EMERGING MINDS
JOURNAL FOR STUDENT RESEARCH

ISSN 2976 - 9094
EMJSR 2023, (1):81-89
https://doi.org/10.59973/emjsr.24

Received: 2023-07-18
Accepted: 2023-07-28
Published: 2023-07-29

Electrochemical Etching Method to Fabricate Tips for Scanning Tunnelling Microscopes using Tungsten

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Abstract – The goal of this project was to create a tungsten tip for use in STM machines. This project started with the research of existing methods for creating STM tips through electrochemical etching. During initial testing, the electrolyte solution was identified as a powerful variable. Once a suitable solution had been found and optimized, we made changes to the etching procedure while observing the difference between outcomes. In this way we developed a method, which could create consistently sharp tips. The focus moved from finding a method for constant power etching to pulse etching. The advantage of constant power etching was that it gave a good indication of how sharp the tips could get while being very fast, allowing for rapid testing of variables and their impact on the outcome. The advantage of pulsed etching was the ability to control how sharp the tips created were. The final procedure was to pass 4V through the equipment (see figure 9), pulsed on for 1 second and off for 8 seconds. When the wire breaks the voltage is to be turned off and the tip retrieved. Excellent tips have been produced using this method, as evidenced in this report.

Keywords – STM tips; Electrochemical etching; Tungsten tips.

1. Introduction

Tungsten STM tips are crucial for atomic level material imaging [1], which is useful in quality control of high precision components like computer transistors. This paper outlines what appears to be a more entry level setup for STM tip creation compared to other papers. Many papers use specialist equipment that will not be present in this paper and will instead use basic lab equipment: A DC power supply, Crocodile clips, a clamp stand and a 100ml beaker.

To make this project a success it would be important first to observe what work has already been done in this field of research and how it is possible to adapt and develop that work. The paper "Method of electrochemical etching of tungsten tips with controllable profiles" by Chang, Wei-Tse, et al. [2] contained a lot of information that was directly applicable to the goal of the project and was used as a baseline for any experimentation and modifications. This paper is an expansion of this, combined with other methods.

As well as presenting a unique method for tungsten tip etching, this project also shows how one might adapt a method like the one described by Chang et al. [2] to fit their own application, as it is unlikely that identical equipment is available as well as wanting the same outcome.

2. Theory

To understand the decisions made in this project there are two separate concepts that need to be understood:

a) How STM works and why a sharp tip is needed;
b) Electrochemical Etching;

STM is a type of microscope that can take atomic level images (including atoms) on a materials surface. To understand this project, it is important to understand why a tip needs to be sharp. The process involves placing a

sample on a conductive mount and applying a voltage to a very sharp tip. Electrons from the tip will travel to the sample creating a current, this current can then be measured and observed to see if the tip is close or far away from a surface atom. If the tip is close to the surface the current will increase and if it is far away from the surface the current will decrease. This process is then repeated thousands of times to produce an image of the surface, the tip scans line by line to produce an output like figure 1.

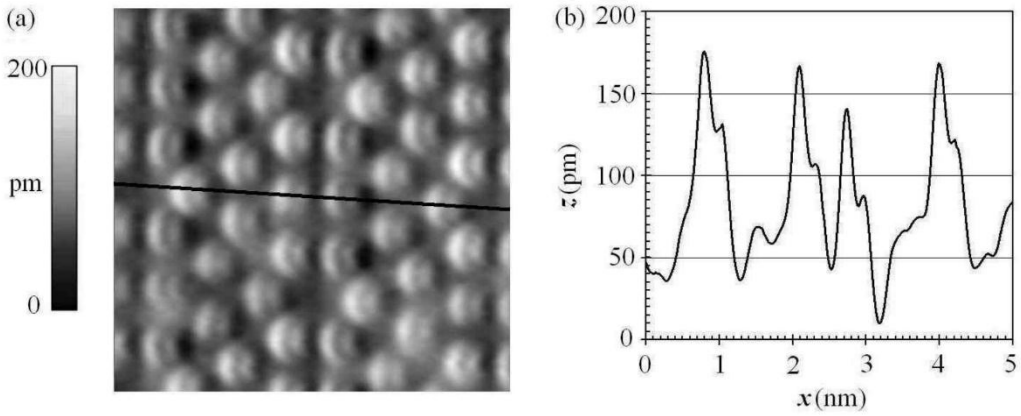


Figure 1. STM output examples [1].

On the left of figure 1 a black line can be seen representing the path the tip would have taken to produce the graph on the right. This process of scanning can only take place if the tip being used is extremely sharp, the best images would use a tip that is a single atom wide. This is because all the atoms at the top of the tip would be able to tunnel and other atoms on the surface of the material than the one directly below could be closer. As a result of this the image would be lower resolution or if the tip is too poor it would be entirely noise.

Electrochemical etching is a process by which applying a voltage between two electrodes in an electrolyte solution one is reduced to nothing and deposited onto the other. The electrode that loses the atoms is called the Anode and the one that receives them is the Cathode. For this application we want to remove tungsten from the wire until a tip is formed, so tungsten wire is used as an anode. Copper cathodes are commonly used however other conductive materials can be used instead. For this application a cathode ring must be used as the etch must be even the entire way around the tip. If a cathode like a carbon rod was used it is possible that the tip would etch more on the side closer to the rod. The solution used in this application is sodium hydroxide its purpose it to allow the current to flow from anode to cathode which allows the transfer of particles to take place.
The reason why a tip is created, and the whole wire is not just destroyed is because etching takes place at an increased rate around the meniscus of the liquid. This results in the wire becoming thinner until it can no longer support the weight of the still thick wire below it, this causes the wire to stretch until it breaks. This process forms a very sharp tungsten tip. When a voltage is applied across the cathode and anode constantly there is a lot of gas created at the anode. This can interrupt the etching process or result in an uneven surface on the tip. Pulsed etching has a ratio of roughly 1:8 where for every 1 second of active etching there is 8 seconds of reset where the gas is allowed to leave the solution, this results in a very smooth tip.

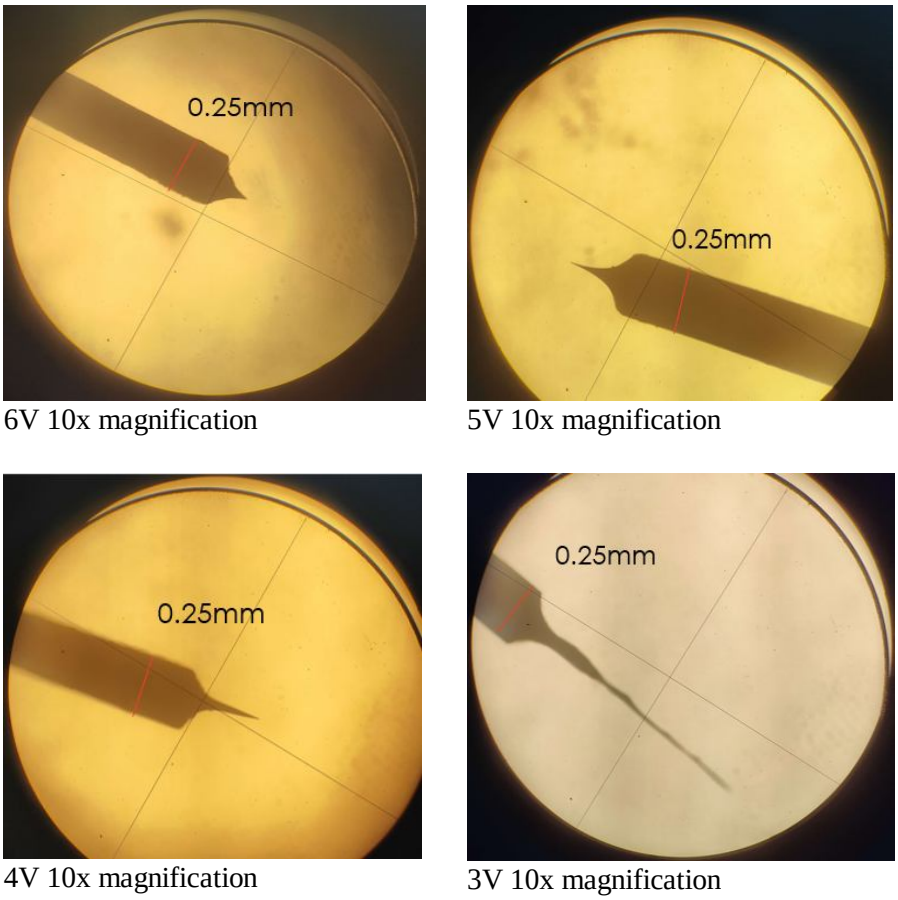
3. Arriving at a methodology

As a reference point, the equipment was set up as close as possible to that described by Chang, Wei-Tse, et al. in the paper "Method of electrochemical etching of tungsten tips with controllable profiles" [2]. The etching was initially unsuccessful, fully etching the tungsten wire and not just at the meniscus which resulted in a blunt piece of tungsten wire as the product.

It was not initially clear what was causing the issue with the etching, so each part of the experiment was altered individually. Initially it was suspected that the voltage was not high enough as the power usage was very low

compared to other etching setups. Despite going up to a voltage of 12V the etch quality did not improve. The equipment like wires and crocodile clips were substituted which had no impact. The sodium hydroxide solution was then diluted from 12 mol to 6 mol. After this change the tip successfully etched although it was still a poor tip.

The first variable that was important to test now that etching was taking place was the voltage. Voltage should have a direct impact on the etch time and therefore the amount of time the tip draws out before it breaks, with a low voltage drawing out a lot and a high voltage creating a very short tip. These predictions were confirmed and observed through the following trial runs.



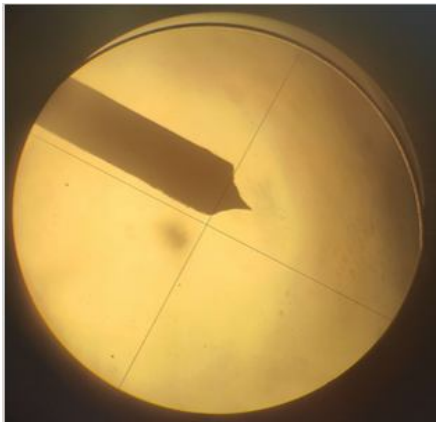
6V 10x magnification | 5V 10x magnification

4V 10x magnification | 3V 10x magnification

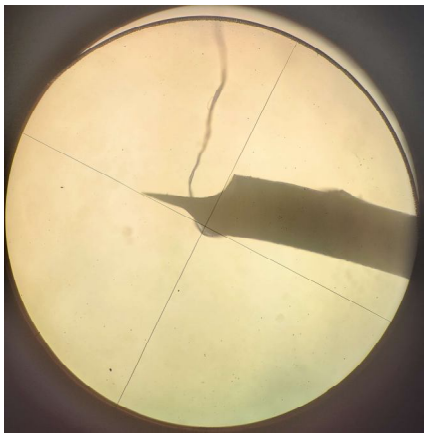
Figure 2. Tungsten tips under optical microscope.

There were multiple tips created for each voltage and the results seemed consistent with 6V being far too short and 3V either failing to etch or having an unusal tip shape as shown above in figure 2. From these experiments it was decided that 4V was the optimal voltage for the application of this paper. It is important to note that the thickness of the wire will have an impact on the voltage required. 0.25mm wire used in this paper is thick compared to other STM tips and so a lower voltage may be needed for smaller diameter wire.

The next variable to optomise was the weight of the tip. Unitl this point the wire had just been submerged in electrolyte solution until it was almost touching the bottom of the beaker. It is also possible to add some weight to the wire so that it will draw out sooner. This should allow control over the tip profile.



6V No weight 10x Magnification



6V Weighted Tip 10x Magnification

Figure 3. Comparison of weighted vs unweighted.

In figure 3 we can see on the left that the tip is extremely short from base to tip compared to the tip on the right that for a 6V tip is long. This increase in length shows that it is possible to influence the tip profile with weight. Although these results are promising as they would allow for tips with good profiles to be made faster (higher voltages take less time) it was another point of possible failure for making this method repeatable. There was no way to convey to another person using a different set of equipment how much wire was below the meniscus as it wasn't possible to measure accurately. With an unweighted tip the amount of wire submerged is roughly the height of the fluid level however with a weighted tip where you wrap the wire around itself to get more mass and it is difficult to replicate. As a result of these two trials, it was decided that 4V unweighted would be the optimal setup.

If this method was to be developed further, it would be important to adjust the other variables that were not explored in this paper:

- Cathode Shape and diameter;
- Cathode material;
- Different voltages at different stages;
- Sodium Hydroxide solution concentration;

There are also variables that were not controlled effectively, and methods should be found to control them:

- Wire weight below meniscus;
- Tungsten wire oxidation;
- Position of anode;

The cathode shape, diameter and material will all impact the effective electric field created. By reducing the distance between the anode and cathode it should increase the speed of the process. Using a carbon cathode instead of copper could influence the conductivity or cost of the setup and would be worth exploring further. As the copper cathode was visibly covered in tungsten after roughly 10 etches, it had a small impact on the current flow.

A combination of voltages could produce the most optimal tips at acceptable speeds. With etch speeds varying from 2 – 10 minutes based on voltage it could be beneficial to etch at 6V for the first minute and then 4V for the remainder. This could take a 4V etch from 6 minutes to 3 minutes.

After the issue with the initial sodium hydroxide solution was fixed it was decided that as long as the tips would etch then the concentration should be kept the same because it was the most difficult variable to change due to COSHH safety concerns.

Although control variables were kept the same as much as possible some things were not possible to accurately control. For example, the wire weight below the meniscus was not constant between runs, the wire was roughly the same as it was kept a few millimetres from the base of the beaker however there would have been some variation.

Oxidation of tungsten wire could have effects on the etch of the tungsten wire, in the future it could be good to put the tungsten wire in the vacuum furnace before etching and remove the oxide coating. This would achieve two things: first it would make etching more consistent as all runs would have the same composition of wire and second it would reduce the chance of damage to the tip after fabrication. Any manipulation of the tip after fabrication risks damage. Heating tungsten to 850^0 C will however affect the mechanical properties of the wire and it is possible that these changes will make it unsuitable for etching, for example the wire might become too brittle.

Once a satisfactory method had been found for constant current etching, some minor modifications had to be made for pulse etching. The power supply had to be programmed such that it would pulse for 1s and then off for 8s. This ratio could be changed however all bubbles and visible evidence of the reaction had fully dispersed at 8s, so it was a good benchmark.

The pulsed tips were then analysed under SEM and compared to constant current tips to see if the added complexity of pulsing was necessary.

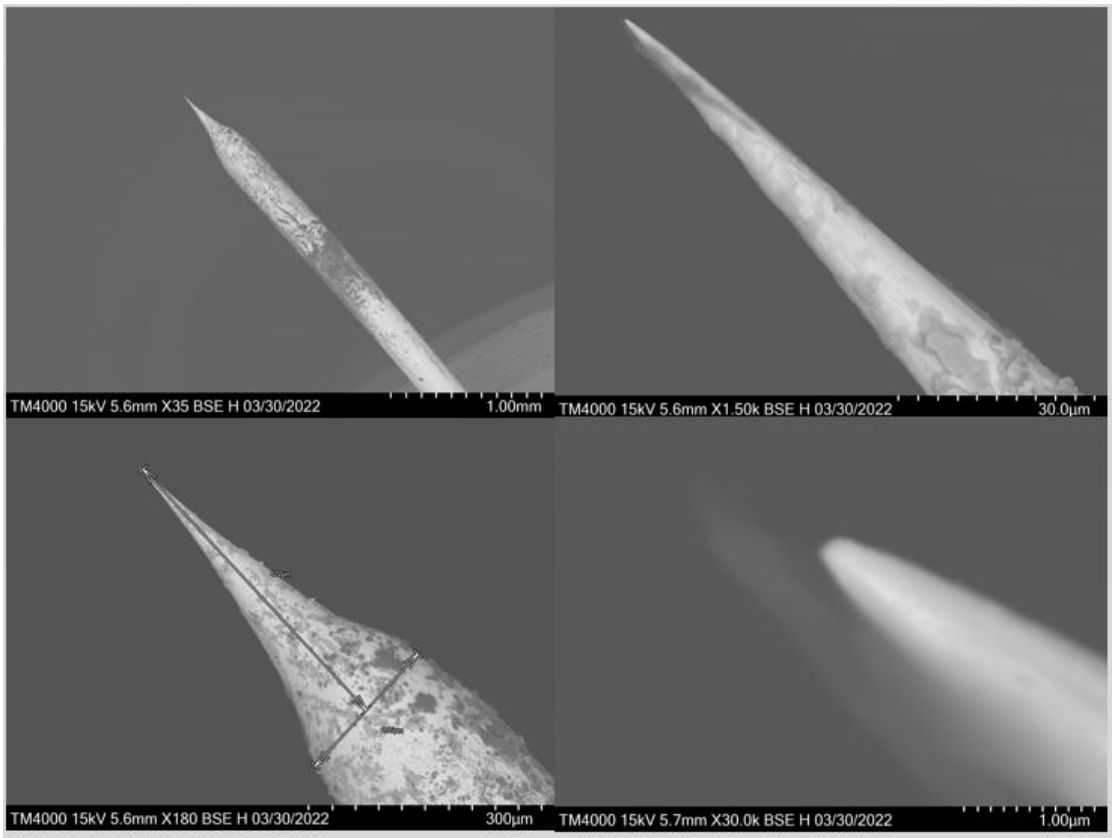


Figure 4. 4V pulsed tip SEM various magnifications.

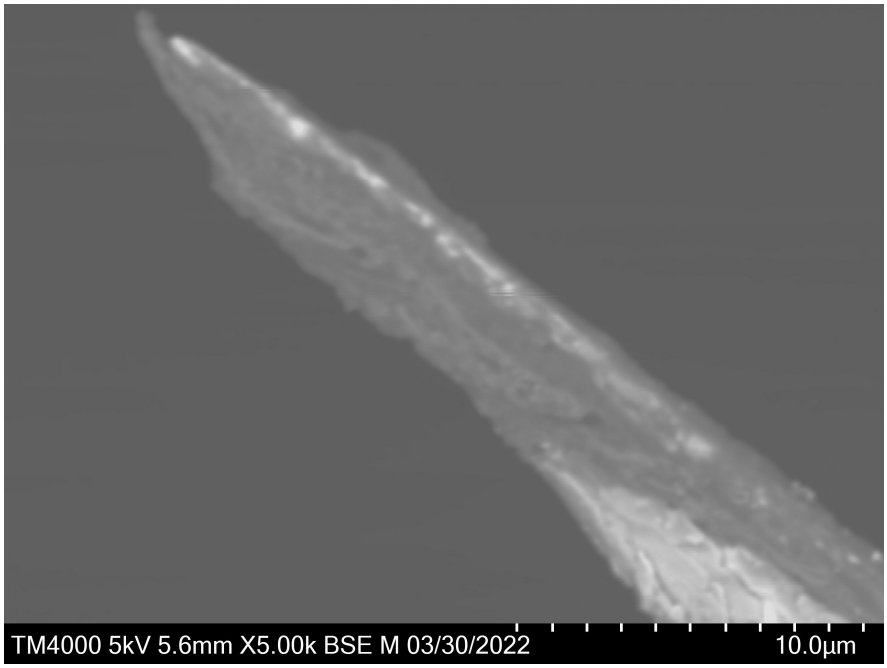


Figure 5. 4V Pulsed tip SEM 5000x magnification.

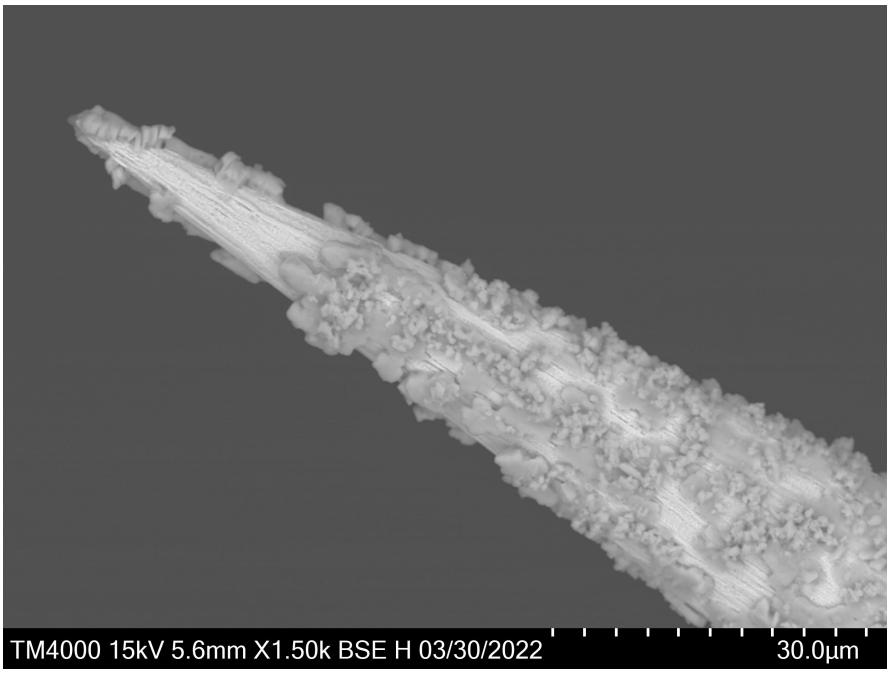


Figure 6. 4V Constant.

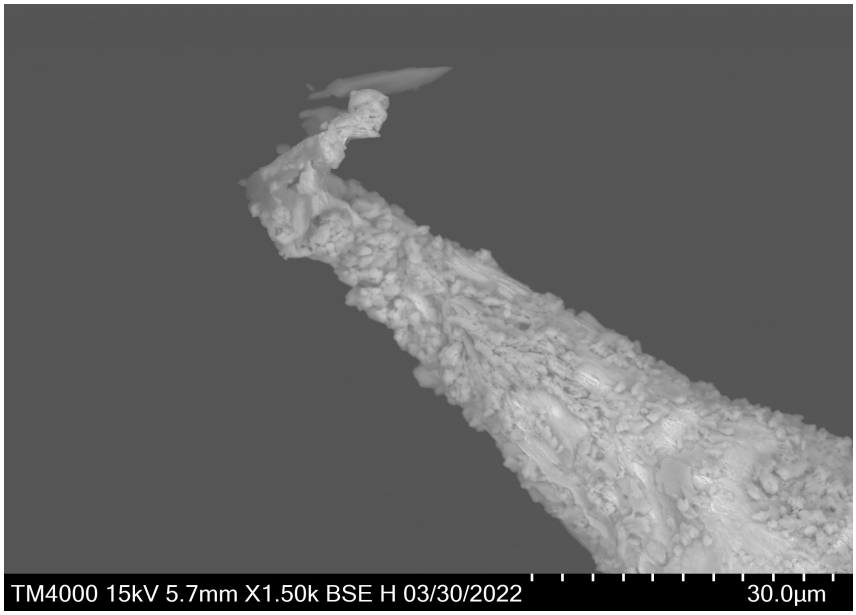


Figure 7. 4V Constant.

By observing Figures 4-7 it can be seen that constant current etching produces tips with crystal growth. However pulsed etching created clean and sharp tips. It is possible that there is some modification that can be made to the method that reduces the crystal growth however no method could be found.

The next stage was to attempt to use these tips in STM [3]. Unfortunately, as expected the tips were not conductive due to the oxide layer and failed to get any tunnelling current. After creating 10 tips and placing them in a vacuum furnace at 850^0 C for 30 minutes (Brought up to 850 and held there for 30 minutes) the tips were used in STM. These tips also produced no images however they did successfully get a tunnelling current even though the output was entirely noise.

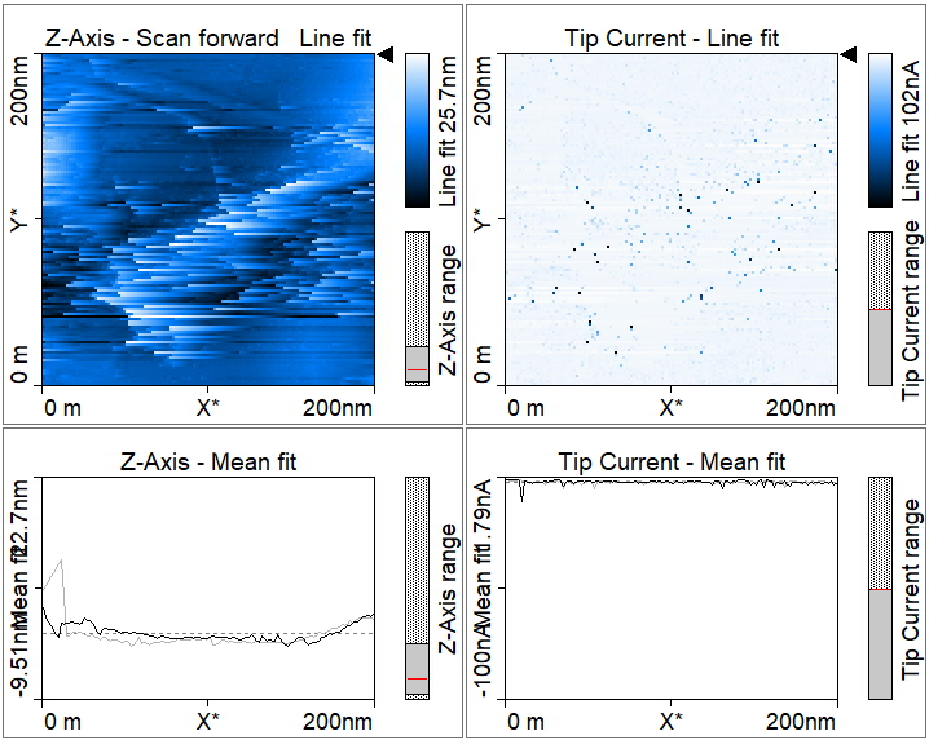


Figure 8. STM output.

4. Methodology

The following equipment has been used:

12V DC power supply
2 cables
2 crocodile clips
Copper Cathode
Tungsten Wire
30ml 6mol NAOH solution
100ml Beaker
Clamp stand

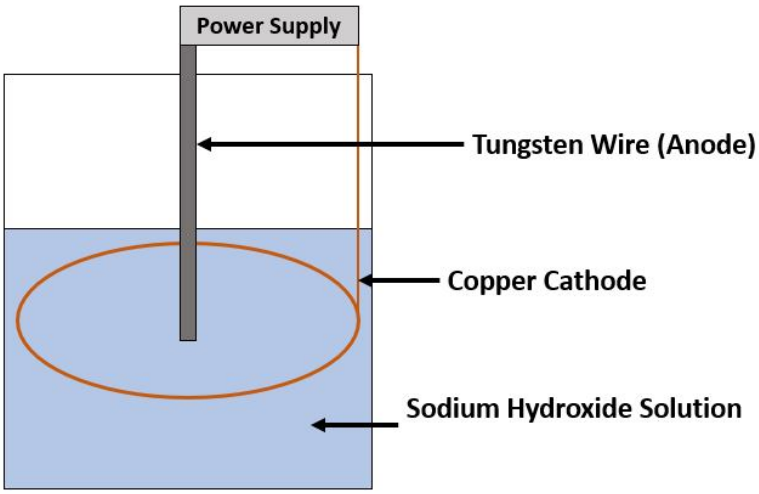


Figure 9. Schematic diagram of the experiment.

The equipment should be connected as shown in figure 9 with the tungsten wire suspended in the solution from the clamp stand almost touching the bottom of the beaker. The anode must be as close to the centre of the cathode as possible.

Constant Voltage
Apply a 4V output from the power supply and stop the power when the wire breaks off at the meniscus.

Pulsed Voltage
Configure the power supply such that it has a ratio of 1:8 on: off. For example, if your power supply is on for 1 second then it should be off for 8 seconds. Apply a 4V output with this ratio of on/off until the wire breaks off at the meniscus.

The section of wire still in the crocodile clips will be the tip and the section of wire that falls to the bottom of the beaker must be removed and discarded.

This method will produce extremely sharp tips as shown in figure 4.

For removing the layer of oxide from the tips place them in a crucible and heat at 850^0 C for 30 minutes in an atmosphere of Argon. Place the tips in membrane boxes as soon as possible after allowing them to cool in Argon atmosphere. This process has very limited evidence of being effective. The tips that underwent heating did successfully get a tunnelling current however the image produced was entirely noise so another method should be explored.

There are some possible adaptations that can be made if the equipment is available:

Place the beaker on a jack stand and never adjust the clamp stand. This will ensure that the wire is always in the exact same place relative to the cathode each time. It will not help to centre the wire, but it will give consistent results.
Highly accurate scales could measure the amount of wire submerged. The amount of water displaced by the wire is about 20 milligrams, so it is possible to measure this by placing the beaker on scales before submerging the wire.

5. Conclusion

No STM images were produced from this project. However the combination of SEM images and Optical microscope images of the tips shows that with small modifications to the process a high-quality tip could be produced. The main factors that caused this method to fail are: Unknown furnace procedure, Poor transportation and storage procedures and the use of a weak STM machine. The core method could be significantly improved upon, but it has been demonstrated that sharp tips are produced so it must be a combination of these final three processes that either ruin, fail to remove contaminants or damage the tips.

For this method to be consistent at producing sharp tungsten tips more research should be focused primarily on the removal of oxide layer from the tungsten. Due to time restrictions, it was only possible to heat a single set of tips. There was limited literature available for removal of oxide layer from tungsten using only a vacuum furnace so a generic method of heating the tips rapidly to 850^0 C, holding them there for 30 minutes and rapidly cooling was used. SEM images compared to tips that had not been heated would have been useful in assessing the impact of this process.

When considering the outcome of this project it is also important to acknowledge the limited equipment available. Other than the vacuum furnace all equipment used is extremely low cost compared to other STM tip manufacturer setups. If modifications could be made to this method that allowed for pre-de-oxidised wire to be used, then the method would provide a real option for tip creation in facilities that cannot afford to buy STM tips. The method used in this paper will probably not be applicable to most research however for industrial applications it is foreseeable that it would be cheaper to produce STM tips on site using a refined and adapted version of this method than to purchase them.

Acknowledgements

I would like to thank Dr. Esmaeil Namvar for their guidance throughout the project as well as Callum Price for supervising my lab work and making themselves available.

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