Pt-Ir Tip Etching Techniques for Scanning Tunneling Microscopy

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Abstract

Superconductors have gained significant attention in the last decade. Understanding the properties of superconducting materials is a critical step both in the field of condensed matter physics and the next advances in engineering. Our group sought to investigate the topic of magnetic vortices in Type II superconductors through low-temperature, ultra high vacuum scanning tunneling microscopy. An important component of a successful STM image is the quality of the tips used in the microscope. Two platinum iridium tip-making methods were tested: the Argonne method and a variation on a method introduced in a paper by Lindahl et al[1]. Sample images taken on an open-air STM by Professor Kandel's group in chemistry, as well as electron microscope pictures of the products of the two tip-making procedures are included and discussed.

1 Argonne Method

The idea behind the Argonne method is to use a two-step chemical etching setup (coarse etch then fine etch/micropolishing) in order to shape the tips. The advantage of this two step method is the short preparation time (less than 20 minutes per tip) and decent control over tip shaping. Some papers advocate a one-step coarse etch instead of the additional micropolishing step. However, various factors in the coarse etch step make any fine control or observation of the tip difficult, including the rapidity of the reaction and wide range of etching times that vary with voltage, length of wire in solution, and even the chemical batch of calcium chloride used to make the solution. The opacity of the precipitate that is produced also makes it difficult to judge the progress of the etching. It is these uncertainities that make single-step coarse etching of tips usually unreliable, especially because the end of the wire breaking off tends to produce tips with ball-shaped ends. This feature is necessary for a sharp result from fine-etching but detrimental to immidiate use as a STM tip.
A note on the cut-off time (the time between when the end of the wire drops off and the time when the power to the etching steup is shut off); it is advantageous to minimize this time as much as possible. A longer cut-off time will result in the tip being etched after the desired shape has been obtained. This leads to blunt tips and destroys the ball at the end of the tip. Some groups propose building an automatic cut-off circuit in order to minimize the cut-off time, but it was found that these cut-off circuits still had a significant delay (500 ns at minimum, but usually on the order of miliseconds). This is an improvement on manual shut-off times but the desire to finely control the last stages of this etching is what motivated the alternate approach in section 2 of this paper. If a manual shut off is used, the sound that the reaction produces can be used as a rough guide to determine when etching may be close to completion, with a noticeable decrease in volume when the end of the wire is about to break off.

1.1 Procedure

1. Cut a clean piece of 0.25mm diameter Pt-Ir wire with wire cutters about 12-15mm long.
2. Insert the wire into the copper clips attached to the coarse etching setup. Make sure the wire protruding is as close to vertical as possible in order to ensure that the etched mass on the end falls off cleanly and without bending the tip.

Figure 1: Coarse etching setup showing: AC powder supply, multimeter, voltmeter, cupper clip, carbon counter electrode, and stand with solution beaker.

3. Fill the beaker with 30-40ml of 1.5M calcium chloride.
4. Lower the wire into the solution, making sure that the amount of wire in the solution is no less than 1.3mm and no more than 2mm. [1]
5. Set the power supply to 35 V AC and start the timer.[2] A rough guide to the steps and the duration is provided below, but it will vary, depending on the setup. It must be kept in mind that it is advantageous for the etch to finish on the lowest voltage, as this produces a finer tip shape. It is acceptable to decrease the time of steps one and two, but it must be kept in mind that the subsequent stage times will be longer the shorter the time spent on higher voltage steps.

Voltage Setting	Etching Time
35 V AC	~90 seconds
30 V AC	~45 seconds
28 V AC	Until process is complete

6. Lower the beaker and solution and carefully extract the tip from the copper clip, being careful not to touch or knock the etched end. The solution can be used up to four times, but was discarded after two in our setup, as it became difficult to determine how much of the tip was in the solution when much precipitate was present. Clean and dry the tip using the following steps, being careful to immerse the tip cut-end first and to hold the etched end facing down when it is placed under running water in order to preserve the tip shape.

- Immerse in deionized water for 10 seconds.
- Rinse under hot running water for 2 minutes.
- Immerse again in deionised water for 20 seconds.
- Dry with nitrogen gas.

7. Secure the tip in the fine etching setup and wet the tungsten loop with calcium chloride solution. The solution will need to be replaced frequently, as precipitate builds up rapidly and the available chloride ions are depleted.
8. Set up the electronics for fine etching. This setup is described in detail in the Argonne procedure paper[2], but it consists most basically of an AC power supply set to about 2.5 V AC[3], a switch box with a button to apply current, and a multimeter to verify the voltage. A microscope stage was modified to hold a copper clip to hold the tip in place, a platform to mount the tungsten loop and an additional two-way adjustable stage in order to easier position the loop in relation to the fixed position of the clip.

[1] It was found that less than 1.3mm led to the entire end of the wire being etched off, with no 'neck' that was thinned and eventually broken off. More than 2mm was found to deform the tip after the drop off. This is speculated to be due to the increased weight and bulk of the end that forces the drop off to occur sooner, when the neck of the wire is not as thin, and strains the wire. Around 1.5mm was found to be a good length for this step.

[2] AC power is absolutely necessary, as DC power will not circulate the chloride ions around the wire as much as AC power will. This will result with an etching time on the order of hours instead of minutes.

[3] It may be tempting to use voltages of 10 V or above in order to speed the fine etch. However, around 10 V or higher, the small amount of solution in the loop is used up very quickly and must be replaced a few times every minute. Voltages higher than 15 V were found to lead to rapid bubble formation in the loop and give blunt tips. It is therefore advisable to restrict voltages for this step below 10 V.

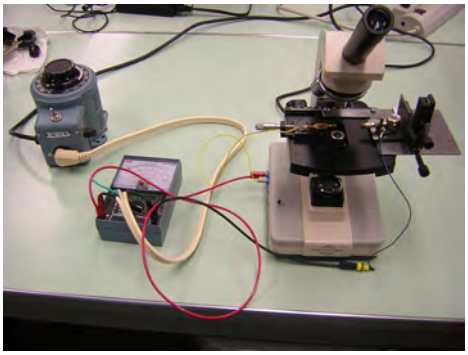
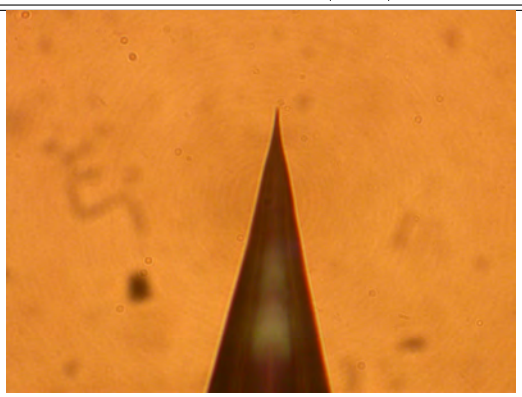
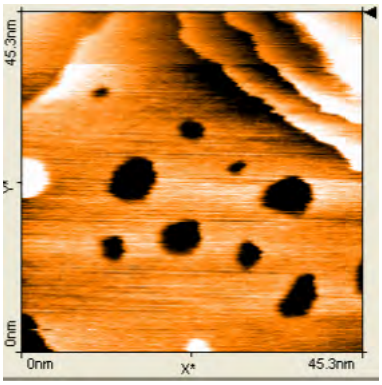
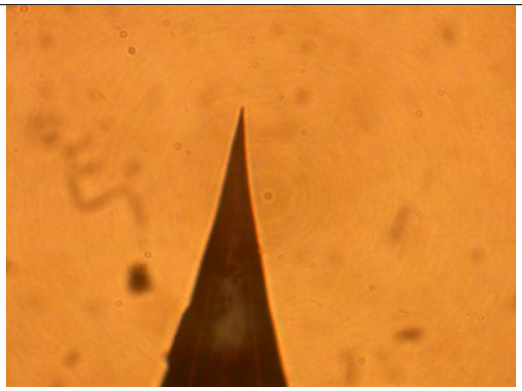
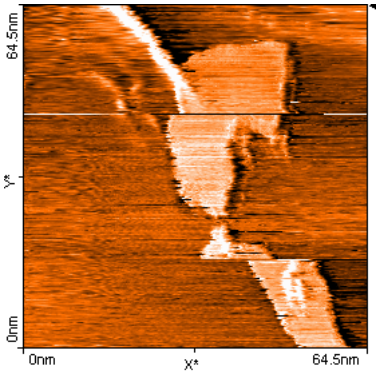
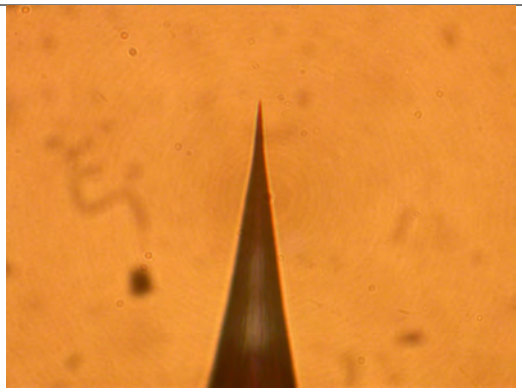
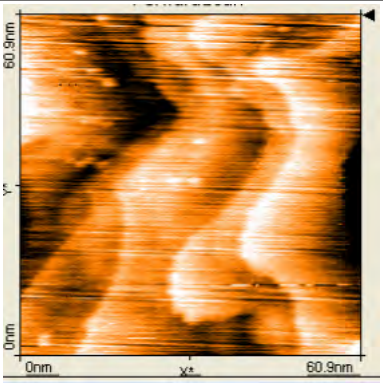


Figure 2: Fine etching setup, showing voltmeter, AC power supply, modified microscope, stage, tungsten loop, and copper clip.

9. Align the tip with the center of the loop. Position the loop behind the ball on the end of the tip, and pull the loop back slowly while pressing the switch box. It is important to apply the power in ONE direction only for proper tip shaping.
10. This process is repeated (changing solution as necessary) until the section of wire just behind the ball is thinned enough to be etched away, leaving a very sharp tip with no ball or other tip anomalies.
11. The tip is the cleaned again, using the same procedure as outlined in step 6 and placed under an optical microscope for characterization and cataloging.

1.2 Tips and Resulting Images

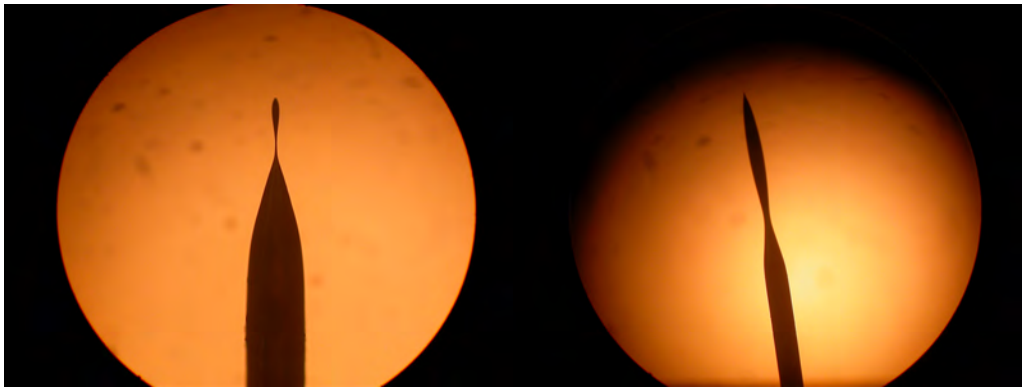
Tip Number/Operator/Sample	Optical Pictures (400x)	Open-Air STM Images
#5/Chris/Octanediol on gold		
#8/Guido/Octanediol on gold		
#9/Chris/Octanediol on gold		

1.3 Discussion

One immidiately obvious feature of this experiment is that tip grading by an optical microscope is very difficult. No good measurement of sharpness can be made at 400x magnification and all three tips look roughly the same in terms of apex shape. The optical microscope pictures are best used as a method to check tips for obvious deformities or crashes. However, tip #5 produced the best images by far and no anomalies occured in either stage of its preparation. Tip #8 had a average quality fine etch and produced a good image, despite the discontinuity in the middle third of the picture. Tip #9 had a slightly longer cut-off time than recommended but still managed to produce a reasonably coherent image at 60.9nm. It can be concluded that the Argonne method produces good tips when the procedure works and has some resilience against minor errors in tip preparation.

2 Experimental Method

The prime motivation behind the experimental method was inspired by a paper published by Lindahl et al[1]. In it, a method of etching is outlined that stops the coarse etch just before the end of the wire drops off, bends the wire 90° and then continues the etch in sulfuric acid and then does some amount of micropolishing. Their method was found to be unworkable for our group (the bending of the wire did not seem to have a purpose and the entire process was very labor intensive) but the idea of stopping the coarse etch earlier was incorporated into our experimental tip procedure. The idea behind this inclusion was to stop the etching when the neck of the wire is thin and close to dropping off, but finish the etching in the micropolishing setup under a microscope.



Figures 3a and 3b: (L) Properly etched tip, showing a thinned neck section. (R) Improperly etched tip with a thick neck and very large bulk section on the end.

In this way, there is no possibility for over-etching through long cut-off times in the rapid coarse etching step. Tip shaping is finished in the fine etching stage, where the voltage is much lower, the control finer, and there is more influence on the final tip shape. Additionally, the progress of the tip shaping can be seen easily under the microscope, unlike the coarse etching setup. The disadvantage of this method is that it is difficult to stop the etching late enough so that enough of a neck is formed to be easily etched away (if the thinned sections not sufficiently small compared to the tip shank, the etching will not progress correctly and will lead to a blunt tip) but early enough so that the end does not drop off or become so thin that the end section bends and deforms during cleaning or micropolishing. With practice, it is not difficult to tell when etching should be stopped. Our group relied on sound (the fizzing of the reaction will taper off just before it is done) and monitoring the current. When the current dropped to 10-20% of its initial value, the etching was almost complete and the power was shut off.[4]

There is one problem that will be explored in the future and that was the issue of the neck of the tip bending when pulled through the wire loop in the fine etching step. This bending is believed to be caused by the surface tension of the solution in the loop. This could be solved by dabbing some of the solution in the loop away with a piece of paper towel, leaving a film instead of a droplet in the loop, or with a slightly larger loop. The tips produced by this method were the sharpest our group has produced (despite the bend in the tip apex) and show great promise as STM tips if a better method of preventing the strain on the neck of the wire in the last step could be found.

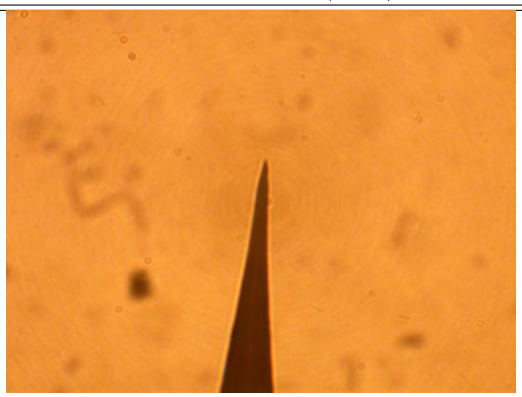
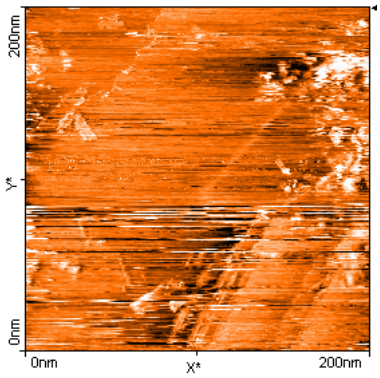
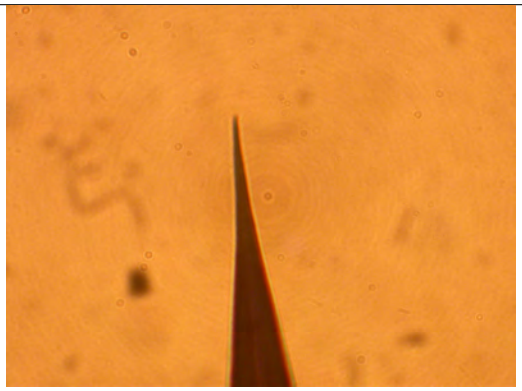
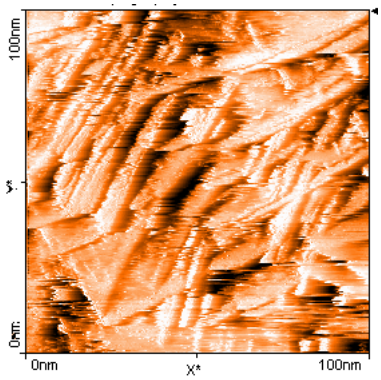
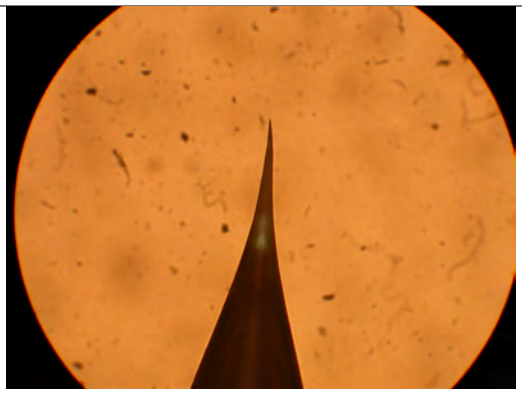
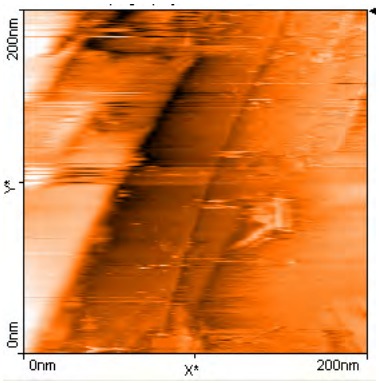
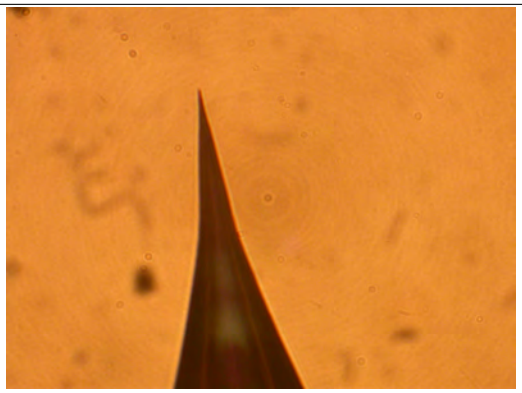
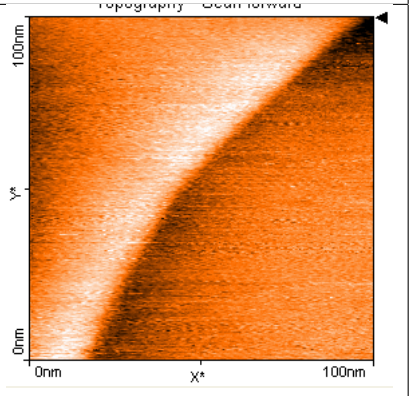
[4]It should be noted that the current does not decrease uniformly to zero as the reaction finishes. Our group found that it reached a finite value at about 10% of the initial value and then discontinuously fell to zero when the end of the tip dropped.

2.1 Procedure

1. The experimental method follows the same steps 1-4 as the Argonne method outlined in section 1.1.
2. Set the power supply to 35 V and start the timer. The time table for this step is the same as step 5 in section 2.1, with the important exception of cutting the reaction short just before the end of the wire breaks off. [5]
3. Clean and dry the tip as in step 6 in section 1.1, being careful when handling the tip, as the end of the tip is quite prone to bending.
4. Insert the tip into the optical microscope micropolishing setup and dip the loop in the 1.5M calcium chloride solution. Dab off some solution with a Kimwipe such that a thin film is left in the loop instead of a droplet.
5. Move the loop onto the wire behind the thinned section.
6. Draw the loop off of the wire while holding the switch button. It is not necessary to draw the entire loop past the neck of the wire each time, as the strain from the wicking between the wire and solution bends the thinned section to the side at late stages in micropolishing.
7. Refresh the solution as necessary and cease etching once the thinned section is removed.
8. Clean and dry the tip using the same method as in step 3.

[5] Details on determining when the reaction is about to finish and what a tip should look like after this step can be found in the introduction to section 2.

2.2 Tips and Resulting Images

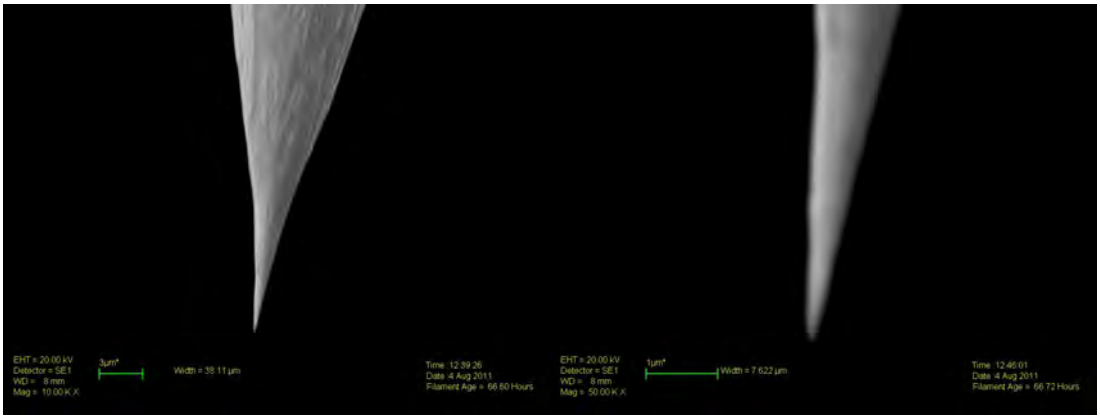
Tip Number/Operator/Sample	Optical Pictures (400x)	Open-Air STM Images
#1/Guido/DTC2		
#2/Guido/DTC2		
#3/Guido/DTC2		
#6/Guido/DTC2		

2.3 Discussion

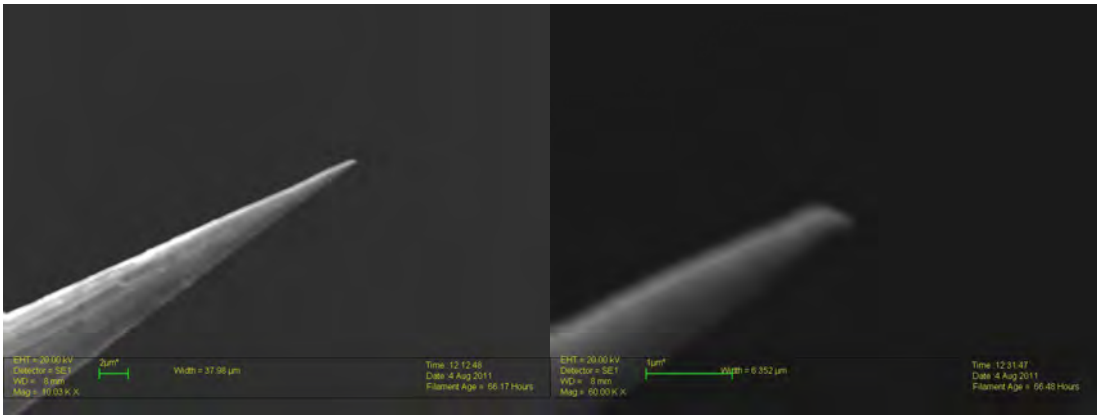
As exemplified in the optical pictures for tips #2 and #3, this method does produce significant bending at the tip apex. This makes it very difficult to align the tip properly with respect to the sample in order for tunneling to occur. Tips #1 and #3 produced fairly decent image resolution at 200nm scales, but it was difficult to get any more detail and all three images show significant smearing and noise. This method is still incomplete and not reliable in its current form. However, it does show promise as part of a different procedure as a way to control more of the etching in the micropolishing step instead of the difficult coarse etching step. Tips #1 and #2 had the thinned sections broken off and then etched a few times to sharpen. #3 had the thinned section broken off and then etching immidiately ceased. #6 had the thinned section fold completely over during micropolishing and produced the worst image.

3 Electron Microscope Images

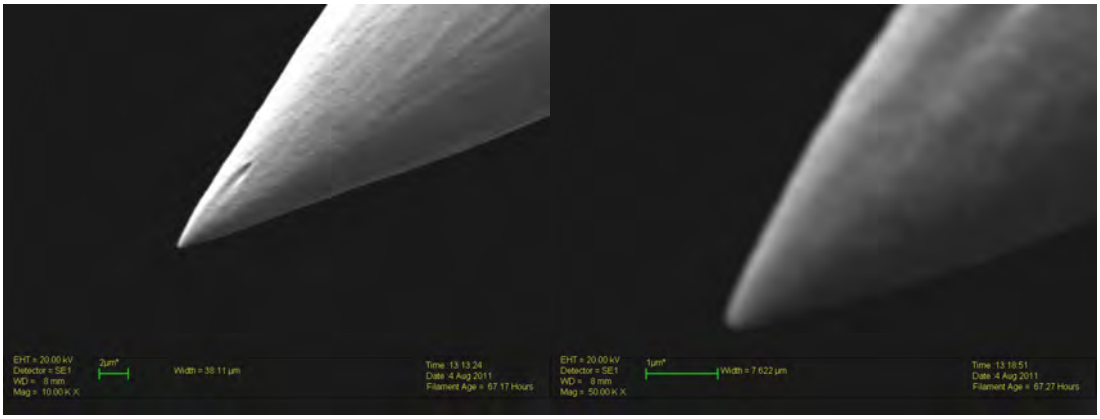
Our group took three tip samples mounted on carbon tape to the Notre Dame Integrated Imaging Facility and used a Leo SEM (scanning electron microscope) under Dr. Alexander Mukasyan in order to produce a series of images at x10,000 and x50,000 of three tip-making methods; the Argonne method, the experimental method, and the Geneva method used primarily by our group up to this point.



Figures 4a and 4b: Argonne method tip at (L) x10,000 and (R) x50,000



Figures 5a and 5b: Experimental method tip at (L) x10,000 and (R) x60,000



Figures 6a and 6b: Geneva method tip at (L) x10,000 and (R) x50,000

As one can see, though the electron microscope we used was not able to resolve much below $1\mu m$, the Argonne method produces much sharper tips (less than 100nm) than the currently used Geneva method (about 300nm). The experimental method also produced sharper tips than the Geneva method, however the bend at the apex is obvious and must be refined before useable tips are produced. A more detailed measurement of the tips' radii of curvature could be made in a higher resolution electron microscope, if additional accuracy or more information about the last few nanometers of the tip are desired.

4 Conclusions and Suggestions

The recommendation for the method at this time is the Argonne procedure. It produced atomic-resolution images, was not difficult to implement, and showed resilience to errors in the etching stages. The experimental method explored different ways to avoid run away etching at the end of the coarse etching step, but suffered from the problem of producing a delicate tip that deformed in the last stages of fine etching and produced tips with bent ends. Various other tip production techniques were not explored, but would be interesting to study in the future. These include tip annealing with a Bunsen burner in order to smooth out the tip apexs and eliminate multi-tips, using various other solutions (including hydrochloric acid, sulfuric acid, and acetone), and building a cut-off circuit to further minimize cut-off time.

References

[1] J. Lindahl, T. Takanen, and L. Montelius, *J. Vac. Sci. Technol. B* 16 (6), Nov/Dec (1998).

[2] Center for Nanoscale Materials, *STM Tip Fabrication and Characterization Procedure*, (Argonne National Labs, Argonne, IL 2010) pp. 1-15.