Preparation and Characterization of Optically-active Metal Probes for Scanning Chemical Microscopy

Jae Cho
Isaac Riisness
Professor Gordon
Chemical Engineering
UC LEADS, UCSB
August 25, 2011
Innovations in imaging tools enabled nanoscience and nanotechnology.

Catalysis
Nanosphere lithography
Nanoparticle synthesis
Nanorods
How do we see at the nanoscale?

- Light microscopy (diffraction limit 100s nm)
How do we see at the nanoscale?

- Light microscopy (diffraction limit 100s nm)
- Electron microscopy (only atom ID)
How do we see at the nanoscale?

- Light microscopy (diffraction limit 100s nm)
- Electron microscopy (only atom ID)
- Scanning probe microscopy (SPM) (no chemical ID)

SPM monitors tip-surface interaction as it probes the surface.
How do we see at the nanoscale?

- Light microscopy (diffraction limit 100s nm)
- Electron microscopy (only atom ID)
- Scanning probe microscopy (SPM) (no chemical ID)
- Tip-enhanced Raman spectroscopy (TERS) enables spatially correlated surface topography and chemistry at the nanoscale
Tip size and optical activity determines TERS performance

PROBLEM: Hard to make sharp, optically-active tips
Tip preparation via electrochemical etching

What’s important?
- Electrolyte
- Voltage
- Material

\[ W + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2 \]
\[ 2Ag + 2OH^- \rightarrow Ag_2O + H_2O + 2e^- \]
\[ Au + 4Cl^- \rightarrow AuCl_4^- + 3e^- \]

Less than 100 nm!

Etching needs feedback
Etching currents for same conditions, different results

Does current give useful info?
More info during etching needed?
Informative, but not enough...
GOAL: Make a diagnostic tool for etching

Use tuning fork oscillator for feedback:

- Mass changes
- Surface area changes
- Etching dynamics
- Hydrodynamic effects

...by attaching wire to tuning fork
GOAL: Make a diagnostic tool for etching

Use tuning fork oscillator for feedback:

- Mass changes
- Surface area changes
- Etching dynamics
- Hydrodynamic effects

...by attaching wire to tuning fork

![Tuning fork oscillator](image1.png)

![Vortex, Film flow, Bubbles, Electrolyte ions, Wire ions, Dissolving out](image2.png)
What affects resonance curve?
- Mass attached changes
- Force on wire changes

Use tuning fork resonance to follow tip etching

---

Combine two different control loops

- Analyze oscillation and current vs. time
- Connect oscillation changes to etching dynamics
Is the tuning fork sensitive to the local environment of the wire?

Correlate wire environment to changes in key resonance parameters: $\omega_0$, $A$, and $Q$
How does resonant frequency change?

- Immersion ↑ → mass ↑ → frequency ↓
- Area of fluid interaction scales with immersion

Linear resonant frequency shift agrees with theory
How does amplitude change?

Amplitude dampening

- Immersion $\uparrow \rightarrow$ area $\uparrow \rightarrow$ drag $\uparrow \rightarrow$ amplitude $\downarrow$

Fork oscillation amplitude decreases as expected

\begin{equation}
F_D = \frac{1}{2} \rho v^2 C_d A
\end{equation}

$A = 2\pi rh$
How does Q factor change?

- Q measures viscous dissipation
- Viscosity $\uparrow \rightarrow Q \downarrow$

Tuning fork can probe viscous dissipation
Summary

- Developed tuning fork analysis system to investigate tip etching
- Tuning fork $\omega_0$, $A$, and $Q$ reveals local wire environment
- Tuning fork is a promising approach to learn more about the tip etching process

Future studies

- Tuning fork to diagnose tip etching
- Quantitative studies:
  - Fork and wire oscillations
  - Mass transport and chemical reactions during etching
Acknowledgements

- Mentor Isaac Riisness for teachings, guidance, and inspiration
- Arica for support