

# Nanowire Growth for Sensor Arrays

Minhee Yun\*, Nosang V. Myung, and Richard P. Vasquez  
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

## ABSTRACT

A nanowire-based sensor array for in-situ gas and biochemical sensing including spacecraft safety monitoring, gas emission monitoring, air and water quality monitoring, and fire detection are designed. To prove our concept, we have fabricated bundled metal (e.g. Pd, Au), metal oxide (e.g.  $\text{Sb}_2\text{O}_3$ ,  $\text{IrO}_x$ ), and conducting polymer (polyaniline) nanowires to detect  $\text{H}_2$ , glutamate, and thyroid hormone using a cost-effective, and high-yield electrodeposition method. Our final form of nanowire-based sensor array will reduce power consumption at least by a factor of 10 by replacing the 100 nW bundled nanowire sensor array with a single nanowire pixel for each sensing material design. Innovative concepts employed in this work include the fabrication of a nanowire array with individually addressable sensors that allow single nanowires to sense gases and biomolecules.

Keywords: Nanowire, Sensor

## 1. INTRODUCTION

The greatest interest in nanostructures stems from their numerous potential applications in such area as electronics, biochemistry, materials, and medicine. One-dimensional structured materials, such as nanowires and nanotubes (NTs), are the best candidate materials for these applications in nanotechnology. Many researchers have also developed nanosensors based on Si nanowires or carbon nanotubes (CNTs). For example, Cui *et al.* demonstrated that Si nanowire-based sensors are capable of highly sensitive and selective real-time detection of biomolecules<sup>1</sup>. Star *et al.* demonstrated CNT based FET devices<sup>2</sup>. However, these building blocks have some limitations. Existing fabrication methods for CNTs produce mixtures of doped and semiconducting nanotubes, which make them difficult to use as sensing materials since metallic and semiconducting nanowires will function differently. In addition, surface modification methods for CNTs, which are essential to prepare interfaces selective for binding a wide range of chemical and biological analytes<sup>1</sup> are not well established. Silicon nanowires are produced by a laser-assisted vapor-liquid-solid growth method<sup>3</sup> or a supercritical fluid solution phase method<sup>4</sup>. These methods operate at high temperature and low pressure and require sophisticated equipment. Even though Si nanowires and CNT offer good sensing materials, they have intrinsic drawbacks of process controllability and low throughput. These methods also require that nanowires and nanotubes must be manually aligned and then electrically connected by another assembly process.

We report an approach to growing individually addressable nanowires for sensor array application using e-beam lithography, electrodeposition, and room temperature SiO deposition. The growth of nanowire sensors with precisely controlled dimensions is very important in a sensor's detection limits and response time. We present a fabrication techniques, that can produce nanowire sensors with precisely controlled dimensions. This technique also produces individually addressable nanowire sensor arrays with multising-sensing capabilities.

In this work, we use a novel, cost-effective, and high-yield, room-temperature, ambient pressure-operated electrodeposition technique to directly fabricate nanowires between contact electrodes, eliminating expensive and tedious post assembly. Electrodeposition is an alternative method to fabricating nanowire sensor arrays with wide ranges of sensing materials available, including metals, alloys, and metal oxides, semiconductors, and conducting polymers. Electrodeposition allows a high degree of specificity in location and chemical identity of a deposit, as well as a high degree of control over thickness<sup>5,6</sup>. It also enables inexpensive scale up for producing fully functional systems.

Previous Li *et al.* work reported molecular detection based on electrodeposited copper nanowires grown between nanogap electrodes<sup>7</sup>. In his work, using a focused ion beam, a pair of Au electrodes facing each other with a gap of 100 nm is

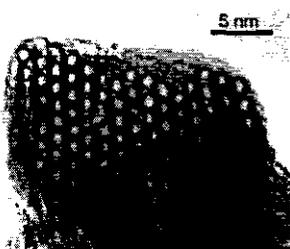
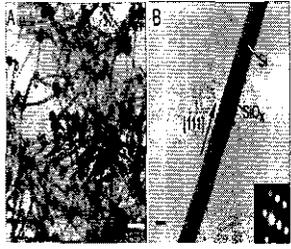
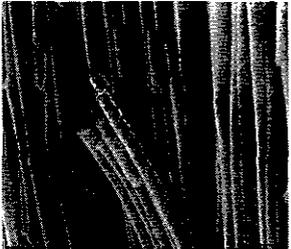
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\* Minhee.Yun@jpl.nasa.gov; phone 1 818 354-3413; fax 1 818 393-4540

fabricated on a Si/SiO<sub>2</sub> substrate, and then the gap is bridged to form a nanowire with the desirable conductance by electrochemically depositing Cu on the ends of the electrodes. Our proposed nanowire-based biochemical sensor will not require use of such an expensive apparatus as a focused ion beam and will require low power consumption compare to 100 nW for Pd mesowire arrays<sup>8</sup>.

Table 1 compares state-of-the art nanosensors with the nanowire. Nanowires for biochemical sensors can overcome the limitations of both CNTs and Si nanowires due to easy fabrication and surface modification. The basic features of nanowire-based biochemical sensors include the detection of small concentrations by measuring changes in the electrical conductance of nanowires produced by the adsorption or bioreaction of the chemical species and changes in the electrochemical potential or current of nanowires produced by bioreaction on the nanowire surface. To detect biomolecules, surface modification of the nanowire is necessary. In this work, a nanowire sensor for sugar detection has been designed for biochemical sensing. For biomedical applications, we have designed a sensor to detect thyroid hormones. Detection of thyroid hormones (e.g., the early molecular signature of disease) using radio-immunoassay or immuno-precipitation is the most popular way to measure 3,5,3'-triiodo-L-thyronine (T3) and thyroxine (T4) hormones. And the detection limits are about 1 nM. Disadvantages of these methods are the use of radioactive isotopes or overly complex procedures. Our nanowire-based sensors can provide simple and safe analysis with equivalent or higher sensitivity compared to the above approaches.

Table 1. The comparison of state-of-the art nanosensor materials

	CNTs	SNWs	This work
<b>Materials</b>	Carbon	Silicon	Metal alloy, metal oxide, conducting polymers
<b>Deposition Techniques</b>	1.Arc-discharge method 2.Laser assisted 3.Chemical vapor deposition	1.Laser assisted 2.Supercritical fluid solution method	1.Electrochemical method
<b>Manufacturability</b>	Difficult	Difficult	Easy
<b>Surface Modification</b>	Limited	Well-known	Well-known
<b>Functionality</b>	Single	Single	Individual multi-functioning capability
	 From ref. #9	 From ref. #6	 Fabricated in this work

## 2. FABRICATION

Figure 1 shows the schematic procedure for electrodepositing nanowire sensors with controlled dimensions. 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 deposition, are standard semiconductor fabrication techniques. First, the (100) oriented Si with the thickness of 350- $\mu$ m Si wafers was cleaned with standard RCA cleaning. Then, a 1- $\mu$ m layer of low stress Si<sub>3</sub>N<sub>4</sub>, which acts as an insulator, was deposited on the wafer using LPCVD. Ti-Au metal films are deposited using a liftoff technique to form the contact layer. The thickness of the Au layer deposited on the contact pads is chosen for optimal electrical readout, which is up to 300 nm. In this work, we used a thermal SiO deposition technique to fabricate the electrolyte channel due to the advantage of the room temperature process. The SiO was deposited on the top of metal. The wafer is then e-beam patterned to define the nanochannels, and etched using an reactive-ion etch. Electrochemical deposition was performed by adding one drop of

electroplating solution on top of the nanochannel. When an electrical potential is applied between the electrodes, a nanowire grows from cathode to anode through the nanochannel because of the local high voltage electric field.

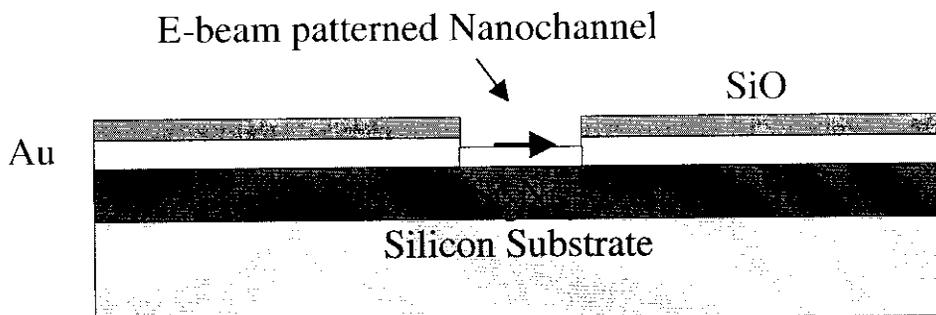
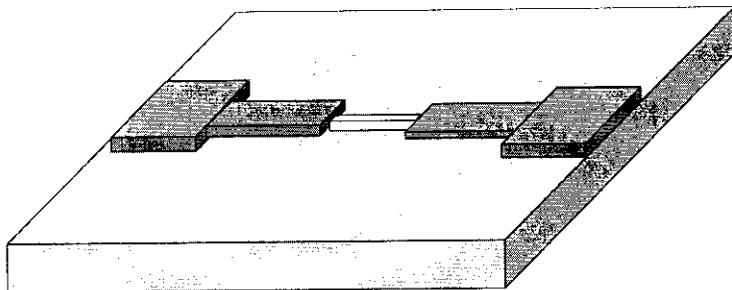


Figure 1. Schematic of nanowire sensor

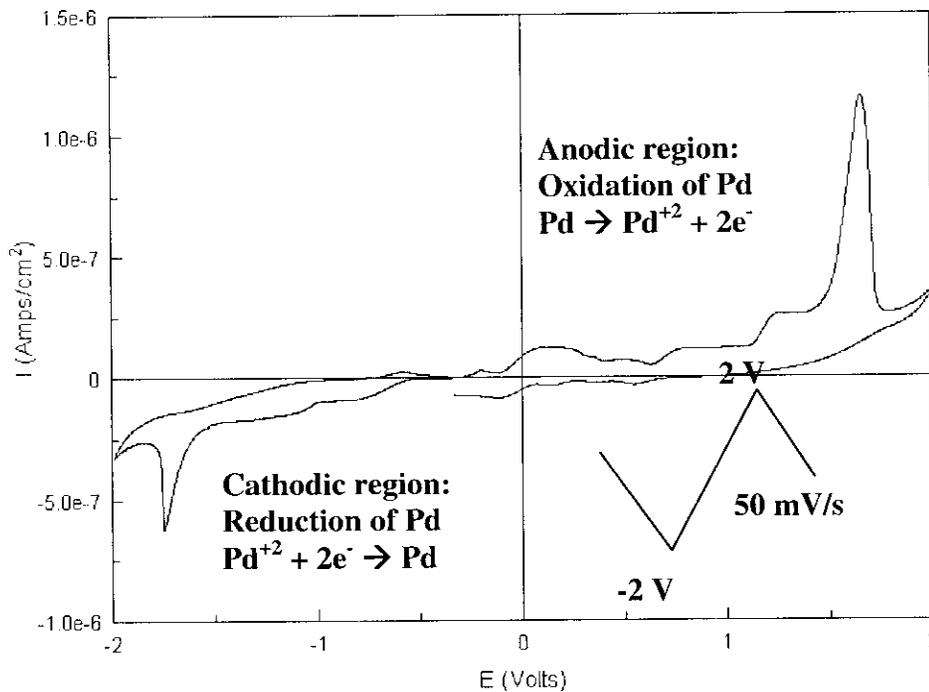


Figure 2. Cyclic voltammogram of Pd electrodeposition in Pd P-salt plating baths: two electrode configuration. scan rate=50 mV/s

The dimensions of the nanowire, including its length and diameter, are predetermined by the width of the nanochannel and the distance between electrodes.

For the demonstration, Pd wires with 1  $\mu\text{m}$  diameter and 3  $\mu\text{m}$  and 7  $\mu\text{m}$  lengths were electrodeposited. Two different electrodeposition solutions (i.e. palladium chloride acid bath and palladium p-salt alkaline bath) were initially considered. However, the preliminary experimental results indicated that Pd p-salt solution produces a smoother deposit with minimum dendrite formation at higher cathodic potentials.

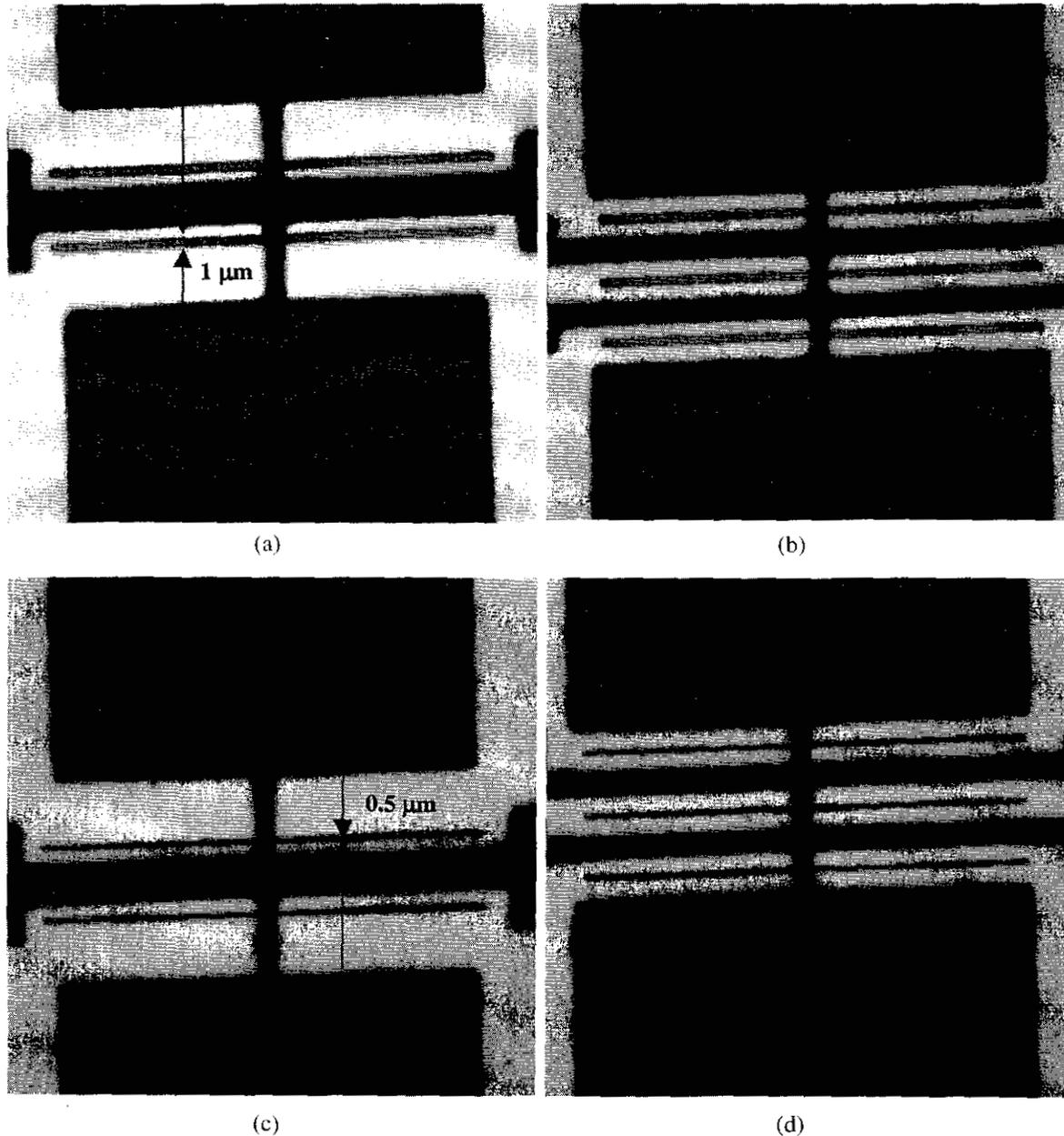
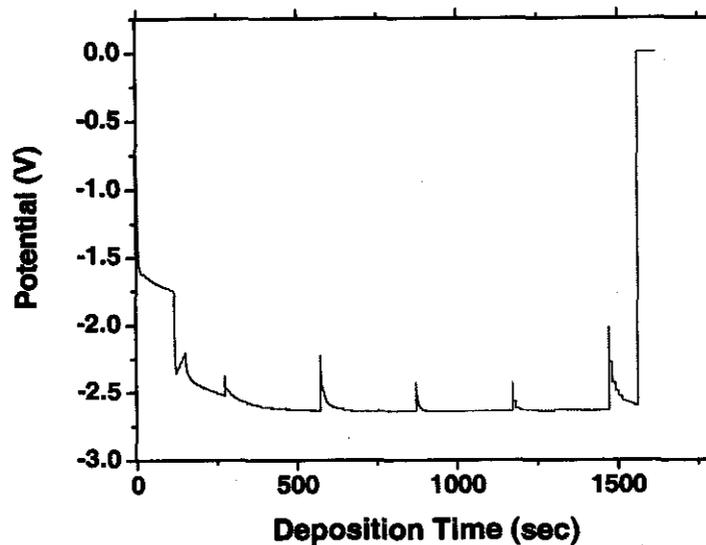


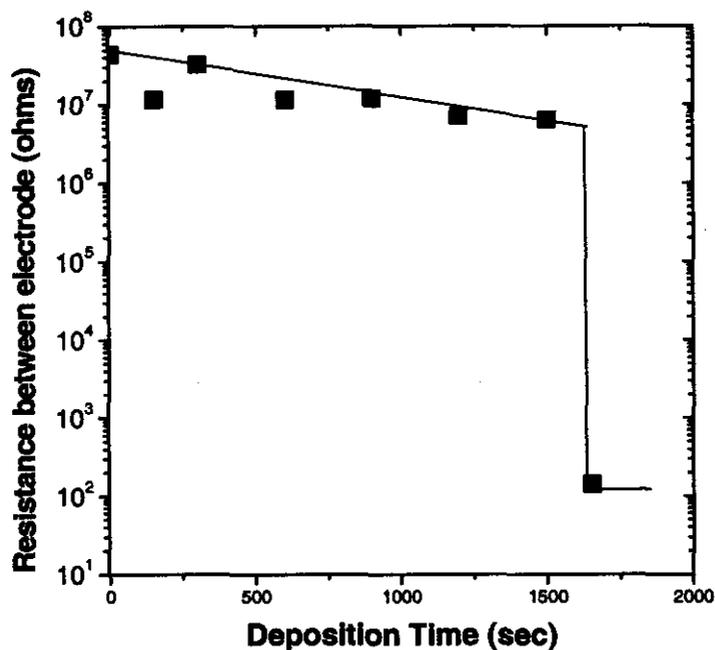
Figure 3. Digital images of e-beam patterned arrays of (a) 1  $\mu\text{m}$  width and 3  $\mu\text{m}$  length with two electrodes, (b) 1  $\mu\text{m}$  width and 3  $\mu\text{m}$  length with three electrodes, (c) 500 nm width and 3  $\mu\text{m}$  length with two electrodes, and (d) 500 nm width and 3  $\mu\text{m}$  length with three electrodes.

The Pd electrolyte consisted of  $\text{Pd}(\text{NH}_2)_2(\text{NO}_2)_2$  (10g/l), and  $\text{NH}_4\text{NH}_2\text{SO}_3$  (100 g/l). The pH of the solution was adjusted to 8.0 by addition of  $\text{H}_3\text{NO}_3\text{S}$  and  $\text{NaOH}$ . Figure 2 shows a cyclic voltammogram of Pd p-salt plating solution using two electrodes configuration. The reduction peak of Pd ions to Pd are observed at  $-1.7$  V. When more negative

potential than  $-1.7$  V is applied to electrode, a significant increase in the current density was observed which is due to  $H_2$  gas evolution.



(a) Cathode potential responses as a function of deposition time: Applied current was  $-1000$  nA.



(b) Resistance change between anode and cathode as a function of time: Deposition current was kept at  $-1000$  nA.

Figure 4. Electrical properties of (a) deposition potential versus deposition time and (b) resistance changes versus deposition time on no-nanochannel devices.

A computer controlled EG&G 273 potentiostat/galvanostat was used to grow Pd wire in galvanostatic mode. The applying currents were varied from  $-10$  nA,  $-20$  nA, and  $-100$  nA and corresponding potentials were monitored for nanochannel devices.

Figure 3 shows nanochannel devices with 1  $\mu\text{m}$  and 500 nm diameters. The line length is 70  $\mu\text{m}$  and electrode gap is 3  $\mu\text{m}$ , respectively. A precisely controlled drop in the concentration of electroplating solution will be on the top of the devices and then electrodeposition proceeds by applying potentials between electrodes. These devices are designed for two and three sensing elements. Reducing the width of the e-beam patterned channels, which is currently under investigation, can further reduce the width of electrodeposited wires to a few tens of nm. We are also currently investigating utilizing different electrolytes to fabricate small arrays with wires of different compositions, and hence different chemical sensing capabilities.

Figure 4 (a) shows cathode potential responses during electrodeposition of a Pd wire at applied currents of  $-1000$  nA for non-nanochannel devices. The cathode potential initially approaches a negative value steeply, followed by a gradual increase in the potential as the Pd wire grows from cathode to anode. When a wire is fully grown and makes contact to the anode, the potential drops to zero and the applied potential is turned off. Lower cathode potentials and shorter deposition times are observed at a deposition current as expected due to a higher deposition rate. The seven- $\mu\text{m}$ -long Pd wires were grown within 1500 seconds with  $-1000$  nA, respectively. Figure 4 (b) shows the changes in electrical resistance of Au electrodes during Pd wire growth at  $-1000$  nA. As expected, the electrical resistance gradually decreases as the Pd wire grows from cathode to anode and reduces the gap. When the Pd wire makes contact to the anode, the measured resistance is less than 100  $\Omega$  in the liquid electrolyte. The optical images of electrochemically grown Pd wire between Au electrodes are shown Fig. 5. The length of the wire is of the order of 7  $\mu\text{m}$  and the width is approximately 1  $\mu\text{m}$ . Fig. 5(b) shows double Pd wires directly grown on single Au electrode.

### 3. SENSOR ARRAY

#### Gas Sensor

By analyzing gas species in space, this sensor could be an important contribution not only to space chemistry, but also to space life detection, subjects of significant effort throughout NASA and other industries. The physical properties limiting sensor devices fabricated in planar structures can be readily overcome by exploiting nanowire technology. The nanowire-based sensor in this research will detect gas species and will exhibit a fast response with a substantially 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 conductance in nanowires produced by the adsorption of the chemical species or phase changes in nanowires.

In this work, we will design and fabricate single Pd nanowires and demonstrate their capability to sense  $\text{H}_2$ . Pd has low contact resistance and high sensitivity to  $\text{H}_2$ . Favier et al. demonstrated the activity of electrodeposited Pd multi-nanowires prepared on graphite surfaces as  $\text{H}_2$  sensors and hydrogen-activated switches by applying a constant voltage of 5 mV between Ag contacts and measuring current<sup>8</sup>. The resistance change is caused by a phase change from metallic Pd to  $\text{PdH}_2$ . These Pd multi-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  $\text{O}_2$ , CO, and  $\text{CH}_4$ . In this work, single Pd nanowires rather than multi-nanowires were electrodeposited with controlled width and length from electrolytes based on Pd salts.

#### pH and Biochemical Sensors

The concentration of the  $\text{H}_3\text{O}^+$  is the most critical parameter to be measured for monitoring the condition of 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  $\text{IrO}_x$  sensors. They have fast response time, "drift-free" behavior, and show good stability in aggressive environments. In contrast to bulk glass pH electrodes, solid-state metal oxide electrodes are also easily microfabricated. A pH  $\text{IrO}_x$  nanowire sensor will be fabricated by electrodepositing  $\text{IrO}_x$  coating on prefabricated inert nanowire (e.g. Au or Pt).

Amperometric biosensors are created by electronically coupling the appropriate redox enzymes to a metal electrode modified with a self-assembled monolayer (SAM) to facilitate enzyme immobilization and to reject interfering species. Conductometric biosensors are assembled by entrapping the relevant enzymes in conjugated polymer nanowires (e.g., polyaniline) on an electrode. Both approaches entail straightforward synthesis protocols, yet the SAM-based system on

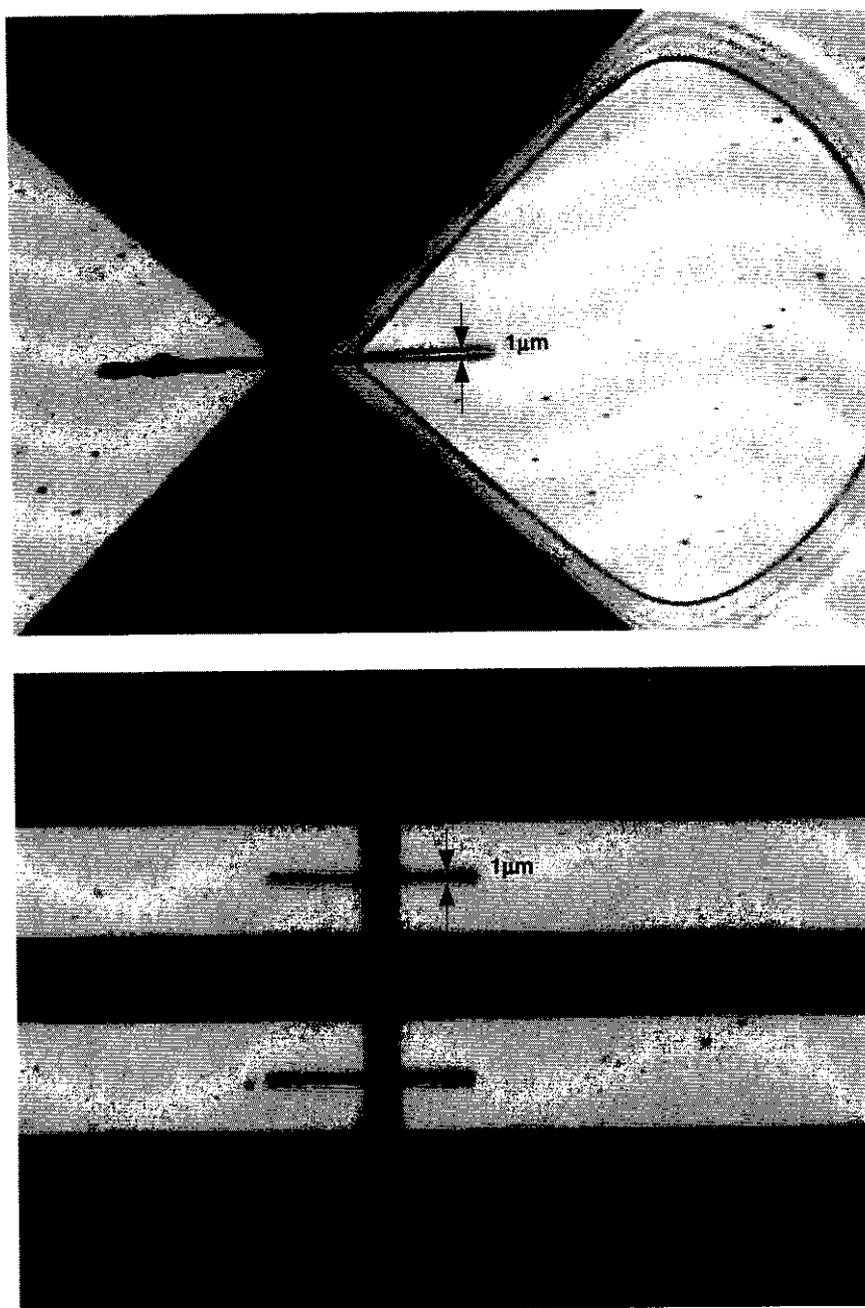
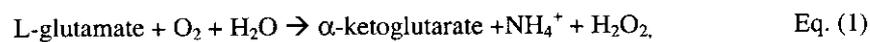


Figure 5. Optimal images of electrodeposited Pd wire grown between electrodes: (A) single wire (B) double wires on same electrode.

Au provides for better interferent rejection while the conductometric system gives substantial signal amplification due to the large change in polymer conductivity in response to small perturbations in its microenvironment.

Amperometric glutamate biosensors have been described based on the enzyme, glutamate oxidase (gluOX). Glutamate oxidase, immobilized to the electrode surface by a variety of techniques, catalyzes the oxidation of glutamate (amino acid) to  $\alpha$ -ketoglutarate and ammonia using oxygen as the electron acceptor.



The hydrogen peroxide generated as a result of the enzyme catalyzed reaction can be oxidized at the electrode surface to give a measurable current that can be correlated to the glutamate concentration.

**A Biomedical Sensor**, like a hormone sensor, can be fabricated using Au and polyaniline nanowires. We are presently investigating fabricating hormone sensor to detect thyroid hormones, 3,5,3'-triiodo-L-thyronine (T3), thyroxine (T4) hormones.

#### 4. SUMMARY

We have developed a fabrication technique that is potentially capable of producing arrays of individually addressable nanowire sensors with controlled dimensions, positions, alignments, and chemical compositions and are in the process of fabricating sensor arrays to detect gases, biochemicals, and hormones. The concept has been demonstrated by growing Pd wires with 1- $\mu\text{m}$  diameters and 7- $\mu\text{m}$  lengths. Reducing the width of the e-beam patterned channels, which is currently under investigation, can further reduce the width of electrodeposited wires to a few tens of nm. It is envisioned that these are the first steps towards producing nanowire sensor arrays capable of simultaneously detecting multiple chemical species. Large-scale arrays may also be possible, e.g. by utilizing integrated large-scale microfluidic networks<sup>10</sup> to control flow of different electrolytes to nanowire growth electrodes. We have successfully demonstrated a biochemical sensor capable of detecting glutamate and a biomedical sensor capable of detecting thyroid hormones using bundled nanowires. Currently, we are investigating the use of single nanowires for gas, biochemical, and biomedical sensor applications.

#### ACKNOWLEDGMENTS

This research was performed at Jet Propulsion Laboratory, California Institute of Technology, under a contract with National Aeronautics and Space Administration.

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