NanoSonic, Inc.

Wireless Networked Sensors in Water for Heavy Metal Detection

2019 Crosscutting Research Project Review

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Dr. Hang Ruan, Principal Investigator, VP of Sensors and Systems
NanoSonic, Inc.
Adjunct Professor, Department of Mechanical Engineering,
Virginia Tech

TPOC
Dr. Jessica Mullen
National Energy Technology Laboratory
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Program Objective

Objective: Develop wireless networked sensors using conformal nanomembrane based chemical field effect transistors (ChemFET) for heavy metal detection in water for energy sector.

Electrostatic self-assembly (ESA) + conformal nanomembrane ChemFET + wireless sensor network → in situ environmental monitoring

Key Expectations:
- Heavy metal selectivity: RCRA 8s (arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver)
- Heavy metal ion sensitivity: <0.01 ppm, with minimal cross-sensitivities
- Sensor element size: <(100 micron)$^2$
- Dynamic range: >40dB
- Frequency response: DC to >10kHz
- Operating temperature: -40°C to 100°C
- Multiplexing capability: >100 individual sensor elements
- Power supply: Battery or integrated energy harvesting device
- Transmission band: 2.4 GHz, IEEE 802.15.4 protocol; BLE protocol
- Packaging options: Patch, Conformal, Portable, and Flowable
- Operation mode: wake-up, measurement, data transfer, and low-power stand-by
Heavy Metal Detection in Water for Energy Sector

Heavy metals such as lead, arsenic, chromium, mercury, and cadmium in water have attracted a great deal of attention for their impact on human health.

Opportunity for Wireless Sensors for Heavy Metal Detection

To allow efficient monitoring of heavy metal levels for environmental surveillance in water for fossil energy sector, a precise, mobile and highly sensitive/selective/re-usable measuring instrument is required.

- Conventional chemical concentration sensing is typically done by taking soil or water samples on-site and transporting them back to a laboratory for analysis, or hand-carrying a sensor unit around an area and making, recording and mapping data.
- Multiple sensor devices can be configured in a small, lightweight and low cost array to analyze multiple sensor targets simultaneously. It can be used as an in-situ sensor attachable for permanent installation or portable inspection in a field.
- Such systems can be used to
  - detect and map multiple environmentally-hazardous chemical concentrations,
  - locate sources of pollution from analysis of concentration gradients, and
  - identify chemical concentrations potentially harmful to people and/or destructive to industry/agriculture.
Example of Potential Use - Flue Gas Desulfurization (FGD) Wastewater Treatment

Potential use of RCRA 8 sensor to monitor the heavy metals of treated effluent for real-time close loop control

**Initial Nanomembrane ChemFET Sensor Configuration**

- High Carrier Mobility
- High Sensitivity
- High Selectivity
- Ultralightweight
- Ultraflexibility
- Array Configuration

**I-V characteristics of ChemFET**

**Mask Design**
Electrostatic Self-Assembly (ESA)

- Conformal, homogeneous molecular layer by layer process
- Precise nanoscale control over thickness
- Excellent long-term environmental robustness
- Environmentally-friendly process
- Multifunction – conductors, polymers, semiconductors, ceramics

Self Assembly Process:
- polymer/polymer
- polymer/particle
- particle/particle

Metal Rubber™
10⁻⁵ Ω·cm
# Partial Library of Demonstrated ESA Material Functions

<table>
<thead>
<tr>
<th>Material Properties</th>
<th>Precursors</th>
<th>Measured Properties</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Detection</td>
<td>Semiconductor nanocrystals</td>
<td>Chemical Sensitivity and Selectivity</td>
<td>Surface modification on nanocrystals</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>Noble metal nanoclusters (Ag, Cu, Au, Pt)</td>
<td>0.1 – 1.0 Ω•cm, 10^{-4} Ω•cm</td>
<td>Mechanically flexible, optically transparent</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>Polymers and polymer / nanocluster combinations</td>
<td>n = 1.2 to 1.8</td>
<td>Tailored Transparent stacks</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>Noble metal nanoclusters (Ag, Cu, Au, Pt), Carbon nanotubes</td>
<td>0.1 MPa – 1.0 Gpa</td>
<td>Mechanically flexible</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Polymers and nanoclusters</td>
<td>2 W/mK</td>
<td>20 W/mK feasible based on current work</td>
</tr>
<tr>
<td>Mechanical Robustness</td>
<td>Oxide nanoclusters (TiO_{2}, ZrO_{2}, Al_{2}O_{3}, SiO_{2})</td>
<td>Good Taber abrasion and haze results</td>
<td>Nanohardness 1 GPa</td>
</tr>
</tbody>
</table>

Monitoring Fabry-Perot Cavity Growth Buildup of ([ZrO_{2+}/PSS^{-}]_{10}) by ESA
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Silicon Nanomembrane

- Thin
- Flexible
- Can be strain engineered
- Transparent
- Transferable

- Bondable
- Stackable
- Conformable
- Patternable (wires, ribbons, tubes)

Nanomembrane-based ChemFET sensors

- 1974: Epitaxial Ga_{1-x}Al_{x}As (X>0.6) sacrificial layer for separating a GaAs/Ga_{1-x}Al_{x}As (x=0.3) from GaAs with HCl etchant
- 1987: Yablonocitch: spin on wax to strain film for efficient release, enable removal of high quality GaAs films as large as 0.8*2mm² and as thin as 80nm
- 2004: Rogers: transferred membranes of Si from silicon-on-insulator (SOI) to fabricate Si flexible thin-film electronics
- 2012: NanoSonic: Si nanomembrane based flexible solar cells
- 2015: NanoSonic: Nanomembraned based ChemFET sensors

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Process Monitoring During Fabrication

I-V characteristics of bulk and nanostructures with oxide mask and channel length of 5 µm, the sensor operates in the linear region.

Phosphorus doping profile at the channel-drain side for bulk Si (left) and SOI nanomembranes (right) after source and drain doping. Oxide mask shown in dark red and buried oxide in SOI in dark red.
Standard Sensor Packages

Standard Sensor Package Can be “Flowable” (Left), “Portable” (Center) and “Attachable” (Right) for Sensor Applications
Self-Assembly of Gold/Thiol Functionalization Layers

Hand dipping (a, b) and Robot (c) Set Up Used to Self-Assemble the Gold/Thiol Functionalization Layers. (d) Microphotograph of a Completed Device with 9 Bilayers of Gold Nanoparticles in the 100 um by 100 um Channel Region.
Initial Modification Example #1: Self-Assembled Au and Thioglycolic Acid-Functionalized ChemFET Sensor

Testing results of the self assembled Au and thioglycolic acid functionalized ChemFET sensor after exposure to different concentrations of (a) Hg, (b) Pb, (c) Cs, (d) Cr, and (e) As ion solutions, as well as (f) different targets with the same concentration of 10ppm. The response for the Hg ion is significantly higher than for other ions.
Initial Modification Example #2: Sensor Modification for Lead Ion Selectivity

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Abbreviation</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetrahydrofuran</td>
<td>THF</td>
<td></td>
</tr>
<tr>
<td>polyvinylchloride</td>
<td>PVC</td>
<td>42.1</td>
</tr>
<tr>
<td>bis(2-ethylhexyl)sebacate</td>
<td>DOS</td>
<td>54.9</td>
</tr>
<tr>
<td>Sodium tetrakis(4-fluorophenyl)borate dihydrate</td>
<td>NaTFPB</td>
<td>0.44</td>
</tr>
<tr>
<td>N,N,N',N'-Tetradecyl-3,6-dioxaoctanethioamide</td>
<td>ETH 5435</td>
<td>1.39</td>
</tr>
<tr>
<td>Tetrakis(4-chlorophenyl)borate tetradecylammonium salt</td>
<td>ETH 500</td>
<td>1.15</td>
</tr>
</tbody>
</table>

N,N,N’,N’-Tetradecyl-3,6-dioxaoctanethioamide

Sodium tetrakis(4-fluorophenyl)borate dihydrate
Multi-Target Selectivity Results for Self Assembled Au Sensor and Lead Ionophore Sensor

Cross sensitivity results with Bar Plot (a) and Radar Plot (b) for self assembled Au sensor and Lead ionophore sensor.
Testing results of a self assembled gold nanoparticles and selenium ionophore (in-house) functionalized chemical sensor in response to Se solutions. The selenium concentration from the sample is measured as 0.78ppm, which is in good agreement with the concentration level of 0.86ppm obtained from a third party laboratory.
Development of Wireless Sensor Electronics

- **a) Wireless Sensor Node**
- **b) Schematic**
- **c) Modular Hardware**

Multiplexing capability: >100 individual sensor elements; Transmission band: 2.4 GHz, IEEE 802.15.4 protocol; Operation mode: wake-up, measurement, data transfer, and stand-by
Low power tablet App with code to read, process and output the data wirelessly from the sensor to tablet.
Power Management of Wireless Sensor Network

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For Additional Information:

Dr. Hang Ruan
NanoSonic, Inc.
hruan@nanosonic.com