Individually Addressable Conducting Polymer Nanowires Array

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ABSTRACT

A facile technique for fabrication of individually addressable, conducting polymer nanowire arrays of controlled dimension, high aspect ratio, and site-specific positioning using electrodeposition between electrodes in channels created on semiconducting and insulating surfaces that can be easily scaled up is reported. In addition, the ability to create "arrays" of conducting polymer nanowires of same or different materials on the same chip has been demonstrated. The fidelity, quality, and electrical properties of single polypyrrole and polyaniline nanowires have been examined by SEM and I–V characteristics. Dendrite-free conducting polymer nanowires completely confined within the channels with full dimension control were observed. I–V characteristic of such nanowires show the ohmic nature of the contact with Au electrode.

Nanowires and nanotubes are promising materials for a variety of applications including optical and electronic nanodevices and chemical and biological sensors.[1] Successful application of these nanostructured materials into functional nanodevices requires controlled patterning at micro- and nanometer scale. Semiconductor and metal nanowires (NWs) and carbon nanotubes (CNTs) have been the materials of choice for fabricating sensor devices. Although several examples of uses of these materials as nanosensors have been reported, many properties of these materials and fabrication methods have significantly limited their full-scale development, particularly for high-density arrays.[2–5] For example, (1) current synthetic methods are unable to selectively grow sensor-suitable semiconducting CNTs, (2) limitation of dopants and inability to functionalize materials other than silicon limits the diversity of semiconductor NWs, (3) nanodevice fabrication requires complex post-synthesis assembly using sophisticated manipulating tools and (4) functionalization/modification for incorporation of specific sensing capabilities can only be performed as post-assembly processes.

Conducting polymers are emerging as a promising material for synthesis of nanostructured materials and devices. They are particularly appealing because they exhibit electrical, electronic, magnetic, and optical properties similar to metals or semiconductors while retaining their flexibility, ease of processing, and modifiable electrical conductivity. The electrical conductivity of these polymers can vary from an insulator to almost the metallic state and can be reversibly modulated over 15 orders of magnitude by controlling the dopant type and level.[6–8] Their porous structures are very amenable to entrapping biomolecules.[9] A variety of conducting polymers have shown promise as sensor materials, including biosensors, because their properties can be tailored to detect a wide range of chemical compounds.[10–12] While the properties of conducting polymers offer many advantages over semiconductor and metallic NWs and CNTs, application of these materials for high-density nanosensor arrays is limited by some of the similar problems. Although successful in satisfying some criteria, photolithography,[13] microcontact printing,[14] template assisted synthesis,[15] scanning electrochemical microlithography,[16] mechanical stretching,[17] and electrochemical dip-pen lithography[18] techniques for fabricating micro- and nanoscale structures from conducting polymers still have limitations in terms of yield, resolution, material multiplicity, positioning, production of high-density arrays, and most of all cost.

We recently reported a facile technique for synthesis of micron/submicron width metallic and conducting polymer wires by electrodeposition within channels between two electrodes on the surface of silicon wafers.[19] In this communication, we extend this method to synthesize single and multiple individually addressable controlled dimension, high aspect ratio (100 nm wide by up to 13 μm long) and dendrite-free nanowires of conducting polymers polyaniline and polypyrrole. In addition, we demonstrate the ability to create

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scalable high density "arrays" by site-specific positioning of conducting polymer nanowires of same and different composition on the same chip.

The deposition and growth of the nanowire chains are based on well-known electrochemical oxidative polymerization, starting with monomers and dopants. Multiple channels can be etched between gold electrode pairs in the form of arrays to provide formation of any number of individual nanowires. The procedure is a single-step deposition process for each nanowire, and multiple-nanowire arrays of different materials can be deposited on the same wafer sequentially. Polypyrrole (PPY) and polyaniline (PANI) are used as models for demonstration.

The fabrication of the electrode structure used for the growth of the conducting polymer wire was described elsewhere.[19] In a typical experiment, the electrode chip/wafer was mounted on a probe station and the contact is established using metallic pins. The contact pins were precleaned with 2-propanol. A three-electrode setup was used for the deposition. Two microliters of deoxygenated pyrrole (0.06 M in 0.01 M KCl) or aniline (0.1 M in 0.1 M HCl) were placed in the electrolyte channel between the two electrodes, and the electropolymerization was performed in galvanostatic mode by applying a desired current while the potential of the working electrode was monitored continuously with respect to a pseudo reference electrode. Simultaneously, a multimeter (connected in the circuit) was programmed to record the resistance values every 1 s and continuously transfer data to a computer file. The electropolymerization was initiated by impressing a 100 nA current between the two gold electrodes. Typically, the potential increased from the open circuit potential to a value of 2 V followed by a gradual decrease as the wire grew. When the wire was fully grown and made a contact with the cathode, the potential dropped to 0.6 V for PANI and 0 V for PPY. At this time, the process was terminated, the electrolyte solution siphoned out, and the wafer was rinsed three times with deionized distilled water and dried. The resistance, on the other hand, started from a value of 20 MΩ and decreased to a few KΩ. The evaporation of water from the 2 μL drop was minimal and did not affect the process, at least up to 4 min.

After formation, resistance of the nanowire was 0.2−0.8 kΩ (wet) and 6−7 kΩ (dry) for a 500 nm wide nanowire, while it was about 1 MΩ for a 100 nm wide dry nanowire. The resistance of the nanowire in the dry state was dependent on the thickness and uniformity of the nanowire, humidity levels, and the deposition conditions. The nanowire resistance was stable at least for 9 h after formation. In the absence of the monomer, nanowire formation was not observed.

Figure 1 shows the SEM image of a 100 nm wide and 4 μm long electrochemically grown PANI nanowire. As observed, the nanowire was continuous, well-confined, and nondendrite, spanning the entire length and making contact between the two electrodes. The quality and fidelity of the nanowire obtained in this study were far superior compared to the earlier work where the overgrowth is clearly observed, even in the optical images at the ends of wires that are 5 to 10-fold thicker.[19]
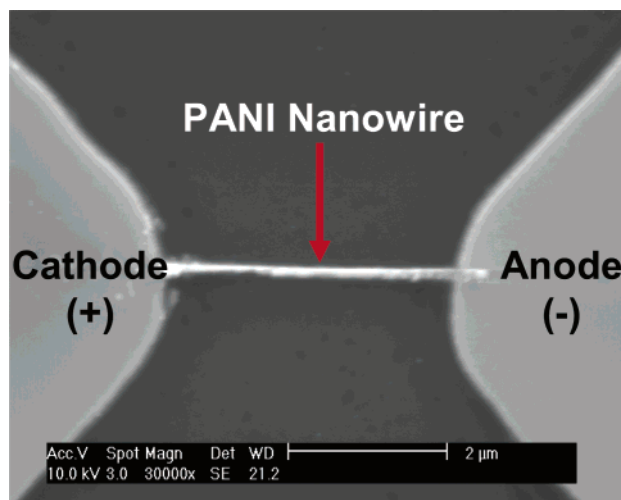
Figure 1. SEM image of a 100 nm wide by 4 μm long PANI nanowire. Scale bar: 2 μm.
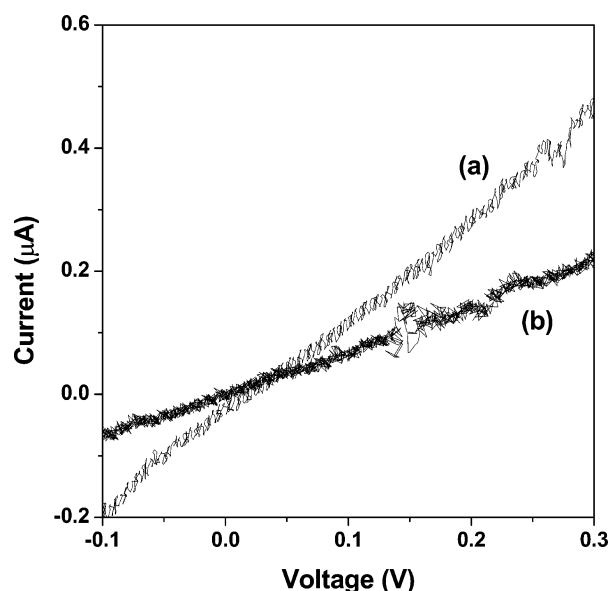

Figure 2. Current vs potential for a PANI (a) and PPY nanowire (b) at 50 mV/s scan rate.

To confirm the wire integrity and contact with the gold electrodes, current vs voltage studies were performed for dry PANI and PPY nanowires (Figure 2). A linear dependence of the current on the applied potential confirmed ohmic contact at both electrodes necessary for the passage of current through the nanowire in the dry state.

The ability to make individually addressable nanowires in high density was evaluated by making two 200 nm wide by 2.5 μm long PPY nanowires separated by 6 μm sequentially. The SEM image (Figure 3) demonstrates that fabrication of arrays of electrodeposited wires of same or different materials at a precise location is feasible.

In multiple deposition studies, uniform nanowires between 0.5 and 13 μm in length within 1 μm, 500, 200, and 100 nm wide channels were formed from both PANI and PPY.

While the electropolymerization in this work was performed using aniline and pyrrole in aqueous medium, the
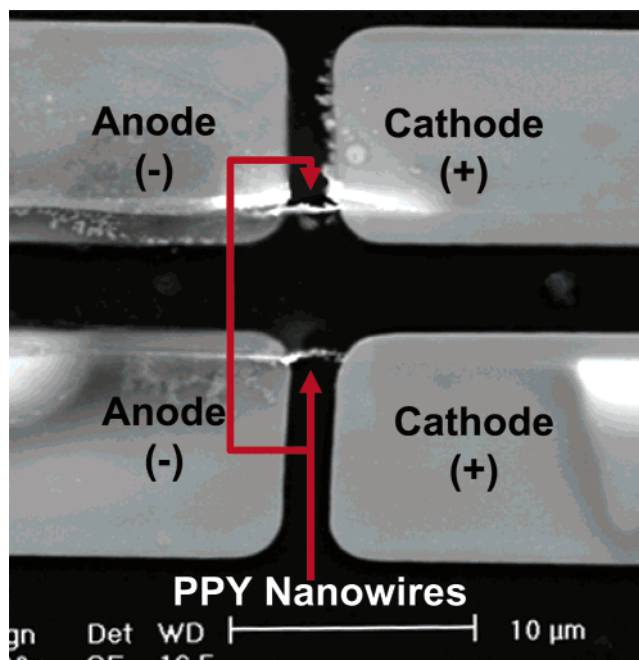
Figure 3. SEM image of two 200 nm wide by 2.5 μm long PPY nanowires separated by 10 μm deposited one at a time. Scale bar: 10 μm.

methodology can be extended to electropolymerization of other conducting polymer monomers and also nonaqueous media.

For demonstration of the conducting polymer nanowire as a sensor, the change in resistance of PANI as a function of environment pH was evaluated. Addition of 0.1 M HCl decreased the resistance by 4 orders of magnitude. The resistance could be switched by 2−3 orders of magnitude by repeatedly cycling with water and 0.1 M HCl. A similar but lower resistance change was observed for PPY. The 4 order of magnitude resistance change observed with the nanowire illustrates the superiority of nanowires over micron or submicron wires.[19]

In summary, we report a facile technique for fabrication of conducting polymer nanowires of controlled dimension and high aspect ratio using a single-step electrodeposition between electrodes in channels created on insulating surfaces. The technique is capable of producing arrays of individually addressable nanowire sensors, with site-specific positioning, alignment, and chemical compositions. The diversity of monomers, dopants, and electropolymerization conditions, for example, monomer and dopant concentration, solvent, and deposition mode, can provide "tailored" materials for specific applications. Additionally, the benign operating conditions for electropolymerization make this process ideal for fabrication of nanobiosensors by the direct deposition of conducting polymer nanowires with embedded bioreceptors in one step rather than the multiple steps needed in surface-modified nanowires and CNTs.

References

(1) He, H.; Tao, N. J. Electrochemical fabrication of metal nanowires, in *Encyclopedia of Nanoscience and Nanotechnology*; Nalwa, H. S., Ed.; American Scientific Publishers: New York, 2003; Vol. X, pp 1−18.
(2) Cui, Y.; Wei, Q.; Park, H.; Lieber, C. M. *Science* **2001**, *293*, 1289−1292.
(3) Kong, J.; Franklin, N. R.; Zhou, C. W.; Chapline, M. G.; Peng, S.; Cho, K. J.; Dai, H. *Science* **2000**, *287*, 622−625.
(4) Li, C. Z.; He, H. X.; Bogozi, A.; Bunch, J. S.; Tao, N. J. *Appl. Phys. Lett.* **2000**, *76*, 1333−1335.
(5) Favier, F.; Walter, E. C.; Zach, M. P.; Benter, T.; Penner, R. M. *Science* **2001**, *293*, 2227−2231.
(6) MacDiarmid, A. G. *Synth. Met.* **2002**, *125*, 11−22.
(7) Heeger, A. J. *Synth. Met.* **2002**, *125*, 23−42.
(8) Shirakawa, H. *Synth. Met.* **2002**, *125*, 3−10.
(9) Ramanathan, K.; Annapoorni, S.; Malhotra, B. D. *Sens. Actuators, B* **1994**, *21*, 165−169.
(10) Dai, L.; Soundarrajan, P.; Kim, T. *Pure Appl. Chem.* **2002**, *74*, 1753−1772.
(11) Bidan, G. *Sens. Actuators, B* **1992**, *6*, 45−56.
(12) Schuhmann, W. Enzyme sensor based on conducting polymer, in *Enzyme and Microbial Biosensors: Techniques and Protocols*; Mulchandani, A., Rogers, K. R., Eds.; Humana Press: Totowa, N. J., 1998; pp 143−156.
(13) Jager, E. W. H.; Smela, E.; Inganas, O. *Science* **2000**, *290*, 1540−1545.
(14) Yu, J. F.; Holdcroft, S. *Chem. Commun.* **2001**, 1274−1275.
(15) Marck, C.; Borgwarth, K.; Heinze, J. *Chem. Mater.* **2001**, *13*, 747−752.
(16) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739−1746.
(17) He, H. X.; Li, C. Z.; Tao, N. J. *Appl. Phys. Lett.* **2004**, *84*, 828−830.
(18) Maynor, B. W.; Filocamo, S. F.; Grinstaff, M. W.; Liu, J. *J. Am. Chem. Soc.* **2002**, *124*, 522−523.
(19) Yun, M.; Myung, N. V.; Vasquez, R. P.; Lee, C.; Menke, E.; Pender, R. M. *Nano Lett.* **2004**, *4*, 419−422.

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