Electrochemical Etching of Silver Scanning Tunneling Microscope Tips in Dilute Acetic Acid

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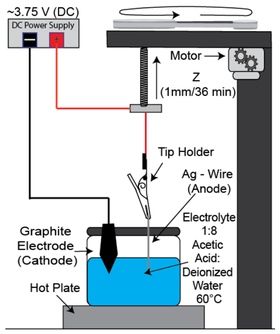
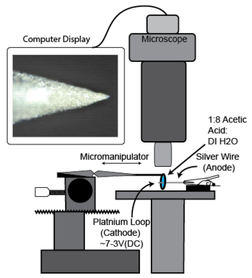
Scanning Tunneling Microscopy

Scanning Tunneling Microscopy (STM) is used to image, manipulate, and spectroscopically characterize individual atoms and molecules to further develop an understanding of materials that have application in the semiconductor field. The fabrication of sharp and smooth metallic tips is an essential part of STM as the radius of curvature of tips used in STM directly influences resolution, ideally tips have an atomically defined apex to avoid having multiple active probes. The smaller the radius of curvature, the finer the resolution. We report a reproducible fabrication procedure of silver STM tips.

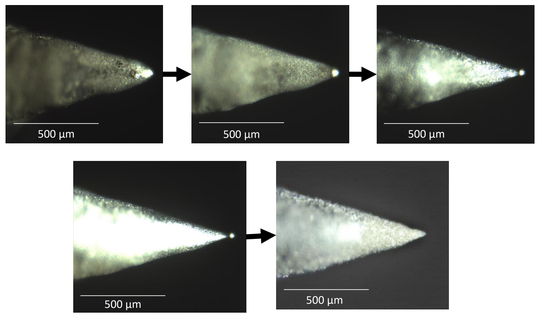
Primary Etching Apparatus



Secondary Zone Dynamic Electropolishing Apparatus



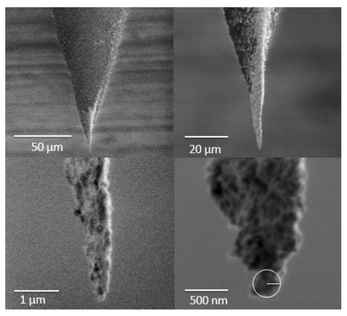
Necking Process with Secondary Etching Apparatus



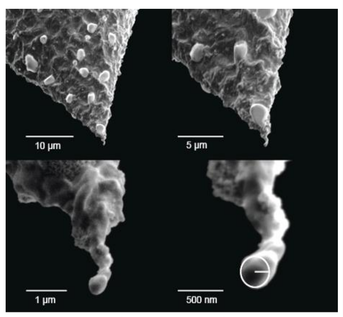
Heat Treatment

To remove contaminants such as silver oxide, the tip is heated at 300°C for one hour. Heat is an effective treatment because it becomes thermodynamically favorable to remove silver oxide at temperatures above 195°C. The removal of silver oxide is advantageous as silver oxides adversely affect STM imaging.[1]

$$2AgO_2(s) + Heat \geq 195℃ \rightarrow 2\mathrm{Ag}\,(\mathrm{s}) + (O_2)\,(g)\,^{2}$$



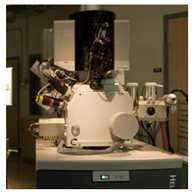
SEM Images of unheated Method 1 Silver STM Tips at Various Magnification



SEM Images of Heat Treated 300°C Method 1 Silver STM Tips at Various Magnification

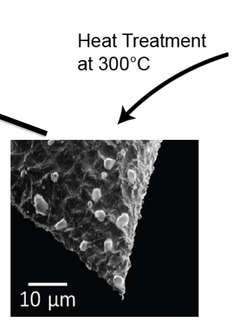
[1] Gorbunov, a. a., B. Wolf, and J. Edelmann. "The Use of Silver Tips in Scanning Tunneling Microscopy." *Review of Scientific Instruments* 64.8 (1993): 2393–2394.
[2] Lide, David. "CRC Handbook of Chemistry and Physics, 88th Edition." 89.

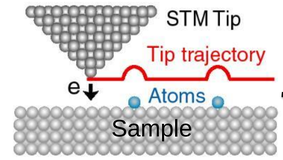
Tip Fabrication Process



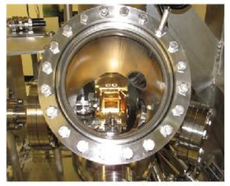
SEM/EDX for Tip Characterization and Analysis

Heat Treatment at 300°C





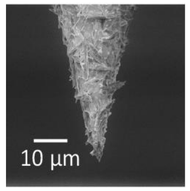
Tip and Sample interaction in STM

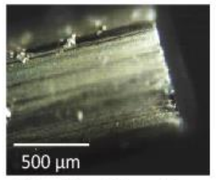


STM Chamber

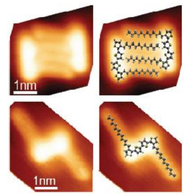
Electrochemical Etching

With 1:8 Acetic Acid: DI H_2O



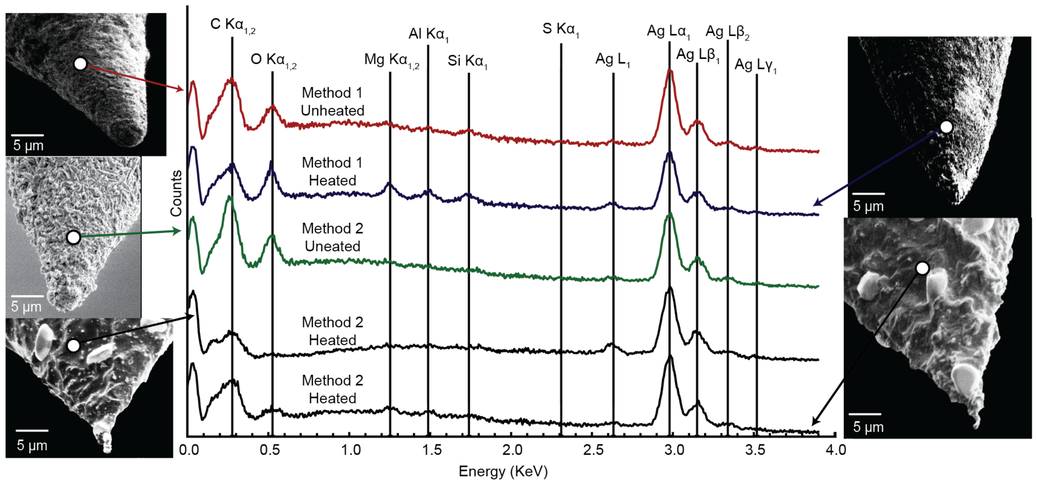


Silver Wire 0.5 mm Dia.



Didodecylquaterthiophene (DDQT)

Elemental Comparison by Fabrication Method: Stacked Energy Dispersive X-ray Spectra



Tip Characterization by Method

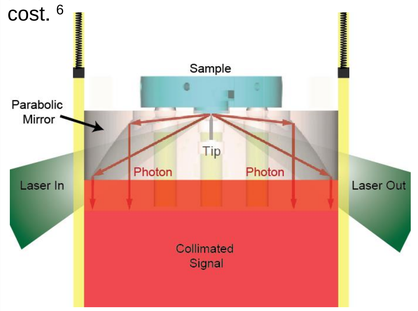
Our fabrication of silver STM tips shown as method 1 involves a multi-step electroetching process of a 0.5 mm diameter silver wire of 99.9985% purity. We use a of volume ratio 1:8 CH_3COOH: DI H_2O electrolyte solution. Acetic acid is favorable for its stability, environmentally innocuous properties, and low surface tension. Method 2 replicates a previously published fabrication method with a 6:1 ammonia and water electrolyte.[3]

Heat treatment on tips fabricated with method 1 had a distinct effect on surface morphology. The change in morphology can be attributed to the level of contamination. In unheated tips there was an elevated number of carbon (0.277 KeV) and oxygen (0.525 KeV) counts relative to the silver Lα1 peak (2.98 KeV). The elevated level of contaminates contributed to the formation of a rough crystalline surface. Correspondingly, in heat treated tips the surface smoothness is a result of lower level of contamination.

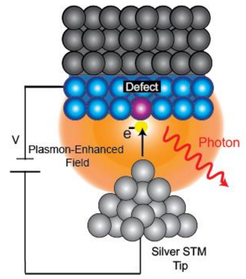
[3] Sasaki, Stephen S. et al. "Note: Automated Electrochemical Etching and Polishing of Silver Scanning Tunneling Microscope Tips." *Review of Scientific Instruments* 84.2013 (2013): 2013–2016.

Benefits of Silver: Plasmonic Enhancement

Silver is an ideal tip material for scanning probe microscopy because the plasmon propagation lengths of silver in the relevant spectral range are longer than other metals that exhibit plasmonic properties, such as gold.[4] In particular, silver is responsible for plasmonic enchantments of at least 10^3 and up to 10^7.[5] These enhancements are needed for shortened acquisition times and more accurate measurements. In addition to its plasmonic properties, silver is favorable for its low dielectric losses and its relative low cost. [6]



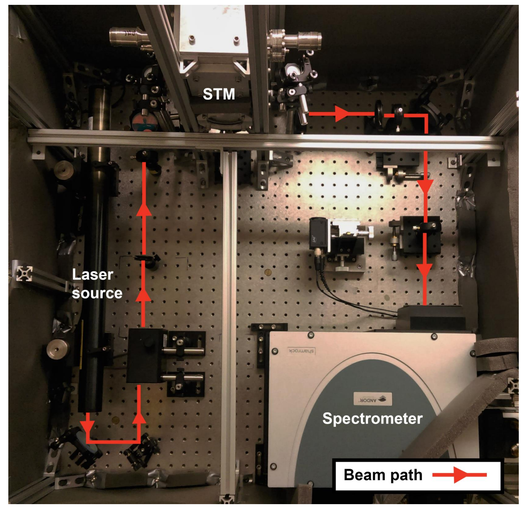
Parabolic mirror collects photons emitted from STM junction during laser induced emission



Plasmonic Enhancement at STM Junction

Future Work

Future work involves adjusting optics to allow optimal collection of photons emitted from the STM to produce a stronger signal at the spectrometer. After optimization, we will then take a series of emission measurements with silver STM tips to determine the magnitude of plasmonic enhancement. After emission studies we plan to our publish findings in the Review of Scientific Instrumentation.



Optics Table

Acknowledgements

This research was supported by the Undergraduate Research Opportunity Program (UROP) Grant. Thanks to the Nazin Group and the Center for Sustainable Chemistry, as without their support this project would not be possible. Special thanks to Ben Taber for continued guidance throughout the research process.

[4] H. Raether, "Surface Plasmons on Smooth and Rough Surfaces and on Gratings" Springer, New York, 1988
[5] Hodgson, P. a. et al. "Note: Electrochemical Etching of Silver Tips in Concentrated Sulfuric Acid." *Review of Scientific Instruments*. Vol. 84. N.p., 2013. 8–11.
[6] Zhang, C et al. "Fabrication of Silver Tips for Scanning Tunneling Microscope Induced Luminescence." *The Review of scientific instruments* 82.8 (2011): 083101.

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