NANO LETTERS

2002
Vol. 2, No. 3
191−193

# Reproducible Electrochemical Etching of Tungsten Probe Tips

**Olivier L. Guise, Joachim W. Ahner, Moon-Chul Jung, Peter C. Goughnour, and John T. Yates, Jr.***

*Department of Chemistry, Surface Science Center, University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

*Received November 20, 2001; Revised Manuscript Received January 8, 2002*



## ABSTRACT

**An electrochemical procedure in KOH electrolyte has been developed to reproducibly produce ∼5 nm radius tungsten probe tips. It has been found that a spurious electrochemical etching process, driven by the natural potential difference between an Ir electrode and the W tip, causes rapid tip blunting at the end of the electrochemical etching period. By electrically reversing this potential difference within 500 ns following tip separation, the blunting process is eliminated yielding sharp tips with varying cone angles.**

The preparation of ultra sharp tips is essential for nanometer probe techniques, including STM. Many tip preparation techniques have been developed over the years such as mechanical cutting or electrochemical etching. In this letter, we report the discovery of a post-etching phenomenon during electrochemical etching, which causes tip blunting. We have studied this effect and developed a procedure to prevent such tip blunting. This technique allows the reliable and reproducible fabrication of ultra sharp tips, with a probe radius of 5 nm or less.

Tips are prepared from tungsten wire (Goodfellow, 0.38 mm diameter, 99.95%) and electrochemically etched using the standard "drop off" technique.[1−7] As shown in Figure 1, the tungsten wire is immersed in a droplet of KOH solution (etchant) held by an iridium loop (Alfa Aesar, 99.8%). A voltage is applied between the tip and the loop, so that the tip is the anode and the loop is the cathode. The electrochemical etching reaction then takes place.[8]

The tungsten wire is etched in 2 steps. In the first step (coarse etching), a DC voltage (typically 3 V) is applied between the electrodes using a 2 M KOH etchant solution. In the second step (fine etching), a DC voltage of 0.5 V is applied using a 0.1 M KOH solution as the etchant. We use a special power supply for fine etching. As shown in Figure 2, the current steadily decreases during fine etching. At the end of the etching, a discontinuity of current occurs as the lower part of the wire drops away. The fine etching power supply records this discontinuity and automatically switches off the applied voltage in 500 ns. We added a feature to this power supply. Instead of simply switching off at the end of the etching period, the power supply may also reverse the potential applied between the electrodes. The user can set up the power supply to select between these two options. During etching, the potential $V_1$ is applied between the electrodes. At the end of etching, the potential $V_2$ is either the reverse potential or the natural potential, which exists between tungsten and iridium in the KOH electrolyte.

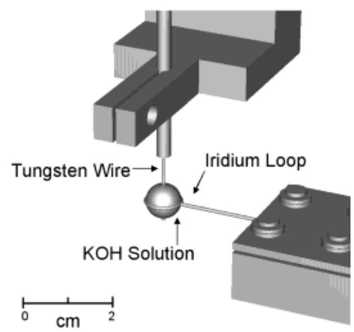


**Figure 1.** Electrochemical apparatus for tungsten tip etching.

After proper cleaning (tips are rinsed with deionized water and methanol after each etching step), tips are characterized by SEM (Cambridge S-90) and by TEM (Hitachi H-800). SEM and TEM images are transferred to a computer and analyzed. We define two parameters to describe a tip, as shown in the inset of Figure 3: the tip radius and the tip cone angle. We approximate the tip end as a sphere whose diameter can be precisely determined by computer image analysis.

In Figure 3, we present measurements of the radius of the tips as a function of the time spent in the etching solution at potential $V_2$. In the first case (flat curve), $V_2$ corresponds to the reverse applied potential, and in the second case $V_2$ corresponds to the natural potential difference between the two electrodes. Time $t = 0$ corresponds to the end of the

* Corresponding author. Tel: +412 624 8320. Fax: +412 624 6003. E-mail: jyates@imap.pitt.edu.

10.1021/nl010094q CCC: $22.00 
**Published on Web 02/27/2002**

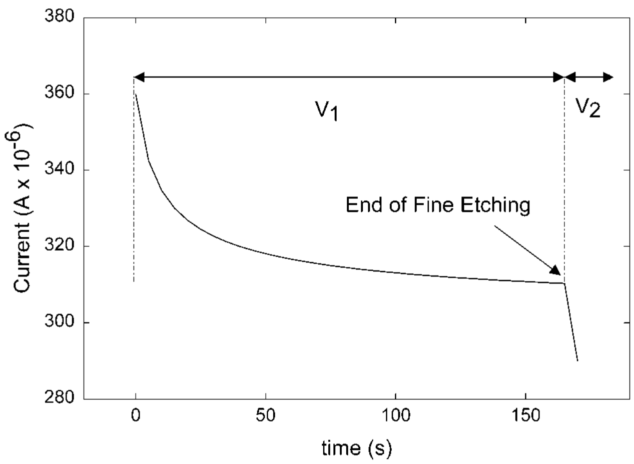


**Figure 2.** Evolution of the cell current during fine etching. The discontinuity in current corresponds to the drop of the lower part of the wire as the etching ends, and activates the automatic power supply switch-off.

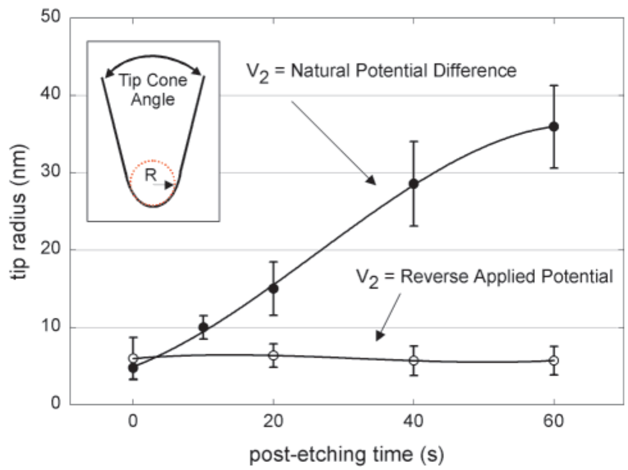


**Figure 3.** Comparison of tip radius evolution for tips prepared with potential $V_2$ as natural bias or reverse bias. Tips have a cone angle of 5°. Inset: Definition of tip radius and tip cone angle.

fine etching. At each etching time, the tip was immediately rinsed with deionized water and withdrawn from the solution. The tips are then characterized by TEM and the tip radius measured. Each data point corresponds to an average of at least 5 tips. The tip cone angle is about 5° for each tip in Figure 3. A rapid increase of the tip radius with time of "post-etching" under natural bias is observed. This increase cannot be solely attributed to the formation in air of an oxide layer since the oxide layer grows by only about 2 nm during 2 days of atmospheric exposure[5] after the tip preparation, whereas the tip radius increases by more than 30 nm for a tip after 60 s of post-etching under the natural potential difference in our case. We believe that this effect is due to electrochemical action under the natural bias occurring between the tungsten wire and the iridium loop when the power supply is switched off. The literature difference between the work function of tungsten and the work function of iridium is 800 mV[9] (for reasonably clean surfaces). The measured open circuit potential difference during an experiment is ~420 mV, with the W tip being positive with respect to the Ir electrode.

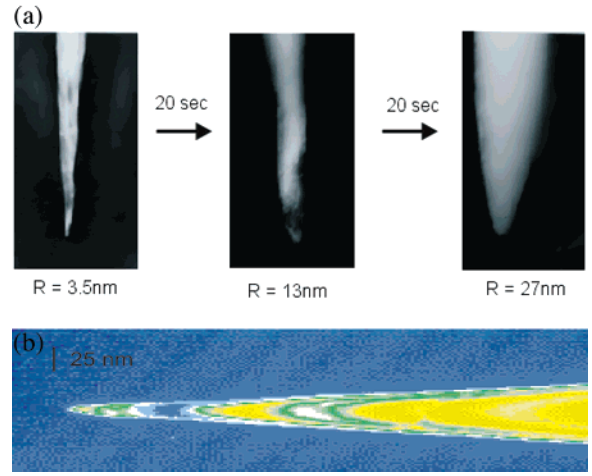


**Figure 4.** (a) Images showing a sharp tip, the same tip after 20 s post-etching, and the same tip after 40 s post-etching. Radius increases from 3.5 nm to 13 nm to 27 nm. (b) TEM image of a typical tip prepared by reverse bias technique. Tip radius is less than 4 nm.

**Table 1.** Effect of Cone Angle on the Rate of Tip Blunting at the Natural Potential Difference

| post-etching time (s) | tip radius (nm) cone angle | | | |
|---|---|---|---|---|
| | 5° | 15° | 25° | 35° |
| 0 | 5 | 5 | 5 | 5 |
| 10 | 10 | 15 | 25 | 30 |
| 20 | 20 | 25 | 36 | 40 |
| 40 | 39 | 43 | 48 | 50 |
| 60 | 46 | 55 | 55 | 59 |

In Figure 3, we note that the use of the reverse applied potential, $V_2$, following the tip separation, results in complete retardation of the increase of the tip radius which occurs when the natural open circuit potential exists.

In Table 1 we provide data for a number of post-etching experiments under the natural bias for tips with various cone angles, ranging from 5° to 35°. The same effect is observed: a rapid increase of the tip radius occurs for all cone angles. It is interesting to notice that the magnitude of the blunting effect increases for increasing tip cone angles.

These experiments demonstrate that the electronic shut-off of the power supply upon tip separation is not by itself a sufficient condition for the production of very sharp tips. If the power supply switches off but the tip is left immersed at the natural potential difference in the solution, the tip radius will then increase with time and the tip will have a blunted-end shape. These observations provide an explanation for a remark by Méndez et al.[4] stating that the lower tip, which falls away, is always sharper than the upper one. The lower tip does not spend as much time as the upper part in the solution after the completion of the etching since after it falls out of the droplet it is not subject to further etching due to the natural bias between W and Ir in KOH solution.

In Figure 4, we present TEM images showing the effect of post-etching. Figure 4a shows first the image of a sharp tip, prepared by applying a reverse potential at the end of

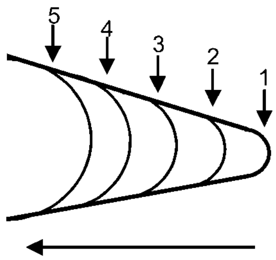


**Figure 5.** Schematic of tip blunting under the natural bias due to post-etching after tip separation. In the case of a tip with a cone angle of 5°, position 1 corresponds to the etched tip with a tip radius of ∼5 nm, position 2 corresponds to the tip radius after 10 s post-etching (tip radius ∼10 nm), position 3 corresponds to the tip radius after 20 s post-etching, and so on.

the etching. The tip radius is determined to be 3.5 nm. After TEM characterization, the tip was dipped again in the etching solution for 20 s with potential $V_2$ corresponding to the natural electrodes bias. A second TEM image shows that the radius increases to 13 nm. The same operation is repeated for an additional 20 s. The tip radius jumps to 27 nm. Figure 4b shows a typical example of a tip prepared by applying a reverse potential at the end of the etching. This very sharp tip has a radius less than 4 nm.

It is important to notice that applying a reverse potential does not eliminate the need for cleaning a tip before use. Cleaning remains a necessary step to remove the contaminants. Instead, the reverse bias freezes any further electrochemical reaction caused by the natural electrode bias in KOH solution.

Figure 5 presents a schematic of the post-etching process. After fine etching, if the reverse bias is applied, a sharp tip can be produced. This corresponds to position 1 on the schematic and a tip radius of about 5 nm. As the tip is dipped again in the solution (power supply off, potential $V_2$ is the natural cell potential) the tungsten wire is etched down moving from condition 1 to condition 5, depending on the time of storage in the electrolyte at the natural potential difference.

The electrical current flowing between the W tip and the Ir electrode under the natural bias condition was measured using an electrometer and found to be in the range $10^{-8}$ to $10^{-7}$A. For the geometrical blunting process shown in Figure 5, the calculated average current to etch from a 3.5 nm radius to a 35 nm radius in 60 s (cone angle = 5°) is only of the order of $10^{-12}$A, assuming a redox process producing $W^{6+}$ as $WO_4^{2-}$. On the basis of this 4−5 order of magnitude ratio of currents, the schematic etching process shown in Figure 5 must be accompanied by electrochemical etching along the shank of the tip.

Additionally, on the basis of these studies, we developed a second technique for preventing further etching due to the natural bias: we added an electrically actuated valve connected to a reservoir of deionized water. When the power supply switches off, the valve opens quickly, releasing the water. The tip is then automatically rinsed and no further etching occurs. This system is not as efficient as the automated bias reverse, since the time required for the automated rinsing is about 2 s compared to 500 ns for freezing the electrochemical reaction by reversing the electrical bias.

In conclusion, we have developed a simple procedure for the preparation of very sharp tungsten tips with radius of 5 nm or less. This method produces tips in a very controlled and reproducible manner. These tips are useful for STM and other probe applications.


**Acknowledgment.** We thank ARO under DURIP sponsorship and DARPA for support of this project.


## References


(1) Anwei, L.; Xiaotang, H.; Wenhui, L.; Guijun, J. *Rev. Sci. Instrum.* **1997**, *68*, 3811.
(2) Bourque, H.; Leblanc, R. M. *Rev. Sci. Instrum.* **1995**, *66*, 2695.
(3) Klein, M.; Schwitzgebel, G. *Rev. Sci. Instrum.* **1997**, *68*, 3099.
(4) Méndez, J.; Luna, M.; Baró, A. M. *Surf. Sci.* **1992**, *266*, 294.
(5) Müller, A.-D.; Müller, F.; Hietschold, M.; Demming, F.; Jersch, J.; Dickmann, K. *Rev. Sci. Instrum.* **1999**, *70*, 3970.
(6) Nakamura, J.; Mera, Y.; Maeda, K. *Rev. Sci. Instrum.* **1999**, *70*, 3373.
(7) Oliva, A. I.; Romero, A.; Peña, J. L.; Anguiano, E.; Aguilar, M. *Rev. Sci. Instrum.* **1996**, *67*, 1917.
(8) Chen, C. *Introduction to Scanning Tunneling Microscopy*; Oxford University Press: New York, 1993.
(9) Fomenko, V. S. *Handbook of Thermionic Properties: Electronic Work Functions and Richardson Constants of Elements and Compounds*; Plenum Press: New York, 1966.



NL010094Q