An integrated approach for producing nanometer radius tungsten probes

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ABSTRACT:

A fundamental requirement in the quest for atomic resolution in NSOM, and STM is that the end of the tapered tip diameter used in the probes must be atomic. In this report, we present a fairly reproducible electrochemical etching procedure of tungsten wire to produce probe tips.

Introduction:

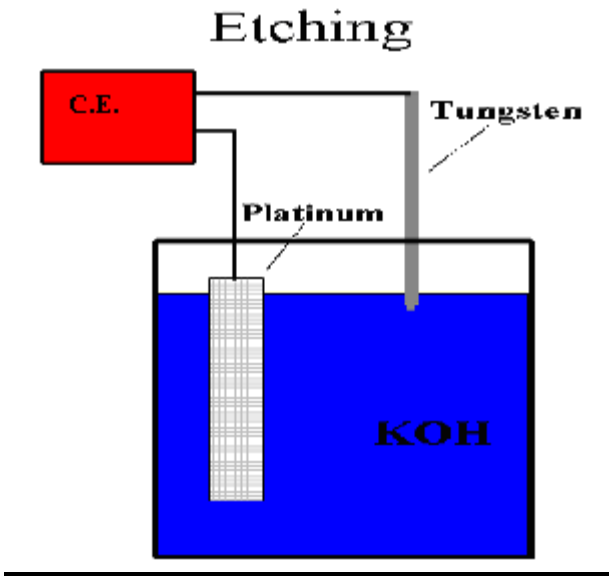
Near field, optical microscopy is based on the detection of non-propagating waves in the near-field region. The near-field region is defined as the region away from the sample that is less than the wavelength of the incident light. Near field optics has been developed to attain a spatial resolution with optical imaging to limits well below the limits λ of Abbe and Raleigh criterion. The Abbe-Raleigh resolution is overcome in two ways: aperture and aperture less NSOM. In the apertureless NSOM , a sharp metallic tip is used[1].

Etching Metallic tips

The size, shape, and cleanliness of metallic tips are very important for the resolution of NSOM and STM. Tips not well prepared or cleaned can yield several mini-tips, if there are several tips, the tip from which the electrons tunnel might change during a scan yielding multiplying imaging features [2].

A popular procedure to generate metallic tips is by electrochemical etching of a metal wire. Tungsten wire is mostly adopted for such purposes due to a number of reasons. The most important reason is that tungsten (W) can produce an extremely sharp tip in a single electrochemical reaction involving fairly mild chemicals [1]. Our tips are made from 0.010" diameter tungsten wires. Smaller diameters are little

difficult to find appropriate holders and bigger ones do not produce the same fineness as this diameter.



Experimental details

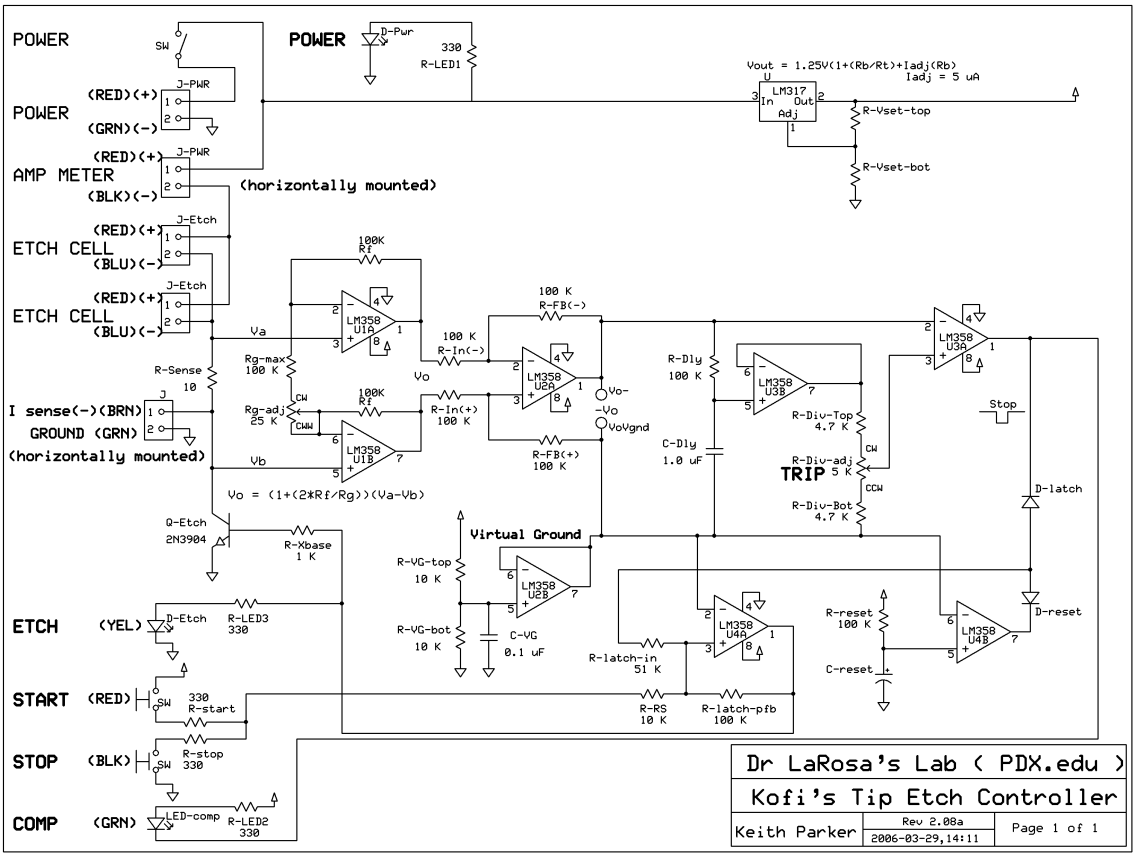
A sketch of the experimental set-up is shown in figure (I) above. The wire is partially submerged into a base solution of potassium hydroxide (KOH) which also contains a counter electrode. A potential difference is then applied to the solution with the tungsten being the anode and a counter electrode for a specified amount of time using the control electronics (C.E.), this simple procedure yields a tip. In the production of tips, accuracy is paramount and delay in shutting of etching current will lead to blunting of the tips, thus far, this approach of using controller electronics to control the start, monitor the current and automatically shut of the current makes our approach comparable to others in literature. The real advantage in our procedure is the fact that it can be easily implemented and the tips are reproducible.

Details of the control electronics of the C.E. are discussed in the next section.

CONTROL ELECTRONICS:

A schematic diagram of the control circuit is shown in figure three below

Figure 3. Schematic set up of tip Etch Controller



Overview of the C.E. :

The purpose of this circuit is to monitor the current flowing through R-sense and cut-off the current (and holding it off with a latch) when there is a sudden significant drop in the sensed current draw.

V-in(max) = 12 VDC

I-etch(max) = 150 mA

VIRTUAL GROUND: (U2B)

The Virtual Ground provides a low-impedance voltage at Vcc/2 for the instrumentation amplifier that requires a "virtual" pair of positive and negative power supplies from a single voltage.

A voltage (R-VG-top & R-VG-top) provides Vcc/2 which is buffered by the voltage

follower configured op-amp (U2B) to form the Virtual Ground. A decoupling capacitor (C-VG) is used to reduce noise. The Virtual Ground is also used as a reference voltage for the ground based reset circuit.

CURRENT SENSE & CONTROL: (R-Sense & Q-Etch)

The current is sensed by measuring the voltage developed across the sense resistor (R-Sense).Current flow is controlled by the transistor (Q-Etch) operating in a saturated mode. While base current is limited by a resistor (R-Xbase).

INSTRUMENTATION AMPLIFIER: (U1A, U1B, U2A)

The Instrumentation Amplifier is a classic design that uses a high-impedance differential input stage and a differential to single-ended op-amp with the output referenced to the Virtual Ground

REFERENCE DELAY: (U3B)

A sample of the voltage is delayed by the resistor (R-Dly) and capacitor (C-Dly), buffered by a voltage followered configured op-amp (U3B), and then divided by the resistive voltage divider (R-Div-Top, R-Div-adj, & R-Div-Bot) to for the delayed reference voltage.

COMPARATOR: (U3A)

The comparator compares the current voltage to the delayed reference voltage. When the current voltage is less that the delayed reference voltage (from the reference voltage divider) the output of the open-loop op-amp (U3A) goes low.

An isolation diode (D-latch) forms an effective "open collector" output so that only a low output forces the cut-off latch to the OFF state and a high output has no effect on the cut-off latch.

CUT-OFF LATCH: (U4A)

This section latches the current off when the comparator circuit commands it to with the "Stop" signal and provides manual START & STOP switch inputs.

OP-AMP LATCH: - The latch is implemented with an op-amp (U4A) that uses positive feed back (via R-latch-pfb) to hold its state. The latch input resistor (R-latch-in) sets the latch to OFF because it has significantly lower resistance than the positive feedback resistor (R-latch-pfb). Diodes (D-latch & D-reset) prevent the latch from being reset to ON.

START/STOP SWITCH: - The START/STOP switch is a momentary action SPDT (single pole double throw) with a center (default) OFF position. It connects either Vcc (START) or ground (STOP) via resistor R-RS to the cut-off latch to manually force it to the desired state. The START/STOP switch always dominates the latch setting because the resistor R-RS is significantly lower in resistance than the resistor R-latch-in.

RESET CIRCUIT: (U4B)

The reset is simply an RC delay (R-reset & C-reset) compared to the Virtual Ground (Vcc/2) by an op-amp (U4B). An isolation diode (D-reset) forms an effective "open collector" output so that only a low output forces the cut-off latch to the OFF state and a high output has no effect on the cut-off latch.

INDICATORS:

The "ETCH" LED (D-Etch) is on while the etch current transistor is on, supplying etche current. The "POWER" LED (D-Pwr) is on while power is applied to the circuit.

Etching Parameters

Once etching is complete the probe formed has a conical shape ending with a diameter in the order of hundreds of nm. We observed that the final shape of the tip is dependent on several parameters such as:

- The choice of the counter electrode
- The concentration of the electrolyte
- The etching time/cut of current
- The immersion of the wire

The choice of counter electrode is extremely important, since it can affect you overall results. Platinum emerges to be a suitable candidate since it has a higher redox potential than tungsten. Therefore platinum would not take part in the reaction [3]. Stainless steel also works very well as a counter electrode

The wire is partially submerged into a base solution of potassium hydroxide (KOH) for electrochemical etching. A potential difference is then applied to the solution with the tungsten being the anode for a specified amount of time. The following reactions take place [3]

$$\text{cathode}: 6H_2O + 6e^- \rightarrow 3H_2(g) + 6OH^-$$

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

$$W(s) + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2(g)$$

From the above reaction equation, it is obvious that gaseous hydrogen is produced at the cathode, disturbing the meniscus area. To avoid this disturbance the cathode is shielded from the anode either by placing the electrodes in separate beakers connected with a bridge or by surrounding it with a glass tube [1].

A limitation of this etching process is that a lot of contaminants consisting of H, C, O, etching residuals and tungsten oxide. These oxides cause unstable tunnel currents and the tip loses some of its metallic behavior, as SEM results showed in later in the section suggest.

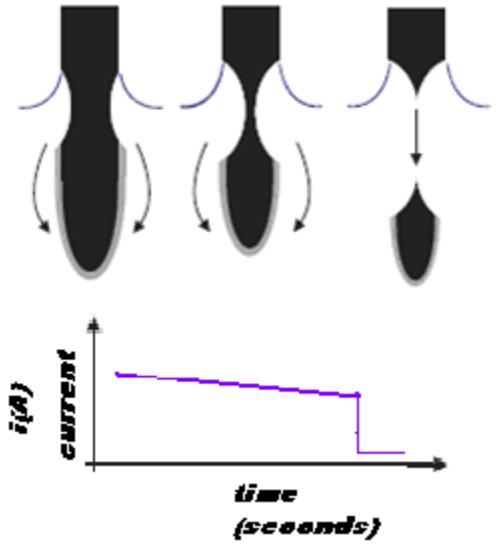


Figure ii. Schematic diagram showing the wire breaking off at the neck. The graph indicates the variation of current as a function of time. The tip is formed at the moment the current drops suddenly

Choice and Concentration of electrolyte

Some publications report of using Noah as an alternative with good results [3] . However, we observed that that using a KOH (potassium hydroxide) as an electrolyte yields favorable results. A 2M KOH is used as an electrolyte and 3.0V Dc is used to provide a bias voltage for the etching reaction. As the etching progresses the current between the anode and the cathode decreases, because the resistance of the cell increases when the area of the wire in the electrolyte decreases.

The wire breaks at the neck that is formed during etching (see figure ii), in this case the whole etching takes place within several minutes. The current is usually between 200mA and decreases steadily, till the critical current at which at which the more dense layer formed at the meniscus breaks off, at this point the multi-meter registers zero current.

The concentration of electrolyte is very crucial, our investigations using 2M, 3M, up to 7M KOH reveals that, for a fixed applied voltage, lower concentration implies longer etching time while increasing concentration leads to rapid etching periods. The reaction is extremely rapid and violent at high concentration and applied voltages; sometimes the violent nature of the reaction does not make it feasible to obtain a tip with appropriate dimensions.

Increasing the applied voltage using a fixed concentration of an electrolyte also leads to a similar effect of a very rapid reaction. We observed that a low Dc voltage unlike an Ac voltage does not encourage the formation of abundant gas bubbles. The rapid production of abundant bubbles at a given time tends to disturb the meniscus of the electrolyte.

The etch-cut off current:

The etch-off current is very crucial to the formation of a sharp tip, the longer current continues to flow in the through the circuit after the drop off, etching would continue and

the tip would be blunt. To avoid this situation, we used controller electronics to automatically shuts of the current once "drop off" occurs.

The length of immersion and the shape of the meniscus:

Inserting an appropriate length perpendicularly would yield a suitable tip. In the next few pages, I present an SEM picture of a tip that was inserted perpendicularly into the electrolyte by about 0.2mm. In this case, no visible drop off occurred and the tip formed is not suitable for NSOM applications.

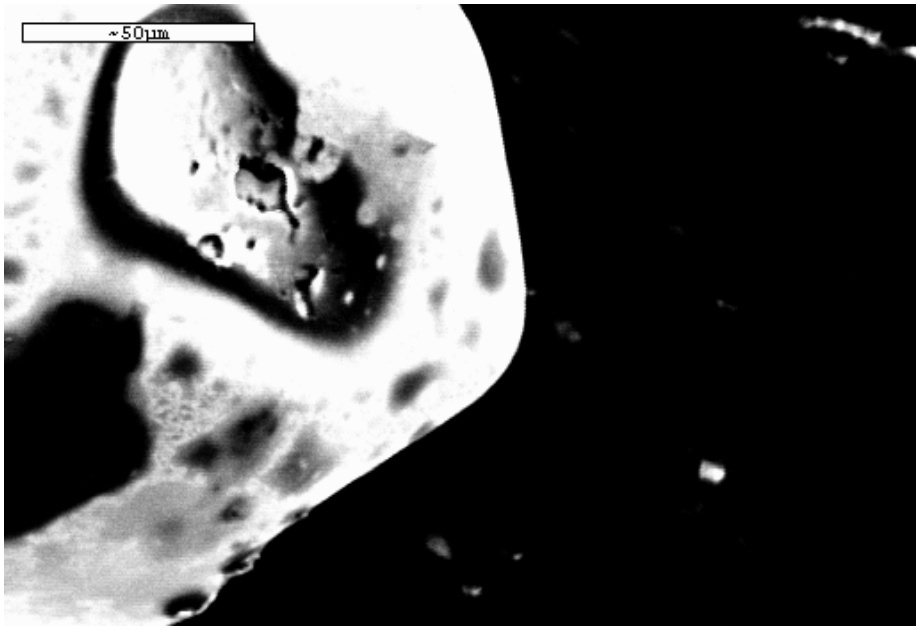


Figure 3. Short immersion of tungsten wire yields a blunt tip. Note that in this case there is no drop off, just erosion of the tungsten metal

Next we inserted a tip perpendicular and the length of the immersion was about 4mm. The tip formed in this case is symmetrical. An SEM image formed is shown below

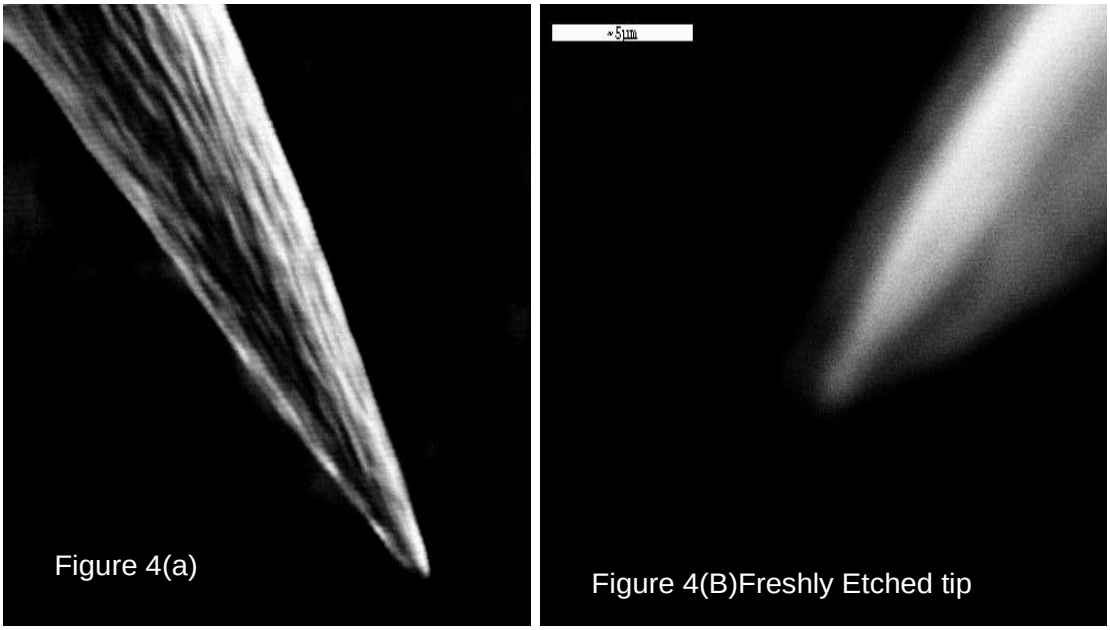


Figure 4. SEM Pictures of tips formed by perpendicular insertion of tungsten wire, length of immersion was (a) 7mm, here the tapered end of the tip is very long (b) 4mm the tapered end of the tip is shorter and the tip forms a cone angle of less than 45 degrees.

From figure 4 and further trials seem to suggest that an insertion length of 4mm yields a probe with a suitable tip aspect ratio.

Further trials were done using the optimum immersed in length of 4mm; the tips were inserted into the electrolyte at an angle other than 90 degrees and figure 5 shows a typical result.

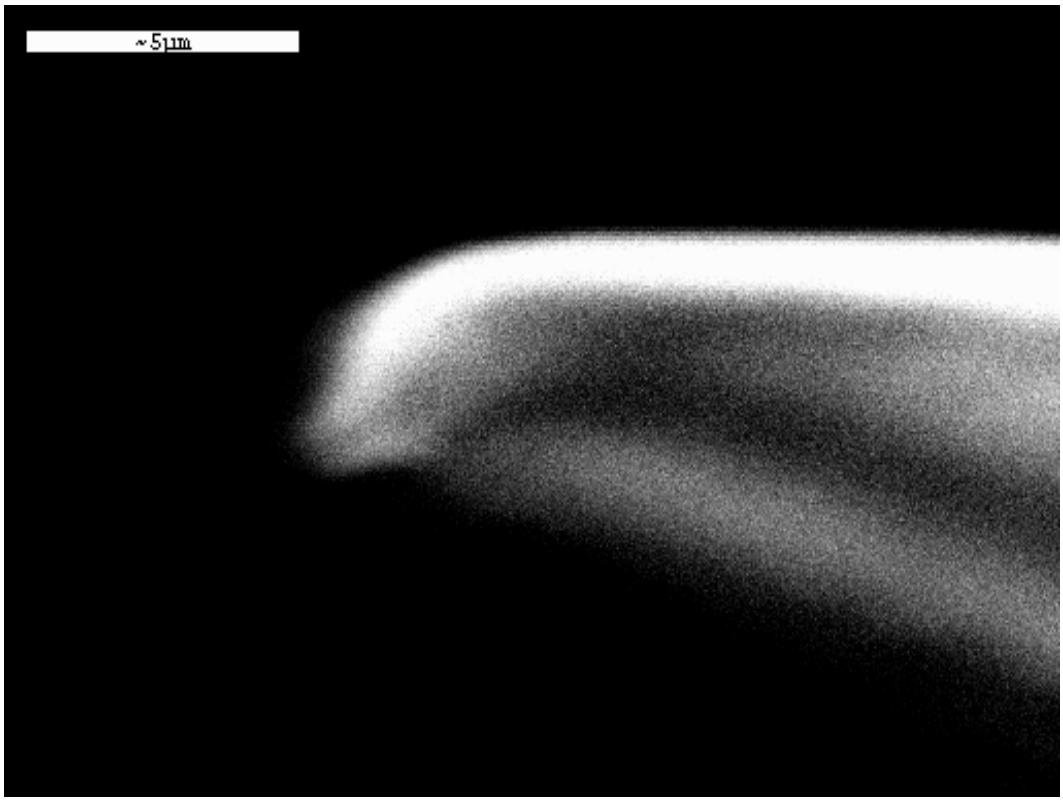


Figure 5. Oblique insertion yields asymmetrical tips. Even when you are using the optimum immersion length

Why tungsten tips require further cleaning

The presence of hydrocarbons and the residuals of etching process are easily removed by carefully dipping the etched tip in distilled water, followed by dipping acetone and ethanol. Analysis of the tip using the X-ray energy-dispersive spectrometer (EDS) gives a lot of information about the surface composition of the tungsten tip. An X-ray spectrum of the etched and carefully cleaned tip is shown in figure six,

This spectrum suggests that contaminants of oxygen (O) and sodium (Na) still exist on the etched portion of the wire. Some authors refer to this oxide layer as tungsten oxide layer (W03)

this may have developed during the etching period. It is worth noting that the tungsten K edges energy are out of range for this detector, the L edge is also not detected because of the low energy used in this case. Only M_{α} peak (1.775) peak of W is completely resolved.

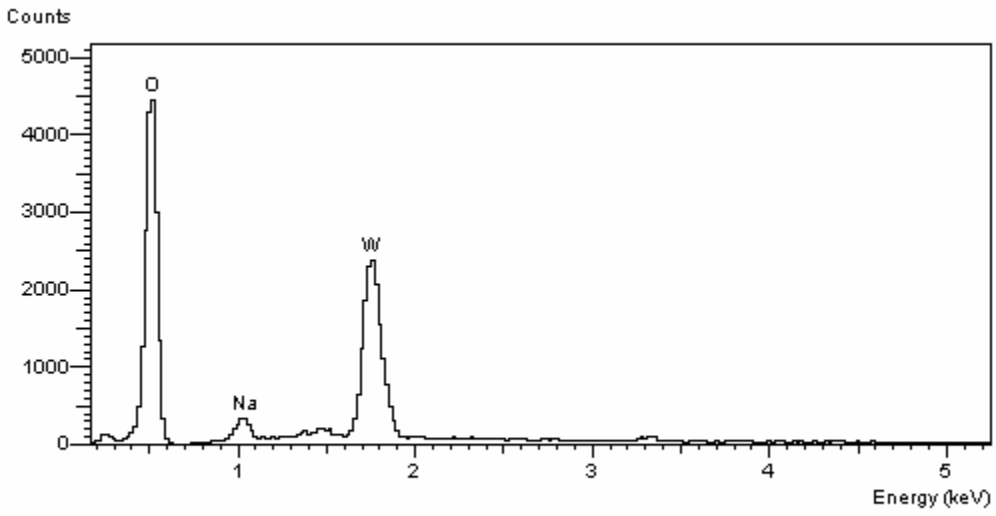


Figure 6. Spectrum of thoroughly cleaned tungsten tip using a lower energy beam.

Although the level of this insulating layer is acceptably and the tip can be used for NSOM and STM experiments a pure metallic tip is more desirable. The important question to be answered is which portion of the metallic tip has a higher distribution of oxide form, is it formed at the shaft of the tip or at the apex of the tip. The answer to this question lies in the preparation of the tip. However, more conclusive evidence can be reached by using the TEM to study the insulating layer of the tip using different preparation methods.

A number of ways has been suggested by various authors to remove the tungsten oxide layer [3,4]. In this section I discuss three effective methods used commonly to clean the tip .

Annealing Method **:**

A very popular method is the annealing process.

At very high temperatures in the ultra high vacuum, the following reaction takes place

$2WO_3 + W \rightarrow 3WO_2$, [3]

the volatile tungsten dioxide formed is volatile and sublimates at higher temperatures of about 1075 K. An undesirable effect of annealing is the blunting of the tip. However this

can be avoided if the annealing is done extremely carefully. The end result of careful annealing is tip with a very high degree of tungsten present.

*HF chemical cleaning***:**

Here an etched portion of the tip is dipped into hydrofluoric acid immediately after electrochemical etching for about half a minute. Since the oxides of tungsten are soluble in HF while tungsten is not, this method is highly preferred.

*Ion Milling***:**

Ion milling is a process applied to a sample under vacuum whereby a selected area of the surface can be bombarded by an energetic beam of ions. The bombardment erodes the surface, and is very desirable in this case since this action sharpens the tip. Thus rotation and angle of attack is important. Generally using rotation and grazing bombardment angles promote even erosion of the sample surface and minimizes damage effects [2, 5].

Post etching procedure:

To further reduce the probe diameter without using FIB, we follow a similar technique to that of Olivier et al. [6] , the etched is cleaned and then etched in 0.1M KOH for a few seconds, this reduces the diameter of the probe without blunting the tip. Some of the tips formed this way are shown in Appendix One.

For the sake of comparison, I would like to show the X-ray spectrum for a cut wire etched immediately after cutting.

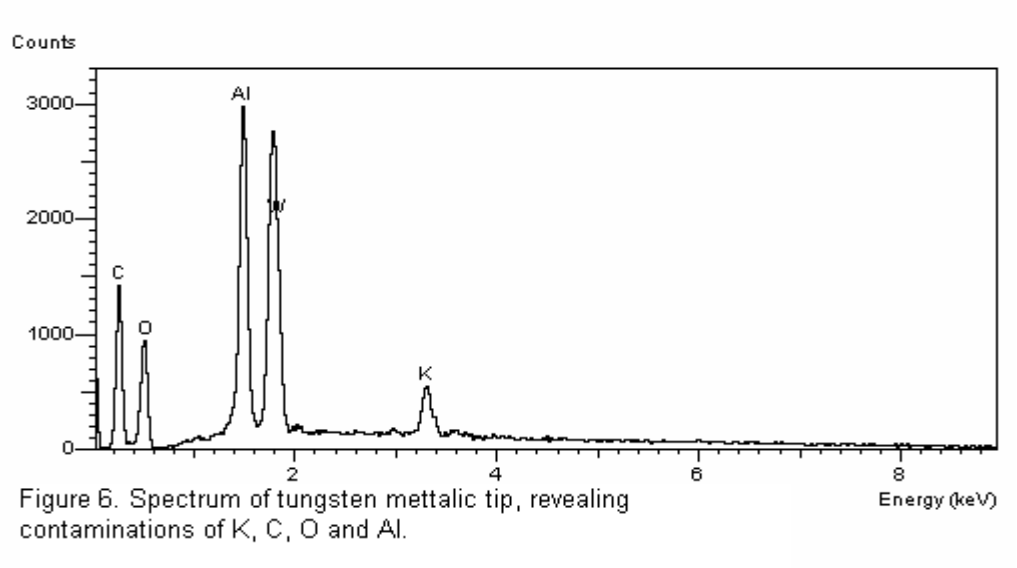


Figure 6. Spectrum of tungsten mettalic tip, revealing contaminations of K, C, O and Al.

The spectrum seems to suggest that more contaminants are present. As a result, we strongly recommend pre-etching away some portion of the cut wire before etching for the actual tip. This spectrum was taken before cleaning the tip, after thoroughly cleaning the tip the all the other contaminants initially present remained except carbon.

Conclusion: Our procedure for producing tungsten probes is not only reproducibly but also easily implemented

In future we intend to monitor the current just before drop off using computer interface, this may prove vital in understanding how the drop off occurs. The next step is to implement this probe diameter in NSUM experiments and ultimately use this property to study thin films

Reference:

[1] D. Courjon, Near-Field Microscopy and Near-Field Optics, Imperial College Press [2003]

[2] Inger Ekvall *et al* 1999 *Meas. Sci. Technol.* **10** 11-18

[3] Anne- Sophie Lucier- Masters Thesis, McGill University, Canada [2004]

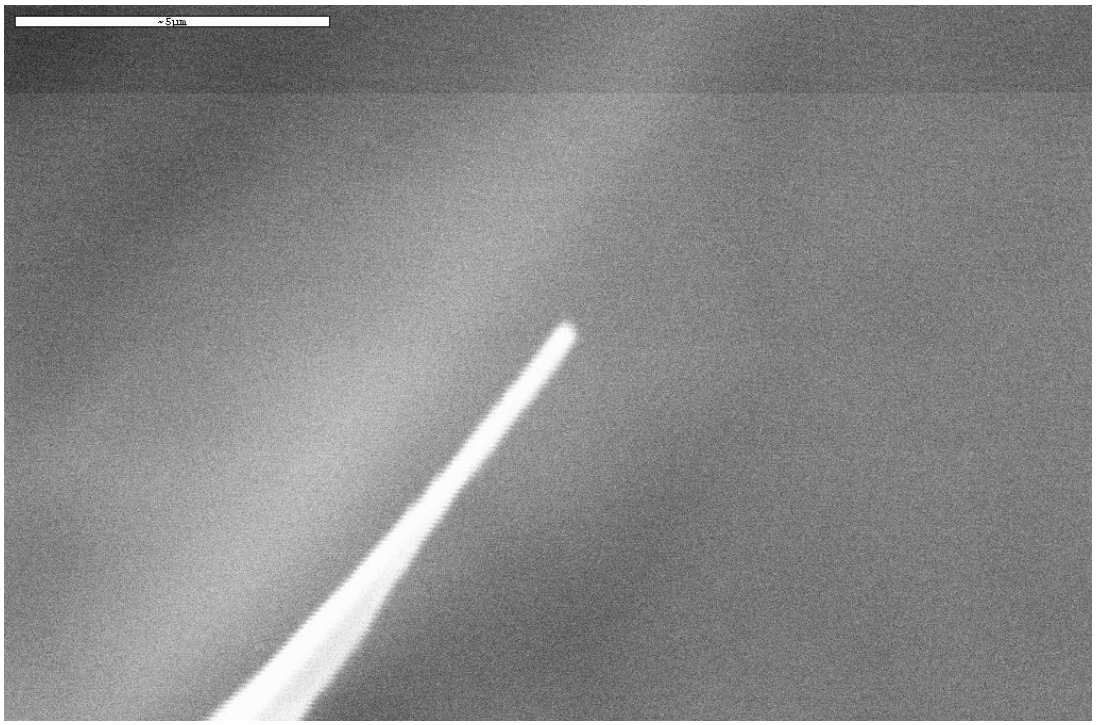
[4] K. C. Li and C. Y Wang. Tungsten: Sources, Metallurgy , Properties and Applications. Plenum Press, 1979.

[5] http://www.ebsd.com/sampleprep7.htm

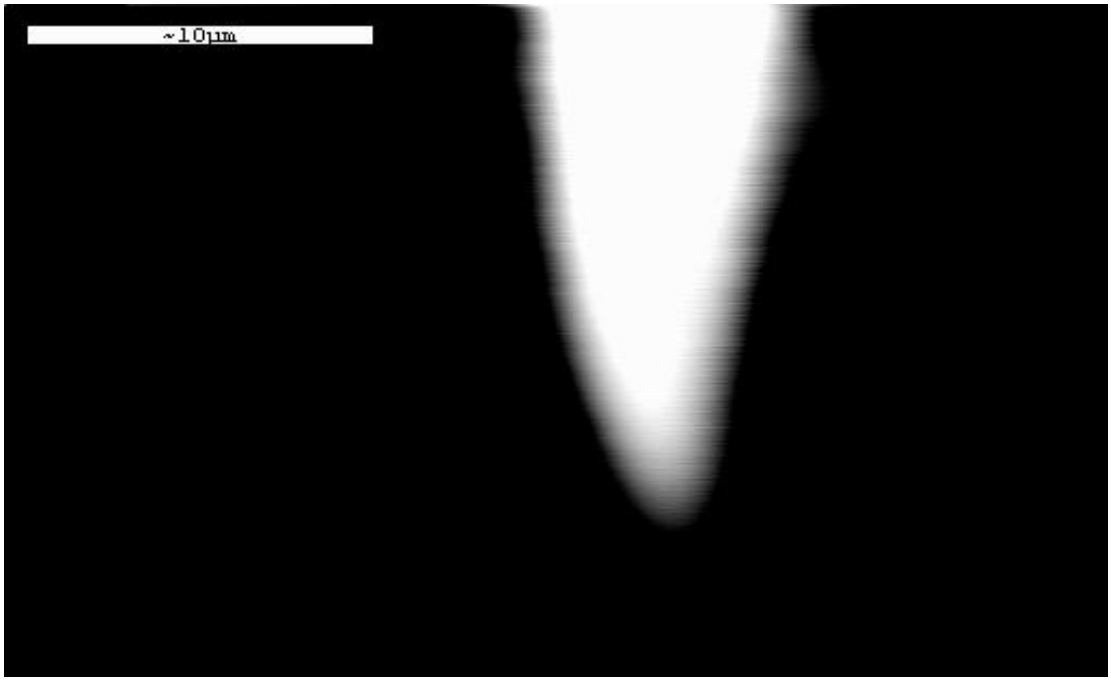
[6] Olivier L. Guise et al. Nano letters 2002, Vol.2, No. 3 191-193

Additional SEM images shown in the appendix: following pages:.

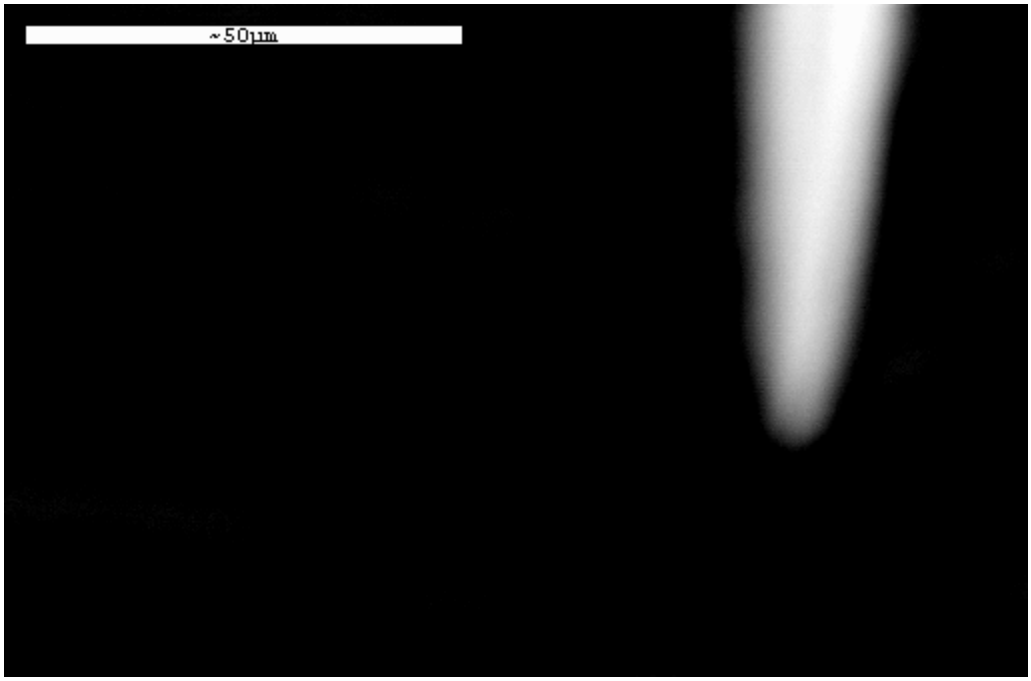
Figure below taken with Z=15mm, 6200X, concentration of KOH used is 2M



270306C, Z=20mm, Magnification 3400X, concentration of electrolyte, 3M KOH



270306b , Z=20mm, 920X, etched in 4M KOH



270306e, Z=20mm, 2070X, 5M KOH

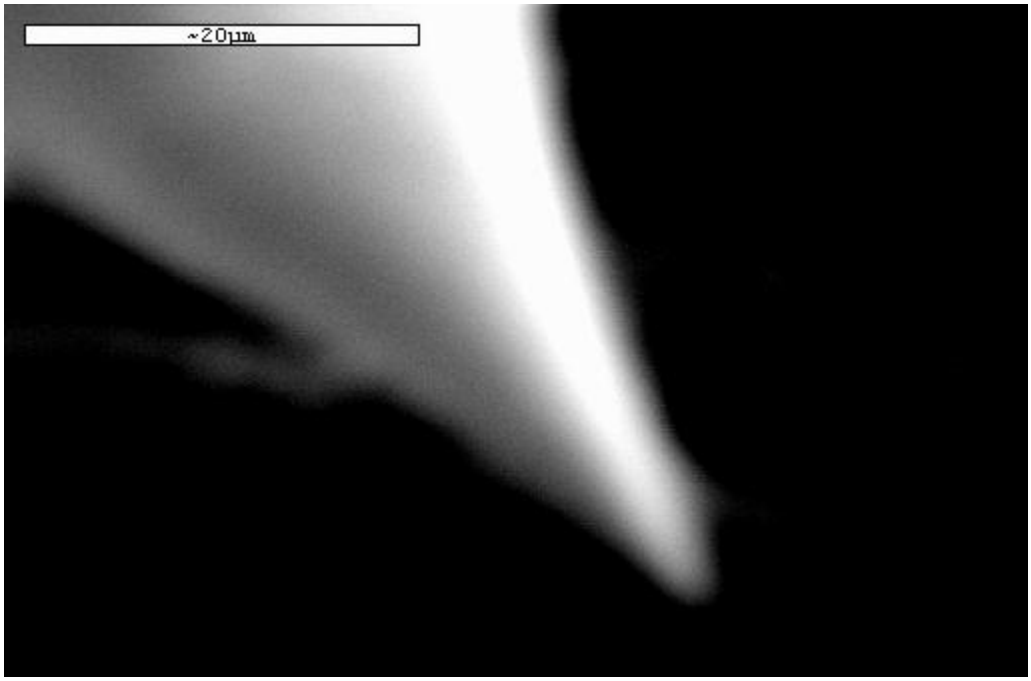
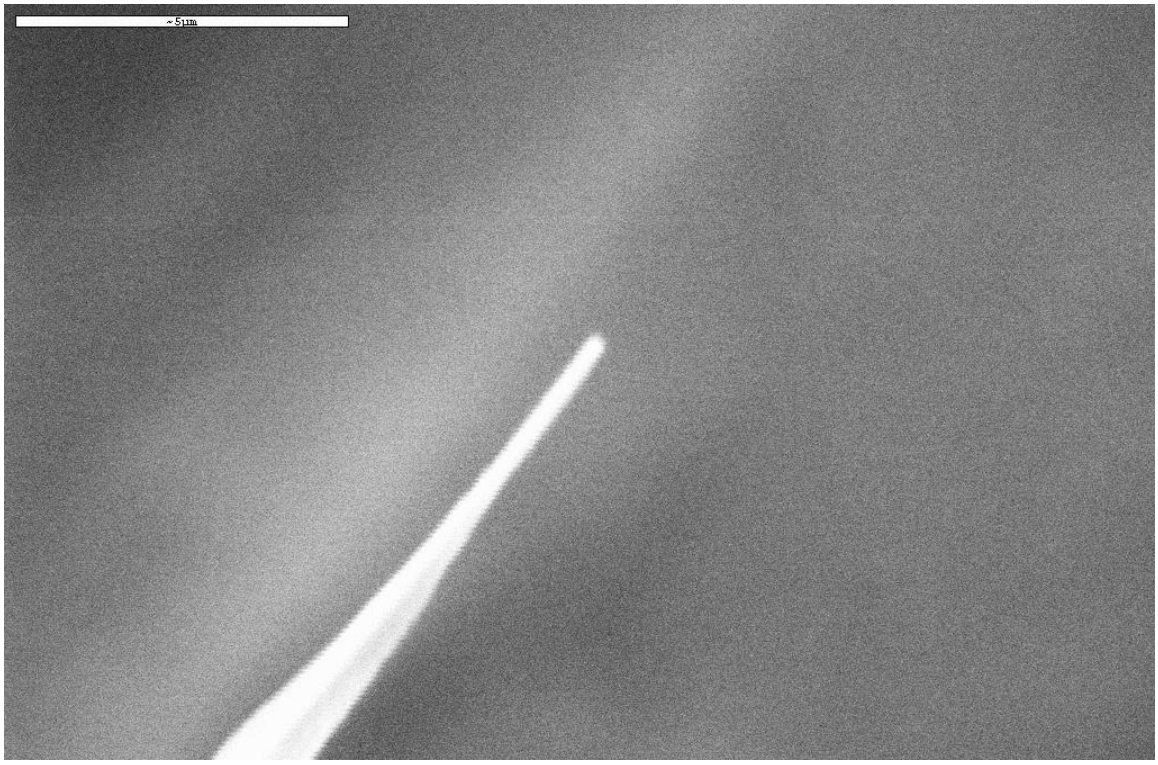
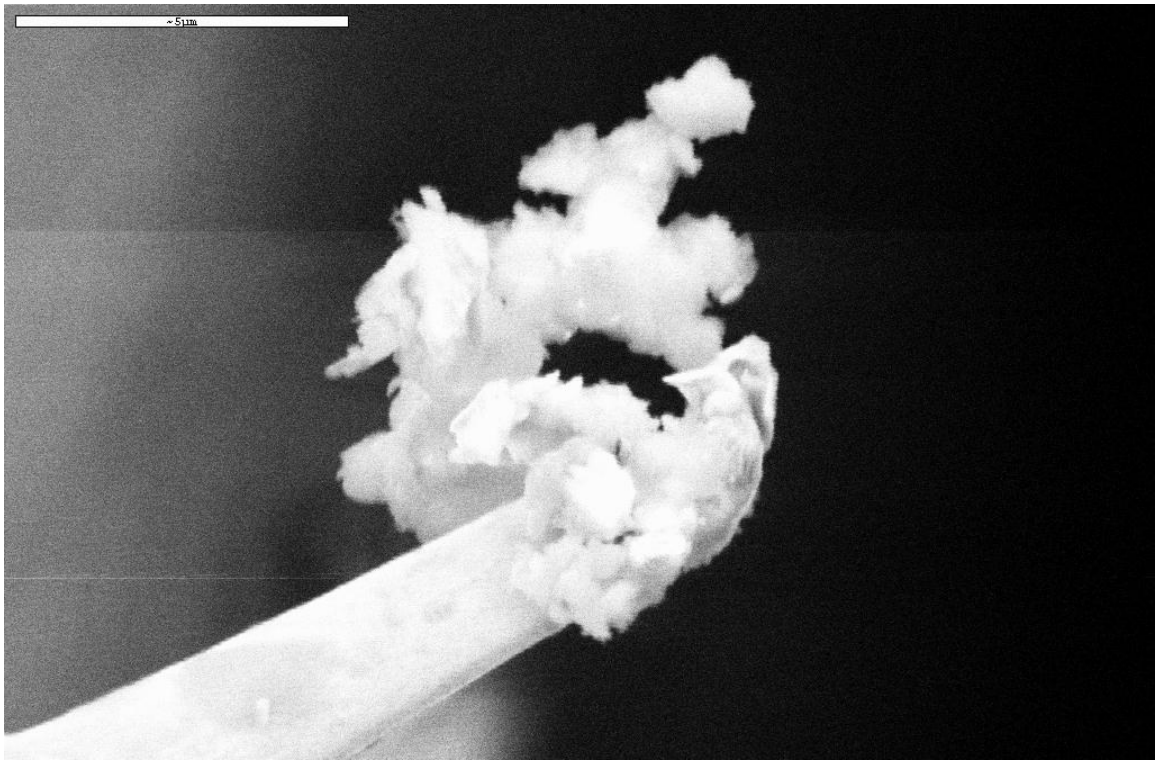


Figure below taken with Z=15mm, 5500X





APPENDIX TWO: SET UP OF THE WORK STATION