Preparation and Characterization of Metal Tips for Tip Enhanced Raman Spectroscopy

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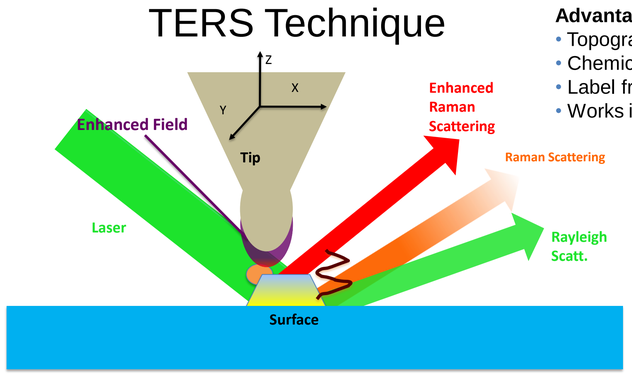
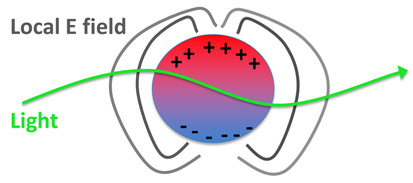
Introduction

Raman Spectroscopy is a form of light scattering where a vibrational mode of a molecule is momentarily excited, followed by emission of a photon with different energy; based on the energy difference between the incident and scattered beams, chemical moieties in the molecule can be identified from the energy loss spectrum. The problem with Raman spectroscopy is that it is extremely weak, occurring ~once in 10^6 scattered photons. Tip Enhanced Raman Spectroscopy (TERS) is a means by which an enhanced electromagnetic field is created by coupling far-field laser light to surface plasmons in a nanostructured gold or silver tip. The enhanced field acts like an antenna to increase Raman scattering, enabling chemical surface imaging on a nanometer length scale. The lateral resolution of the technique is determined by the size of the tip; therefore, sharp tips with a small (10-20 nm) apex are of utmost importance for the TERS experiment. To that end, work this summer focused on the preparation and characterization of nanostructured tips via electrochemical etching.

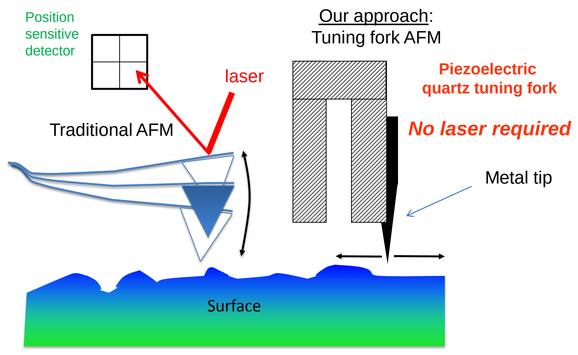
TERS Technique



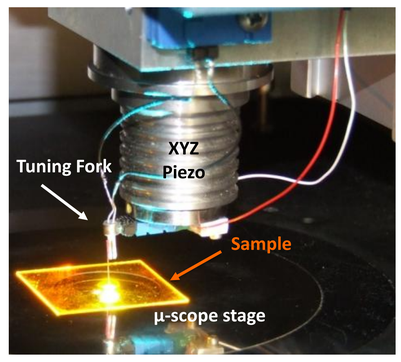
Advantages of TERS:
- Topography
- Chemical composition
- Label free
- Works in various environments



The enhanced field created by surface plasmon* resonances in a metal nanoparticle.



Traditional AFM:
- Cantilever scanned over surface
- Tip-surface forces change cantilever oscillation
- Changes laser deflection on position sensitive detector



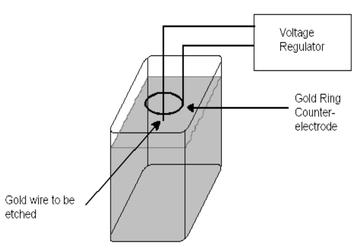
Tuning fork AFM:
- Tip scanned over surface
- Tip-surface forces change tuning fork oscillation
- Changes in piezoelectric tuning fork current

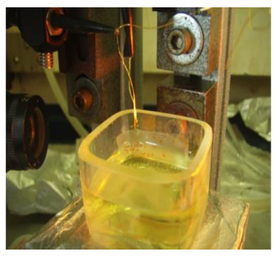
Surface Topography

Plasmons are coherent oscillations of the free electrons in a metal.

Tip Preparation

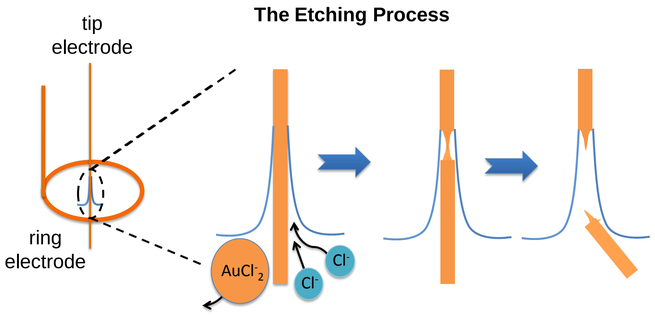
Electrochemical Etching Setup for Gold Tips





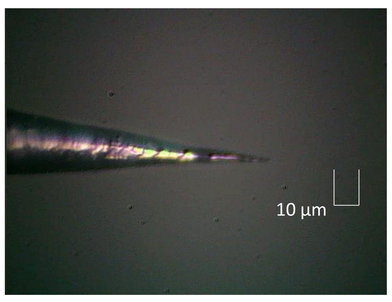
Setup:
- Electrolyte composed of 1:1 HCl and ethanol by volume.
- The gold ring and wire are suspended from hooks which are in turn connected to a voltage regulator.
- The anode is connected to the (+). The cathode is connected to the (-).

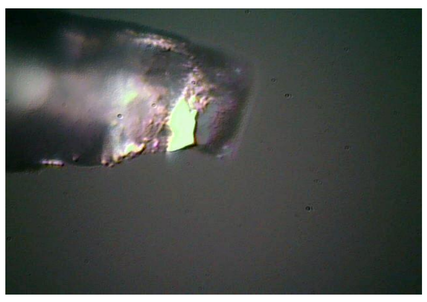
The Etching Process



- Chloride ions react with the gold wire, producing $AuCl_2$ in solution.
- The Cl ions continue to react with the gold in the wire until the tip falls.
- Voltage regulator stops the etching process.

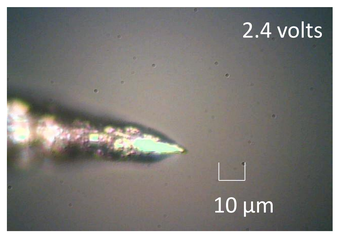
Gold Tip Etching

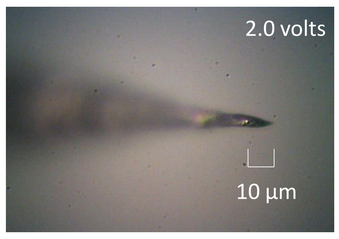




Above, 0.250 mm wire:
- **Electrolyte:** 1:1 HCl and Ethanol
- **Voltage:** 2.4 V

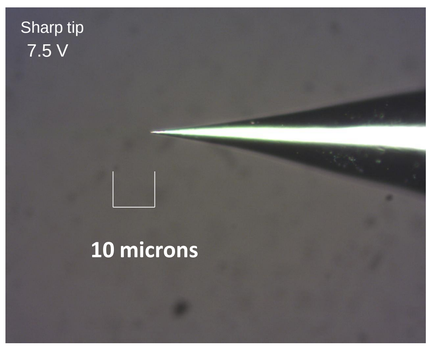
"Crashed tip"
- Gold is a very sensitive material
- Slight impacts can destroy tips

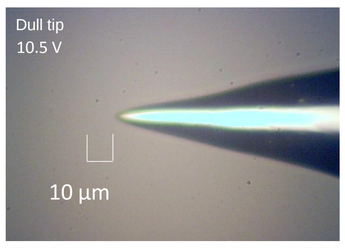


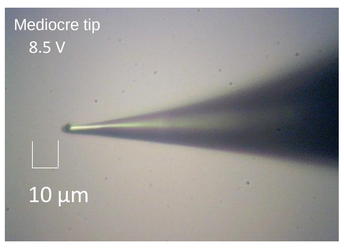


0.04 mm wire:
- **2.4 V**: dull tip
- **2.0 V**: sharper tip
- **Conclusion**: Smaller wire requires smaller voltage

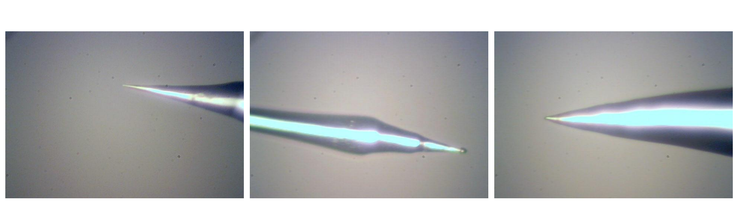
Tungsten Tip Etching







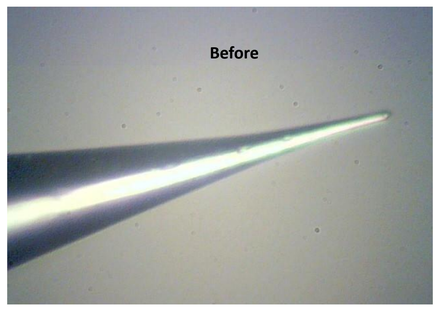
- **Electrolyte**: 3M KOH
- **Optimum voltage**: 7.5 V



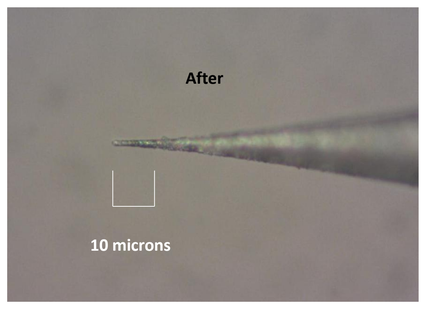
Fresh solution → Used solution

Solution freshness experimentation:
Fresher solution makes sharper tips

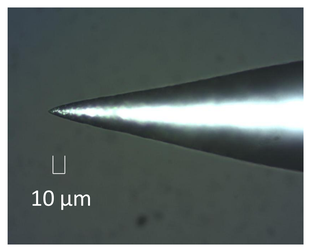
Silver Plating of Tungsten Tips



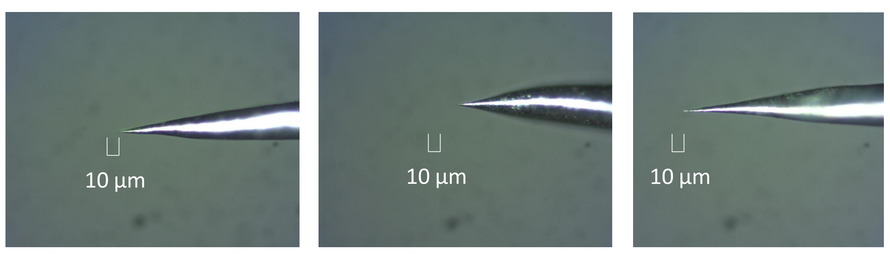
- **Electrolyte:** $AgNO_3$, KI, and H_2SO_4
- **Reaction time:** 20-30 sec
- **Plating Voltage:** 3.0 V



Silver Tip Etching



First Etching
- **Electrolyte**: Ethanol, hydrogen peroxide, and ammonium hydroxide
- **Voltage**: 20-24 V
- **Result**: Dull tips



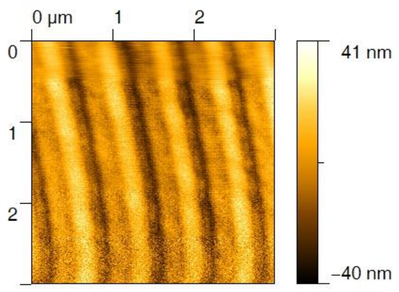
New etching
- **Electrolyte**: 5:1 ammonium hydroxide and ethanol by volume
- **Voltage**: 10.5 V
- **Results**: Sharp tips

Summary

Several different tips were made with different solutions and voltages.

- **Gold**: smaller wire requires smaller voltage.
- **Tungsten**:7.5 volts gave sharper tips. Reuse of solution produces less fine tips over time. Successful silver plating.
- **Silver**: produced successful tips with ammonia-ethanol electrolyte

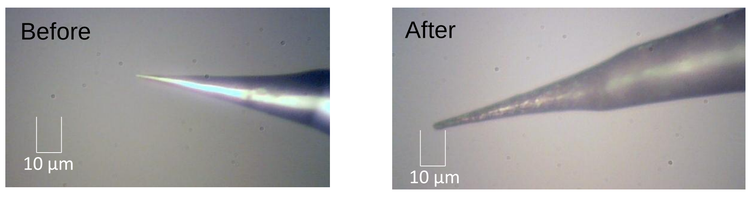
- Tungsten tips created this summer were used for tuning fork AFM calibration



Metal grating on a silicon wafer imaged by tuning fork AFM and tungsten tip.

Future work

- Implementation of TERS
- Continue improvement of tip preparation techniques
- Evaluate optical activity of other noble metal tips



Future tip preparation techniques include surface roughening via chemical etching, as shown above.

Acknowledgments

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