Electrical Characterization of Polyaniline/Polyethylene Oxide Nanofibers for Field Effect Transistors

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ABSTRACT

Nanofibers comprised of polyaniline/polyethylene oxide (PANI/PEO) are being developed for novel logic devices. We report the electrical conductivity of PANI/PEO nanofibers with diameters in the 100 – 200 nm range. We measured conductivity values of ~ 0.3 – 1.0 S/cm, which is higher than the values reported for thicker nanofibers, but less than the bulk value of PANI. The electrical measurements were performed by depositing the fibers on pre-electroded, oxidized silicon (Si) substrates. The excellent adherence of the nanofibers to the SiO_2 as well as the gold (Au) electrodes may be useful in the design of future devices.

Keywords: Polyaniline, nanofiber, electrical, conductivity, transistors

1 INTRODUCTION

Novel transistors and logic devices based on nanotechnology concepts are under intense development. The potential for ultra-low power, high-density circuitry is attractive for applications such as digital electronics and sensors. For NASA applications, nanotechnology offers tremendous opportunities for increased on-board data processing and thus autonomous decision-making ability, and novel sensors that detect and respond to environmental stimulus with little oversight requirements. To date, much of the research in nanoscale electronics has focused on carbon nanotubes, and great progress has been shown. This progress is demonstrated by logic devices that utilize both p- and n-type field effect transistors (FET) in a single integrated circuit[1, 2]. Furthermore, the robustness and sensitivity of carbon nanotube FETs in aqueous environments make them highly attractive for biosensing applications[3].

The early successes of carbon nanotube FETs make us optimistic that electronic devices with different functionalities can be achieved using different materials. In this study we report on our initial studies of nanofibers comprised of polyaniline (PANI) and polyethylene oxide (PEO). PANI is an interesting material because its electrical properties are in a range that is attractive for semiconductor devices, it is highly stable, and is sensitive to optical and electrochemical processes[4]. Furthermore, it can be processed into very long fibers using a simple electrospinning process. In this work, the objective is to develop semiconducting PANI/PEO nanofibers, where the current level is controlled by a gate voltage. Accomplishment of these goals would be a basis for the future development of self-assembled, nano-sized logic devices, and create a foundation for ultra-efficient memories and processors.

Because of the rapidly evolving nature of this field, verification of the feasibility of our proposed technology could be expedited by using a simple, low cost, and reliable deposition technique, such as electrospinning. Electrospinning is well-known, but not widely used technique for fabricating nanofibers. However, with the recent surge of interest in nanotechnology, new interest in electrospinning has attracted attention because it is capable of producing nanofibers that are very useful for emerging nanotechnology applications. To date, much of the interest in electrospinning is centered on the mechanical properties of nanofibers that are produced using this method; it is a low-cost means of creating fibers with diameters in the 40 – 2000 nm range, and lengths up to 1 km[5]. Electrospun nanofibers are promising for the structural elements of nanoscale machines, such as wires, ropes, and fabrics. In addition, these nanofibers may provide connections between the nanoscale world and macroscale world, since the diameters are in the nanometer range and the lengths are much larger.

The electrical conductivity of PANI can be varied from 10^{-10} S/cm to 6000 S/cm, depending on how it's processed[6, 7]. For our applications, we are interested in stabilizing the emeraldine salt form, which is semiconducting and has a bulk conductivity of ~ 10 S/cm in air. Prior work demonstrated that nanofibers comprised of doped polyaniline and polyethylene oxide, with diameters in the 450 – 2000 nm range, have conductivities of approximately 0.1 S/cm[8,9]. Understanding the reason for

the difference between the bulk and fiber conductivities is important if we are to develop charge control devices based on these materials. In this study, we report electrical conductivity measurements of PANI/PEO nanofibers with diameters of 100 – 200 nm. We also demonstrate that nanofibers deposited directly onto gold (Au) electrodes display ohmic behavior, which may be useful for the future development of self-assembled structures.

2 EXPERIMENTAL

The nanofibers were fabricated using an electrospinning technique, similar to that reported earlier[5,6]. In this technique, a mixture of polymer solutions is placed inside a hypodermic syringe or in a glass pipette. Inside the syringe is a metal cathode, and the anode, upon which the nanofibers are to be deposited, is typically located 25 – 30 cm away from the cathode. When a sufficiently high voltage is applied so as to overcome the surface tension forces of the polymer droplet, a jet is formed and the charged polymer molecules are accelerated to the target substrate, where they form nanofibers. The electrospinning apparatus used in these experiments is schematically illustrated in figure 1. PANI-based nanofibers are of interest because they have conductivities that can be changed from 10^{-10} S/cm to 6000 S/cm, by varying the doping levels and conformations of the polymer chain.

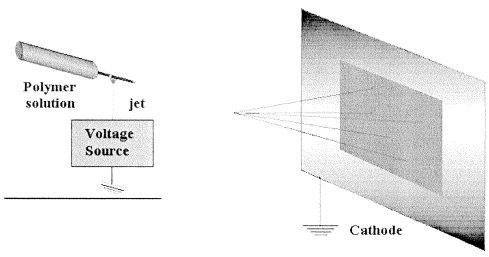

Figure 1. Basic electrospinning apparatus used to prepare PANI/PEO nanofibers.

Although PEO is an insulator, it acts as a plasticizer and is needed in order to form viscous polymer droplets and thus is an important ingredient in the formation of the nanofibers.

In this set of experiments, the electrically conductive portion of the nanofibers was formed by combining 100 mg of PANI with 129 mg of camphosulfonic acid, and dissolving in 10 ml of chloroform ($CHCl_3$) for 6 – 8 hours. The resulting deep green solution was filtered and 10 mg of polyethylene oxide (PEO), with a molecular weight of 900,000, was added to the solution and stirred for an additional two hours. Prior to electrospinning, this solution was filtered using a 0.45 μm PTFE filter to give a homogenous solution. Approximately 1 ml of the solution was placed in a B-D® 1 ml26$^{3/8}$ hypodermic syringe that was mounted a few degrees below horizontal, and the metal tip of the needle connected to 8 kV. The fibers were collected on an oxidized Si substrate, with Ti (20 nm)/Au (400 nm) electrodes already deposited. The oxide was thermally grown, and was 300 nm thick. The electrodes were spaced 2 – 10 microns apart, and the width of the Au electrodes was 20 μm. The distance between the tip of the hypodermic needle and Si substrate was 30 cm. Our goal was to maximize the doped PANI content, and thus the conductivity of the fiber, while minimizing the fiber diameter. We calculate polyethylene oxide comprised about 9 weight percent of the composite fiber.

Electrical resistance measurements were made using a Keithley model 6430 Sub-Femtoamp Remote Source Meter. Low current measurements were taken using a two-contact configuration. So as to minimize measurement errors due to the high resistance values (> 1 GΩ) of the nanofibers, measurements were taken in the source voltage/measure current configurations, wherein a series of positive and negative voltages is applied to the sample, and current is measured[10]. The test apparatus used to characterize the electrical behavior of the nanofibers is schematically illustrated in figure 2, and a photograph of the instrumentation is shown in figure 3. To further minimize the possibility of extraneous noise influencing the measurement, the samples were enclosed in a Faraday cage. For this set of experiments, a series of five positive and negative voltages cycles was applied to the nanofibers for each voltage, with each voltage being held for one minute. At the end of one minute, the current was measured. To calculate the current for each bias point, the average of five measurements was calculated.

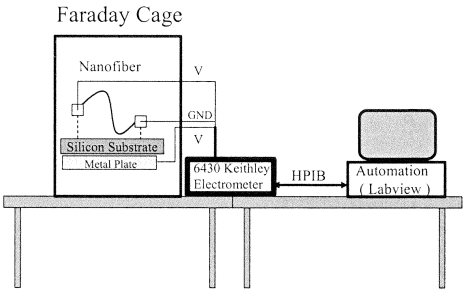

Figure 2. Schematic diagram of test apparatus used to characterize electrical properties of nanwires.

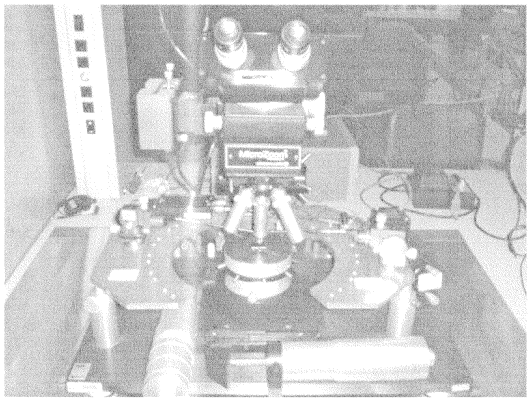

Figure 3. Photograph of test apparatus used to measure electrical properties of PANI/PEO nanofibers. During measurements, the entire apparatus is enclosed by a Faraday cage so as to minimize noise.

3 RESULTS AND DISCUSSION

The PANI/PEO nanofibers analyzed in this study displayed properties which could be important for future logic and active devices. Nanofibers with diameters of approximately 100 nm, and lengths that routinely exceeded 300 μm were demonstrated. A low magnification scanning electron (SEM) image of one of the nanofibers is shown in figure 4. This figure demonstrates that long, high quality, and isolated nanofibers were obtained. Furthermore, the nanofiber adhered well to both the gold pads and oxidized Si surface. This could have significance for the future development of self-assembled devices, wherein the nanofibers will be expected to attach themselves to selected sites using via surface modification or some type of electrical bias induced assembly process.

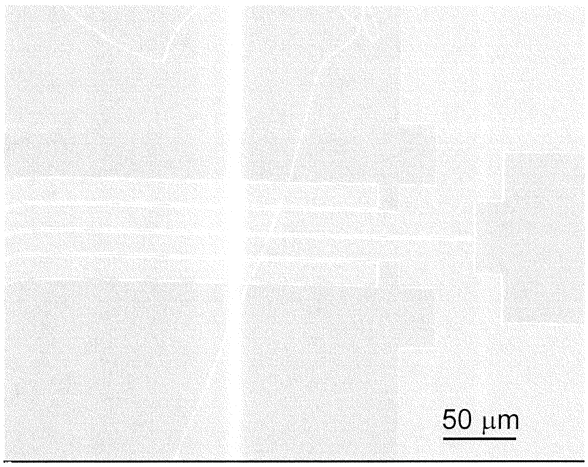

Figure 4. Low-magnification scanning electron micrograph of polyaniline/polyethylene oxide nanofiber deposited across Ti/Au electrodes, on an oxidized Si substrate. Two-terminal resistance measurements were made across adjacent electrodes.

A more highly magnified image of a nanofiber is shown in figure 5. With respect to potential devices, the fact that the nanofiber is securely attached to the SiO_2 layer as well as the Au electrodes is significant because it opens the possibility for self-assembled devices. We believe that the excellent adherence is largely due to the low surface energy of polyaniline (70 mN/m) relative to that of SiO_2 or Au (300 and 1200 mN/m, respectively), thus making it energetically favorable for the nanofiber to adhere to the surface[11]. However, it is also likely that the nanofibers are highly charged as they impinge on the surface, which may also contribute to the tenacity of the nanofiber/substrate bond.

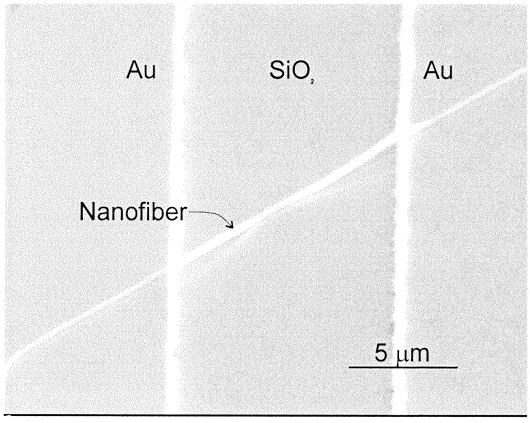

Figure 5. Scanning electron micrograph of PANI/PEO nanofiber. The fiber is approximately 100 nm in diameter, makes electrical contact to two gold electrodes, and extends across a 10 micron wide, 300 nm thick SiO_2 layer. The gold electrodes are 400 nm thick.

Electrical current versus applied voltage for a 100 nm diameter nanofiber is shown in figure 6. This data shows ohmic resistance behavior, indicating the contact resistance at the Au/nanofiber interface is negligible compared to the nanofiber resistance. The calculated conductivity of this fiber was approximately 1 S/cm, which is somewhat higher than values previously reported for thicker (450 nm) diameter fibers. The observed conductivity value is in a range where most materials are semiconducting, which opens the possibility that the current will be controllable via a gating mechanism, and three-terminal logic devices will be forthcoming.

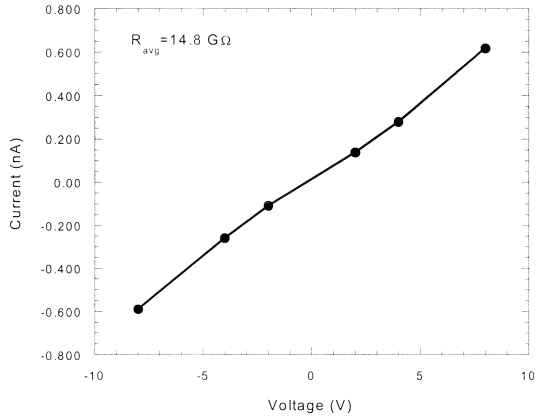

Figure 5. Current versus voltage behavior of PANI/PEO nanofiber. The diameter of the fiber was approximately 100 nm, as measured by Atomic Force Microscopy. The electrode spacing was 10 μm.

4 CONCLUSIONS

We report the electrical conductivity of PANI/PEO nanofibers with diameters in the 100 – 200 nm range. We measured conductivity values of ~ 0.3 – 1.0 S/cm, which is higher than the values reported for thicker nanofibers, but less than the bulk value of PANI. The electrical measurements were performed by depositing the fibers on pre-electroded, oxidized Si substrates. The excellent adherence of the nanofibers to the SiO_2 as well as Au electrodes may be useful in the design of future devices

ACKNOWLEDGEMENTS

We are grateful to Nicolas Varaljay (NASA-GRC) for thermally growing the oxide layer on the silicon wafers, fabricating the metallization pattern that was used to characterize the electrical properties of the nanofibers, and for performing scanning electron microscopy analysis of the nanofibers. One of the authors (N.J.P) acknowledges NASA's support under NASA Grant NCC3-963.

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