Investigation of a Single Pd Nanowire for Use as a Hydrogen Sensor**

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Interest in nanowire technology has grown significantly over the past several years, due to their potentially broad applications in optics, electronics, and sensors (e.g., resonators,[1] molecular detection,[2] nanoconnectors,[3] biosensors,[4] and gas sensors[5]). Due to their small size, sensitivity, real-time detection, and ultra-low power demands, nanowire sensors are being investigated for detection of a wide range of chemical and biochemical species. The techniques used to fabricate these sensors include laser ablation cluster formation,[6] focused ion-beam etching of electrodes to create a small gap (≈100 nm),[7] use of ion-track membranes,[8] use of alumina templates,[9] and electrochemical step-edge decoration.[10] These techniques have drawbacks of limited controllability and manufacturability, therefore reliable and controllable nanowire fabrication remains a significant challenge.

We have previously reported a method of electrodepositing Pd wires with micrometer diameters[11] and conducting polymer nanowires of polyaniline and polypyrrole with diameters of 100 nm.[12] In this work, single Pd nanowires are fabricated by electrodeposition in electrolyte channels patterned with electron-beam lithography, and hydrogen sensing is demonstrated. This fabrication technique can produce nanowires with controlled dimensions, positions, alignments, and chemical compositions, and potentially enables the use of a wide range of materials for creating arrays of single-nanowire sensors. Additionally, the growth of nanowires using this technique would allow for easy integration with existing silicon technology.

Figure 1 shows SEM images of typical electrodeposited nanowires between electrodes. The magnified image in Figure 1b shows a single Pd nanowire with a diameter ranging from 70 to 85 nm. An EDS (energy dispersive spectroscopy) elemental analysis detected only Pd metal in the nanowire.

Figure 2 shows various nanowire diameters, ranging from as small as 100 nm to as large as 1 μm, with lengths up to 7 μm. Figure 2a shows a nanowire with a diameter of 100–150 nm that is 3 μm long. This nanowire has a high surface area with a bristle structure due to the electric field inside the nanochannel. I–V characterization shows ohmic and metallic behavior with a resistance of 875 Ω at room temperature. This is much larger than the value of about 1–5 Ω expected for bulk Pd resistivity. The additional resistance may be attributed to nanocontacts and the grain-boundary scattering effect.[13] For small film thickness the mean grain size is smaller, which leads to the presence of more grain boundaries and, hence, higher resistivity.[14] The diameters of the other Pd single nanowires shown in Figure 2 are approximately 100 nm to 1 μm (b), 100–300 nm (c), and 250–350 nm (d); the initial resistances of these nanowires are 85, 248, and 235 Ω, respectively. In general, the resistance of a nanowire is dependent on the diameter of the
nanowire, with the narrowest region determining the final resistance. Our nanowires have the same height, but different growth conditions give different lengths. The nanowires in Figures 2a and b have lengths of 3 \( \mu \text{m} \), whereas those in Figures 2c and d have lengths of 5 \( \mu \text{m} \) between the electrodes. Even though tapered structure electrodes (c and d) have longer distances between electrodes, they show more stable nanowire growth.

The sensing of different hydrogen concentrations (between 0.02 and 10\% in N\textsubscript{2} gas) was demonstrated with the single electrodeposited Pd nanowire shown in Figure 2a. Figure 3a shows an increased output voltage (decreased nanowire resistance) with hydrogen gas-flow and a return to the original state when no hydrogen gas is present. The sensor responds to hydrogen across the entire concentration range studied. We were not able to obtain hydrogen gas concentrations lower than 0.02\% due to the limitations of the hydrogen gas-flow controller, so the lower limit of sensitivity could not be determined. However, the demonstrated sensitivity is comparable to, or better than, previously reported H\textsubscript{2} gas sensors such as those based on Pd\textsuperscript{15,16} field-effect transistors\textsuperscript{17} and metal oxides\textsuperscript{18}, with lower power consumption.

Figure 3b shows the variation of output voltage in a single Pd nanowire while the hydrogen gas-flow is cycled to yield hydrogen concentrations in the range 0.1\% to 10\%. The Pd sensor response is rapid, reversible, and reproducible, as shown in Figure 3b. Hydrogen gas with concentrations of 0.1, 1, 5, and 10\% was cycled three times in 370 s and each concentration showed about the same response between cycles. The observed decrease of the nanowire resistance (output voltage increase) may be due to improved intergrain contacts and closing of the nanogaps when hydrogen absorption causes the Pd grains to expand\textsuperscript{5}.

Figure 3c shows the measured output voltages when hydrogen concentrations of 0.1, 1, 5, and 10\% are cycled three times (Ex1-1, -2, and -3), and with hydrogen concentrations of 0.1, 1, and 10\% cycled three times (Ex2-1, -2, and -3) to confirm reproducibility. There is little scatter in the measured output voltages between cycles and the hydrogen concentration can be uniquely determined for hydrogen concentrations above 1\%. However, for concentrations of 1\% or below the measurements are more variable and are not dependent on the hydrogen concentration. Although the values of low hydrogen concentrations cannot be determined, the Pd nanowire sensors do detect the presence of hydrogen down to the lowest concentration obtainable (0.02\%) in this work.

In conclusion, this report describes the fabrication of single Pd nanowires with diameters ranging from 70 to 300 nm and up to 7 \( \mu \text{m} \) in length using standard semiconductor processing techniques and electrodeposition. This process can, in principle, produce sensor arrays that are capable of sensing multiple chemical species simultaneously. We have demonstrated hydrogen sensing in the concentration range of 0.02\% to 10\%. This Pd nanowire sensor exhibits a fast response time (<300 ms) with ultralow power consumption (<25 mW).

**Experimental Section**

Fabrication of the Pd nanowires was similar to the procedure described previously\textsuperscript{10}. A 0.5-\( \mu \text{m} \)-thick SiO\textsubscript{2} insulator layer was grown on a Si(100) wafer by wet oxidation. A Ti (25 NYL3B) adhesion layer and thick Au (approx. 1500 Å) contact layer were then deposited, with electrodes and contacts being patterned by liftoff. Thermally evaporated SiO (\( \approx 1500 \) Å) was then deposited on top of the electrodes. A poly(methyl methacrylate) layer was selectively opened by e-beam lithography, and electrolyte channels were formed in the SiO by reactive-ion etching. One drop of electroplating solution—[Pd(NH\textsubscript{2})\textsubscript{2}(NO\textsubscript{2})\textsubscript{2}] (10 gL\textsuperscript{-1}) and NH\textsubscript{4}NH\textsubscript{2}SO\textsubscript{3} (100 gL\textsuperscript{-1})—was placed into each channel with a micropipette. The nanowire grew from the cathode to the anode through the channel when an electric potential was applied. The diameter and length of each nanowire can be predetermined by the width of the electrolyte channel and the distance between the elec-
measured the variation of output voltage caused by the resistance change in a single Pd nanowire to which a constant voltage of 5 mV was applied. An ammeter with a current amplifier with a gain of $10^6$ was placed in series with the nanowire, and the output voltage of the current amplifier was measured with a fixed output resistance of 2 Ω.

**Keywords:**
hydrogen · lithography · nanowires · palladium · sensors


Received: September 24, 2005
Published online on January 13, 2006

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**Figure 3.** Electrical signals as a function of time for various concentrations of hydrogen in nitrogen using a Pd single nanowire: a) signals for various concentrations between 0.02 and 0.2% hydrogen, b) a comparison of signals for concentrations of 0.1, 1, 5, and 10% over 360 s, and c) a comparison of signals for concentrations of 0.1, 1, 5%, and 10% hydrogen versus output voltage.