

Electrochemically Grown Wires for Individually Addressable Sensor Arrays

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ABSTRACT

We report on the electrochemical growth of micro/nanowire devices using e-beam-patterned electrolyte channels, potentially enabling the controlled fabrication of individually addressable arrays. The concept of growing single wires and small arrays using this technique is demonstrated by single and double wires of Pd and polypyrrole with 500-nm and 1- μ m widths up to 7- μ m lengths and 200-nm thicknesses. The use of Pd wires as hydrogen sensors and polypyrrole wires as pH sensors is demonstrated.

Semiconductor and metal nanowires and carbon nanotubes have been the subject of intense interest as sensors^{1–4} and electronic devices for high-density circuits.^{5–16} The techniques used to fabricate these devices have included using an atomic force microscope to manipulate individual carbon nanotubes onto prepatterned electrodes,⁵ the random dispersion of suspended carbon nanotubes in solution onto a substrate with prepatterned electrodes,^{6–8} and using catalysts (as carbon nanotube nucleation sites) lithographically patterned on electrodes.^{13,15} Although these methods have been adequate for demonstrating the operational characteristics of individual devices, they have intrinsic drawbacks of low throughput and limited controllability, which make them unattractive for large-scale circuits. Attempts to improve fabrication controllability have included applying an electric field for the postgrowth alignment of metal and semiconductor nanowires^{9,10} or for alignment during the growth of carbon nanotubes,¹⁴ the growth of metal nanowire arrays on a selectively etched superlattice template followed by manual transfer to the desired substrate,¹⁶ and the fluidic alignment of semiconductor nanowires on a substrate followed by e-beam lithography to form contacts.^{2,11,12} Nanowire logic gates and a small-scale circuit have been successfully fabricated and demonstrated utilizing a layer-by-layer fluidic alignment.¹² However, device fabrication with controllability, reproducibility, and yield suitable for large-scale circuits remains a significant challenge.

Electrodeposited nanowire sensors can overcome the limitations of both CNTs and Si nanowires because of the relative ease of fabrication and surface modification. Electrodeposition is a promising and versatile method for the fabrication of nanowire sensor arrays, with a wide range of available sensing materials that can be electrodeposited, including metals, alloys, metal oxides, semiconductors, and conducting polymers. For example, electrodeposited IrO₂, Sb/Sb₂O₃, Pt, Pd, polyaniline, and polypyrrole are good pH-sensing materials.^{17,18} Electrodeposited Ru oxide/cyanide films have been used to detect inorganic and organic species (e.g., aliphatic alcohols).¹⁹ The sensitive detection of molecules by Cu nanocontacts electrodeposited between electrodes¹ and hydrogen sensing by Pd wires electrodeposited on graphite step edges³ have been demonstrated. Electrodeposition is also potentially scalable for producing nanowire arrays (e.g., in combination with large-scale integrated microfluidic networks²⁰). Finally, the electrodeposition of nanowires between contact electrodes would eliminate time-consuming and tedious postgrowth device assembly, and the nanowires would inherently be individually addressable.

As the first step toward the fabrication of individually addressable nanowire sensor arrays, sensors based on bundled nanowires electrochemically grown using nanoporous alumina templates are also being investigated. This approach allows for the development of nanowire surface-modification techniques and the characterization of sensor sensitivity and selectivity in parallel with the development of single wire array fabrication. To demonstrate our concept, we have previously reported the electrochemical growth of single Pd

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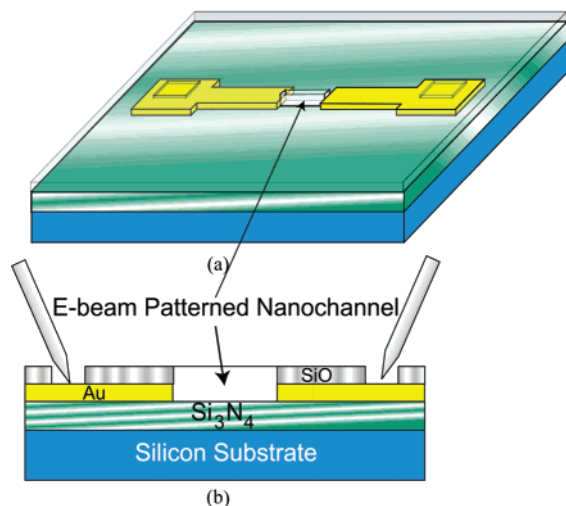


Figure 1. Schematic diagram of a structure used for the electrochemical wire growth. (a) Electrodeposited wire connected between electrodes. (b) Cross-sectional view of the Si substrate, silicon nitride (1 μm), Au contacts, and thermally evaporated SiO. Channels for the electrolyte solution are formed between electrodes by e-beam patterning of the SiO.

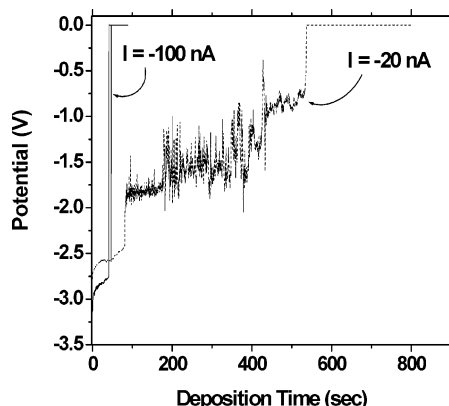


Figure 2. Measured wire growth potential responses as a function of deposition time. The applied currents were -20 and -100 nA.

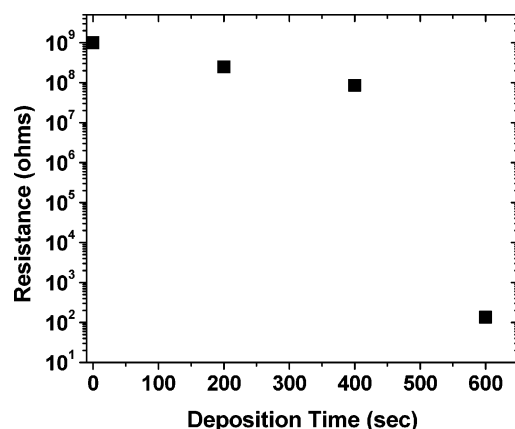
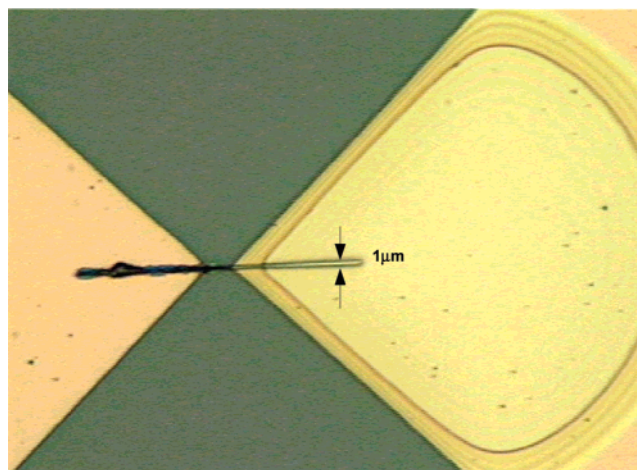
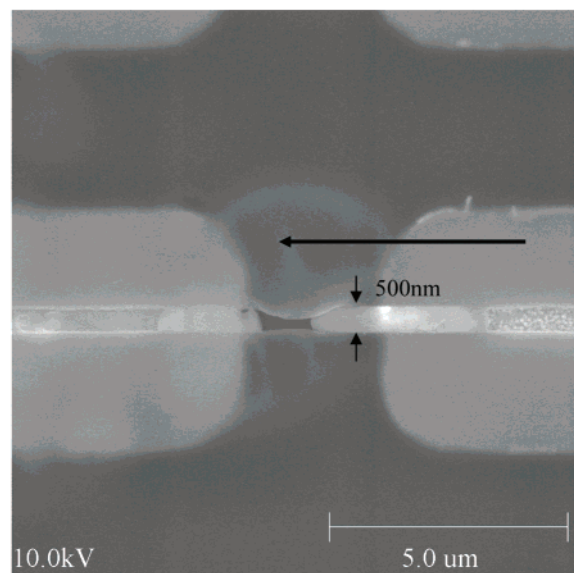


Figure 3. Resistance change between anode and cathode as a function of time. The deposition current was kept at -20 nA.

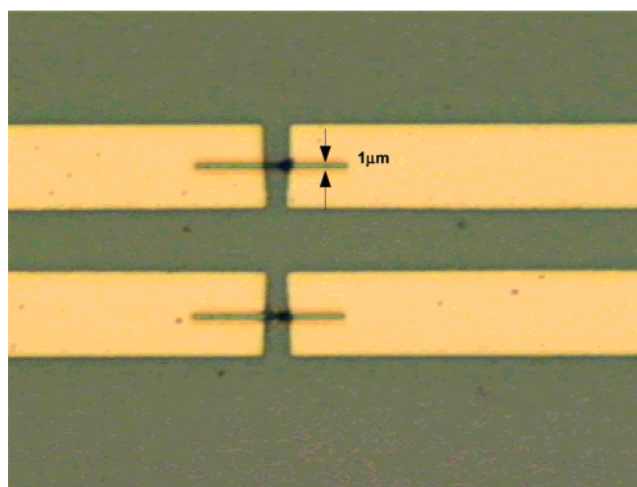
wires with $1\text{-}\mu\text{m}$ width between lithographically patterned Au contact electrodes and a glucose sensor using bundled Pt nanowires with $100\text{--}200\text{-nm}$ diameter.²¹ The glucose amperometric sensor was constructed by co-deposition from a solution of glucose oxidase and polypyrrole onto the Pt-



(a)



(b)



(c)

Figure 4. Images of electrodeposited palladium wires grown between electrodes. (a) Single wire with $1\text{-}\mu\text{m}$ diameter, $7\text{-}\mu\text{m}$ length, and 200-nm thickness. (b) Partially grown single wire with 500-nm diameter, $3\text{-}\mu\text{m}$ length, and 200-nm thickness. (c) Double wires with a common electrode with $3\text{--}5\text{-}\mu\text{m}$ length.

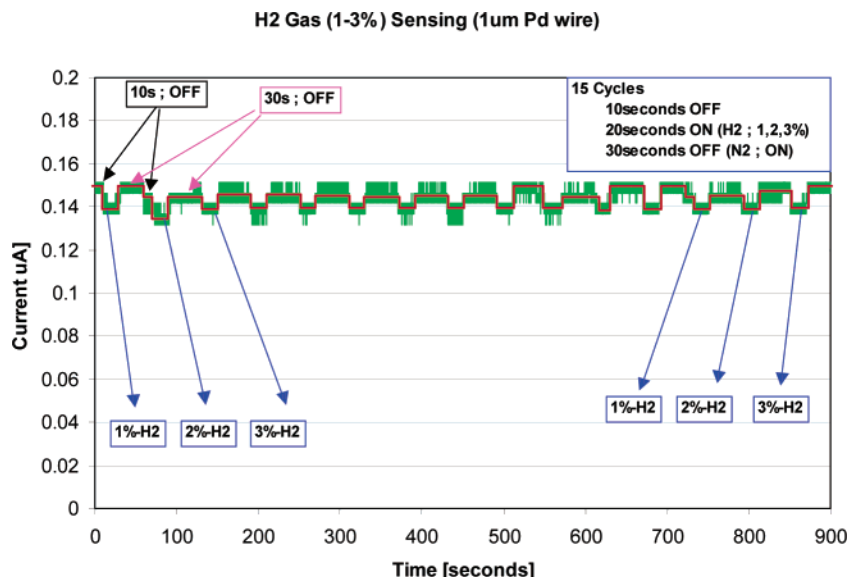


Figure 5. Hydrogen gas sensing results using a single Pd wire with 1- μm diameter and 7- μm length for 1, 2, and 3% H_2 concentration in nitrogen.

bundled nanowires, thus immobilizing the enzyme within the polymer film. This electrochemically assisted enzyme-immobilization technique not only controls the polymer thickness accurately but also enables enzyme deposition on small electrodes. Compared to that of a Pt thin film, the response to glucose is improved by 3 orders of magnitude by using Pt nanowires as the substrate. This is attributed to the much higher surface area of the Pt nanowire bundle.

In this report, we demonstrate the electrochemical growth of single Pd wires grown as previously described,²¹ with smaller widths of 500 nm, and demonstrate their use as H_2 sensors. We also report the electrochemical growth of single polypyrrole wires with widths of 500 nm and 1 μm and demonstrate their use as pH sensors. In general, with decreasing film diameter the mean grain size decreases, leading to the presence of more grain boundaries and hence an increase in resistivity.²² This growth technique potentially enables the fabrication of nanowire sensors with controlled dimensions, positions, alignments, and chemical compositions. The technique involves e-beam lithography to form an electrolyte channel for the electrodeposition of wires between electrodes. In arrays, each channel can have a different electrolyte, and hence the electrodeposited wires can have different compositions. This technique potentially enables the fabrication of individually addressable nanowire sensor arrays with the capability of simultaneously detecting multiple chemical species.

Figure 1 shows a schematic diagram of the structure used for the growth of a single electrodeposited wire. A (100)-oriented silicon wafer is cleaned with standard RCA cleaning. A 1- μm -thick insulator layer of low-stress Si_3N_4 is deposited on the wafer using low-pressure chemical vapor deposition. A Ti adhesion layer and an $\sim 3000\text{-}\text{\AA}$ -thick Au contact layer are then deposited, with contacts being patterned by liftoff. Thermally evaporated SiO_x is then deposited on the wafer at room temperature. Using e-beam lithographic patterning, the deposited SiO_x is selectively opened with reactive ion etching to form electrolyte channels. One drop of electroplat-

ing solution is placed into each channel with a micropipet. The wire grows from the cathode to the anode through the channel when an electric potential is applied. The dimensions of the wire are predetermined by the width of the channel and the distance between electrodes, and the channel also limits dendrite branching during growth.

To demonstrate the technique, palladium and polypyrrole wires of 500-nm and 1- μm widths with 3- to 7- μm lengths and 200-nm thickness have been electrodeposited. To grow the Pd wires, we have used a palladium p-salt plating solution with a two-electrode configuration. The palladium electrolyte consists of $\text{Pd}(\text{NH}_2)_2(\text{NO}_2)_2$ (10 g/L) and ammonium sulfate (100 g/L). The pH of the solution was adjusted to 8.0 by the addition of sulfamic acid and sodium hydroxide. A potentiostat/galvanostat is used to grow palladium wires in galvanostatic mode. The applied currents are -10 , -20 , and -100 nA, and the corresponding potentials are monitored. Polypyrrole wires with 500-nm and 1- μm widths are grown under the same conditions using a solution of pyrrole (0.24 M) and NaCl (0.1 M).

Figure 2 shows cathode potential responses during the electrodeposition of a palladium wire at applied currents of -100 and -20 nA. The cathode potential initially steeply approaches a negative value, followed by a gradual increase in the potential as the palladium wire grows from cathode to anode. When a wire is fully grown and makes contact with the anode, the potential drops to zero, and the applied potential is turned off. Lower cathode potentials and shorter deposition times are observed at deposition currents of -100 than -20 nA as expected from the higher deposition rate. Palladium wires (7 μm long) were grown within 50 s with -100 nA and within 500 s with -20 nA. Figure 3 shows the electrical resistance change of the gold electrodes during palladium wire growth at -20 nA. As expected, the electrical resistance gradually decreases as the palladium wire grows from cathode to anode and reduces the gap. When the palladium wire makes contact with the anode, the measured resistance is less than 100 Ω in the liquid electrolyte.

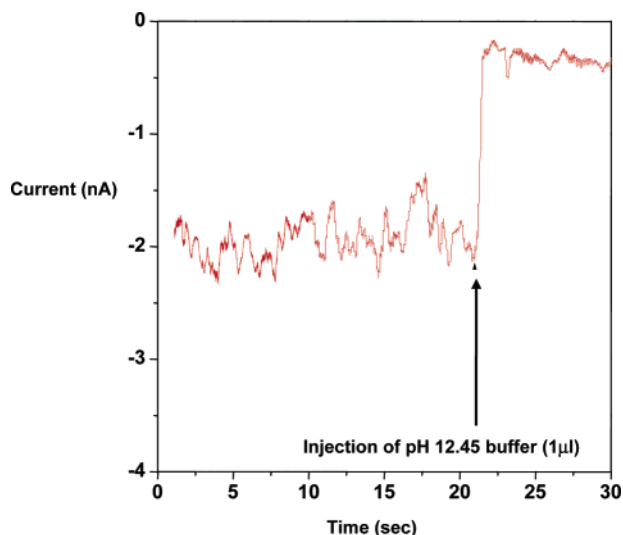


Figure 6. Demonstration of pH sensing by adding 1 μL of pH 12.45 buffered solution on top of a single polypyrrole wire (500-nm width).

Optical images of electrochemically grown palladium wires between gold electrodes are shown in Figure 4. The length of the wire is approximately 7 μm , and the width is approximately (a) 1 μm and (b) 500 nm with 200-nm thicknesses. The arrow in Figure 4b indicates the wire growth direction from cathode to anode. The wire growth shown in Figure 4b was interrupted to illustrate the growth mechanism. Figure 4c shows an image of double Pd wires grown using common Au electrodes, demonstrating that arrays of electrodeposited wires are feasible.

Using a single electrodeposited Pd wire with 1- μm diameter and 7- μm length, we have demonstrated the sensing of different concentrations of hydrogen gas (1, 2, and 3% in N_2 gas). Upon exposure to H_2 , the Pd wire reacts reversibly to form more resistive palladium hydride. Figure 5 shows the measured current in the single Pd wire at a constant voltage of 2.5 mV while the hydrogen gas flow is cycled on and off. The line shows the mean value of the sensing currents in the graph. The sensing currents decrease with hydrogen gas flow and returned to the original state when no hydrogen gas is present.

We have also fabricated a single conducting polymer wire (polypyrrole) with 200-nm thickness, 500-nm width, with 3- μm length and have demonstrated pH sensing. The conductivity of polypyrrole is directly proportional to the pH.²³ Figure 6 shows the current change observed upon the change in resistance when 1 μL of buffered solution at pH 12.45 is placed on top of the single polypyrrole wire.

The electrochemical growth of nanowires of other materials is also currently being investigated for different sensing capabilities. Using nanoporous alumina templates, we have grown bundles of 100–200-nm-diameter nanowires of Pd, Pt, Au, polyaniline, Sb_2O_3 , and IrO_x .

In conclusion, 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 the growth of palladium

and polypyrrole wires of 500-nm and 1- μm widths with up to 7- μm lengths and 200-nm thicknesses. Using these single wires, we have successfully demonstrated hydrogen sensing with Pd wires and pH sensing with polypyrrole wires. Reducing the width of the e-beam patterned channels, which is currently under investigation, can in principle further reduce the width of electrodeposited wires to a few tens of nanometers. We are also currently investigating the utilization of different electrolytes to fabricate small arrays with wires of different compositions and hence different chemical sensing capabilities. It is envisioned that these are the first steps toward nanowire sensor arrays capable of simultaneously detecting multiple chemical species.

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