Electrochemically Grown Single Nanowire Sensors

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ABSTRACT

We report a fabrication technique that is potentially capable of producing arrays of individually addressable nanowire sensors with controlled dimensions, positions, alignments, and chemical compositions. The concept has been demonstrated with electrodeposition of palladium wires with 75 nm to 350 nm widths. We have also fabricated single and double conducting polymer nanowires (polyaniline and polypyrrole) with 100 nm and 200 nm widths using electrochemical direct growth. Using single Pd nanowires, we have also demonstrated hydrogen sensing. It is envisioned that these are the first steps towards nanowire sensor arrays capable of simultaneously detecting multiple chemical species.

Keywords: Nanowire, Conducting Polymer Nanowires, Hydrogen Sensor

1. INTRODUCTION

Sensors based on semiconductor and metal nanowires (NW) and carbon nanotubes (CNT) are under investigation for applications including optical\textsuperscript{1}, electronic\textsuperscript{2}, chemical\textsuperscript{3}, and biological sensors\textsuperscript{4}. Sensors based on nanowires of various materials have been demonstrated for molecular detection\textsuperscript{5}, nanoconnectors\textsuperscript{6}, biosensors\textsuperscript{7}, and gas sensors\textsuperscript{8}. Successful applications of these NW and CNT materials into functional sensors require controlled processing at the micro- and nano-meter scale. Techniques previously used to fabricate CNT and nanowire sensors have the drawbacks of low throughput, time consuming fabrication, and limited controllability. Nanowire sensor fabrication with reproducibility and good yield remains a significant challenge.

We have previously demonstrated electrodeposition\textsuperscript{9} of single Pd wires\textsuperscript{10} with diameter of 1 micron and conducting polyaniline and polypyrrole nanowires\textsuperscript{11} with diameters of 100 nm. The fabrication technique involves electrodeposition to directly grow nanowires between patterned thin film contact electrodes, eliminating expensive and tedious post-growth device assembly. Table 1 summarizes features of nanowire sensors based on carbon nanotubes, Si nanowires, and electrodeposited nanowires. Electrodeposition has advantages of a high degree of specificity in location and chemical identity of a deposit, as well as control of thickness during the process\textsuperscript{12} and a wide range of potential sensing materials. In this work, electrodeposition of single wires and small arrays with wire diameters of 75 nm is demonstrated. \text{H}_2\text{ sensing with single Pd nanowires and pH sensing using single conducting polymer nanowires are demonstrated.}

2. FABRICATION

Single Pd nanowire \text{H}_2\text{ gas sensors and the nanowire fabrication method have been previously described\textsuperscript{9, 10}. Figure 1 shows a schematic diagram of the growth of electrodeposited wires. A (100)-oriented silicon wafer is cleaned with standard RCA cleaning. The processes used in this work, including cleaning, dry etching, low-pressure chemical vapor deposition (LPCVD), lithography, dielectric deposition, e-beam lithography, metallization and electrochemical

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Table 1. The comparison of nanosensor materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>CNTs</th>
<th>Si NWs</th>
<th>Electrodeposited NWs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Deposition Techniques</strong></td>
<td>• Arc-discharge method</td>
<td>• Laser assisted</td>
<td>• Electrochemical method</td>
</tr>
<tr>
<td>• Chemical vapor deposition</td>
<td>• Supercritical fluid solution method</td>
<td></td>
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<tr>
<td><strong>Manufacturability</strong></td>
<td>Difficult</td>
<td>Difficult</td>
<td>Easy</td>
</tr>
<tr>
<td><strong>Surface Modification</strong></td>
<td>Limited</td>
<td>Well-known</td>
<td>Well-known</td>
</tr>
<tr>
<td><strong>Functionality</strong></td>
<td>Single species</td>
<td>Single species</td>
<td>Individually Addressable Array</td>
</tr>
</tbody>
</table>

Table from ref. #13

The electrolyte channel is patterned with e-beam lithography, and etched using reactive ion etching. One drop of Pd electroplating solution is placed into each channel with a micropipette. The Pd electrolyte consists of Pd(NH₂)₂(NO₂)₂ (10g/l), and NH₂NH₂SO₃ (100 g/l). The pH of the solution is adjusted to 8.0 by addition of H₂NO₃S and NaOH. A nanowire starts to grow from cathode to anode through the e-beam patterned channel when a potential is applied between contact electrodes. The dimensions of the nanowire, including its length and width, are predetermined by the width of the nanochannel and the distance between electrodes. 
Figure 2(a) Single Pd nanowire with a width of 75 nm to 85 nm.

Figure 2(b) Single Pd nanowire with a width of 90 nm to 150 nm.

Figure 2(c) Single Pd nanowire with a width of 250 nm to 350 nm.
This fabrication method shows several advantages over other approaches\textsuperscript{15-19}, including controlled growth, reproducibility, easy alignment, and extensive material choices. Fig. 2 shows various nanowire diameters ranging from as small as 750 nm to as large as 350 nm. These single Pd nanowires with lengths of up to 7 microns have been synthesized by e-beam lithography and electrodeposition, respectively. Fig. 2(a) shows a nanowire with diameter of 75 nm to 85 nm with 3 microns length. The fabricated nanowire has a high surface area due to dendrite formation during growth. I-V characterization of the palladium wire shows ohmic and metallic behavior with a resistance of 875 ohms at room temperature. This is much larger than the value of about 1 to 5 ohms expected using bulk Pd resistivity. The additional resistance may be due to the grain-boundary scattering effect. With decreasing film thickness the mean grain size decreases, leading to the presence of more grain boundaries and hence an increase in resistivity\textsuperscript{30}. The diameter of the Pd single nanowire shown in Fig. 2(b) is approximately 90 nm to 150 nm and the length is 5 microns, and the Pd nanowire in Fig. 2(c) has a width of 250 nm to 350 nm and a length of 5 microns. The tapered electrodes in Figs. 2(b) and 2(c) have longer distances between electrodes compared to the 3 micron distance in Fig. 2(a), but still show a stable nanowire growth across the electrodes due to the confined electric field.

3. CONDUCTING POLYMER NANOWIRES

(a) A single polyaniline nanowire 100nm wide and 4 microns long.

(b) A single polypyrrole nanowire 200nm wide and 3 microns long.

Figure 3. (from ref. 11).
Electrodeposited polypyrrole and polyaniline nanowires have also been fabricated as described previously\textsuperscript{11}. The fabrication of the electrode structure used for the growth of the conducting polymer wires is the same as for Pd fabrication. We have used two microliters of deoxygenated pyrrole (0.06 M in 0.01 M KCl) or aniline (0.1 M in 0.1 M HCl) solutions as the electrolytes. These electrolytes are placed in the e-beam patterned channel between the two electrodes. Then the electrodeposition was carried out in galvanostatic mode by applying 100 nA current while the potential of the working electrode was monitored continuously with respect to a pseudo reference electrode. At the same time, we used a programmed multimeter to record resistances of the growing nanowires. The potential changes from the open circuit potential to a value of 2 V followed by a gradual decrease as the wire grows. When the wire was fully grown and made a contact with the cathode, the potential dropped to 0 V and the electrodeposition process was stopped. Finally, the wafer was rinsed three times with DI water. The measured resistances of grown conducting polymer nanowires are in the range of a few Kilo-ohms to Mega-ohms. Examples of electrodeposited polyaniline and polypyrrole nanowires are shown in Fig. 3.

4. SENSING

Nanowire-based sensors can potentially exhibit a fast response with higher sensitivity and selectivity than existing sensors. The basic principle behind nanowire-based gas sensors is the detection of small concentrations by measuring changes in electrical resistances in nanowires caused by the absorption or desorption of the chemical species or by phase changes in the nanowires\textsuperscript{9}.

Pd is a commonly used material in hydrogen sensors because Pd has low contact resistance and high sensitivity to H\textsubscript{2}. There are two known mechanisms for hydrogen sensor using Pd materials. First, the Pd reacts reversibly to form more resistive palladium hydride upon exposure to H\textsubscript{2}\textsuperscript{21}. Second, Penner et al. demonstrated electrodeposited multiple Pd nanowires as H\textsubscript{2} sensors and hydrogen-activated switches with the nanowires grown using a step edge decoration method\textsuperscript{21}. In that work, resistance decreases upon exposure to hydrogen gases due to hydrogen molecules filling between break junctions\textsuperscript{20}. These multiple Pd nanowire sensors operate at room temperature, have a fast response time (<75 msec), require low power (<100 nW), and are resistant to poisoning by reactive gases, including O\textsubscript{2}, CO, and CH\textsubscript{4}\textsuperscript{21}.

![Figure 4. Hydrogen gas sensing results using a single Pd wire with 150 nm diameter and 3 \( \mu \)m length for 0.1%, 1.0%, and 10% H\textsubscript{2} concentration in nitrogen carrier gas.](image)

In this work, we demonstrate sensing of different concentrations of hydrogen gas (from 0.02% to 10% in N\textsubscript{2} carrier gas) using a single electrodeposited Pd wire. We have measured the variation of output voltage caused by the resistance change in a single Pd nanowire to which a constant voltage of 5 mV has been applied. An ammeter with a current amplifier with a gain of 10\textsuperscript{4} has been serially inserted to measure the current during the sensing. The output voltage of the current amplifier is measured with a fixed output resistance of 2 ohms. The output voltage increases (nanowire resistance decreases) with hydrogen gas flow and returns to the original state when no hydrogen gas is present as shown in Fig 4. Figure 4 shows hydrogen gas sensing with concentrations of 0.1, 1.0, and 10% cycled every 180 seconds, to
confirm reproducible resistance changes for those concentrations. As shown in Fig. 4, the measured output voltage is approximately the same for hydrogen gas concentrations of 1% or less, and has higher values for hydrogen concentrations greater than 1%.

The concentration of the H⁺ is an important environmental parameter for aqueous biological species, or for predicting the path of chemical reactions. The most widely used solid-state metal oxides used for pH sensing have been potentiometric Sb₂O₃ sensors. We have previously demonstrated pH sensing using a single conducting polypyrrole nanowire. The conductivity of polypyrrole is directly proportional to the pH.

4. SUMMARY

We have demonstrated a fabrication technique that has the potential to produce arrays of individually addressable nanowire sensors. 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 between 75 nm and 350 nm and conducting polymer nanowires with diameters between 100 nm and 500 nm. Using these single wires, we have successfully demonstrated hydrogen sensing with Pd nanowires and pH sensing with polypyrrole nanowires. Our nanowire fabrication technique is ideal for nano-biosensor fabrication by the direct fabrication of metal-oxide and conducting polymer nanowires with embedded bioreceptors in one step rather than multiple steps needed in surface-modified nanowires and CNTs. Reducing the width of the e-beam patterned channels, which is currently under investigation, can potentially further reduce the width of electrodeposited wires to a few tens of nm. We are also currently investigating utilizing different electrolytes to fabricate sensor arrays with nanowires of different compositions for different chemical sensing capabilities. It is envisioned that these are the first steps towards nanowire sensor arrays capable of simultaneously detecting multiple chemical species.

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