Polymeric Nanowire Architectures and Nanodevices

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We devised a method, named as scanned electrospinning technique, to form a variety of one-dimensional polymeric nanostructures. It is a straightforward technique that enables the rapid fabrication of oriented polymeric nanowires as well as their integration with lithographically defined and micromachined surfaces. As a result, these orientated polymeric nanowires can be used as building blocks for nanodevices. Using this method we have made and tested a prototype of high-speed single polymeric nanowire chemical detector that is capable of sensing ultra low concentrations of ammonia gas, with rapid and reversible resistance change. As an example of the nanomechanical resonator, mechanical oscillations of individual suspended silica fibers were measured, with a resonant frequency of 10.8 MHz and a mechanical quality factor of 1600. The general approach represents a significant step toward realizing the potential of organized self-assembled nanostructures in nanoscale device architectures.

Keywords: polymeric, nanowire, nanodevice, sensor, resonator.

One-dimensional (1D) nanostructures have received considerable attention in recent years due to their unique electrical, mechanical, optical characteristics and potential device applications. For example, carbon nanotubes and semiconductor nanowires have been intensively investigated because of their unique characteristics, different from the bulk materials. Polymeric nanowires have not been investigated as thoroughly, due in part to the limited ability to fabricate 1D nanostructures from polymeric materials as well as the difficulty of interfacing them with macro systems. Electrospinning is an electrostatically induced self-assembly process wherein ultra-fine fibers are produced, which is by far one of the simplest approaches to generate 1D nanostructure from a rich wealth of organic polymers. The conventional electrospinning technique however has very limited control on the deposition. To overcome the limitation, we devised a method, named as scanned electrospinning technique, to form a variety of 1D polymeric nanostructures. It is a straightforward technique that enables the rapid fabrication of oriented polymeric nanowires as well as their integration with lithographically defined and micromachined surfaces, which can be used as building blocks for different kinds of nanodevices. By this approach, we have been made high-speed polymeric nanowire chemical sensor, suspended silica nanomechanical resonator, polymeric nanowire field-effect transistor, polymeric waveguide, etc [1-5].

Polymeric Nanowire Chemical Sensor

Nanoscale sensors have been attracting considerable attention in recent years. Although the use of nanotubes and nanowires offers the prospect of high sensitivity and rapid detection, the ability to incorporate nanowires into sensor device architectures is limited by the difficulty in manipulating and locating the nanostructures with respect to the microelectrodes. A variety of conducting polymers have shown promise as sensor materials because their properties can be tailored to detect a wide range of chemical compounds. Conducting polymers also have attractive features such as mechanical flexibility, ease of processing, and modifiable electrical conductivity. In this report, we demonstrate an approach for creating polymeric nanowire sensors that has the advantages of sensitivity, spatial resolution, and rapid response associated with individual nanowires along with the material advantages associated with organic conductors.

By using the scanned-tip electrospinning approach for depositing isolated oriented polymeric nanowires, we created individual polyaniline/poly(ethylene oxide) (PANI/PEO) nanowire sensors that can detect NH_3 gas at concentrations as low as 0.5 ppm with rapid response and recovery time. The controllable geometry and high surface-to-volume ratio associated with the nanowires yield improved response and increased sensitivity compared to the same properties for previously described polyaniline sensors based on films and random fiber networks. The organized geometry also allows for better measurement of the wire electrical properties and yields a predictable and reproducible response for the sensor devices.

This electrical conductivity of conducting polymers results from the existence of charge carriers (through doping) and from the ability of those charge carriers to move along the π bonds of the polymer chains. The polymers may show chemical selectivity, which allows them to act as excellent materials or the immobilization of gas or biological molecules, and they also exhibit highly reversible redox behavior with a distinguishable chemical memory. Conducting polymer nanowires (CPNWs) also have the potential for use as molecular electronic architectures and devices. Electrospinning has been widely used to make PANI and other polymer wires, but these wires have not been deposited as oriented single wires. As a sensor, the high surface-tovolume ratio of the single nanowires and its small dimensions permit the rapid depletion or accumulation of charge carriers in the nanowires.

Among conducting polymers, PANI has received widespread attention because of its simple and reversible

doping/dedoping chemistry, stable electrical conduction mechanism, and high environmental stability. PANI has an affinity for NH_3, resulting from the similarity of the coordinative roles of nitrogen atoms in PANI and NH_3. PANI exhibits p-type semiconductor characteristics; consequently, electron-supplying gases such as NH_3 reduce the charge-carrier concentration and decrease the conductivity.

In our approach, a droplet of PANI/PEO solution was placed on an arrow-shaped tip that acted as a scanned electrospinning source. The polymer jet, electrostatically extracted from the tip, dried in transit to a substrate on a rotating counterelectrode. This process produced oriented PANI/PEO nanowires with diameters in the range of 100-500 nm. Photolithographically patterned four-terminal gold electrodes were positioned on the counterelectrode plate in an orientation perpendicular to the wire deposition direction. A typical scanning electron micrograph showing a single CPNW lying across the gold electrodes is shown in Figure 1. The polymer-blend solution was 2 wt % PANI doped with 10-camphorsulfonic acid in chloroform, and 0.25 wt% PEO. The scanned tip was fixed at a distance of 1.5 cm from the substrate and held at a potential of 8.5 kV with respect to the grounded counterelectrode. The substrate was rotated, producing a relative velocity of about 200 cm/s for the tip in relation to the substrate.

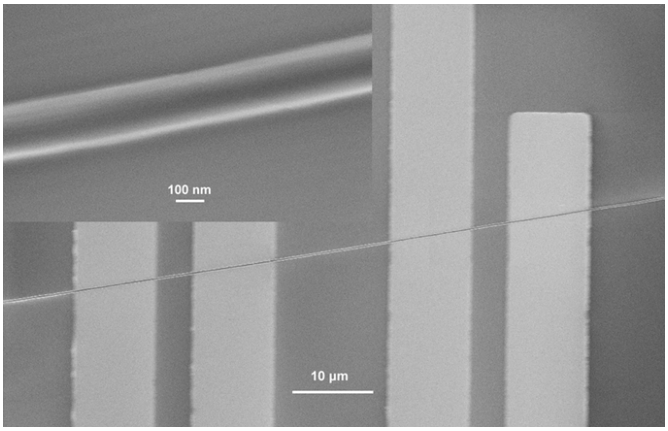

Figure 1. Scanning electron micrograph of a single PANI nanowire lying across four-terminal gold electrodes used for conductivity measurements. (Inset) Higher-magnification view of the CPNW of diameter 180 nm.

The typical conductivity of our individual PANI/PEO nanowires was about 0.5 S/cm before exposure to NH_3. This compares to conductivity on the order of 0.1 S/cm that is normally observed in PANI films based on the same doping method. It is expected that better alignment of polymer chains in the disordered regions can facilitate the hopping transport between the crystalline regions. Although the microstructure mechanism for increased conductivity of the oriented single wires is not known, the process includes some stretching of the wires as they are deposited on the moving substrate, which is likely to have an impact on the microstructure and molecular orientation.

The electrical conductance properties of the CPNW were measured using both two-terminal and four-terminal resistance measurements. Resistance measured by the two terminal method deviated less than 4% from that of the four terminal method (data not shown), which indicates that the contact resistances between the wires and the electrodes are small. By using either measurement method, current versus voltage behavior was observed to be linear for all of the devices studied, which indicates that the gold electrodes made ohmic contact to the CPNW. The current through the wire during the dedoping and doping of the PANI nanowire by the addition and removal of the NH_3 gas was recorded at a constant applied potential of 0.5 V. The time dependent conductance response of the CPNW upon exposure to different concentrations of NH_3 gas showed dramatic drop, and was proportional to the concentrations of gas exposed. As a control, nitrogen flowed over the sensor, and no change in the conductivity of the CPNW was observed. The threshold detection concentration level was 0.5 ppm NH_3.

The time response of the nanowire sensors can be understood by considering the diffusion of ammonia into the wire and the reaction of NH3 with doped PANI. We describe this process with a model of diffusion into a solid cylinder and instantaneous chemical reaction to change the doping. Upon exposure to NH3, the gas molecules diffuse into the PANI wire, and the dedoping of the H^+-doped PANI by NH_3 occurs rapidly. Electroneutrality must be maintained in the polymer, which is achieved by charge transfer between the NH_3 molecule and the specific active sites (the H^+-doped imine-nitrogen sites of PANI), and this leads to a decrease in the charge-carrier density. We assume that the electrical conductivity of the polymer is proportional to the time-dependent H+ concentration $[H^+]$ and that this is equal to the concentration prior to NH_3 exposure minus the concentration of NH_4^+. We assume that the chemical reaction by which NH_4^+ is formed proceeds much more rapidly than the diffusion process and that local equilibrium exists between bound and free NH_3 such that $[NH_4^+] = K[NH_3]$. The time-dependent conductance of the wire $S(t)$ is proportional to the total number of NH_3 molecules entering the wire by diffusion. This can be obtained from the solution of the diffusion equation for a cylinder:

$$\frac{S(t)}{S_0} = 1 - \frac{K[NH_3]_0}{[H^+]_0}\left(1 - \sum_{n=1}^{\infty} \frac{4}{\alpha_n^{\,2}} e^{\frac{-\alpha_n^{\,2} Dt}{a^2}}\right) \qquad (1)$$

where S_0 is the initial conductance of the wire, $[NH_3]_0$ is the supplied constant NH_3 concentration, a is the radius of the wire, and D is the apparent diffusion coefficient. α_n are roots of $J_0(\alpha_n)=0$, where J_0 is the Bessel function of the first kind of order zero.

We measured the response times of CPNW sensors of different wire diameters. The conductance changes as a function of time for 335- and 490-nm-diameter wires are shown in Figure 2. The response times (defined as the time duration for the conductance to decrease to $1/e$ of the whole conductance change) for the two wires are 74.8 s for the nominal 335-nm-diameter wire and 162.3 s for the nominal 490-nm-diameter wire. A least-squares fit was applied to the

experimental data using Equation (1), and the apparent diffusion coefficients for the two wires were determined to be 5.47×10^{-13} cm^2/s for the nominal 335-nm-diameter wire and 5.25×10^{-13} cm^2/s for the nominal 490-nm-diameter wire. The fact that these apparent diffusion coefficient values agree essentially to within our experimental error indicates that the differences in wire response are due to radius-dependent diffusion, not material differences.

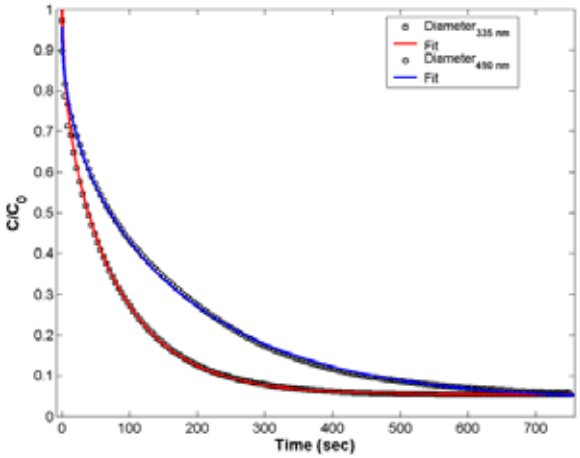

Figure 2. Timedependent conductance change for two CPNW sensors with wire diameters of 335 and 490 nm, measured upon exposure to 50 ppm NH3.

The results indicate that the wire diameter affects the response time of the sensor, with the smaller-diameter wires having a faster response associated with the more rapid diffusion of gas molecules through the wire.

A typical response of the single CPNW to cyclic NH_3/air exposure (10 s on/2-4 min off) demonstrates the speed of the CPNW sensing performance (Figure 3). Devices were cycled up to 40-50 times while retaining resistance reversibility.

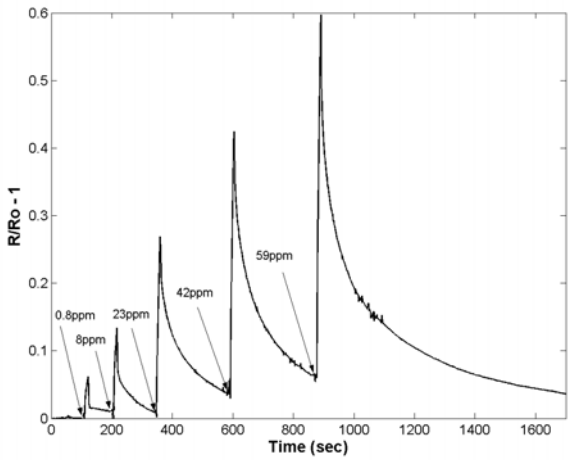

Figure 3. Real-time CPNW response to different concentrations of NH_3 gas. Cyclic NH_3/air exposure (10 s on/2-4 min off).

This work demonstrates a new approach to forming organized self-assembled polymeric electronic devices. It represents a possible manufacturing approach, utilizing the best aspects and diversity of polymers and self-assembled materials combined with the best aspects of microelectronics technology.

Suspended Silica nanofiber as nanomechanical resonator

The scanned electrospinning method was utilized to extrude polymeric nanofibers from a blended polymeric solution and deposit oriented nanofibers on patterned surfaces to form suspended structures. The deposited polymeric nanofibers were converted to silicon oxide by calcination without changing their morphologies. We measured the mechanical oscillations of individual suspended fibers, driven by a piezoelectric actuator. The resonant frequencies of these nanostructures were measured using laser interference techniques.

By utilizing this approach without the complexion of e-bean lithography and multiplayer thin film deposition process, a suspended nanofiber with a diameter of 120 nm was fabricated with a resonant frequency of 10.8 MHz and a mechanical quality factor of 1600. Because of the simplicity of the process steps to create organized inorganic nanofibers and the ability to produce suspended structures, this approach opens new opportunities in the study and device use of inorganic nanofibers.

The polymer solution was prepared by dissolving 5 wt % poly(vinyl)pyrrolidone (PVP, MW:1 300 000) polymer in spin-on glass (SOG) intermediate coating solution (IC1-200 from Futurrex, Inc.) and dispensed onto the deposition source. PVP was blended with the SOG to increase the viscosity of the SOG solution, which must be viscous enough to create a continuous polymeric jet during the deposition process. Trenches with 10, 20, 30, and 40 μm widths and depths greater than 2 μm were fabricated on silicon chips using the standard microfabrication processes of contact photolithography and plasma etching. Deposited polymer nanofibers were converted to chemical vapor deposition (CVD) grade SiO_2 nanofibers by heating in air at 850 °C for 3h without changing their suspended morphology. Because the evaporation temperature of PVP is less than 200 °C, the PVP polymer was vaporized. During the calcination process, the SiO_2 molecules were cross-linked.

Due to the evaporation of organic materials and solvents, and cross-linking of the SiO_2, the diameter of the nanofibers decreased by about 18%. A substantial decrease in PVP content during the calcination process has been verified by energy dispersive X-ray analysis (EDX). Using a scanning electron microscope equipped with an EDX detector, the carbon content of several fibers was examined. Fibers examined included freshly electrospun fibers that had not yet been baked and fibers that had gone through the calcination process on both evaporated gold and bare silicon substrates. The average carbon peak amplitude for the postcalcination samples, with fibers of diameter on the order of 1 μm examined, was 30% of the carbon peak amplitude for the fibers that had not yet been baked. The average background carbon signal was 23% of the unbaked fiber carbon peak, due

to carbon contamination of the substrate and detector equipment. This significant reduction in carbon content to near-background levels, as shown by a reduction of the average EDX carbon peak, is consistent with a significant reduction in fiber PVP concentration during the calcination process.

Scanning electron micrographs of cylindrical suspended nanomechanical structures, created by the scanned electrospinning technique, after the calcination process, can be seen in Figure 4.

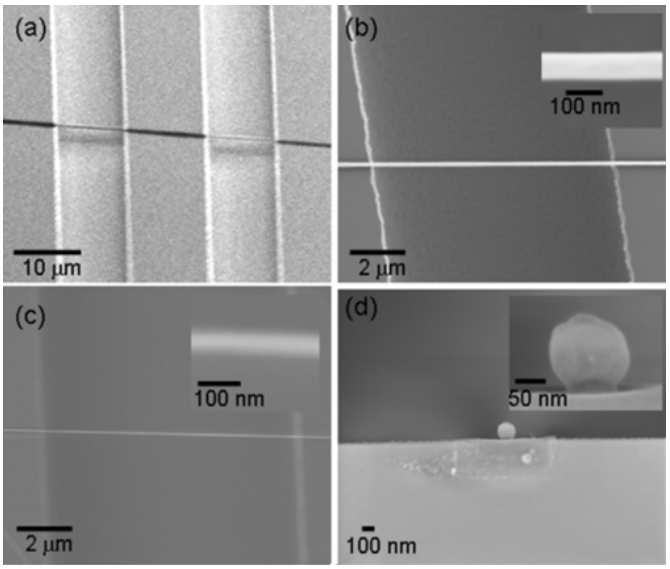

Figure 4. Scanning electron micrographs of suspended silica nanofibers after calcination. The diameter and length of the resonators were (a) 160 nm and 10 μm, (b) 120 nm and 10 μm, (c) 70 nm and 10 μm. (d) Scanning electron micrograph of the cross section of a silica nanofiber deposited on the silicon surface.

The nanomechanical resonators were placed in a vacuum chamber and pumped down to pressures below 10^{-5} Torr. The chip containing the nanofibers was attached to a piezoelectric transducer inside the vacuum chamber for mechanical actuation. A 5 mW He-Ne laser was focused on the center of the cylinder through a microscope objective lens. The laser light, reflected from the cylinder and the bottom of trench, was directed into a photodiode to detect the oscillation. The location of the laser spot on the cylinder was adjusted to obtain the maximum reflected light modulation detected by the photodiode. A spectrum analyzer was used to observe the frequency response of the fiber oscillation and to determine the resonant frequencies of the nanofiber. A plot of the mechanical response of a 120 nm diameter nanofiber as a function of actuation frequency is shown in Figure 5. The resonant oscillation frequency of this device was 10.8 MHz with a quality factor of approximately 1600. This peak is the fundamental resonant frequency, and this frequency is consistent with SOG doubly clamped beams made by electron beam lithography.

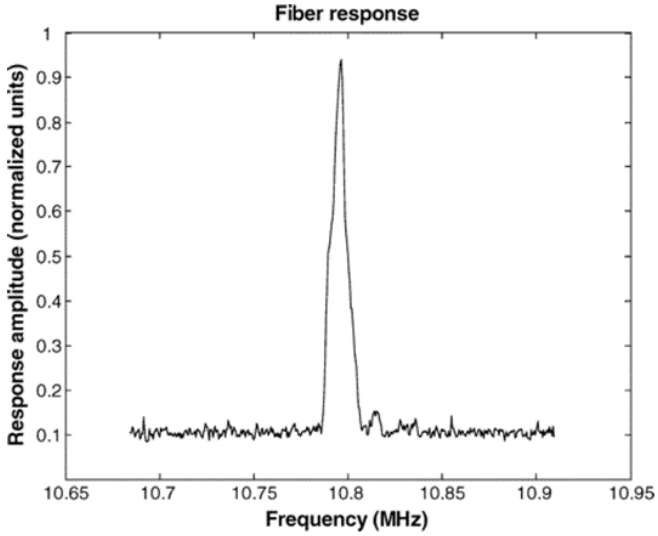

Figure 5. Plot of the mechanical frequency response of a 10 μm long, 120 nm diameter oscillator showing a resonance at 10.8 MHz. The quality factor of the oscillator is approximately 1600.

In conclusion, we have developed a nanomaching process for fabricating silica nanofibers. Suspended fibers were formed by combining a scanning electrospinning deposition method with contact photolithography, and a calcinations process to convert polymeric nanofibers to inorganic nanofibers. This fabrication approach offers an alternative to the conventional method of thin film deposition, electron beam lithography, and plasma etching for the formation of nanomechanical devices. We demonstrated the use of these nanofibers as mechanical resonators, but similar geometries could be used for optical or other nanomechanical devices.

This review describes a new method for rapid fabrication of one-dimensional self-assembled polymeric nanostructures over macroscopic distances, and suggests an approach to nanowire and nanofiber device manufacturing. The generality of this method can be perspective for design and fabrication of highly ordered and controlled morphology of the 1D nanostructure for applications in the wide realm of nanotechnology.

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