Nanowire Sensors and Arrays for Chemical/Biomolecule Detection

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ABSTRACT

We report electrochemical growth of single nanowire based sensors using e-beam patterned electrolyte channels, potentially enabling the controlled fabrication of individually addressable high density arrays[1]. The electrodeposition technique results in nanowires with controlled dimensions, positions, alignments, and chemical compositions. Using this technique, we have fabricated single palladium nanowires with diameters ragning between 75 nm and 300 nm and conducting polymer nanowires[2] (polypyrrole and polyaniline) with diameters between 100 nm and 200 nm. Using these single nanowires, we have successfully demonstrated gas sensing with Pd nanowires and pH sensing with polypyrrole nanowires. In addition, biologically functionalized conducting polymer (polypyrrole) nanowires were formed and application to biosensing was also demonstrated[3]. The biologically functionalized polypyrrole nanowires were formed by the electropolymerization of monomer pyrrole with simultaneous entrapment of biomolecules in a single step (avidin, biotin and streptavidin conjugated CdSe quantum dots). When exposed to biotin-DNA, the avidin- and streptavidin-polypyrrole nanowires exhibit a rapid change in resistance at concentrations as low as 1 nM, demonstrating the utility of the biomolecule-functionalized nanowires as biosensors.

Keywords: nanowire, sensor array, conducting polymer nanowires

1 INTRODUCTRION

Due to the high interest in one dimensional nano-structured sensors[4-6], significant research and development efforts have been made to fabricate nanoscale sensors for potential applications in electronics[4], biochemistry[5], and medicine[6]. These one-demensional nano-structured materials, such as nanowires and carbon nanotubes (CNTs), are of interest due to their small size, sensitivity, real time detection, and ultra-low power demands. However, current techniques used to fabricate these nanowire and CNT sensors have drawbacks of limited controllability and manufacturability. Reliable and controllable nanowire fabrication and assembly remains a significant challenge.

Here we report growing nanowires for sensor arrays using standard semiconductor device fabrication techniques. Use of electrodeposition techniques for nanowire fabrication can overcome the limitations of CNT sensors due to the relative ease of fabrication and surface modification. Electrodeposition allows a high degree of specificity in location and chemical identity of a deposit, as well as control over the dimensions of electrodeposits. It also offers a fast and single step method of making single nanowires without the need for tedious post-growth assembly. In addition, a wide range of sensing materials can be deposited by electrodeposition, including metals, alloys, metal oxides, semiconductors, and conducting polymers.

In this work, we have detected hydrogen gas using an electrochemically grown single palladium nanowire, and demonstrated sensing of DNA using avidin functionalized single conducting polymer nanowire. Our growth method for nanowires can potentially produce individually addressable nanowire sensor arrays with the capability of sensing multiple chemical species simultaneously.

2 EXPERIMENTAL

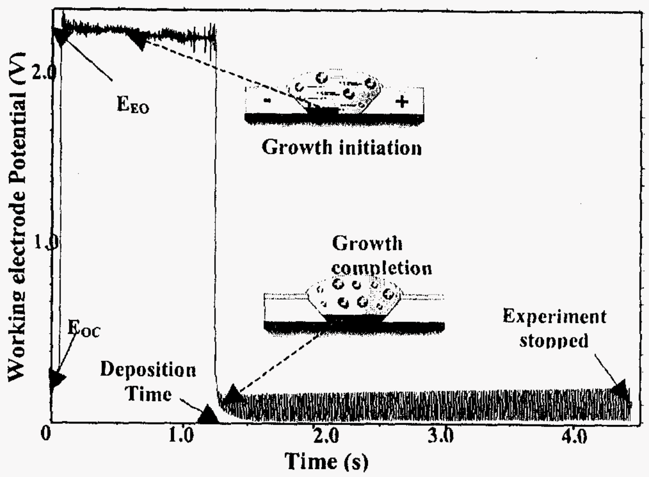

Figure 1. Typical chronopotentiogram of nanowire growth under galvanostatic mode of electrodeposition.

Figure 1 shows a chronopotentiogram of electrodeposited nanowire growth. Using standard microfabrication techniques, electrodes are formed with a 300 nm-thick Ti-Au metal film. SiO is then thermally deposited and the electrolyte channel is e-beam patterned and etched using reactive ion etching. The detailed fabrication process can be found elsewhere[1]. After microfabrication and e-beam patterning, electrochemical deposition is performed by adding one drop of electroplating solution on top of the channel. When an electrical potential is applied between the electrodes, the potential reaches equilibrium at initiation of nanowire growth and then drops to zero at completion of nanowire growth. The nanowire grows from cathode to anode through the nanochannel. The nanowire formation was also confirmed using optical and SEM measurements.

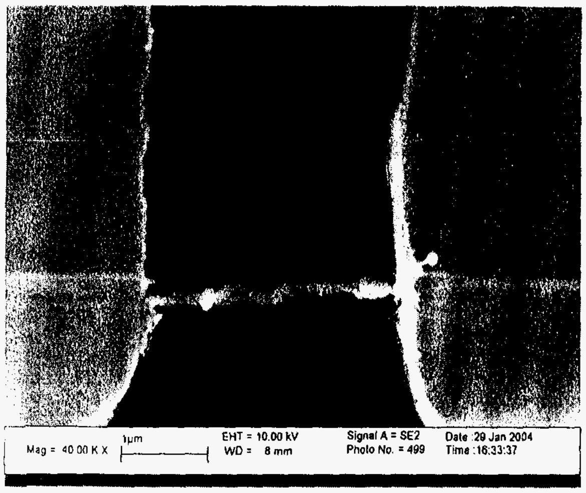

Figure 2. SEM image of electrochemically grown single Pd nanowire between electrodes (ref.7).

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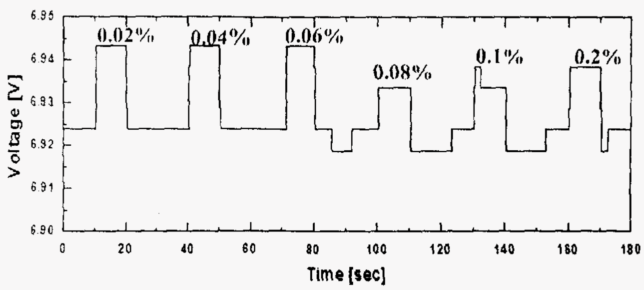

Figure 3. Sensing of hydrogen using a 100 nm Pd nanowire.

In this work, Pd nanowires are being investigated for their capability to sense H_2. The detection of hydrogen gas is important for many applications including fuel cell technology and environmental monitoring applications. Pd has low contact resistance and high sensitivity to H_2. Exposure of palladium to hydrogen results in the formation of palladium hydride and changes the properties of the palladium metal.[7, 8] Using this approach, field effect transistors,[9] microelectronic sensors,[10] optical sensors,[11] mesowire based hydrogen sensors and switches,[12] and carbon nanotube based sensors[16] have been constructed [7].

Figure 3 demonstrates sensing of hydrogen gas, with concentrations ranging from 0.02% H_2 to 0.2% H_2 using a single Pd nanowire with diameter of 100 nm. Upon exposure to H_2, output voltages increase and return to the original state when no hydrogen is present. Hydrogen gas flow is cycled on for 10 seconds and off for 20 seconds in the experiment shown in Figure 3.

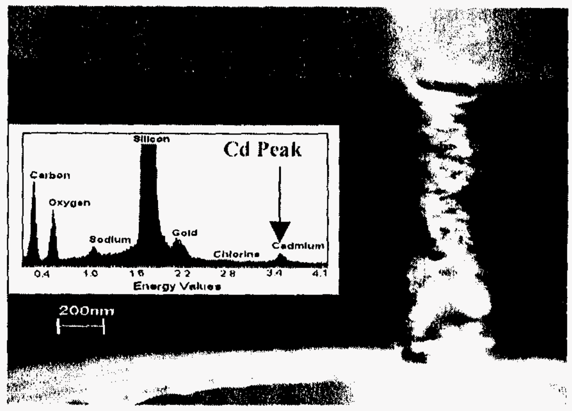

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Figure 4 shows a SEM image of a protein quantum dot conjugate(Aqd)-functionalized polypyrrole nanowire, demonstrating that the nanowire is continuous, well defined, and dendrite free, spanning the entire length of the channel and making a good contact with both electrodes. Energy-dispersive X-ray (EDX) analysis of the nanowires confirmed the presence of Cd within the nanowire, an indication of the presence of quantum dot and thereby streptavidin within the polypyrrole nanowire[3].

The operating principle of nanowire-based biochemical sensors is the detection of low molecular concentrations by measuring changes in the electrical conductance of nanowires produced by the adsorption or bioreaction of the chemical species. Using the protein-functionalized Ppy nanowire, we have demonstrated the utility of functionalized nanowires as sensors. We have sensitively detected 1 nM of a biotin-DNA conjugate using such bio-functionalized nanowire based biosensor. The sensor showed response to analyte additions with increasing concentrations up to 100 nM.

We are currently investigating the utility of different electrolytes to fabricate a sensor array consisting of nanowires of different materials. Figure 5 shows an example of an array of palladium and silver nanowires fabricated on the same electrode. Such an array can offer potentially different chemical sensing capabilities using the same platform. It is envisioned that these are the initial steps towards the fabrication of nanowire sensor arrays capable of simultaneously detecting multiple chemical species.

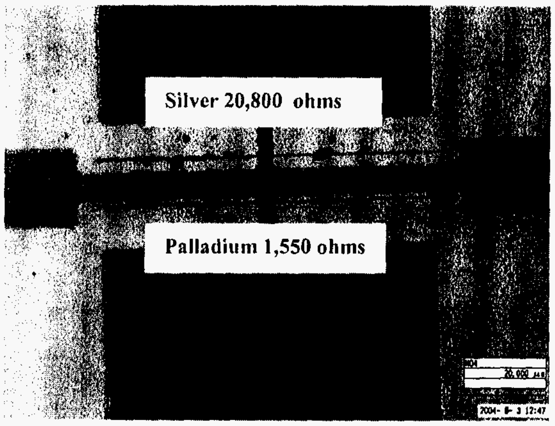

Figure 5. Optical image of Pd and Ag nanowire array

3 CONCLUSION

We have developed a fabrication technique that is capable of producing arrays of individually addressable nanowire sensors with controlled dimensions, positions, alignments, and chemical compositions. The concept has been demonstrated by growing Pd nanowires and conducting polymer nanowires. Using these fabricated Pd and polypyrrole nanowires, we successfully demonstrated gas and biochemical sensors. The use of single nanowires for biomedical sensor applications is also being investigated.

4 ACKNOWLEGEMENT

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REFERENCES

[1] Minhee Yun, Nosang Myung, Richard P. Vasquez, Choonsup Lee, Erik Menke, and Reginald M. Penner, Nano Letters, *4(3)*, 419(2004)

[2] Kumaran Ramanathan, Mangesh Bangar, Minhee Yun, Wilfred Chen, Ashok Mulchandani and Nosang V. Myung, Nano Letters, 4(7), 1237(2004)

[3] K. Ramanathan, M. Bangar, M. Yun, W. Chen, A. Mulchandani, N. V. Myung, J. Am. Chem. Soc., *127*, 496 (2005)

[4] B. H. Hong, S. C. Bae, C.-W. Lee, S. Jeong, and K. S. Kim, *Science*, *2001, 294*, 348.

[5] Y. Cui, Q. Wei, H. Park, and C. M. Lieber, *Science, 293,*1289 (2001)

[6] A. Star, J-P. Gabriel, K. Bradley, and G. Gruner, Nano Letters, **3** (4), 459 (2003)

[7] Mangesh A. Bangar, Kumaran Ramanathan, Minhee Yun, Choonsup Lee, Carlos Hangarter, Nosang V. Myung, Chemistry of Materials, *16*, 4955(2004)

[8] Lewis, F. A. Int. J. Hydrogen Energ, *20*, 587(1995)

[9] Dwivedi, D.; Dwivedi, R.; Srivastava, S. K. Sensors and Actuators B, 71, 161 (2000)

[10] Wolfe, D. B.; Love, J. C.; Paul, K. E.; Chabinyc, M. L.; Whitesides, G. M. Appl. Phys. Lett., 80, 2222 (2002)

[11] Butler, M. A. Appl. Phys. Lett., 45, 1007-1009 (1984)

[12] Favier, F.; Walter, E. C.; Zach, M. P.; Benter, T.; Penner, R. M. Science, 293, 2227(2001).

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AUTHOR(S): M. Yun, C. Lee, R.P. Vasquez, K. Ramanathan, M. A. Bangar, W. Chen, A. Mulchandan, and N.V. Myung

PUBLICATION TITLE: Technical Proceedings of the 2005 Nanotechnology Conference and Trade Show, Nanotech 2005

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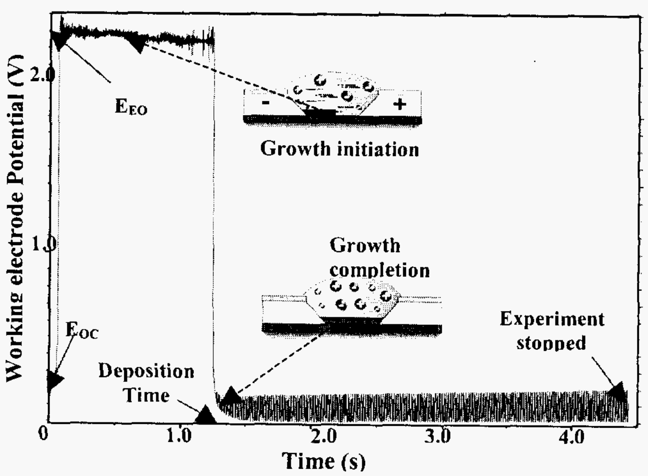
2 EXPERIMENTAL



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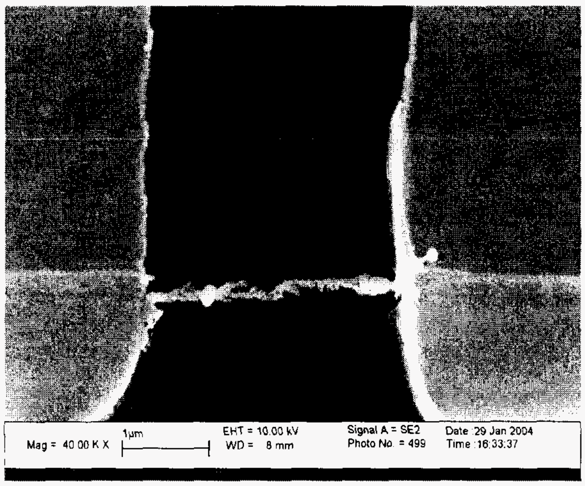

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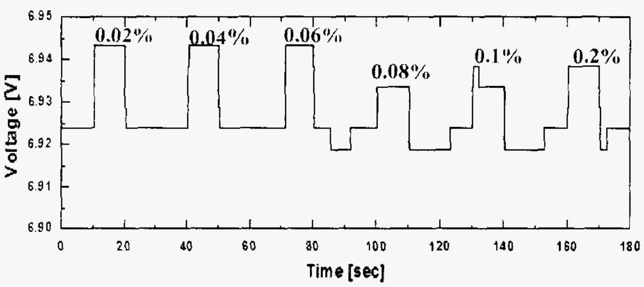

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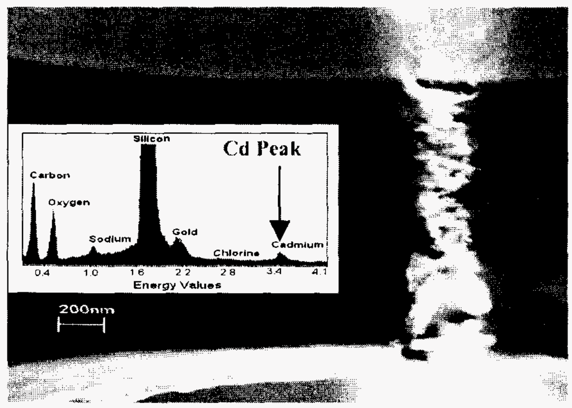

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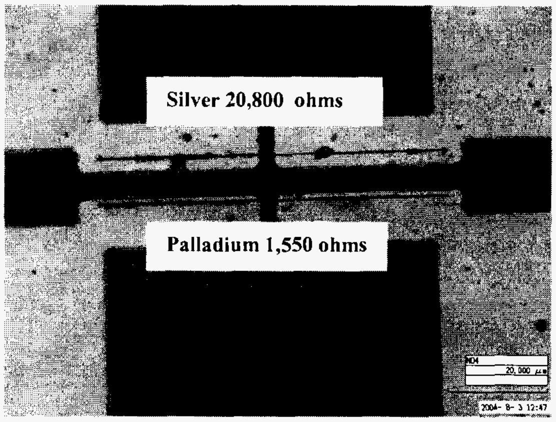

Figure 5. Optical image of Pd and Ag nanowire array

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REFERENCES

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[3] K. Ramanathan, M. Bangar, M. Yun, W. Chen, A. Mulchandani, N. V. Myung, J. Am. Chem. Soc., *127*, 496 (2005)

[4] B. H. Hong, S. C. Bae, C.-W. Lee, S. Jeong, and K. S. Kim, *Science*, *2001, 294*, 348.

[5] Y. Cui, Q. Wei, H. Park, and C. M. Lieber, *Science, 293,*1289 (2001)

[6] A. Star, J-P. Gabriel, K. Bradley, and G. Gruner, Nano Letters, **3** (4), 459 (2003)

[7] Mangesh A. Bangar, Kumaran Ramanathan, Minhee Yun, Choonsup Lee, Carlos Hangarter, Nosang V. Myung, Chemistry of Materials, *16*, 4955(2004)

[8] Lewis, F. A. Int. J. Hydrogen Energ, *20*, 587(1995)

[9] Dwivedi, D.; Dwivedi, R.; Srivastava, S. K. Sensors and Actuators B, 71, 161 (2000)

[10] Wolfe, D. B.; Love, J. C.; Paul, K. E.; Chabinyc, M. L.; Whitesides, G. M. Appl. Phys. Lett., 80, 2222 (2002)

[11] Butler, M. A. Appl. Phys. Lett., 45, 1007-1009 (1984)

[12] Favier, F.; Walter, E. C.; Zach, M. P.; Benter, T.; Penner, R. M. Science, 293, 2227(2001).

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