Nanowire Growth for Sensor Arrays

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Overview

- Motivation, and Challenge
- Bundled Nanwires
  - Fabrication
  - Sensing
- Single Nanwire
  - Fabrication
- Conclusion
Objective & Motivation

The objective of this work is to demonstrate nanowire-based sensor arrays for in-situ biochemical multi-sensing.
**Gas Sensor**

(A) Schematic diagram of a PMA (Palladium mesowire array) based hydrogen sensor or switch.

(B) SEM image [400 micron X 600 micron] of the active area of a PMA-based hydrogen sensor.

(C) PMAs were prepared by electrochemical step edge method at graphite surfaces and transferred to a cyanoacrylate film.

From Favier et al., Science, 293, 2227(2001)
Motivation

pH Sensor and Biomolecule Sensor

Schematic illustrating the conversion of NW nanosensors for pH sensing. The NW is contacted with two electrodes, a source (S) and drain (D), for measuring conductance.

From Lieber et al., Science, 293, 1289(2001)

(A) Cu Nanowire fabricated by combining conventional photolithography and focused ion beam techniques.

(B) The conductance change of the Cu nanowires (Upon molecular adsorption, the conductance typically decreases to a fractional value)

From Tao et al., APL, 76(10), 1333(2000)
## Advantages of EC Nanowire

<table>
<thead>
<tr>
<th></th>
<th>CNT</th>
<th>SNWs</th>
<th>Proposed Nanowires</th>
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</thead>
<tbody>
<tr>
<td><strong>Materials</strong></td>
<td>Carbon</td>
<td>Silicon</td>
<td>Metals alloys, Metal oxides, Conducting polymers</td>
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<tr>
<td>**Deposition</td>
<td>*Arc-discharge Methods</td>
<td>*Laser assisted</td>
<td>*Electrochemical method</td>
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<tr>
<td>Techniques</td>
<td>*Laser</td>
<td>*Supercritical fluid</td>
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<td></td>
<td>*CVD (catalytic</td>
<td>solution method</td>
<td></td>
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<tr>
<td></td>
<td>decomposition)</td>
<td></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>**Surface</td>
<td>Limited</td>
<td>Well-known</td>
<td>Well-known</td>
</tr>
<tr>
<td>Modification</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Functionality</strong></td>
<td>Single</td>
<td>Single</td>
<td>Individually Multi-functioning capability</td>
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</tbody>
</table>

*Baughman et al.* *Morales et al.* *This work*
Gas, pH Sensor and Biomolecule Sensor Array

Individually Addressable Sensor Arrays with Multi-sensing Capabilities

- Metals, Metal Oxides, and Conducting Polymers
  - IrOx
    - pH sensor, fast response, and good stability
  - Au and Cu
    - Antigen-functionalized or immobilized enzyme-biosensor
    - Biomolecule and Hormone sensors
  - Polyaniline
    - Immobilized glucose oxidase
    - Hormone sensors
  - Palladium
    - Hydrogen gas sensor
Challenges

1. Fabricating a single nanowire between electrodes (silicon or metal tips) requires optimizing the electrodes configuration and electrodeposition conditions for different nanowire sensing materials.

2. Biomolecule sensor; Surface modification technique must be developed and "tailored" to functionalize an individual nanowire.

3. In addition, a high precision potentiostat/galvanostat (i.e. electrochemical instrument) is needed to precisely grow nanowires.
Bundled Nanowires
Sensing

• Sensing Techniques:
  - Conductometric and/or Amperometric biosensor

• Sensing Materials:
  - Hydrogen Sensing material
    ; Palladium
  - pH Sensing materials
    ; Iridium oxide, antimony/antimony oxide, polyaniline
    Tin oxide, indium oxide
  - Hydrogen peroxide Sensing materials
    ; Platinum
  - Hormone sensing materials
    ; Au, Polyaniline, Platinum
1. First Anodizing & Removal of First Anodized Alumina

2. Second Anodizing

3. In the case of aluminum foil, patterned Sputtered Au Layer

4. flip the sample and RIE or Chemical Etch Aluminum

5. Pore Widening Barrier removal

See 5219-22, N. Myung et al.
Bundled Nanowires

Antimony nanowires

Iridium oxide nanowires

Tin oxide nanowires

Polyaniline nanowires
Bundled Nanowires

Enzyme hosting nanowires

Platinum nanowires

Gold nanowires
Knowledge of the concentration of $H^+$ (pH) is critical to understand the biological activity and identifying electroactive species in solution.
Enzyme-based Amperometric Detection

- $\text{O}_2$ serves as the electron mediator
- The oxidation current of $\text{H}_2\text{O}_2$ reflects the glutamate concentration
- The optimal oxidation potential of $\text{H}_2\text{O}_2$ is 0.7V vs Ag/AgCl;
- Ascorbic acid and dopamine can also be oxidized by the electrode, if the potential is greater than 0.2V vs Ag/AgCl
Glutamate Sensor

Glucose Sensing (thin film)

\[ 200\text{mM of polypyrrole is an optimal concentration for electrodepositing a permselective polypyrrole film;} \]
Comparison between amperometric response of glucose sensor constructed on Pt (■) thin film and (▼) bundled nanowires. The Pt bundled nanowires have a high roughness factor (RF) X 200 increase in surface area using nanowires

X10 greater sensitivity than bare Platinum
Hormone Sensor

T3 Hormone Sensing

Thyroid hormones (T3 and T4) have profound effects on metabolism, growth, and development. Deficiency or excessive production of the hormones can cause thyroid disorders such as Hashimoto thyroiditis and Graves disease.

T3 detection mechanism using Radio-immunoassay method

3,5,3'-Triiodothyronine (T₃)
Single Nanowire
Deposit low stress $\text{Si}_3\text{N}_4$ (or $\text{SiO}_2$ onto Si wafers)

Metalize top $\text{Si}_3\text{N}_4$ with E-beam evaporation and Lift-off

SiO Deposition

Channel Pattern and Electrodeposition
E-beam Patterns
Fabrication

Electrodeposition

Step 1. Microfabricated Electrodes

Step 2. Applying Current or Potential

Step 5. Interconnected nanowires

\[ \text{SiO Layer} \]
\[ \text{Gold Metal Tips} \]

\[
\begin{align*}
0 & \quad + \quad e^- & \quad \rightarrow & \quad \text{Pd}^+ \\
\text{e}^- & \quad \rightarrow & \quad \text{SiO} & \quad + \quad e^- & \quad \text{(e.g.} \quad 2\text{H}_2\text{O} & \quad \rightarrow & \quad \text{O}_2(g) & \quad + \quad 4\text{H}^+ & \quad + \quad 4e^-) \\
\end{align*}
\]

\[
\begin{align*}
\text{Deposition Time (sec)} & \quad 0 & \quad 100 & \quad 200 & \quad 300 & \quad 400 & \quad 500 & \quad 600 \\
\text{Resistivity (ohms)} & \quad 10^9 & \quad 10^8 & \quad 10^7 & \quad 10^6 & \quad 10^5 & \quad 10^4 & \quad 10^3 & \quad 10^2 \quad \rightarrow \quad \text{(e.g.} \quad \text{Pd}^{2+} & \quad + \quad 2e^- & \quad \rightarrow & \quad \text{Pd}_{\text{ele}}) \\
\end{align*}
\]
Fabrication

Single Wire

Single palladium micronwire grown on single Au electrode
Fabrication

Dual Wires

Final device structure with different nanowire materials

Double palladium micronwire grown on single Au electrode
Fabrication

With channels

Full growth
Between the tips
Fabrication

Without channels

Full growth Between the tips

Potential (V)

Resistance between electrodes (ohms)

Deposition Time (sec)
Fabrication

Wire or Dendrite?
Fabrication

Nano-contact?
Top-view of the a sharp single Si Tips

Top-view of Si multi-tips
Future Works

1. Single wire sensing for gases

2. Single wire sensing for biomolecules

3. Single wire sensing for hormone

4. Sensor array fabrication and integration
1. We developed a novel process to directly grow a micron-wire between Au electrodes with an individually addressable capability using electrochemical deposition. This method has the potential of fabrication of the individual functioning nanowires and could be used for nanoelectronic devices and various sensors.

2. Various bundle of nanowires (e.g. tin, antimony, iridium oxide, gold, platinum, and polyaniline) were electrodeposited and characterized for pH and Glucose sensor.

3. We have improved the sensitivity of glucose using Pt bundle nanowires. Pt nanowires shows 200 X increase in effective surface area and 10 X greater in sensitivity than Pt thin film.

4. Much work remained to accomplish Nanosensor array