

Fabrication and electrical characterization of polyaniline-based nanofibers with diameter below 30 nm

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We fabricate and electrically characterize electrospun nanofibers of doped polyaniline/polyethylene oxide (PAN/PEO) blend with sub-30 nm diameter. Fiber diameters near 5 nm are obtained for optimized process parameters. Scanning conductance microscopy (SCM) shows that fibers with diameter below 15 nm are electrically insulating; the small diameter may allow complete dedoping in air or be smaller than phase-separated grains of PAN and PEO. Electrical contacts to nanofibers are made by shadow mask evaporation with no chemical or thermal damage to the fibers. Single fiber $I-V$ characteristics show that thin fibers conduct more poorly than thick ones, in agreement with SCM data. $I-V$ s of asymmetric fibers are rectifying, consistent with formation of Schottky barriers at the nanofiber-metal contacts. © 2003 American Institute of Physics. [DOI: 10.1063/1.1622108]

One-dimensional nanowires are of interest for fundamental physics and application as interconnects, functional devices, and molecular sensors. Devices have been fabricated from semiconductors, metals, and carbon nanotubes, and most recently electronic (“conducting”) polymers. Polymer-based nanodevices should have advantages of low cost, and flexible, controlled chemistry.¹ Electrospinning is a well-established approach to polymer nanofiber fabrication with the possibility of large-scale production of meters-long fibers for incorporation into smart textiles and wearable electronics.² We showed previously that electrospinning can produce fibers as small as 100 nm, and that fibers with 600 nm diameter have electrical conductivity near that of the bulk.^{3,4}

Here we report the fabrication of electrospun nanofibers with sub-30 nm diameter from conducting polyaniline doped with camphorsulfonic acid (PAN.HCSA) blended with insulating polyethylene oxide (PEO). Nanofibers with diameter as low as 20 nm are uniform and smooth, and discontinuous fibers with diameter as small as 5 nm are present in the sample. Samples were characterized by atomic force microscopy (AFM), scanning conductance microscopy (SCM),⁵ and single-fiber electrical transport measurements. We fabricate submicrometer electrical contacts to single fibers using a shadow mask evaporation process to avoid chemical and

thermal damage to the sample. SCM indicates that fibers with diameter below 15 nm are electrically insulating. The small diameter may allow enhanced dedoping by atmospheric gases (e.g., water vapor) or be smaller than phase separated grains of PAN and PEO. Single-fiber $I-V$ measurements show that fibers of diameter 20 and 70 nm have conductivity of 10^{-3} and 10^{-2} S/cm, respectively, sharply less than bulk material (1 S/cm).³ Fibers with strong diameter variation show rectifying behavior, consistent with the formation of a low-transparency Schottky barrier at the contact to the thin end.

To make the base fiber solution, 100 mg emeraldine base polyaniline was doped with 129 mg camphorsulfonic acid and dissolved in 10 ml chloroform. The solution was stirred for 6 h and filtered. Next, 10 mg PEO (molecular weight 900 000) was added, and the PAN.HCSA/PEO blend solution stirred for 2 h. The sample was left in a capped bottle for 72 h and then filtered with a 450 nm teflon filter to give a homogenous liquid. The electrospinning setup was as reported earlier.⁴ About 1 ml of the solution was placed in a hypodermic syringe (B-D 1 ml 26 3/8) mounted a few degrees below horizontal. The tip of the needle was held at a potential of 8 kV, and electrospun fibers were collected for 20–30 min on an oxidized Si wafer placed 30 cm from the tip.

The nanofibers produced are hundreds of micrometers long, most with diameter below 30 nm, a tenfold improvement over our earlier report.⁴ Figure 1(a) shows a typical AFM image. Fiber A, is straight, with diameter decreasing smoothly from 50 to 25 nm. Other fibers (e.g., fiber B) are curled, with stronger variation in fiber diameter and occasionally “beads” 200–500 nm in size. We observe discontinuous fibers with diameter below 5 nm, suggesting that fibers with diameters corresponding to just a few molecules

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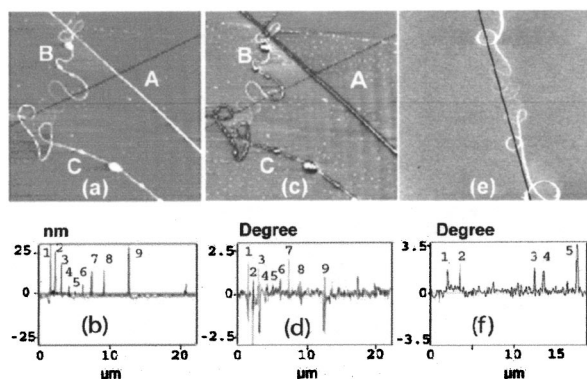


FIG. 1. (a) AFM image of the nanofibers. (b) Line scan along the black line in (a). (c) Simultaneously acquired SCM image. (d) Line scan through the SCM image. Peaks 1, 2, 3, and 9 show negative-positive-negative phase shift contrast that is due to a conducting nanofiber. (e) SCM image of an insulating PEO nanofiber. The fiber diameter varies from 40 nm near the top of the image, to 4 nm at its thinnest, to 60 nm at the bottom of the image (AFM data not shown). (f) Line scan along the black line in (e). The phase shift measured in SCM is *always positive* for insulating nanofibers.

could be fabricated if the instability that breaks the fiber can be suppressed.

We use SCM for initial characterization of nanofiber conductivity.⁵ SCM is a rapid technique that does not require electrical contacts. It has a low detection limit for one-dimensional conductivity ($G_{ID} = GL$; G is the fiber conductance and L its length), estimated at 10^{-16} S cm,⁵ that is set by the $R-C$ time constant of the nanowire. Conducting and insulating fibers can be distinguished by SCM, but fiber conductivity is not quantified. SCM is done on a Digital Instruments Dimension 3000 NS-III-A AFM using gold-coated tips (CSC12A, Micromasch). Topographic AFM and SCM images are acquired simultaneously by tapping mode (tip grounded) and interleave scans with a 100 nm lift height (tip voltage of +8 V), respectively. During the interleave scan, the tip is driven near its resonance frequency. If the tip is near a conducting nanostructure, induced charge alters the tip-sample electric force. This shifts the resonance frequency of the tip, and produces a *negative* phase shift of the tip oscillation. We took many SCM images of single-wall carbon nanotube (SWNT) control samples. As in Ref. 5, we observe that both metal and semiconducting SWNTs appear as conducting in SCM,⁶ that they show a *negative* phase shift (black line contrast) that is *wider* than the nanotube itself due to the long range electric interaction, and that the phase shift is larger for longer nanotubes.

Figures 1(a) and 1(c) are AFM and SCM images of PAn.HCSA/PEO nanofibers. As a control, we did SCM of *insulating* electrospun nanofibers of pure PEO [Figs. 1(e) and 1(f)].⁷ PEO fibers always show a *positive* phase shift of uncertain origin that increases with fiber diameter. In contrast, PAn.HCSA/PEO fibers with diameter larger than 30 nm show a negative-positive-negative phase shift “double dark line” contrast [1, 2, 3, and 9 in Figs. 1(c) and 1(d)] indicating they are conducting. The negative phase shift (dark line contrast) associated with conduction is superimposed upon the positive phase shift associated with an insulating fiber. Sub-15 nm diameter fibers (peaks 4–6) always show a *positive* phase shift *equal* to that found for insulating PEO fibers of the same diameter. PAn.HCSA/PEO fibers with diameter

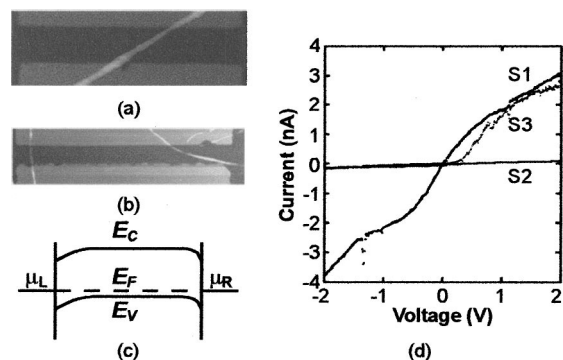


FIG. 2. (a) AFM image of S1 with a 70 nm diameter nanofiber in a 1.5 μ m gap. (b) AFM image of S3 with two nanofibers; the diameter of the rightmost fiber varies sharply. (c) Proposed energy band diagram for the nonuniform fiber of sample S3. Asymmetric Schottky barriers form due to variation in the sample diameter. The left end of the fiber is thinner and has the more opaque barrier. $I-V$ characteristics of nanofiber samples. S3 conducts similarly to S1 for one bias polarity and similarly to S2 for the other.

of 15–25 nm may show the dark line contrast or lack it (peaks 7 and 8). SCM thus indicates a transition from conducting to insulating as the fiber diameter drops below 15 nm. Given the detection limit of 10^{-16} S cm, we infer a bulk fiber conductivity less than 10^{-4} S/cm for sub-15 nm diameter fibers. This transition may be due to full dedoping of thin PAn.HCSA fibers by atmospheric gases, e.g., water vapor.^{1,8} Alternatively, phase separation of PAn.HCSA and PEO in the nanofiber may lead to discrete nanoscale conducting polymer grains separated by insulating PEO regions.⁹

Organic solvents (e.g., acetone) dissolve nanofibers so they cannot be contacted by electron-beam lithography, as is done for other nanowires, e.g., SWNTs.¹⁰ We therefore use chemical-free shadow mask evaporation based on a nanoscale patterned silicon nitride membrane¹¹ to deposit 10 μ m wide electrical leads separated by a micrometer-scale gap.

$I-V$ characteristics are measured in air at room temperature. The AFM image of sample S1 [Fig. 2(a)] shows a single 70 nm diameter nanofiber contacted by leads separated by 1.5 μ m. The $I-V$ for S1 is symmetric and relatively linear with resistance of 600 M Ω over the range -2 to $+2$ V [Fig. 2(d)]. This corresponds to a bulk fiber conductivity of 10^{-2} S/cm, much smaller than that of PAn.HCSA cast films (1 S/cm).³ Sample S2 (AFM image not shown) consists of two nanofibers in parallel, with diameters of 18 and 25 nm. The $I-V$ [Fig. 2(d)] is symmetric and linear, with resistance near 20 G Ω , yielding a fiber conductivity of 10^{-3} S/cm, further reduced from the bulk value. The reduction in conductivity might be a bulk effect (e.g., dedoping) but sample S3, discussed in the next paragraph, provides compelling evidence for formation of opaque Schottky barriers at the nanofiber-electrode contact, as occurs for semiconducting SWNTs¹²

Sample S3 [Fig. 2(b)] consists of two nanofibers in parallel. The leftmost fiber has a uniform diameter of 20 nm, while the diameter of the rightmost nanofiber varies from 20 nm at the top contact to 70 nm at the bottom contact. The $I-V$ for S3 is strongly rectifying: For one bias polarity the conductivity is small and resembles that of S2, while under forward bias the sample conducts strongly, similar to S1.

We interpret this as evidence for the formation of opaque Schottky barriers at metal contacts to nanofibers with diam-

eter below 25 nm. Contacts to the 70 nm diameter fiber are more transparent due to a larger number of free carriers but may still limit transport as argued later. The thin, uniform diameter fibers in S2 and S3 have an opaque Schottky barrier at each end. Under bias of either polarity, one barrier is reverse biased and sharply limits conduction. In contrast, the fiber whose diameter varies from 20 to 70 nm has an opaque barrier only at the thin end. One voltage polarity is a reverse bias for this Schottky barrier, yielding a low current similar to S2. For opposite voltage polarity the barrier is forward biased, and the sample conducts more readily, similar to S1, even though about one-half the length of the asymmetric fiber is of 20 nm diameter. This may indicate that Schottky barriers limit current in all three samples, and the bulk fiber conductivity may be consistently underestimated in experiments of this type. Figure 2(c) is a proposed energy band diagram for this scenario, where we assume that holes are the majority carrier in the nanofiber, as expected for PAn.HCSA.¹³

In conclusion, we fabricated conducting polymer nanofibers with diameters smaller than 100 nm. Fibers with diameters as small as 20 nm are readily formed, and 5 nm diameter fibers may be accessible in the future. We observed behavior in the electronic properties of polymer nanofibers through SCM and single-fiber transport experiments. SCM indicates a crossover from conducting to insulating fibers as the diameter is reduced below 15 nm. I - V characteristics of single fibers give a lower bound on the bulk conductivity of 10^{-2} S/cm for 70 nm diameter fibers and 10^{-3} S/cm for 20 nm diameter samples. Measurements of single fibers with sharply varying diameter provide evidence that Schottky barriers form at the fiber-electrode contact, with a more opaque barrier at the thin end. Further experiments are warranted to completely characterize the contact. These results indicate

clear avenues for future development of engineered nanofiber electronic devices and sensors.

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- ¹A. G. MacDiarmid, *Rev. Mod. Phys.* **73**, 701 (2001).
- ²D. H. Reneker, A. L. Yarin, H. Fong, and S. Koombhongse, *J. Appl. Phys.* **87**, 4531 (2000).
- ³I. D. Norris, M. M. Shaker, F. K. Ko, and A. G. MacDiarmid, *Synth. Met.* **114**, 109 (2000).
- ⁴A. G. MacDiarmid, W. E. Jones, I. D. Norris, J. Gao, A. T. Johnson, N. J. Pinto, J. Hone, B. Han, F. K. Ko, H. Okuzaki, and M. Llaguno, *Synth. Met.* **119**, 27 (2001).
- ⁵M. Bockrath, N. Markovic, A. Shepard, M. Tinkham, L. Gurevich, L. P. Kouwenhoven, M. W. Wu, and L. L. Sohn, *Nano Lett.* **2**, 187 (2002).
- ⁶Semiconducting SWNTs are doped by exposure to atmosphere and have a one-dimensional conductivity well above the SCM detection limit.
- ⁷PEO nanofibers were electrospun from a solution of 50 mg PEO (mol. wt. 900 000) dissolved in 10 ml chloroform and collected on an oxidized silicon wafer. SCM of insulating and conducting fibers will be discussed in detail elsewhere [C. Staii, N. Pinto, and A. T. Johnson (unpublished)].
- ⁸Fibers are dedoped when placed in water, with a color change from green to deep blue. Nanofibers show an age-dependent conductivity if left in air that is minimized if they are stored in a water-free atmosphere [J. Goldsmith, A.G. MacDiarmid, and A.T. Johnson (unpublished)].
- ⁹R. S. Kohlman, A. Zibold, D. B. Tanner, G. G. Ihas, T. Ishiguro, Y. G. Min, A. G. MacDiarmid, and A. J. Epstein, *Phys. Rev. Lett.* **78**, 3915 (1997).
- ¹⁰M. Radosavljevic, M. Freitag, K. V. Thadani, and A. T. Johnson, *Nano Lett.* **2**, 761 (2002).
- ¹¹Y. Zhou, J. Hone, W. F. Smith, and A. T. Johnson, *Nano Lett.* (to be published).
- ¹²M. Freitag, M. Radosavljevic, Y. Zhou, A. T. Johnson, and W. F. Smith, *Appl. Phys. Lett.* **79**, 3326 (2001).
- ¹³C. T. Kuo and W.-H. Chiou, *Synth. Met.* **88**, 23 (1997).