Summer Scholar Report

Pt-Ir Tip Creation for Use with Thiols and Thioethers on Gold Surfaces

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Abstract:

Pt-Ir chemical etching techniques using $CaCl_2$ solutions were studied for creating properly shaped, sharp tips for STM use to study self-assembled monolayers (SAMs) of thioethers and thiols on gold surfaces. Initially, the goal of this research was to study thioethers on gold surfaces using physical tip etching procedures. Physical procedures can be used to create tips for use in STM; however, these procedures have proven to not be as reliable. Therefore, in order to achieve good resolution of images of thiols and thioethers on gold surfaces, chemical etching techniques were adapted. A segment of Pt-Ir wire was held in a solution of $CaCl_2$ and a voltage was applied, causing the wire to taper, forming a tip. Rough etching and fine etching at varying concentrations, wire length, and voltage caused different reaction rates, and the rate of reaction determined the usefulness of the tips. A rate too fast, and the tip would be too dull, but a rate too slow would cause the tip to bend and have poor shape. By studying the different parameters, the best conditions for tip etching were found.

Introduction:

Scanning Tunneling Microscopy is a key analytic technique in studying surfaces and self-assembled monolayers that grow on them. A SAM is formed when compounds in a solution absorb onto a surface in repeating ordered patterns. Both thiols and thioethers have been shown to form SAMs on gold surfaces, and they have many applications.[1] Thiol monolayers have had a variety of uses including electro-chemical processes, adhesion, and modeling membranes.[2] Another monolayer of particular interest is one created by thioethers. It has been shown that thioethers, when anchored to a surface, can create a tiny motor, similar to flagella on bacteria.[3] This means that SAMs of thioethers have great potential for use as a motor for nanoparticles. The SAM surfaces of dioctylsulfide, dodecylsulfide, and octade-canethiol were studied to see how they form on surfaces of gold. This was attempted at different conditions in order to see how these factors affect SAM packing.

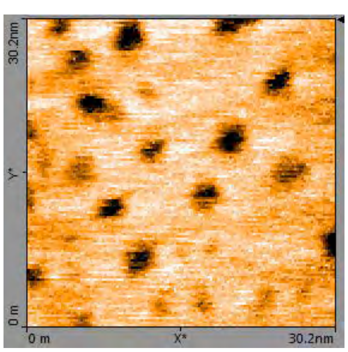

FIGURE 1: *STM Image of Octadecanethiol on Gold surface*

Chemical etching is a process that uses a voltage applied across a solution and a wire in order to cause that wire to taper and create a tip. There are two methods of chemical etching; rough etching and fine etching. In rough etching, a wire is typically etched in the middle, causing the wire to extrude and break, creating a sharp tip. A fine etching procedure usually begins with a wire that has already been rough etched. Then the etching focuses on the tip to make it sharper or better shaped. In order to see the differences in the different SAMs, effective chemical etching techniques of Pt-Ir wire must be found. Several different techniques were used that each affected the tip differently.

Procedure:

The SAM surfaces were created on an Au(111)/mica substrate provided by Agilent Technologies. They were annealed using a hydrogen flame for several seconds, and then viewed using the Nanosurf Easyscan2 STM system to confirm that the annealing was successful. The annealed gold surfaces were placed in sealed beakers of solutions of the dioctanesulfide or dodecylsulfide, and left to sit overnight. When taken out of the solution, the gold surface was dried by gently blowing nitrogen over it. It was then placed in the STM to be viewed.

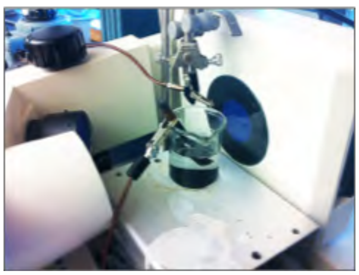

FIGURE 2: *Setup for Etching Pt-Ir Tips*

The Pt-Ir tip was created in a two-step process of rough then fine etching. Figure 2 shows the arrangement for the procedure. In the rough etching process, between 1 to 5 mm of wire would be placed into a solution of $CaCl_2$. The $CaCl_2$ concentrations used were 0.5, 1.5 and 3.0 M. A voltage was applied across the wire at voltages ranging from 10 to 50 V. Figure 3 shows the placement of the wire into the solution at the start of the reaction. The end point of the process, the moment when the wire was cleaved, was signified by a sudden silence and stopping of bubbles.[4]

FIGURE 3: *Close Up of Pt-Ir Etching*

Several different fine etching techniques were tried, but only two had consistent success. The tip focused method was to only place the very tip of the wire into the solution, and etch the tip at voltages between 5 and 10 V.[4] Using an optical microscope, the tip was placed barely touching the solution. The second method was to place 1 mm of the wire into the solution, apply a voltage between 5 and 10 V, and slowly pull the wire out of the solution. This was done between 1 and 10 times for any tip depending on its initial sharpness and shape. The tips were characterized using an optical microscope at 400 and 1000 times magnification.

FIGURE 4: *Tip Results from Different Etching Techniques*

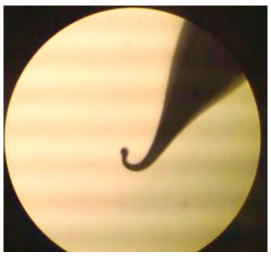	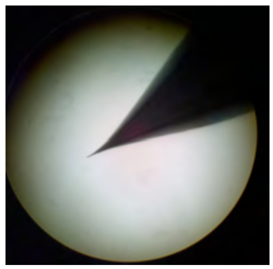	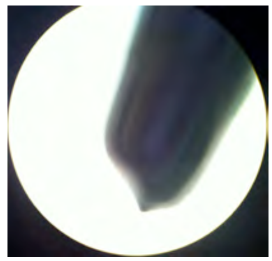	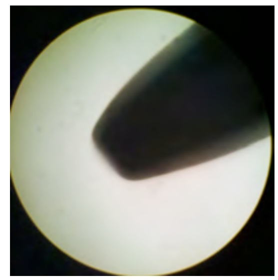
FIGURE 4A: *Rough Etched Tip That Has a Bend Due to a Slow Reaction Rate (400x)*	**FIGURE 4B:** *Rough Etched Tip That is Too Long Due to a Slow Reaction Rate (1000x)*	**FIGURE 4C:** *Rough Etched Tip That is Too Short Due to a Slow Reaction Rate (1000x)*	**FIGURE 4D:** *Rough Etched Tip That is Dull Due to a Fast Reaction Rate (1000x)*

Results:

The rough etching of tips appeared to be affected by several *Rate (1000x)* factors; the voltage applied, concentration of $CaCl_2$ solution, and length of wire inserted into the solution. It was found that medium voltages (25 - 30 V) produced sharp tips that possessed good shape. Voltages higher than this, (40 – 60 V) react too quickly, and do not produce sharp tips. Volt- ages lower than this (10 – 20 V) react too slowly, and take several hours to complete, and also have a poor shape. Higher voltages increased the rate of etching. The poor shape caused by low voltages is created due to an unclean break during the rough etching process. High voltages caused dull tips because they would continue to react with the wire even after wire broke. Placing more of the wire, (3 – 5 mm), into the solution caused the tips to be sharper, however, this often caused the tip to bend and have an unusable shape. This was due to the etching point having too large of a force onto it, causing it to break too soon. Placing less wire, (1 – 2 mm) created tips that were not as sharp, but were usually free from shape defects. Higher concentrated solutions caused the reaction to go faster. This caused the tips to be dull, and without any benefit in shape. Lower concentrations caused the reaction to go slower, and create sharper tips, but did not appear to cause any issues with the shape. It appears that for the rough etching, a medium volt- age with a low concentration using a short amount of wire in the solution makes the best tips. This is because these conditions cause the tip to react at the proper rate. At a higher reaction rate, the tip does not become sharp enough, and at a lower rate, bends and curves in the tip become too common. However, in all cases of rough etching, a fine etching procedure was used to either make the tip sharper, or have a better shape. Examples of tips are shown in Figure 4.

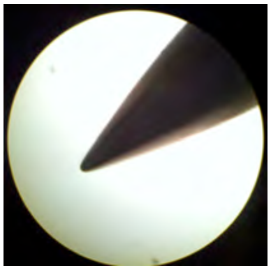

FIGURE 5: *Fine Etched Tip After Both Methods (1000x)*

Two major fine etching procedures were studied, and they each had different uses.[4] The tip focused etching process made tips become sharper. However, this process did not improve tip shape significantly. Lower voltages were better for this method, because if the voltage was too high, the tip would begin to dull. The pull-down method was very effective at removing bends from tips, as well as improving length. This method did not improve tip sharp- ness, and sometimes made tips duller. Depending on the problem with the shape, different voltages were needed. For tips that were bent about 10 V worked best. If the voltage was too high, the bend would just be broken leaving a dull tip. However, if the voltage was too low, the bend would not be corrected. For fixing tips that were too long, a higher voltage is needed, as breaking part of the end of the tip is desirable. For short tips, higher voltage is desirable as well, because it etches the wire more creating a longer tip. Both the pull down and tip focused methods are extremely useful when used together. The pull-down method fixes the shape of the tip, and then the tip focused method can be used to sharpen the tip further. An example of a sharp tip is shown in figure 5. This combination can make almost any tip from the fine etching process into a usable sharp tip.

Conclusion:

Consistently good tips can be created from Pt-Ir wire using these methods. The ideal conditions for rough etching a wire are to have 2 mm go into the solution of 0.5 M $CaCl_2$ and apply 25 V. The wire should turn out to be both rather sharp as well as have a good shape. With this wire, if shape needs to be improved, the pull-down method will work. Then after a good shape is acquired, the tip focused fine etching can be used to sharpen the tip further creating a tip that is suitable for use in the STM to view thiols and thioethers on gold surfaces.

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4. Czerepak, Anna., Pt-Ir Tip Etching Techniques for Scanning Tunneling Microscopy, Physics Department, University of Notre Dame, NSF/REU Program, 2011