Detection of Heavy Metal Ions with Nanojunctions

N.J. Tao

Arizona State University

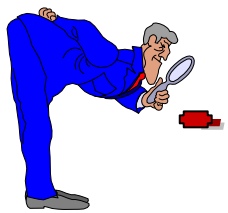
Why Heavy Metal Ion Sensors?

- **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***

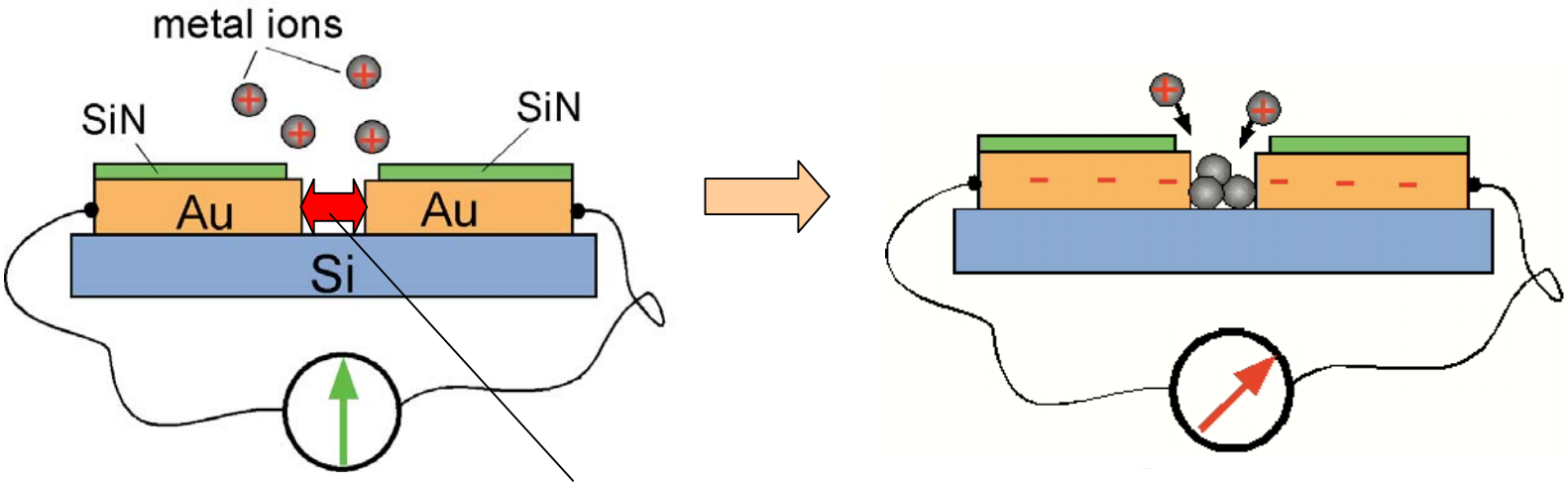
In situ: ***Portable device but less sensitive & reliable***

High sensitivity is necessary for early warning



Nanojunction Approach

Nanocontact Sensor



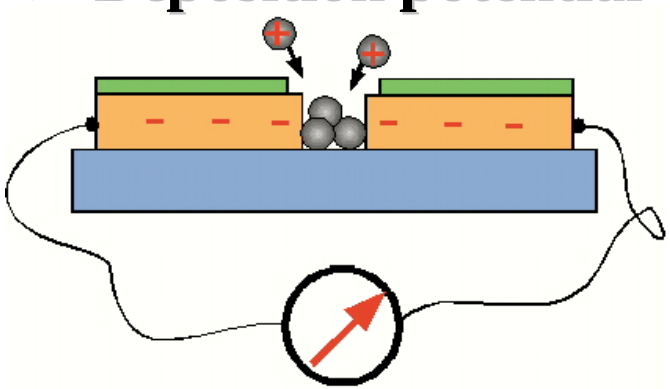
Atomic Scale!

Sensitivity:

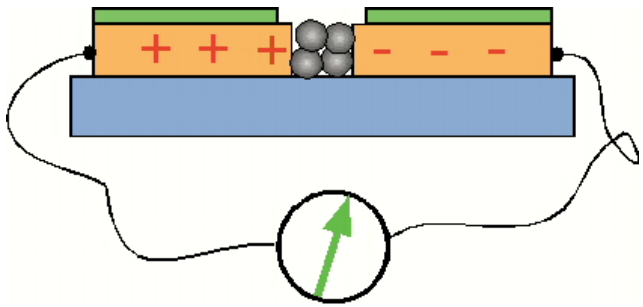
The electrodes are separated with an atomic-scale gap, so **a few ions can be detected**.

Specificity:

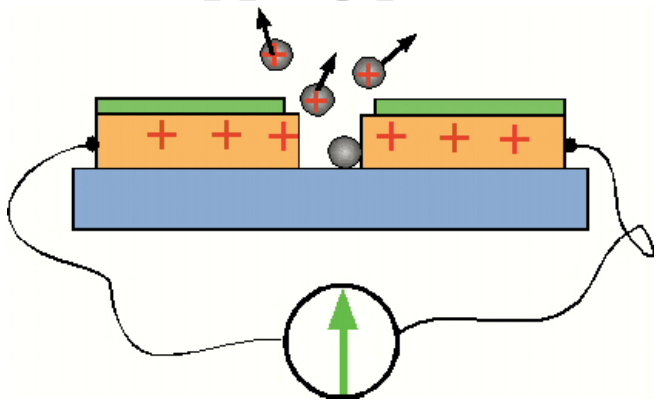
- **Deposition potential**

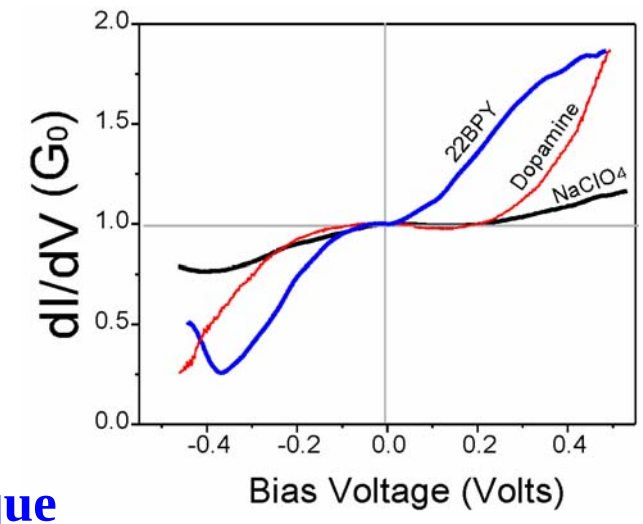


- **Spectroscopy:**
  - Current vs. Bias Voltage



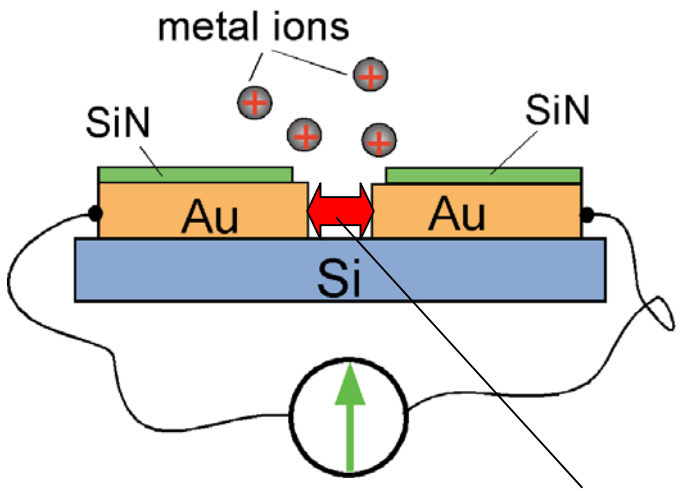
- **Stripping potential**





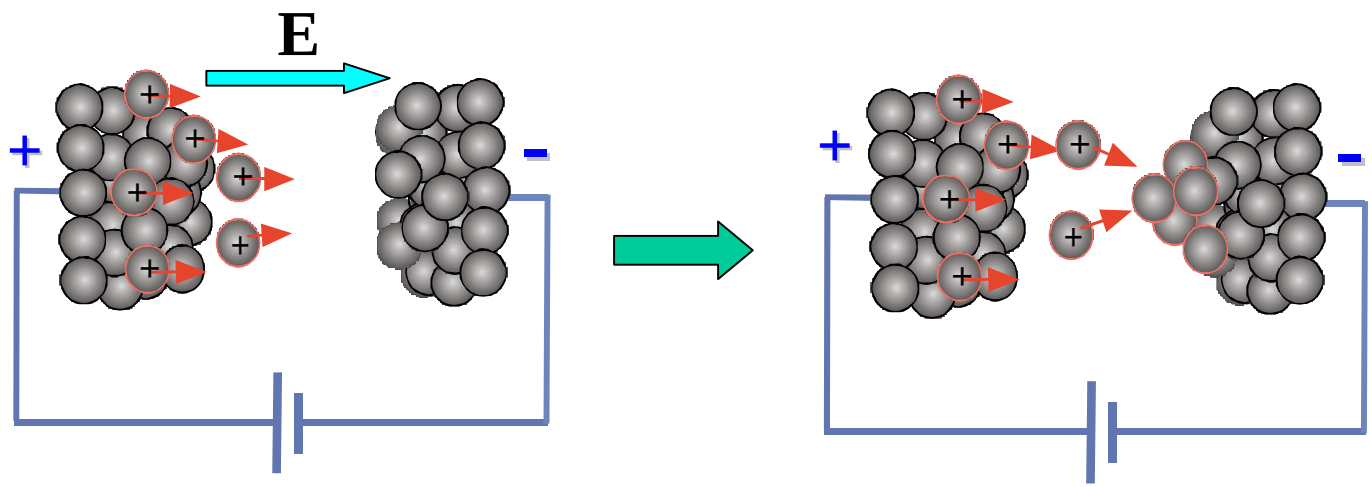
- **Similar to Anodic Stripping Technique**

How to Fabricate Electrodes with Atomic-Scale Separations?



Atomic Scale!

Fabrication Method



Anode: Etching delocalized, but

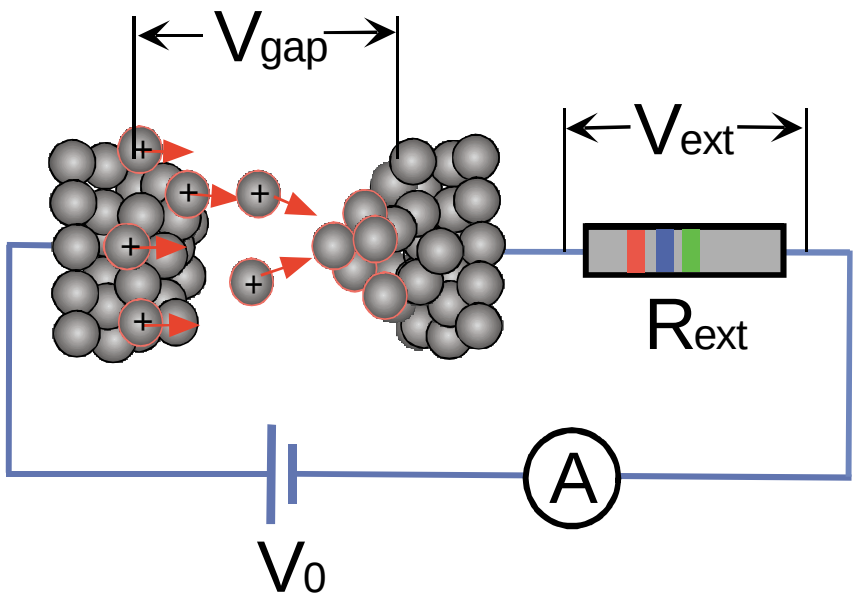
Cathode: Deposition localized at sharpest point,

due to:

- **Self-focusing** – directional growth

Decreasing Gap!

Self-Termination

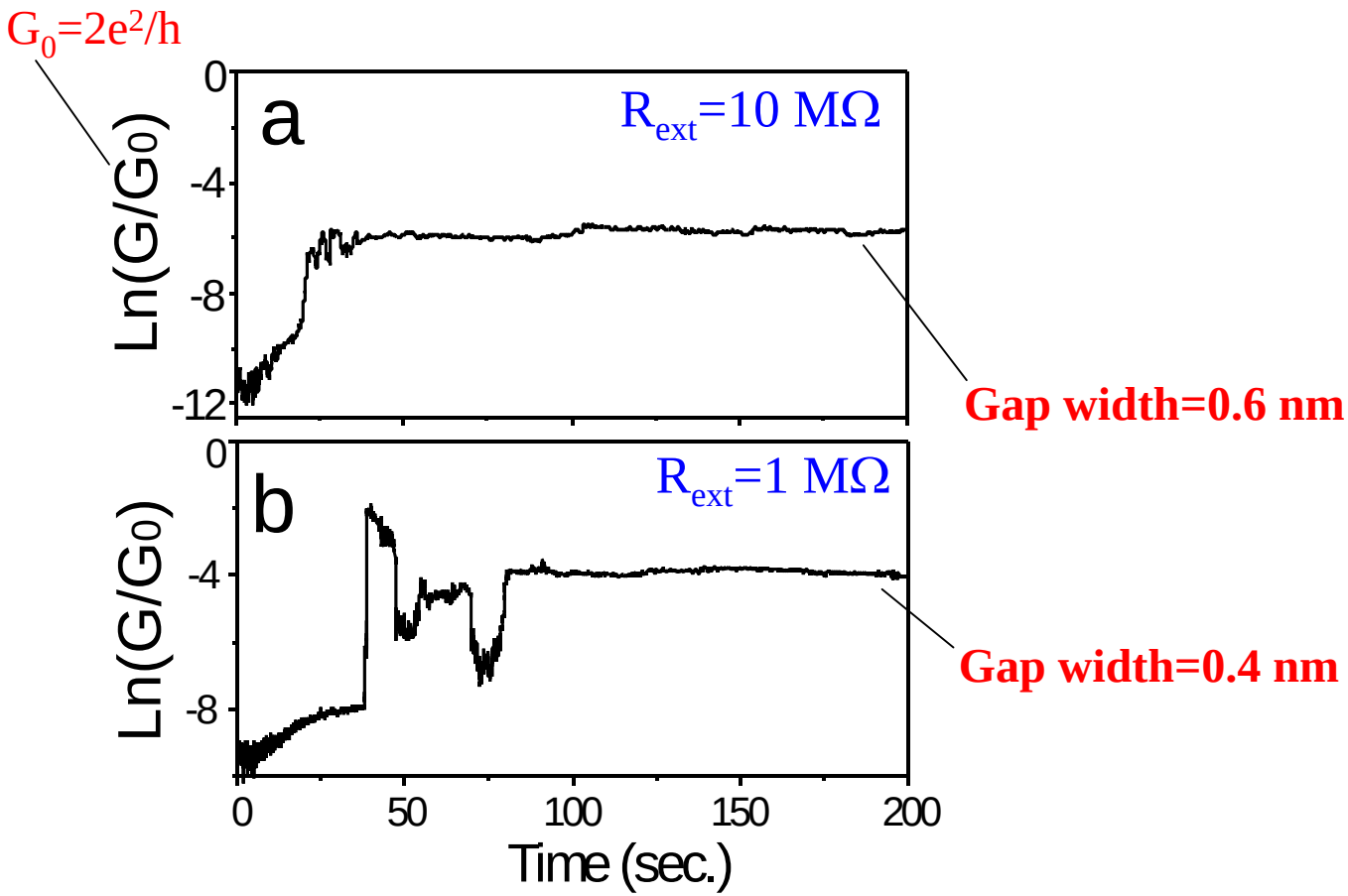


Voltage Divider:

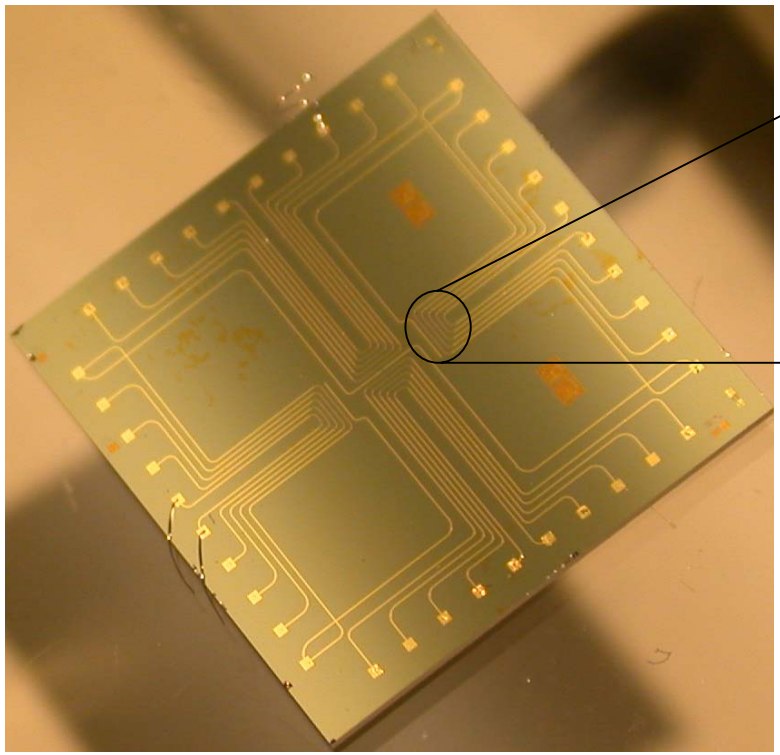
$$V_{gap} = \frac{R_{gap}}{R_{gap} + R_{ext}} V_0$$

- Initially, $R_{gap} >> R_{ext}$, $V_{gap} \sim V_0$ ➡ full speed deposition.
- Finally, $R_{gap} << R_{ext}$, $V_{gap} \sim 0$ ➡ deposition terminates.
- The gap resistance is determined by R_{ext}.

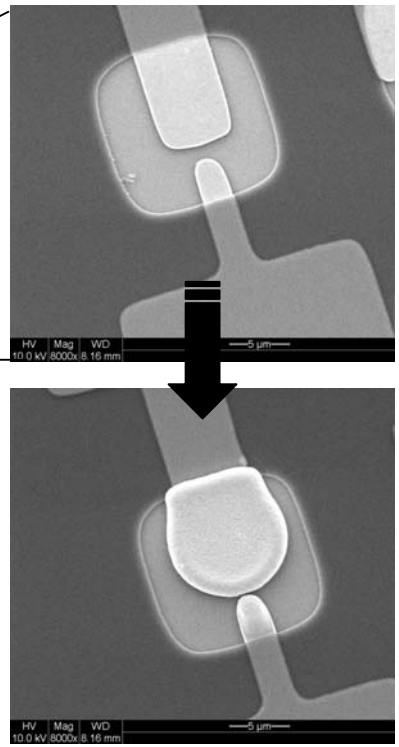
Fabrication of an atomic-scale gap



An Array of Atomic-Scale Gaps

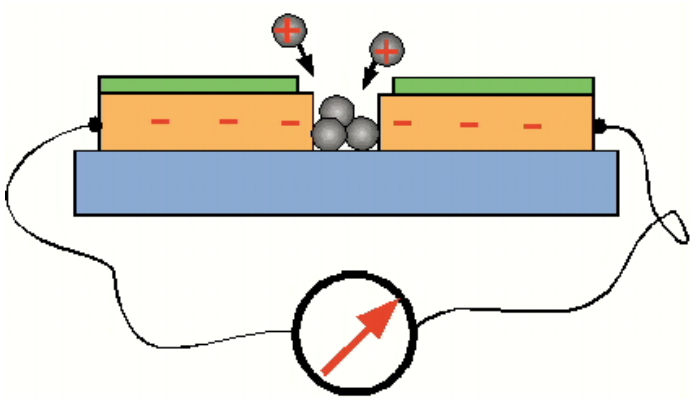


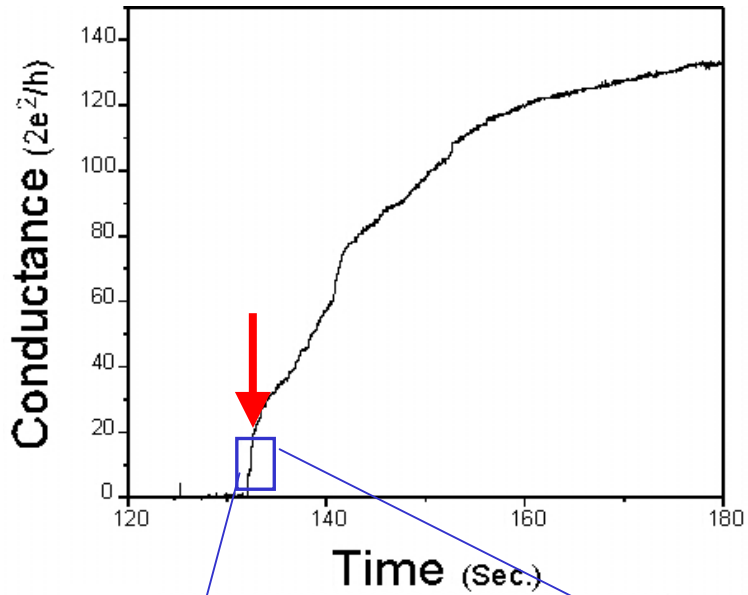
Si_3N_4 / Au / SiO_2 / Si

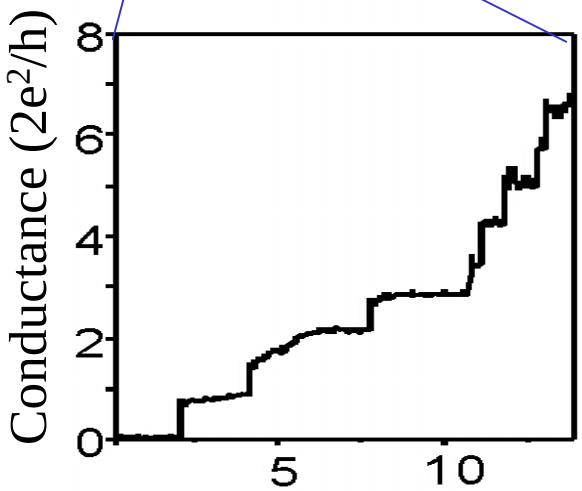


SEM images

Deposition of Metal Ions



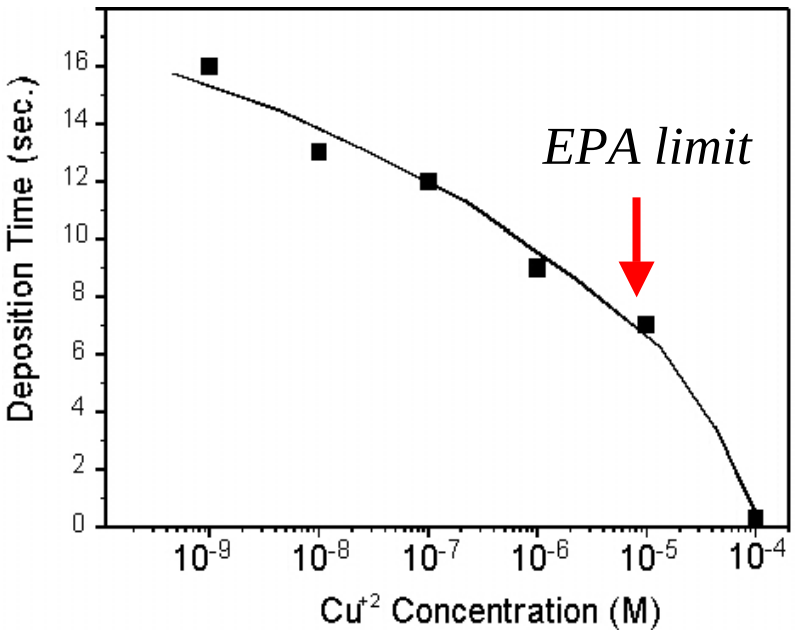




- **Conductance Quantized!**

Number of metal atoms ~ Conductance in quantum unit ($G_0=2e^2/h$).

Detection of Cu ions

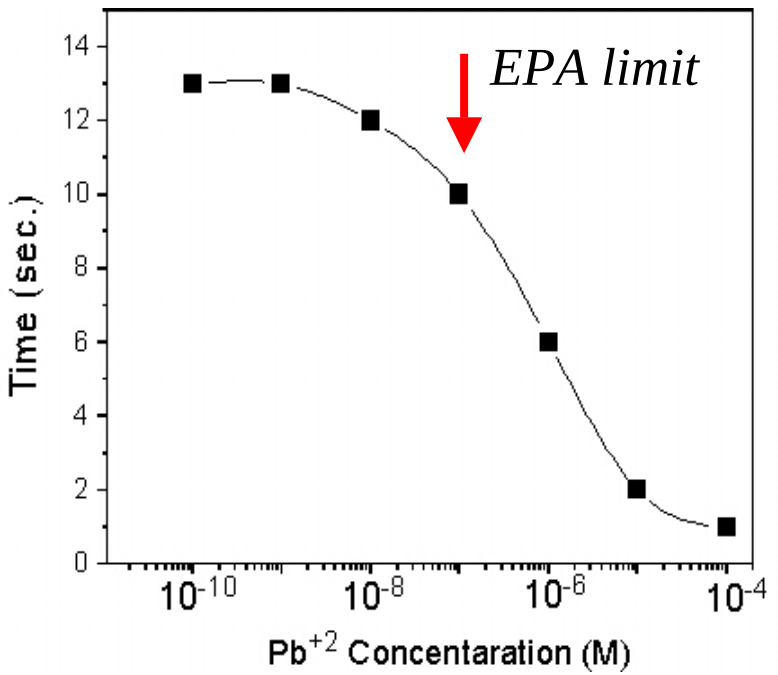


- **Deposition time needed to bridge the gap decreases as the concentration**
  - *determining the concentration from the deposition time*
- **Wide dynamic range**
  - *from mM to at least nM*

Electrodes potential: -0.55V

In $CuSO_4$ electrolytes

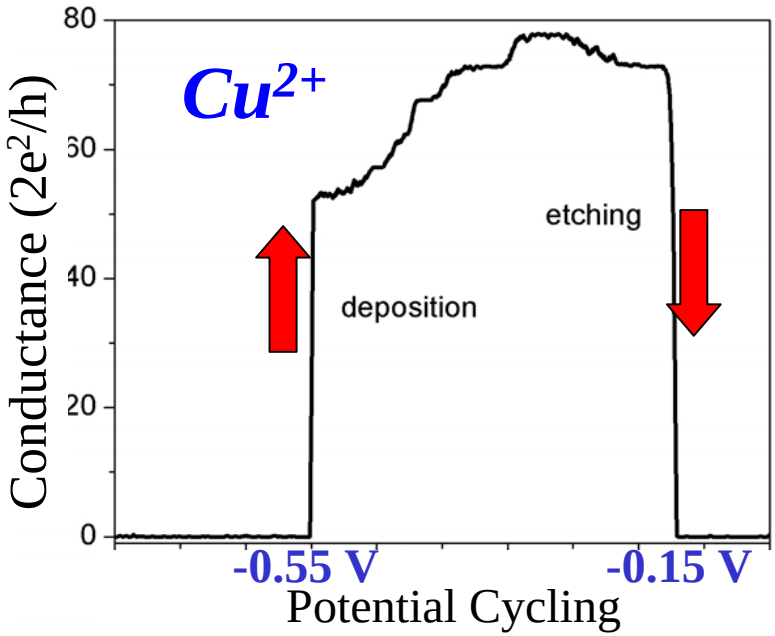
Detection of Pb ions

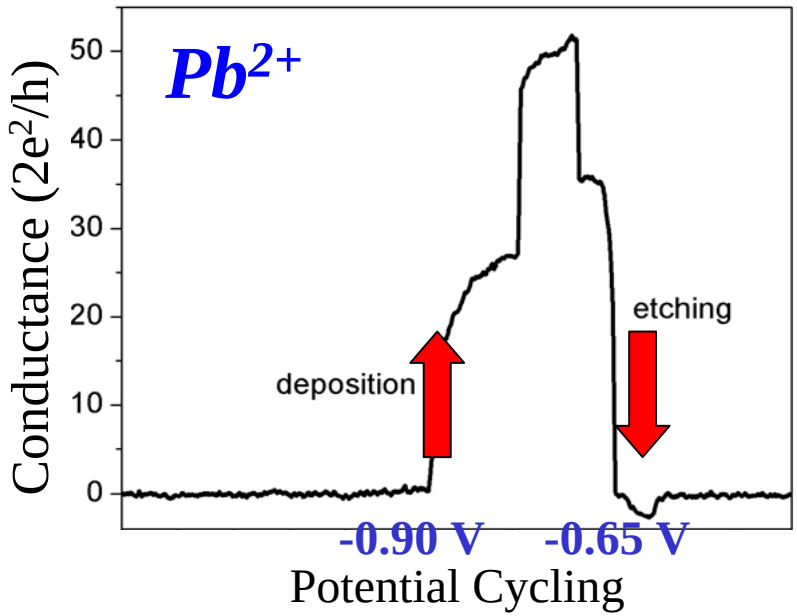


- **Deposition time decreases as the concentration**
  - *similar to Cu ions*
- **0.1 nM *(10 ppt)* concentration is reached**
  - *further improvement can be made to lower the limit*

Electrodes potential: -0.85V
in $Pb(NO_3)_2$ electrolytes

Specificity

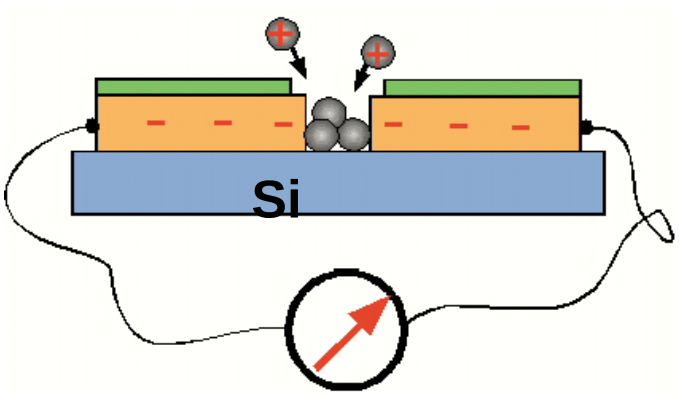




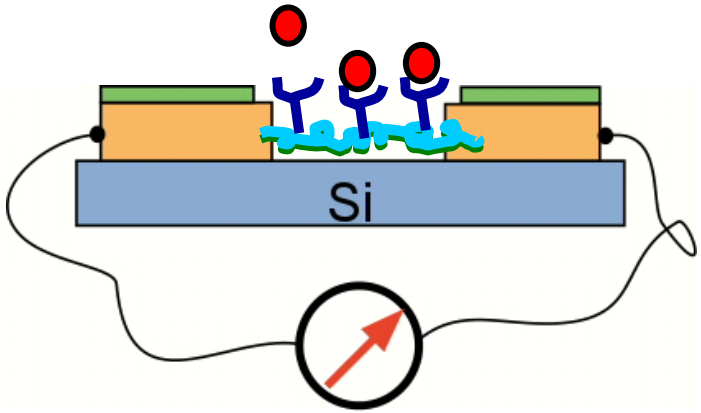
- **Different metals have different deposition & stripping potentials.**

Summary

A Nanocontact Sensor:



A Polymer Nanojunction Sensor:



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