Fabrication of Tungsten Tips

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Abstract

The Scanning Tunneling Microscope(STM) offers us the atomic resolution of the material surface by giving voltage between STM-tip and the surface we want to examine. The digital image can be created when STM-tip is moving around the surface producing a tunnel current that can be detected by the computer.

In our research, we focused on the preparation of the STM-tip by using electrochemical etching of a tungsten wire in KOH solution. The auto cutoff etching circuit and etching devices are designed and constructed by ourselves. The radio of curvature(ROC) of the tip can reach $< 50nm$ under a scanning electron microscope(SEM), the same as many paper showing. To get as sharp and well-defined a geometry tip as possible, we try to figure out how the parameters such as concentration, applied voltage, and wire length inside the solution affect the final tip.

The fabrication of metal tips for spectroscopy measurements is becoming more and more popular and a great amount of work has been done in the tips fabrication process. Sharp metal tips used to examine the surface of different materials play a key role in STM, SEM, and AFM.

Another motivation behind this job is to gain the same sharp tip with a cheaper experimental setup built by ourselves instead of purchasing the expensive and complex device from the company. During the fabrication process, the experiment helped us to understand physics and chemistry knowledge better and cultivate hands-on skills.

List of Figures

List of Tables

Contents

1 Introduction

1.1 Review of STM

The scanning tunneling microscopy (Figure 1[1]) was invented by Rohrer and Binnig in 1981 and promoted by Gerber and Weibel. When tips approach the conducting sample surface about one nanometer after applying a bias voltage between tip and sample, the tunneling current could be produced. Tunneling current depends on the state of the sample, tip position, and value of applied voltage. STM does not show the real atom position but rather an electron density near surfaces.

The theory and basic principles of STM include quantum mechanics and solid physics [2]. STM can provide images of material surfaces with atomic resolution when tips scan a small area of the surface. The quality of images and resolution highly depends on the sharpness and cleanliness of the tip because only the tip with atomically stable apex and no contamination that let current flow through the last atom on the apex. Therefore, more and more researchers are trying to produce this kind of tip with a low aspect ratio. However, most of the preparation methods can not reach that goal.

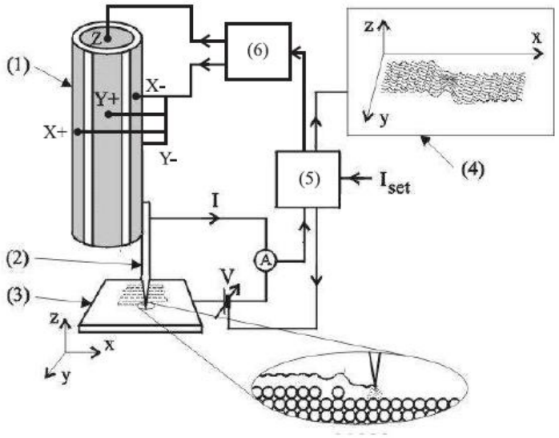


Figure 1: STM device.(1)Piezoelectric tube, (2)STM-tip, (3)Sample, (4)image, (5)control unit, (6)piezoelectric power

1.2 Overview of three common electrical etching methods

Many metal materials can be used as STM tips like tungsten(W), gold(Au), and platinum-iridium($PtIr$). In our experiment, we choose 0.25mm tungsten wire for STM tips because of its great reproducibility and high conductance.

There are a lot of methods and different set-ups to prepare tungsten tips[3][4][5]. The most common way to get well tips is electrochemical etching which includes (1) a submerged electrochemical etching method [6], (2) a single lamella drop-off electrochemical etching, and (3) a double lamella drop-off electrochemical etching [7].

For us, we choose the first method to etch tungsten tips, which the device is shown in Figure 2[8]. The 0.25mm diameter tungsten wire is vertically inserted in the 2 Molar potassium hydroxide (KOH) aqueous solution, serving as an anode while we apply a DC voltage between a diameter of 20mm copper ring and the W wire. The copper ring is kept at a negative potential relative to the W wire mounted on a micrometer to change its position on the z-axis.

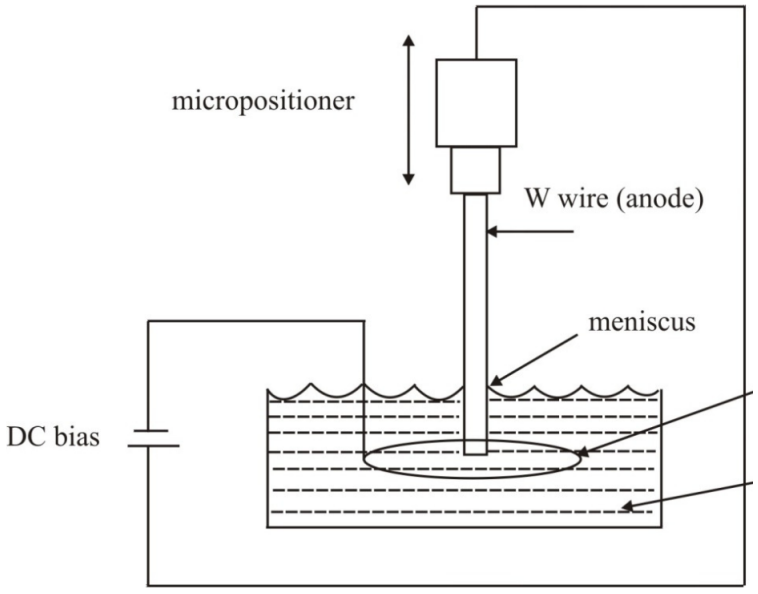


Figure 2: Schematic diagram of the submerged electrochemical etching system

Another two etching equipment are shown in Figure 3[1] and Figure 4[8].

For the single lamella etching system, it consists of a Pt ring, NaOH with de-ionized water, a dc supply power source, a tungsten wire, a glass beaker with a solution allowing to move up and down for making lamella, and a magnetic tip holder for keeping W tips stable. When the lower part of W tips was etched away, the upper part of the tips will suddenly stop etching. We usually use a micromanipulator and magnification microscope to control the electrolyte meniscus around the wire.

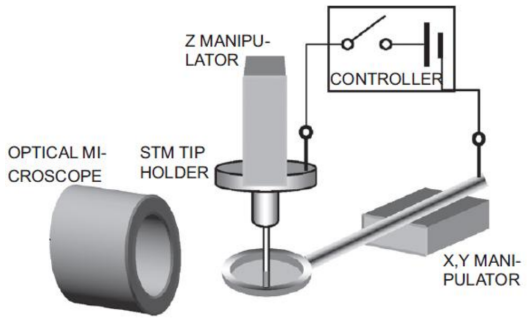


Figure 3: Schematic diagram of the single lamella drop-off etching system

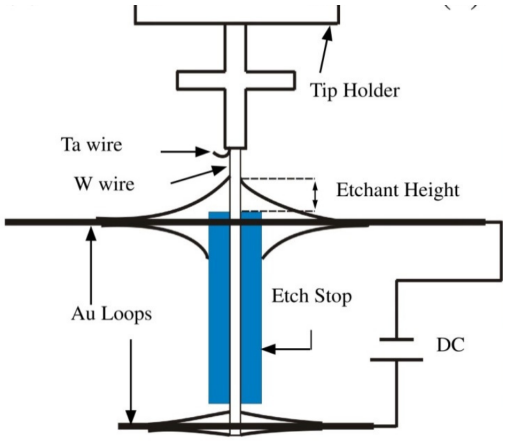


Figure 4: Schematic diagram of the double lamella drop-off etching system

The double lamella etching system is a modified version shown in Figure 4. The partial etch stop(nail polish) W wire inserted into the tip holder with a few lengths of Ta wire

is vertically oriented. The upper gold ring is connected to the negative pole of the power supply while the lower part is connected with the positive pole of the power supply.

1.3 Electrochemical etching and reaction process

For the submerged method, when a dc bias voltage is applied between the W wire and the copper ring, a lot of complicated reactions will happen around the surface of the KOH solution [6]. However, the main overall etching reactions are simple as follows:

$$Cathode : 6H_2O + 6e^- = 3H_{2(g)} + 6OH^- \tag{1}$$

Standard Reduction Potential (SRP) = -2.48V

$$Anode : W(s) + 8OH^- = WO_4^{2-} + 4H_2O + 6e^- \tag{2}$$

Standard Oxidation Potential(SOP) = +1.05V

$$Total : W(s) + 2OH^- + 2H_2O = WO_4^{2-} + 3H_{2(g)} \tag{3}$$

Standard Electrode Potential(E^o) = -1.43V.

In the etching process, $H_{2(g)}$ and OH^- ions shown by equation 1 are generated at the cathode side whereas the tungsten wire becomes anions WO_4^{2-} represented by equation 2. From equation 3, we can know that the WO_4^{2-} will be formed when E^o surpasses 1.43V. However, in real conditions, we need to apply a higher dc bias voltage than the standard electrode potential for the reason that the resistance between the cathode and anode will increase during the etching process.

The electrolyte meniscus which is an important factor in the final shape and size of tips will be formed around the interactive surface between the KOH solution and the wire. The etching mechanism is like the following Figure 5[6].

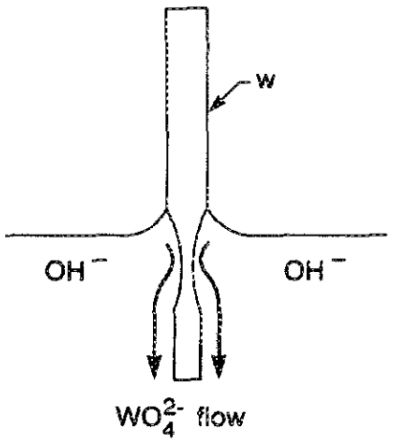


Figure 5: Schematic illustration of the etching mechanism

The OH^- ions flow towards the neck of the wire meanwhile the flow of WO_4^{2-} goes down along the sides of the W wire to the lower part due to a thick layer around the lower part caused by OH^- accumulation.

The electrochemical etching rate decreases along the surface of the meniscus because the concentration of OH^- near the top of the meniscus is lower than that of a major part of the solution. The research found that the etching rate at the top of the meniscus is much lower than at the bottom. As a result, a necking phenomenon occurs around the surface of the solution which is just below the meniscus due to the maximum etching rate.

After some time, the wire will be thin. As a result, the lower part of the wire finally drops because the tensile strength of the W wire is smaller than the weight of the lower part of the wire. The reserved upper part of the tip will be used for the STM tip.

2 Experimental Description

2.1 Experimental device and drop-off circuit

In our lab, we designed the drop-off circuit and experimental device by ourselves according to the classical original circuit[6] and other improved circuits [9]. Figure 6[6] and Figure 7[9] show a similar DC etching circuit. The detailed principle about how the circuit realizes the quick drop-off function can be seen from the paper[6]. However, we found a big mistake in Figure 6 which wasted us lots of time figuring out the problem that the circuit can not work normally. We found that in Figure 6, the two FETs should change their position for the reason that it will cause the comparator to lose its function and prevent the etching process happen. It should be connected like Figure 7 with two FETs.

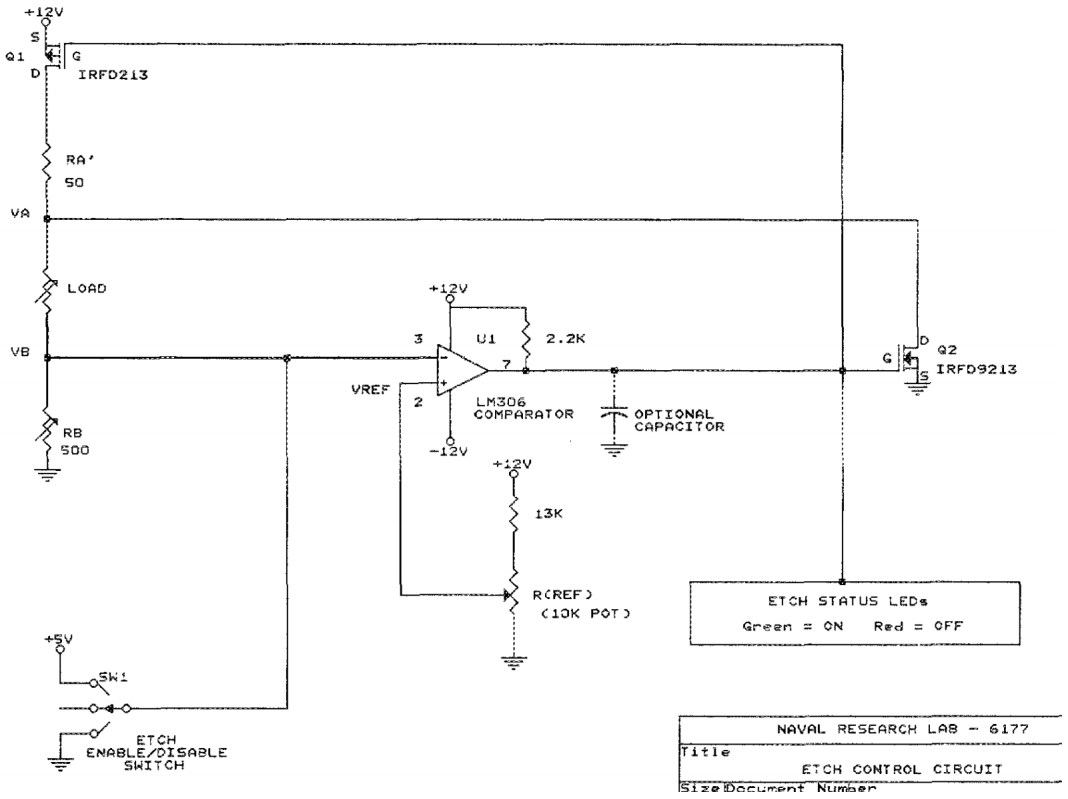


Figure 6: Drop-off etching circuit structure

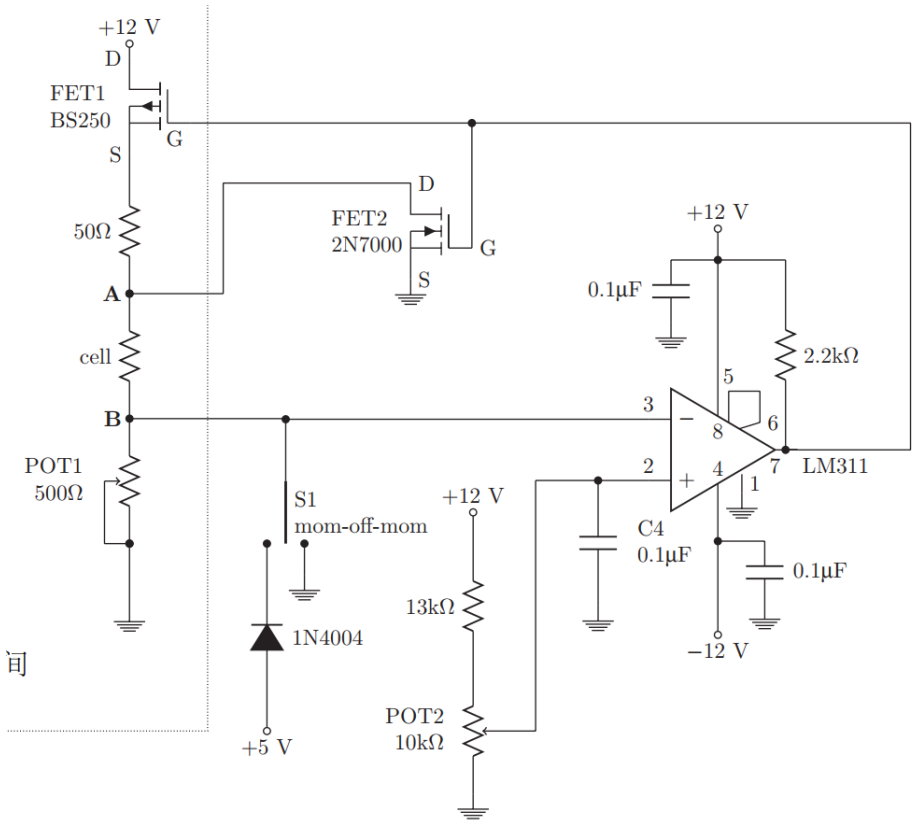


Figure 7: Improved drop-off etching circuit structure

In the Jaecklab, the electrical circuit designed by us is shown in Figure 8 and Figure **??**. The circuit includes one P-type metal-oxide-semiconductor field effect transistor(IRFD9213), one N-type metal-oxide-semiconductor field effect transistor(IRFD213), and one comparator(LM306) which will output different voltage values according to the comparative result in channel 2 and 3, one integrated DC supply power which can output $12V$, $-12V$ and $+5V$, two potentiometers to set reference voltage around $0.138V$ at channel 2 as well as to change the applied voltage between W wire and copper ring, some resistances, and capacitors with $0.1\mu F$ for shorter cut-off time. All the electronics are connected to the breadboard and put inside a big integrated stainless steel box for convenience. During the etching process, we just need to change the 500Ω resistance to frequently make the voltage and current flow stable.

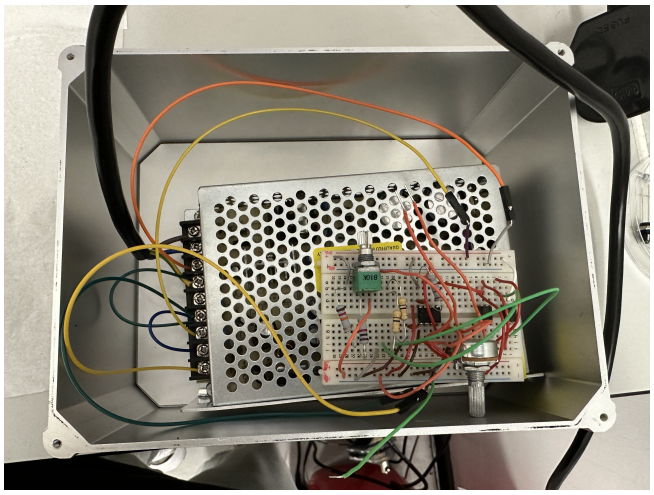


Figure 8: The outside image of etching electronic circuit in Jaecklab

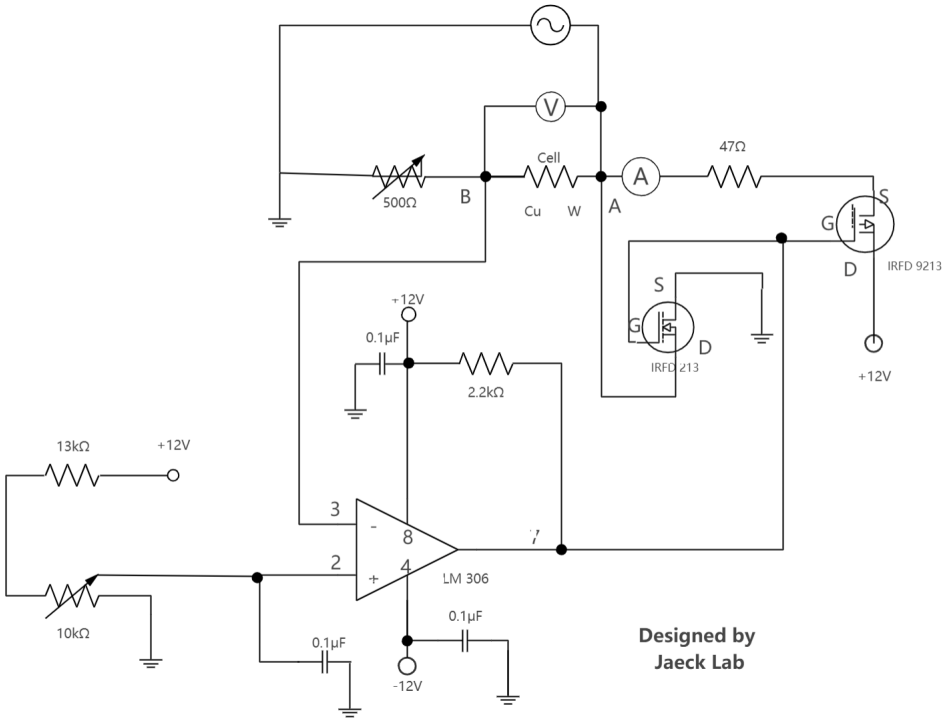


Figure 9: The etching electronic circuit in Jaecklab

As for the tip holding equipment, most of the groups use Omicron tip holders. However, in our group, we design the holder by using Fusion. After the design of the tip holder module, we ask the workshop of HKUST to help us to build it up. The image of the module can be seen in Figure 10. It mainly concludes with a micrometer screw on the top of the metal stand, controlling the Z position and measuring the vertical motion of our tip. The whole system is placed on an isolated experiment set up to prevent any mechanical vibration.

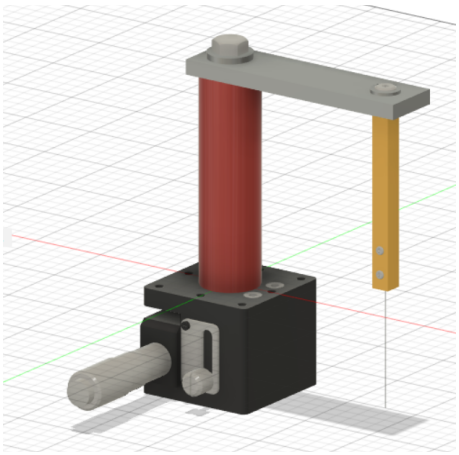


Figure 10: The 3D model of tip holder device by Fusion

2.2 Major parameters we study

Many interesting parameters will effect our final sharpness and shape of the W tips.

First, the most important factor is the cut-off time. The shorter the delay time of the circuit, the better result of our STM tips. The TBS 1052C Series Digital Oscilloscope was used to measure V_B as a function of time for the purpose to record our cut-off time during the drop-off. Usually, the cut-off time is defined as the time that takes V_B to drop to ground potential. In our lab, we consider using a resistance-capacitance circuit to decrease the switching time. The Figure 11shows that our cut-off time is about $600ns$ each time, which is the same as many papers and books.

If we get the cut-off time of about $600ns$ and monitor proper other parameters, it is easy to get a tip with a radius of curvature(ROC) of about $50nm$[6].

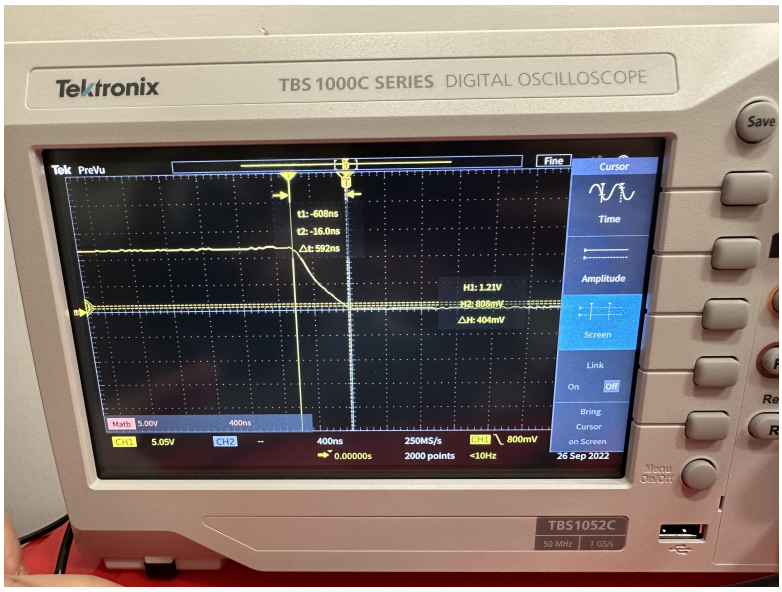


Figure 11: The cut-off time read from oscilloscope

What else, the biased applied potential on the tips at a constant etching current will affect the final products. According to some researches[6][9], the current started to increase when cell potential is about $0.5V$. Increasing the potential from $0.5V$ to $4V$ will increase the reaction rate which means that it will take less time for us to etch one tip. It is only when the voltage larger than $4V$ that the tips will naturally drop off because of the reaction energy in the equation 3. The W tip will generate a thick oxide film which is significant to prevent further reaction at the lower part of the tip inside the KOH solution. Although the oxide does not block 100% of the etching, it does block a significant amount, and it is possible to see the oxide coating the tip and sinking in the water during the etching process.

However, if the etching voltage is too large, the tips could be blunted on the apex owing to the rate of final formation as well as further etching on the tips at the end of the fabrication process. Thus, our lab choose a suitable range of voltage varied from $3.5V$ to $6.5V$ at a constant etching current of 15 mA.

Other parameters include the concentration of the solution and the length of the W tip inside the solution. We found that the etching time will become longer as the OH^- concentration is consumed. If the submerged part of the wire increases, the ROC of the etched tip also increases due to the growing weight of the wire below the electrolyte meniscus. Otherwise, the immersed wire is too short, it is difficult to make it drop off because of the meniscus[10].

Generally, our lab studied the relationship between the radius of curvature of the etched tips and the parameters mentioned before. It is important to note that we only change one parameter each time for more accurate conclusions.

3 Results and Discussion

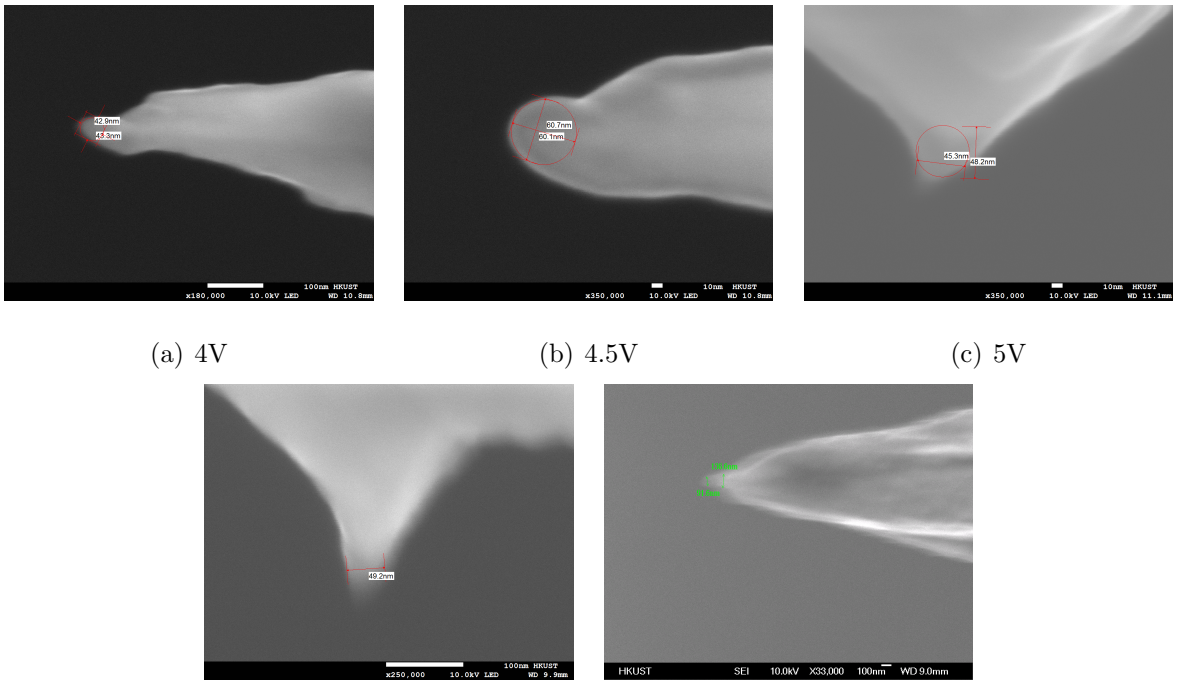
In this part, the results of the submerged etching method over various parameters which were discussed before are presented. All the experiments were conducted at regular room temperature in Room 2237. Some example and their results are shown in Table 1. The images were taken from the optical microscope and scanning electronic microscope(SEM).

Table 1: Parameters and results

Figure in	**Geometry**	**Vol(V)**	El.Conc.(Molar KOH)	Length(mm)	Radius(nm)
Figure 13(a)	Promising	4	2	1	53
Figure 11(a), 12(a)	Promising	4	2	2	21
Figure 13(c)	Not Promising	4	2	5	100
Figure 12(b)	Not Promising	4	3	2	100
Figure 11(b)	Promising	4.5	2	2	30
Figure 11(c)	Not Promising	5	2	2	23
	Not Promising	5	3	2	150
Figure 11(d)	Promising	5.5	2	2	25
Figure 11(e)	Promising	6	2	2	45
	Promising	6	3	2	70

3.1 Applied voltage

In our experiment, we tried voltage from $4V$ to $6V$, the raw data of the etched tips is shown in Table 1.



(a) 4V (b) 4.5V (c) 5V

(d) 5.5V (e) 6V

Figure 12: SEM images of the apex on different voltages

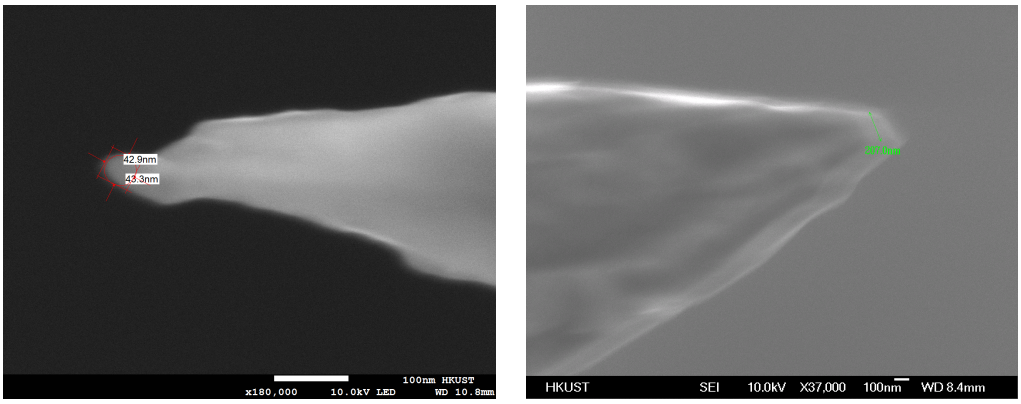
The sample etching condition is shown in Table 2. We experimented with the same condition except for the voltage.

Table 2: sample etching condition 1

Material	**Tungsten**
Electrolyte	2N KOH
Immersion depth	2mm
Counter electrode	Copper
Initial Current	10mA
Reference Vol	0.138V
Etching time	10min

In every case, we kept the voltage constant and the current decreased during the etching as the tungsten wire dissolved. The values of $3, 4, 4.5, 5, 5.5, 6V(Volt)$ have been tested(see Table 1). The high voltage caused a lot of hydrogen gas which bubbled up and disturb the homogenous etching on the wire surface. We have test 3 Volt. However we only get a blunt tip with very bad shape. That means the lowest voltage of 3 Volt resulted in a larger radius of the apex. Thus from the experimental result, we found that the optimal value is around 4 Volt.

3.2 Concentration



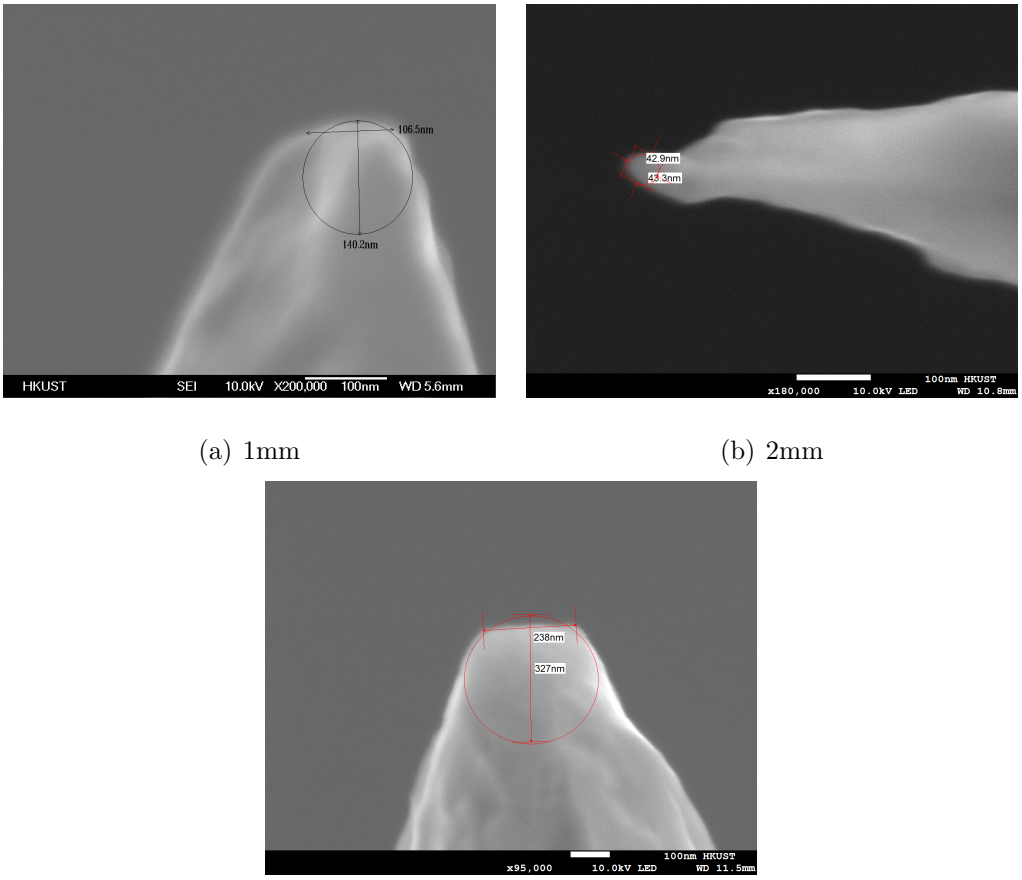
(a) 2M (b) 3M

Figure 13: SEM images of the apex on different concentration

Experiments were carried out using 4 different concentrations of electrolyte(1, 2, 3, and 5 Molar of KOH solution) as presented in Table 1. The high concentration of 5 Molar KOH, caused a very fast and uncontrolled reaction and resulted in a very large radius (which is not shown in Table 1). As the concentration becomes lower, the reaction becomes more controlled and fine generating a very small radius on the apex. However, lower density will increase the etching time. For example, in our experiment, the 1 Molar KOH took us about an hour to complete the etching. As a result, we need to adjust the W wire frequently to prevent it from dirt in the air. It is so difficult to wait and adjust so we did not get a good

tip at 1 Molar solution. From our result, the suitable concentration is around 2 Molar.

3.3 Length of the lower part inside solution



(a) 1mm

(b) 2mm

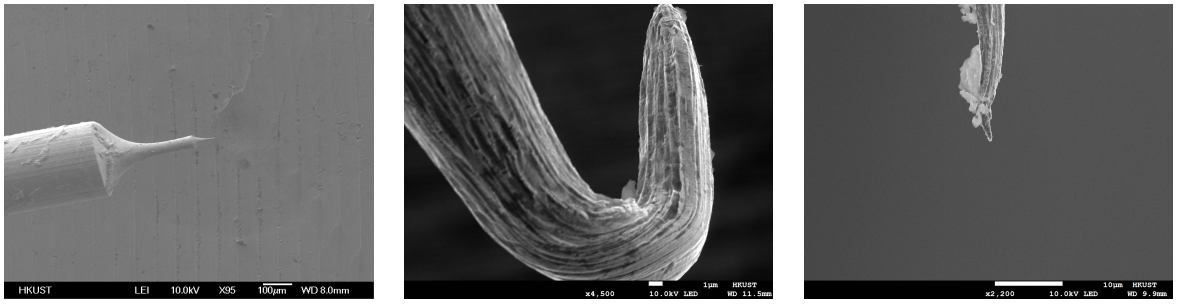
(c) 5mm

Figure 14: SEM images of the apex on different lengths

With the purpose to optimize the mass, the length of the lower part was varied. As shown in Table 1, we etched tips with different lengths like $1, 2$, and $5mm$. For the case of 1mm, the mass of the lower part was not enough to drag the lower part down. For the case of 5mm, the tips started to get a larger radius of the apex. A good explanation is that the gravity force becomes large enough to overcome the ultimate tensile strength for tungsten per the area of a few square nanometers. From our experiment, we found that 2mm was

the best value.

3.4 Unexpected effects



(a) (b) (c)

Figure 15: SEM images of the apex on different unexpected conditions

In our experiment, we met a lot of failures and now want to discuss some common unexpected results. Figure 14.a shows discontinued etching results as a reason for the movement on tips after the start. The vertical position of the tip is very important. We should avoid moving it until it drops off.

Figure 14. b shows a bent tip. The reason is that the tip came in contact with the tweezers when we put it inside the tip holder. Whenever we find such a thing happening, there is no doubt that something went wrong and we should etch another new tip.

Figure 14. c shows a dirty tip. Cleanliness is a very important issue in the etching process. In every step of the process, the wire and tools (tweezers, holders, etc.) have to be cleaned with deionized water, acetone, and isopropanol. The copper ring (cathode) has also to be cleaned in the same way and make control with the optical microscope that the tip is clean before every step. Otherwise, any dirt will destroy the final tip.

Here we offer the correct way to keep the device and products clean. Once completing the etching process, the tips were transferred to the cleaning station. At this station, the tips were washed first with de-ionized water and then with ethanol and isopropanol to remove any kind of contaminants and oxides. The washed tips might still have rides. Finally,

to remove the oxide layer, the tips were whirled in concentrated hydrofluoric acid (HF) for about 30 s. After cleaning, the etched tips were transferred to the optical microscope which was used to image the tip surfaces. The optical microscope is a simple way to identify the etched tips' shapes.

4 Conclusions

In this work, we built up and designed our electronic etching circuit and tip holder device. It showed that our etching facility had almost the same effect as some expensive commercial etching equipment. The aim was to optimize the preparation method for reproducibility. We have produced several well-defined geometry tips with an apex radius of a few nanometers.

We studied many parameters which affect the shape and sharpness of the portion of the wire that remains above the air/electrolyte interface following DC drop-off. After investigation, the following conclusions can be drawn.

We thought the cutoff time of the etching circuit is the most important factor. The faster the cutoff time, the sharper the tip. As for our etching circuit, it has a cutoff time of about $600ns$, which can be seen from Figure 11. For the electrolyte concentration of 3 Molar KOH, the reaction will be very fast and uncontrolled. The lower concentration of 1 Molar KOH produced a smaller apex radius but increased the total etching time. The best choice of concentration is 2 Molar. As for the applied voltage, the higher voltage will create a large number of hydrogen gas molecules which will bubble up and disturb the surface stability. In our case, the optimal value of the voltage was about 4 Volt. The lower voltage of about 3 Volt will cause a bad shape of a larger radius of the tip. When the length of the lower part becomes shorter than $1mm$, it is not heavy enough to drop off. If the length of the lower part inside the solution is longer than 5mm, the gravity force becomes so large that the W tip will drop off before it has a sharper apex.

Keep in mind that it was an experimental work and a different combination of the parameters will give different results. The main focus of our research was to understand the electrochemical etching process and then produced many tips using custom equipment designed by ourselves.

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6 Appendix A: Procedure for STM-tip preparation with electrochemical etching of W wire in KOH solution

Start with filling fresh DI-water from the system put on gloves and clean everything (i.e. tungsten wire, ring, tweezers, tip holders, holders, and reservoirs) with acetone, then isopropanol, and then DI-water.

- Prepare 2 Molar KOH concentration. For 100ml DI-water interferes with 11.2g KOH.
- Cut some tungsten wire. The length depends on your need. Keep in mind to make the W wire straight with tweezers.
- Adjust the W wire to let it go through the center of the copper ring.
- Connect the circuit according to Figure 9. Set the trigger about $1mV$ on the oscilloscope for the record of the cutoff time. The detailed operation of oscilloscope can be seen on the manual. If we want to change the reference voltage,we can adjust the $10k\Omega$ potentiometer.
- Start the electrochemical etching with a voltage of 4 Volt between W and copper ring by adjusting the 500Ω potentiometer. Keep an eye on the process and adjust the resistor frequently to make the voltage or current constant. During the etching process, the current keeps stable at the beginning of the process. After some time, the current will decrease little by little. We can adjust the 500Ω potentiometer counterclockwise. The etching process will take about 10 minutes.
- After drop off, remove the desk and take out the upper part of the W wire. Put it in a tip holder filled with fresh and clean isopropanol. Finally, use the N_2 to blow the dirt on the tip.

7 Appendix B: Some problems and solutions while etching tips

- The end of the W tips could not naturally drop off even after a long time

  Solution: Improve the applied voltage or the concentration of KOH.

- Some oxide dirt attaches to the tip

  Solution: Keep all the things clean and follow the procedure in Appendix A.

- Abnormal shape of the tip

  Solution: Do not move the desk or interfere with the surface dramatically when etching.

- Other things we can add later.