, etc., which would reduce the mean free path for phonon scattering.

**IV. CONCLUSIONS**

We have studied in this work the electrical and thermal properties of carbon nanotube fibers formed by coagulation spinning. Clear correlations between structure and properties are evidenced. Both electrical and thermal conductivity of neat or composite fibers can be improved upon alignment of the carbon nanotubes. The relative improvement is rather modest, by a factor of 3 to 4 for electrical conductivity, for fibers having the same chemical nature. In sharp contrast, annealing the fibers to remove insulating polymers and obtain neat nanotube fibers, leads to significant increase of the conductivity, by several orders of magnitude, and to differences in the intrinsic conductivity mechanisms. While some aspects remain to be clarified, this work demonstrates the critical importance of the structure and chemical composition of nanotube fibers for their transport properties. Nanotubes fibers are potentially useful for the future development of conducting textiles, composites, and electrochemical sensor or actuators. We hope that the present results will help in optimizing the conducting properties of nanotubes fibers for these and other applications.

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