Detection of Heavy Metal Ions with Nanojunctions

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Why Heavy Metal Ion Sensors?

- Heavy metals are toxic
  - dangerous pollutants second only to pesticides in environmental importance

- Heavy metals are not biodegradable
  - accumulate and persist for many years

- Current methods fall in two categories:
  
  **Ex situ:** Sensitive but expensive and complicate
  
  **In situ:** Portable device but less sensitive & reliable

  High sensitivity is necessary for early warning

- Nanojunction Approach
Nanocontact Sensor

Sensitivity:
The electrodes are separated with an atomic-scale gap, so a few ions can be detected.
Specificity:

- **Deposition potential**
  - Similar to Anodic Stripping Technique

- **Stripping potential**

- **Spectroscopy:**
  - Current vs. Bias Voltage

- Similar to Anodic Stripping Technique
How to Fabricate Electrodes with Atomic-Scale Separations?
Fabrication Method

Anode: Etching delocalized, but
Cathode: Deposition localized at sharpest point,

due to:

• **Self-focusing** – directional growth

Decreasing Gap!
Self-Termination

Voltage Divider:

\[ V_{\text{gap}} = \frac{R_{\text{gap}}}{R_{\text{gap}} + R_{\text{ext}}} V_0 \]

- Initially, \( R_{\text{gap}} \gg R_{\text{ext}} \), \( V_{\text{gap}} \sim V_0 \) → full speed deposition.
- Finally, \( R_{\text{gap}} \ll R_{\text{ext}} \), \( V_{\text{gap}} \sim 0 \) → deposition terminates.
- The gap resistance is determined by \( R_{\text{ext}} \).
Fabrication of an atomic-scale gap

$G_0 = 2e^2/h$

$R_{\text{ext}} = 10 \, \text{M}\Omega$

Gap width = 0.6 nm

$R_{\text{ext}} = 1 \, \text{M}\Omega$

Gap width = 0.4 nm
An Array of Atomic-Scale Gaps

Si₃N₄ / Au / SiO₂ / Si

SEM images
Deposition of Metal Ions

- **Conductance Quantized!**
  Number of metal atoms \(\sim\) Conductance in quantum unit \((G_0=2e^2/h)\).

![Diagram of metal deposition and conductance quantization](image)
Detection of Cu ions

- Deposition time needed to bridge the gap decreases as the concentration -- determining the concentration from the deposition time

- Wide dynamic range -- from mM to at least nM

Electrodes potential: -0.55V

*In CuSO₄ electrolytes*
Detection of Pb ions

- Deposition time decreases as the concentration - similar to Cu ions

- 0.1 nM (10 ppt) concentration is reached - further improvement can be made to lower the limit

Electrodes potential: -0.85V in Pb(NO₃)₂ electrolytes
Specificity

Different metals have different deposition & stripping potentials.
Summary

A Nanocontact Sensor:

A Polymer Nanojunction Sensor:
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