Tungsten tips of different diameters for STM prepared by electrochemical etching method

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Abstract

In the Scanning tunneling microscope (STM) different kinds of tips is used. The shape of the tip (cylindrical) is very important for the functioning of an active probe. In the present work, STM tips are fabricated from tungsten metal wire. The electrochemical etching method was used to prepare tungsten tips. This method generally involves the anodic dissolution of the metal electrodes. Two types of etching methods are AC and DC itch. Tips prepared by DC etch method have a hyperbolic shape and are much sharper than AC etch and are preferred for high-resolution STM imaging. In the present work, DC etching process was preferred. During the etching process current with respect to time was noted for different diameters of the tungsten wire. It was observed that current decreases with respect to time because of the decrease in the diameter of the wire during the etching process. The sharpness and shape of the tip depending on the concentration of the electrolyte (KOH) medium, the depth of the wire in the electrolyte medium, natural vibrations, and leveling of the surface. SEM study shows a sharp tip of size in nanometer scale was obtained.

Keywords: Electrochemical etching, tungsten tips, electrolyte

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Introduction

were believed to have nanometer protrusions at the apex which function effectively as an active probe. To avoid multiple active probes, minimize vibrations, and have a high aspect ratio, there is the increased use of tip shapes with cylindrical geometry ending on a point and having an apex. radii significantly less than 100 nm. STM tips are typically fabricated from metal wires of Tungsten (W), Platinum-Iridium (Pt-Ir), or Gold (Au) [1-3]. The requirements of STM tips are based on the condition that we are interested in and should ideally terminate to a single atom but the macroscopic shape of the tip is of little importance. Since the tunneling current is exponentially dependent on the tip surface separation, the tip atom closest to the sample surface always gives the major contribution to tunneling current [4]. For topographic STM studies of larger-scale structures on relatively rough surfaces, the macroscopic shape of the tip also becomes important. A tip with a relatively large cone angle fails to penetrate into deep and narrow grooves on the sample surface. The preparation of the tip should therefore be optimized with regard to its geometry for STM studies of rough surfaces [5].

There are different methods for the preparation of the tip like electrochemical etching, chemical etching, ion milling, cathode sputtering, flame polishing, mechanical shaping, cutting, machining, etc. [6]. Out of these, electrochemical is a very simple method to prepare sharp tips [7]. The sharpness of the tips is one factor, which affects the resolution of the STM images. The shape of the tips is dependent on the meniscus, which surrounds the wire at the air electrolyte interface The sharpness of the tip is related to the tensile strength of the wire, and how quickly the electrochemical reaction can be stopped once the wire. Tip-making by electrolysis method involves the reaction of the specimen with an electrolyte. Ideally, the reaction is not chemical but occurs only under the influence of electric driving forces. The parameters like active electrolyte, solvent, electrolyte concentration type of voltage and magnitude of voltage, etc. are important and should be considered for making specific tips [8].

2. Experimental technique

2.1 Electrochemical etching

The tip has crucial importance for imaging. The etching generally occurs by the removal of material in a selective way, that is its rate is different for different parameters such as crystallographic orientation, composition, microstructure, etc. The electrochemical etching procedure generally involves the anodic dissolution of the metal electrodes. There are two ways of electrochemical etching i.e. AC etch or DC etch. Each procedure gives a different tip shape. The AC etch tips have a conical shape and much larger cone angles than DC etch tips. The DC etched tips, on the other hand, have the shape of a hyperboloid, are much sharper than AC etch, and are preferable for high-resolution STM imaging [9]. Tips are prepared by the DC drop-off method in which etching occurs at the air/electrolyte interface causing the portion of the wire in solution to "drop off" when its weight exceeds the tensile strength of the etched region of the wire [10].

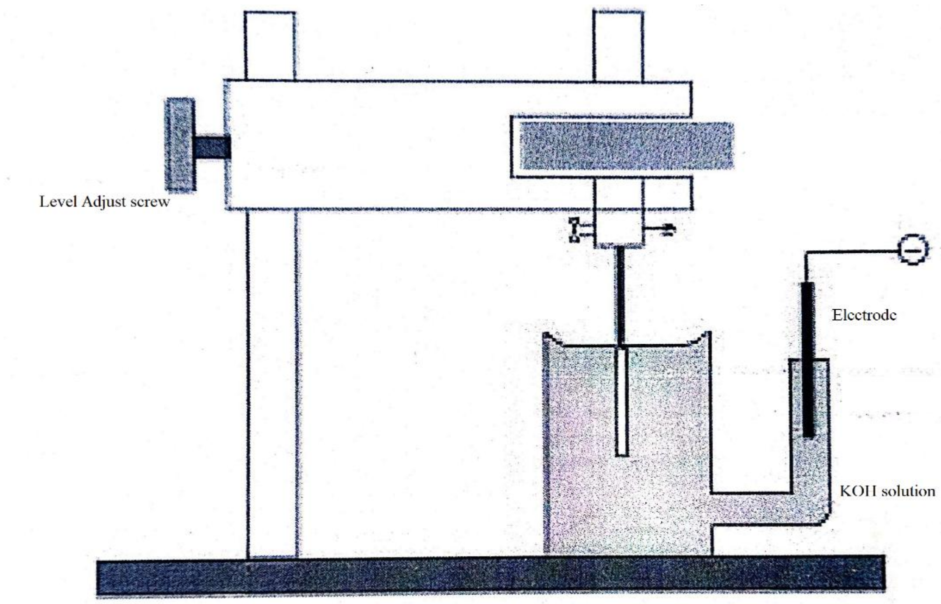

Figure 1. Electrochemical etching process

Equations 1,2, and 3 give the overall reaction governing this particular electrochemical etching[11]

cathode: $2H_2O + 6e^- \rightarrow H_2(g) + 2OH^-$ (1)

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

Resultant: $2W(s) + 2OH^- + 2H_2O \rightarrow 2WO_2 + 3H_2(g)$ (3)

The tungsten is first oxidized to intermediate tungsten oxides; these are in turn non-electrochemically dissolved to yield these soluble tungstate anions which show the greatest stability in a basic medium. The reaction also involves the reduction of water; bubbles of gaseous hydrogen and OH^- ions are thus produced at the cathode (equation 1) [11].

2.2 Generation of the tip

One can wonder how this reaction actually generates a tip shape out of a cylindrical wire. The explanation [equation 3] roots in the fact that capillary forces yield the formation of a meniscus of solution around the tip wire when it is immersed into the electrolyte. The shape of the meniscus plays a very important role in determining the final shape of the tip, as the etching rate at the top of the meniscus is a lot slower than at the bottom. This can be explained by the presence of a concentration gradient due to the diffusion of OH^- ions to the tip.

"Furthermore, the soluble tungstate produced during the reaction flows towards the lower end of the tip wire, generating a dense viscous layer, which prevents this region from being etched away" [11]. Thus, a necking phenomenon is observed in the meniscus where the etching rate is enhanced. At some point, this part of the wire becomes so thin its tensile strength cannot sustain the weight of the lower end of the wire; the latter breaks off, and a sharp tip is left behind. This is commonly referred to as the "drop-off" method [11, 12], and it is illustrated in figure2.

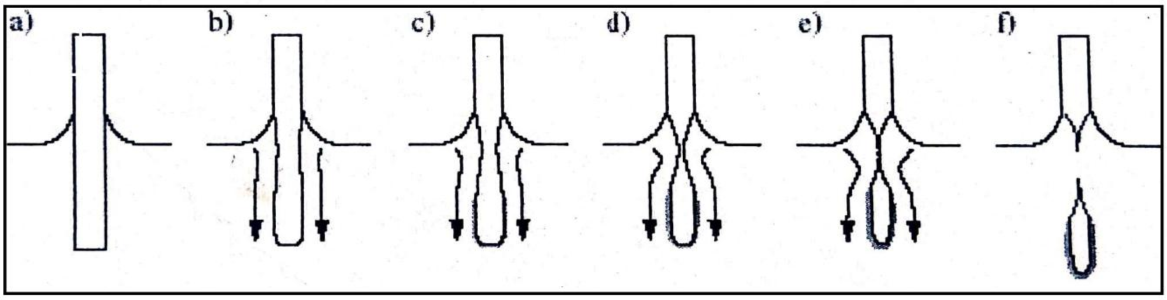

Figure 2. Illustration of the drop-off.

3. Results and Discussions

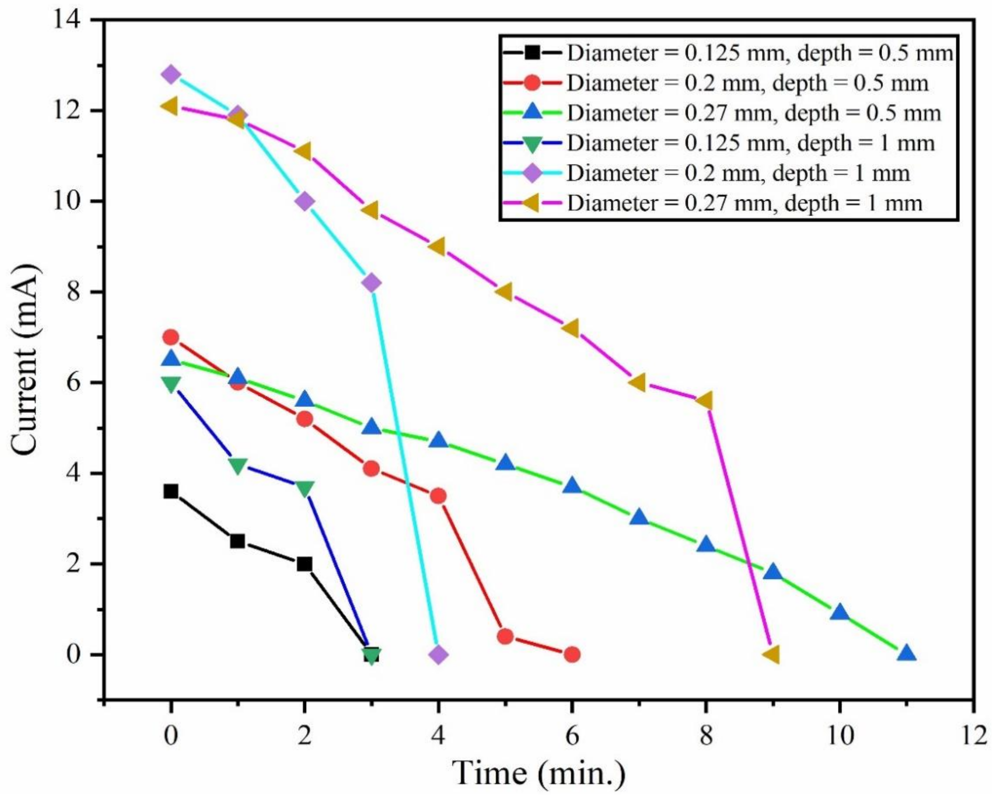

Figure 3. Current against Time plot for different diameter of the tungsten wire.

The graph of current(mA) Versus Time(minute) for the tips of the different diameters shows that during electro-chemical etching current decreases with the progress of time since, as the area of the wire decreases during etching the resistance goes on increasing and gets the value infinity when drop off occurs. The starting value of the current was different for different diameters. The higher diameter has a greater starting value of the current. The starting value of the current reduces with a decrease in the diameter due to a reduction in the area of the cross-section of the wire provided that there was no oxidation of tungsten (W) wire [9,13].

The starting current for different diameters is shown in table 1. The etching time for different diameters of wire was different. It is observed that the higher diameter wire takes more etching time as shown in table1. The time also depends on the concentration of the KOH solution. The concentrated Solution takes less etching time. The etching time also depends on the depth of the wire in the KOH solution. If the diameter of the wire is the same and the depth is different; the etching time is different. The larger depth takes less etching time. Because if the weight was more; then the downward force on the wire goes on increasing and due to this downward force wire breaks [14]. The etching time for different wires is shown in the table given below.

Table 1. Etching time, Starting current for diameter and depth of the wire in electrolyte.

Diameter of the wire (mm)	Depth (mm)	Concentration of the KOH	Etching time (second)	Starting current (mA)
0.125	0.5	2N	154	3.6
0.125	1.0	2N	132	6.0
0.2	0.5	2N	554	3.7
0.2	1.0	2N	360	12.8
0.2	2.0	2N	330	14.4
0.3	0.5	2N	1320	3.9
0.3	2.0	2N	480	22.5

The better sharpness and shape of the tip depending on the following parameters. **i) The depth of the wire in solution:** If the diameter of the wire was smaller and its depth in solution was more, then after etching length of the tip was also larger and such a tip damaged very easily. Therefore, for a good shape of the tip adjust the appropriate depth of a wire in KOH solution If the diameter of a wire is small then adjust less depth of the wire in KOH solution [15]. Some satisfying examples are shown in table 2 given below.

Table 2. Appropriate depth of tungsten wire in electrolyte and concentration of electrolyte for different diameter of the wire

Diameter (mm)	Depth (mm)	Concentration
0.08	Less than 0.5	1 N
0.125	0.5 to 1.0	1 to 2 N
0.2	1.0	2 N
0.3	1.0 to 1.5	2 N
0.4	1.0 to 3.0	2 to 3 N

ii) Effect of concentration: If the tip diameter was less then used a less concentrated KOH solution. Because the Diameter was less and the concentration was more the etching takes place in a few seconds adjustments of this process were not possible accurately [15]. As the diameter increases then use a more concentrated solution for saving time as shown in table 2.

iii) Effect of natural vibration and unlevelled surface: At the time of etching, the system was vibrating which affected on shape and sharpness of the tip. The shape was not uniform and the sharpness was also not well as we required. The non-uniform shape of the tip was also due to the unlevelled surface of the KOH Solution in which the tip was immersed [15]. The figure given below shows the required shape and unexpected shape due Unlevelled surface.

In the present study, we have used metal tungsten wire of different diameters. We are expecting the variation in the radius of curvature with the diameter of a wire. The higher diameter will cause the stub to drop off much sooner due to increased weight. Since drop-off occurs when a small part of the wire has been etched away, these tips will have a corresponding larger radius of curvature than those of a lesser diameter. It is found that many of these tips get bent at the very end of the tip because there are two forces acting on the wire, one is the weight of the stub pulling down on the wire and the other is the wire pulling up on the Stub. as long as the downward force does not exceed the tensile strength of the neck, it will not break. However, when the weight exceeds This strength the stub breaks off removing downward force on the wire. As a result, the material at the end of the tip may experience a slight recoil and bend the tip.

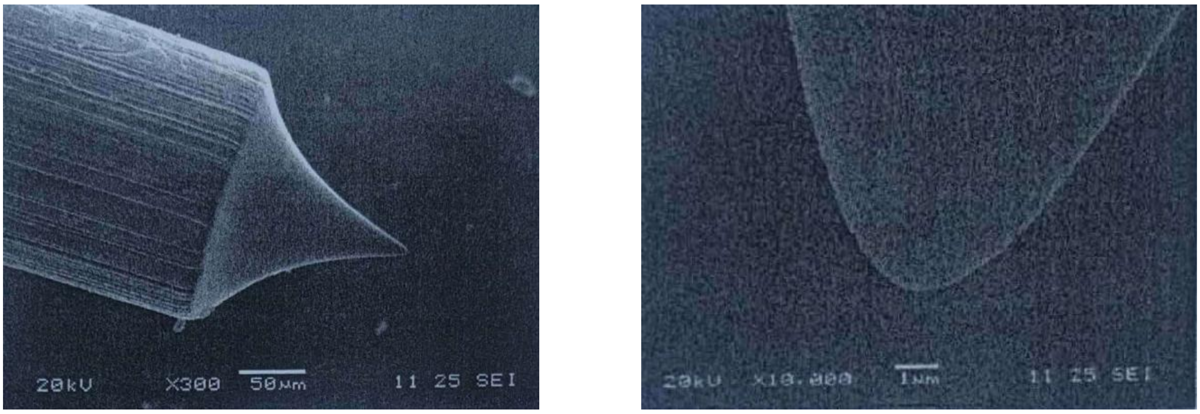

Figure 4 (a) SEM image of tungsten tip (Diameter = 0.2 mm, Depth = 0.5 Conc. = 2 N)

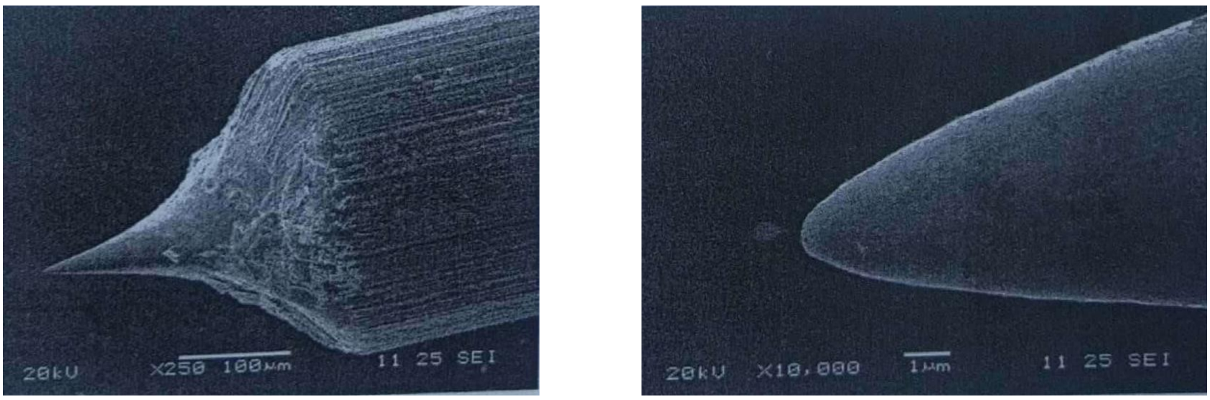

Figure 4 (b) SEM image of tungsten tip (Diameter = 0.2 mm, Depth = 1.0 mm Conc. = 2 N)

4. Conclusion

Current decreases with respect to time for different diameters of the tungsten wire during electrochemical etching. The depth of the wire is very important to get a better shape of the tip. For a smaller diameter of the wire adjust the small depth of the wire in the electrolyte solution during the etching process. The selection of the proper concentration of the electrolyte (KOH solution) is very important to get the appropriate size and shape of the STM tip. The study focused on the anodic dissolution of the tungsten (W) wire in KOH, we believe that the results are generally applicable to the other metals. From the SEM image, it is observed that the size of the tip was obtained on a nanometer scale.

Disclosure statement

No potential conflict of interest was reported by the author(s).

References

1. So/rensen, A. H., Hvid, U., Mortensen, M. W., & Mo/rch, K. A. Preparation of platinum/iridium scanning probe microscopy tips. Review of scientific instruments, 1999, **70(7)**, 3059-3067. doi.org/10.1063/1.1149891
2. Zhang, J., Wang, P., Zhang, X., Ji, H., Luo, J., Wang, H., & Wang, J. Systematic electrochemical etching of various metal tips for tunneling spectroscopy and scanning probe microscopy. Review of Scientific Instruments, 2021, **92(1)**, 015124. doi.org/10.1063/5.0011896
3. Bhushan, B., & Marti, O. Scanning probe microscopy—principle of operation, instrumentation, and probes. In Nanotribology and Nanomechanics. Springer, Cham. 2017, 33-93, doi.org/10.1007/978-3-319-51433-8_2
4. Kolmer, M., Brandimarte, P., Lis, J., Zuzak, R., Godlewski, S., Kawai, H., ... & Szymonski, M. Electronic transport in planar atomic-scale structures measured by two-probe scanning tunneling spectroscopy. Nature communications, 2019, **10(1)**, 1-10. doi.org/10.1038/s41467-019-09315-6
5. Bushan, B. (Ed.). Handbook of micro/nano tribology. CRC press. 2020
6. Ekvall, I., Wahlström, E., Claesson, D., Olin, H., & Olsson, E. Preparation and characterization of electrochemically etched W tips for STM. Measurement Science and Technology, 1999, **10(1)**, 11. Doi.org/10.1088/0957-0233/10/1/006
7. Duong, T. H., & Kim, H. C. Electrochemical etching technique for tungsten electrodes with controllable profiles for micro-electrical discharge machining. International Journal of Precision Engineering and Manufacturing, 2015, **16(6)**, 1053-1060. doi.org/10.1007/s12541-015-0136-8
8. Tahmasebipour, G., Ahmadi, V., Abdullah, A., & Hojjat, Y. Fabrication of STM tungsten nanotip by electrochemical etching method. International Journal of Nanoscience, 2009, **8(03)**, 305-310. doi.org/10.1142/S0219581X09006110
9. Ibe, J. P., Bey Jr, P. P., Brandow, S. L., Brizzolara, R. A., Burnham, N. A., DiLella, D. P., ... & Colton, R. J. On the electrochemical etching of tips for scanning tunneling microscopy. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films,1990, **8(4)**, 3570-3575. doi.org/10.1116/1.576509
10. Khan, Y., Al-Falih, H., Zhang, Y., Ng, T. K., & Ooi, B. S. Two-step controllable electrochemical etching of tungsten scanning probe microscopy tips. Review of Scientific Instruments, 2012, **83(6)**, 063708. doi.org/10.1063/1.4730045

11. Le, D. C., Duong, T. H., & Kim, H. C. Design of characteristic parameters for controlling tungsten tip profile during electrochemical etching. Journal of Mechanical Science and Technology, 2014, **28(5)**, 1833-1839. doi.org/10.1007/s12206-014-0330-0
12. Tahmasebipour, G., Hojjat, Y., Ahmadi, V., & Abdullah, A. Optimization of STM/FIM nanotip aspect ratio based on the Taguchi method. The International Journal of Advanced Manufacturing Technology, 2009, **44(1)**, 80-90. doi.org/10.1007/s00170-008-1799-4
13. Kulawik, M., Nowicki, M., Thielsch, G., Cramer, L., Rust, H.-P., Freund, H.-J., … Weiss, P. S. A double lamellae dropoff etching procedure for tungsten tips attached to tuning fork atomic force microscopy/scanning tunneling microscopy sensors. Review of Scientific Instruments, 2003, **74(2)**, 1027–1030. doi:10.1063/1.1532833
14. Ju, B. F., Chen, Y. L., & Ge, Y. The art of electrochemical etching for preparing tungsten probes with controllable tip profile and characteristic parameters. Review of Scientific Instruments, 2011, **82(1)**, 013707 (1-8). doi:10.1063/1.3529880
15. Tahmasebipour, G., Hojjat, Y., Ahmadi, V., & Abdullah, A. Effect of fabrication process parameters on the apex-radius of STM tungsten nanotip. Scanning, 2009, **31(2)**, 65–74. doi:10.1002/sca.20142