Video Article

Electrochemical Etching and Characterization of Sharp Field Emission Points for Electron Impact Ionization

Tyler L. Van Well[1], Matthew Redshaw[1], Nadeesha D. Gamage[1], R. M. Eranjan B. Kandegedara[1]

[1]Department of Physics, Central Michigan University

Correspondence to: Matthew Redshaw at redsh1m@cmich.edu

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Abstract

A new variation of the drop-off method for fabricating field emission points by electrochemically etching tungsten rods in a NaOH solution is described. The results of studies in which the etching current and the molarity of the NaOH solution used in the etching process were varied are presented. The investigation of the geometry of the tips, by imaging them with a scanning electron microscope, and by operating them in field emission mode is also described. The field emission tips produced are intended to be used as an electron beam source for ion production via electron impact ionization of background gas or vapor in Penning trap mass spectrometry applications.

Video Link

The video component of this article can be found at http://www.jove.com/video/54030/

Introduction

Sharp tips or points have long been used in microscopy applications, such as the field ion microscope (FIM)[1] and the scanning tunneling microscope (STM)[2], and a range of techniques for producing sharp tips of various materials have been developed[3]. These sharp tips can also be operated as field emission points (FEPs) by applying a high voltage to them, and serve as a convenient electron beam source. One application of such as source is ion production via electron impact ionization (EII). The FEP is particularly advantageous in applications where temperature fluctuations produced by thermal emitters are undesirable. For example, ion production via EII of background gas or vapor in high precision Penning traps[4,5].

A simple method for fabricating FEPs is to electrochemically etch tungsten rods in a sodium hydroxide (NaOH) solution. This technique is relatively straightforward to implement with modest equipment and has been shown to be quite reproducible and reliable. A number of methods are described in the literature and improvements to these techniques continue to appear[6]. Here we describe a method for the electrochemical etching of tungsten tips in a NaOH solution. Our method is a variation of the lamella drop-off technique[7,8] and the floating layer technique[9,10]. Like these two methods it enables the production of two tips from a single etching procedure. A picture of the experimental apparatus for etching the tips is shown in **Figure 1**.

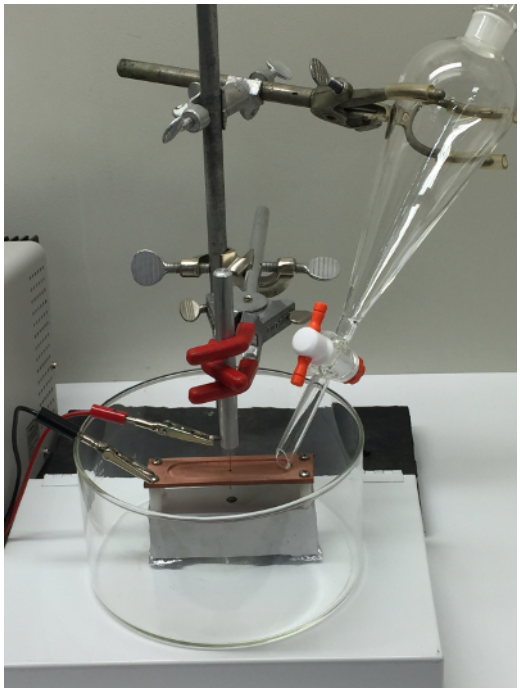

Figure 1. Etching apparatus. Photograph of the experimental apparatus used for electrochemical etching of tungsten rods with NaOH solution. Please click here to view a larger version of this figure.

Electrochemical etching of tungsten in the aqueous NaOH base occurs via a two-stage process. First, intermediate tungsten oxides are formed, and second, these oxides are non-electrochemically dissolved to form the soluble tungstate anion. This process is described, in simplified form, by the two reactions

(1) $W + 6OH^- \rightarrow WO_{3(S)} + 3H_2O + 6e^-$, and

(2) $WO_{3(S)} + 2OH^- \rightarrow WO_4^{2-} + H_2O$.

The etching current and the NaOH solution molarity used affect the time and voltage required to etch through the tungsten rod. Studies of these effects are presented and discussed. More importantly, the etching parameters have an effect on the geometry of the tips and, as such, on their operation in field emission mode. The geometry of the tips we produced were characterized by imaging them with a scanning electron microscope (SEM). These images can be used to estimate, for example, the tip radius. In addition, the tips were operated in field emission mode by applying a negative voltage of typically a few hundred volts to a few kilovolts to them and monitoring the resulting electron emission current. The relationship between field emission current, *I*, and applied bias voltage, *V*, can be described by the Fowler-Nordheim equation[11]

(3) $I = AV^2 e^{-Cr_{eff}/V}$,

where r_{eff} is the effective radius of the tip, *A* is a constant, and *C* is the second Fowler-Nordheim constant $C = bk\alpha\phi^{2/3}$, in which b = 6.83 $eV^{-3/2}V/nm$, ϕ is the work function of tungsten ($\phi \approx 4.5$ eV), k is a factor that depends on geometry ($k \approx 5$), and α is the Nordheim image correction term ($\alpha \approx 1$)[12]. Hence, the effective radius of the tip can be determined by measuring the electron current as a function of bias voltage. Specifically, it can be obtained from the slope of a so-called Fowler-Nordheim (FN) plot of $\ln(I/V^2)$ vs $1/V$.

Protocol

1. Electrochemical Etching

1. **Experimental set-up**
    1. **Apparatus**
    Note: The electrochemically etching set-up requires a standard 0 - 30 V direct current (DC) benchtop power supply and appropriate cables, a separatory funnel, a wide base glass beaker, and standard rod and utility clamp with electrically insulating grips. Small screws, insulated stand-offs, and alligator clips will also be required. Additional items, described below and shown in the picture of the etching apparatus in **Figure 1**, must be fabricated.
        1. Make a tungsten rod holder from an approximately 100 mm long 6 mm diameter aluminum rod. Drill a 0.5 mm diameter approximately 8 mm deep hole in the center, and make a tapped hole for a 4-40 screw in the side to hold the rod in place.
        2. Make a counter electrode from an approximately 100 mm x 30 mm x 3 mm thick copper plate with an approximately 75 mm x 20 mm x 1.5 mm deep reservoir milled into it, and a 1.5 mm diameter hole in the center. Attach approximately 15 mm long insulated stand-offs to the backside of the counter electrode.
        3. Make an FEP catcher by drilling a 6 mm diameter 8 mm deep hole into an approximately 75 x 20 x 20 mm copper block.

2. **Preparation of tungsten rod**
    1. Use wire clippers to cut the 0.5 mm diameter tungsten rods into approximately 25 mm lengths.
    2. Clean the rods in acetone in an ultrasonic bath for 15 min.
    3. Rinse the rods with deionized water.

3. **Etching solution**
    Caution: NaOH solution is a corrosive alkali solution-NFPA 704 label: Flammability (0), Health (3), Instability/Reactivity (0), Special (COR)-and can cause chemical burns if it comes in contact with the skin or eyes. Inhalation of fumes can cause irritation and burns to the respiratory tract. When handling NaOH solution, wear chemical splash goggles and face shield to protect the eyes, and gloves and an apron to protect the skin. Perform the etching procedure in a fume hood or wear a respirator. Care should be taken when performing step 1.1.3.1 to produce the diluted NaOH solution. This process is highly exothermic and can release heat that may cause burns or ignite flammables, and could cause the solution to splash out of the container.
    1. Make a 1.5 M NaOH solution by combining 30 ml of 50% by weight NaOH solution with 370 ml of deionized water to make a 400 ml total volume.
    2. Fill a separatory funnel with the NaOH solution.

4. **Cut-off circuit**
    Note: If the DC power supply is to be operated manually, then the operator will turn the power supply off once the tungsten rod has etched all the way through (see 1.2.2). In case of manual operation, skip to step 1.2. For automatic cut-off of the DC power supply, the cut-off circuit (shown in **Figure 2** and described below), should be constructed. Here, we implement the computer control using a DAQ card.
    1. Connect an ammeter in series with the DC power supply.
    2. Connect two resistors, R_1 and R_2 in series and place in parallel with the tungsten rod/counter electrode etching leg of the circuit. (Nominal values for R_1 and R_2 are R_1 = 5 kΩ and R_2 = 10 kΩ.)
    3. Monitor the voltage across one of the resistors with an analog-to-digital convertor (ADC) and suitable computer control software, *e.g.,* LabVIEW. The monitored voltage, V_{mon}, can be related to the voltage across both resistors and hence, the voltage across the etching leg, V_{etch}, via
        (4) $V_{etch} = \frac{R_1+R_2}{R_1} V_{mon}$,
        where the voltage is being monitored across R_1.
    4. Connect a low resistance resistor, R_L = 1 Ω, in series in the etching circuit. Use a second channel on the ADC to record the voltage across this resistor. The etching current is then found via $i_{etch} \approx V_L/R_L$. (Only about 1 mA flows throw the monitor leg of the circuit.)
    5. In software, create a program to output a 5 V TTL signal from the digital input/output channel (DI/O) when either the etching voltage increases above a set-value, or the etching current drops below a set value, indicating that the tungsten rod has etched all the way through. These values depend on the etching current and NaOH solution molarity being used and should be determined with a test run of the experiment.
    6. As shown in **Figure 2**, arrange for the 5 V TTL signal to open a relay to stop the current flow.

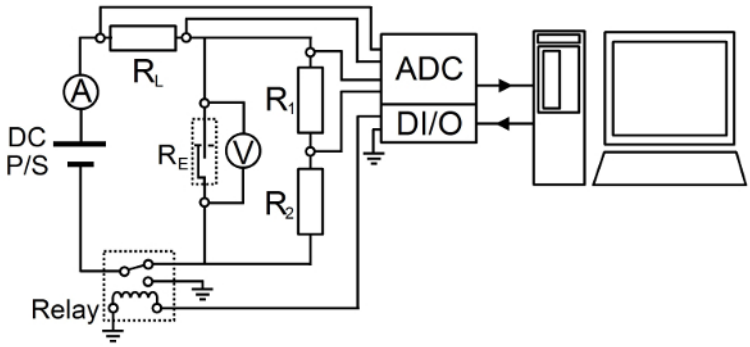

Figure 2. Schematic of etching circuit. A schematic drawing of the etching circuit used to provide the constant DC etching current. The current is determined by monitoring the voltage across a low resistance resistor and the voltage is recorded by monitoring the voltage across a high resistance resistor using an ADC. A computer program monitors the current and provides a 5 V output signal to a relay that opens the etching circuit once the current drops below a specified value. Please click here to view a larger version of this figure.

2. **Etching procedure**
    1. **Apparatus preparation**
        1. Set up the apparatus as shown in **Figure 1**, with the copper FEP catcher block placed inside the wide base glass beaker and the copper cathode located above it, spaced off by the insulating stand-offs.
        2. Set the current on the DC power supply to the desired value, typically 200 mA.
        3. Place a tungsten rod in the holder and connect the positive terminal of the DC power supply to the 4-40 holding screw with an alligator clip.
        4. Insert the tungsten rod through the hole in the copper cathode so that approximately 12 mm of the tungsten rod passes through the hole.
        5. Connect the negative terminal of the power supply to the copper cathode with another alligator clip.

2. **Etching**
    1. Manually adjust the drip rate of the separatory funnel to match the drip rate through the hole, about 1 drip every 3 sec. Wait for the reservoir in the copper cathode to become full.
    2. Turn on the DC power supply to begin etching.
    3. If operating in manual mode, turn off the DC power supply once the bottom part of the tip etches all the way through and drops off. If operating with an automatic shut-off switch, the etching current will be cut-off automatically once the rod etches through.

2. Characterization of Field Emission Points

1. **Inspection of tips**
    1. Carefully remove the bottom tip from the catcher block using pliers or tweezers. Remove the upper tip from the tungsten rod holder by loosening the 4-40 screw and gently pulling the upper tip out with the pliers or tweezers.
    2. Rinse with acetone and then with deionized water.
    3. Examine with an optical microscope. Tips should be seen to taper to a fine point. Those that do not, *e.g.*, because they are bent or do not have a regular cone structure, should be discarded. **Figure 3** shows an example of (a) a good tip and (b) a bent tip.
    4. Store tips in a desiccator.

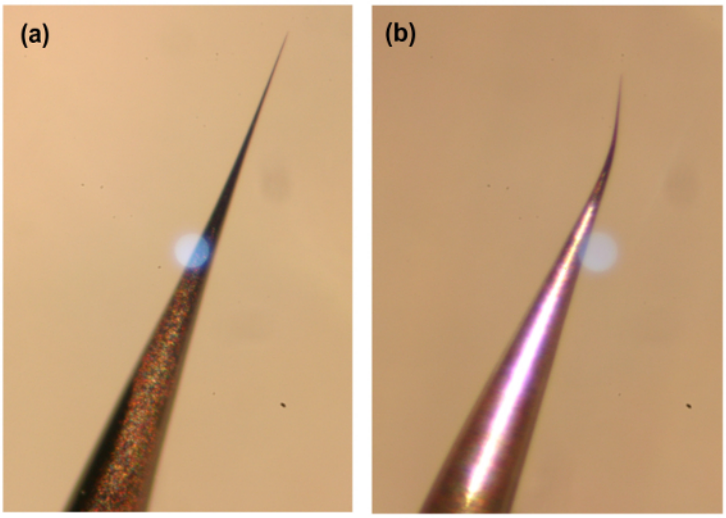

Figure 3. Optical image of FEP tips. Picture of (**a**) a good tip and (**b**) a bad tip, as viewed through an optical microscope. Please click here to view a larger version of this figure.

2. **Scanning Electron Microscope (SEM) Imaging**
    1. For SEM Imaging, secure FEP tips to a conducting holder using conducting tape or by screwing them to it (*e.g.*, see **Figure 4**) and image in a SEM according to manufacturer's protocol at magnifications of approximately 1,800X and 37,000X to view the cone of the tip and the end of the tip, respectively.

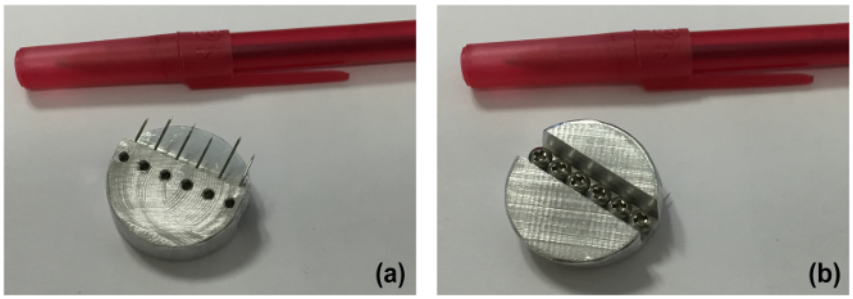

Figure 4. FEP holder for SEM imaging. A picture of (a) the top and (b) the bottom of the holder used to secure FEPs while imaging with the SEM. Please click here to view a larger version of this figure.

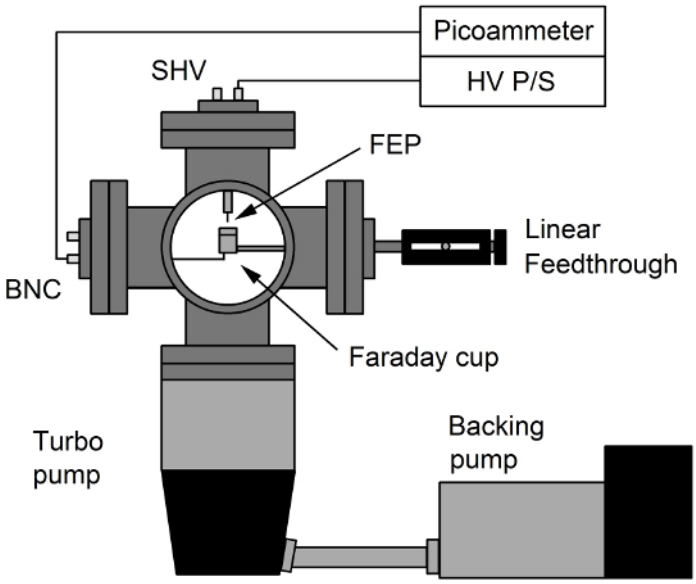

Figure 5. Field emission apparatus. Schematic of the apparatus used to apply a HV to the FEPs while under vacuum to produce an electron beam. The electron beam current is monitored on the Faraday cup with a picoammeter. Please click here to view a larger version of this figure.

3. **Field Emission Tests**
    1. **Apparatus**
    Note: For the field emission tests the following, or similar, equipment is required: a 6-way 6" conflat flange cross to serve as a vacuum chamber, three 6" to 2 ¾" conflat flange zero length adaptors, an SHV (safe high voltage) feedthrough on a 2 ¾" conflat flange, a BNC feedthrough on a 2 ¾" conflat flange, a linear feedthrough on a 2 ¾" conflat flange, a 6" conflat flange window, a 6" conflat flange blank off, a turbo vacuum pump mounted to a 6" conflat flange, and a backing pump (*e.g.,* a scroll pump) for the turbo. A high voltage (HV) power supply capable of delivering up to -5 kV is required to bias the FEP, and a picoammeter is required to monitor the electron current emitted from the FEP and collected on a Faraday cup, see *e.g.,* [13]. In lieu of a Faraday cup, a simple conducting collection plate can be used. A schematic of the field emission set-up is shown in **Figure 5**.
        1. Make a second tungsten rod holder (see step 1.1.1.1). In the opposite end of the holder to the FEP drill a 1 mm diameter hole and drill and tap a hole in the side of the rod for a 4-40 screw to secure it to the vacuum side of the SHV feedthrough.
        2. Set-up the field emission apparatus as shown in **Figure 5**. The Faraday cup should be about 2 cm from the end of the FEP.
        3. Connect the HV supply to the SHV feedthrough that the FEP holder is attached to, and connect the picoammeter to the BNC feedthrough that the Faraday cup is attached to.
        4. Pump down the set-up to a pressure of 10^{-6} mbar or below.

    2. **Field emission**
        1. Gradually increase the bias on the FEP and monitor the electron beam current on the Faraday cup with a picoammeter. When field emission begins, a current will be observed on the picoammeter.
        2. Increase the HV in incremental steps (of around 50 V) and record the average electron beam current on the picoammeter at each step. (This process can be computer controlled *e.g.*, by a LabVIEW program if desired, or can be done manually). Keep the electron beam current below 1 µA.

    3. Conditioning
        1. Condition the tip by operating in field emission mode at 5 nA for 1 hr.
        2. Repeat the current vs HV scan of 2.3.2.2.

Representative Results

Study of etching parameters

During the etching process the power supply is operated in constant current mode. The voltage required to maintain this constant current increases slightly as the tungsten rod is etched away (due to the increase in resistance of the rod). The current drops almost to zero when the tip etches all the way through. A small current continues to flow due to the fact that the upper tip is still in contact with the etching solution. A plot of current and voltage as a function of time during the etching process is shown in **Figure 6**.

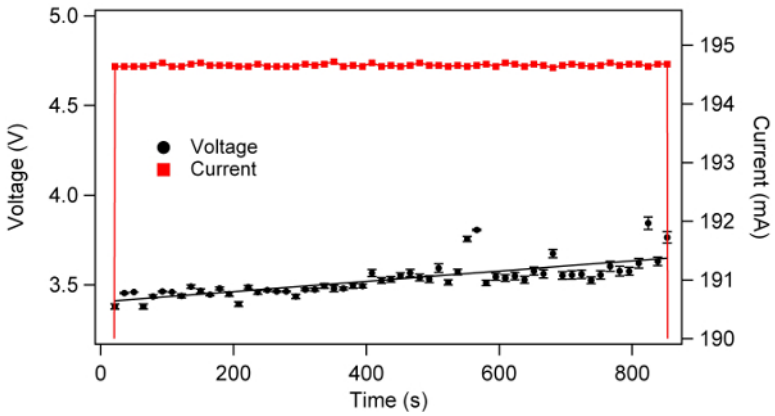

Figure 6. Current and voltage during etching process. The current and voltage supplied by the power supply during the etching process. The voltage required to maintain the constant current increases slightly during the etching process due to the increase in resistance as the tungsten rod etches away. The error bars on the voltage data points, determined as the standard uncertainty in the voltage data averaged in 15 sec bins, also increase in size during the etching period as a result of larger voltage fluctuations. The current drops almost to zero when the tungsten rod etches all the way through and the bottom tip drops off. Please click here to view a larger version of this figure.
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The time required to etch through the tungsten rod depends on the etching current used and on the molarity of the solution. **Figure 7 (a)** shows the time required to etch through a 0.5 mm diameter tungsten rod as a function of etching current for three different molarity NaOH solutions. The etching rate increases linearly with current. Power law fits of etching time as a function of current gave exponents of 1 for all three NaOH solution molarities. **Figure 7 (b)** shows that the etching voltage is linearly proportional to current and that the voltage required to deliver the constant current decreases with increasing molarity. This relationship is to be expected from Ohm's Law: the number of charge carriers available in the solution, and hence the effective conductance, is determined by the molarity of the solution. The dependence of etching time, or inverse etching rate, on current, as seen in **Figure 7 (a)** is expected based on Eqn. (1). However, **Figure 7 (a)** also shows that, for low current settings of 100 mA, the etching rate decreases with increasing molarity. This could result from the lower potential required to maintain this current for the high molarity solution, since etching current also depends on the potential required to drive the reaction[15].

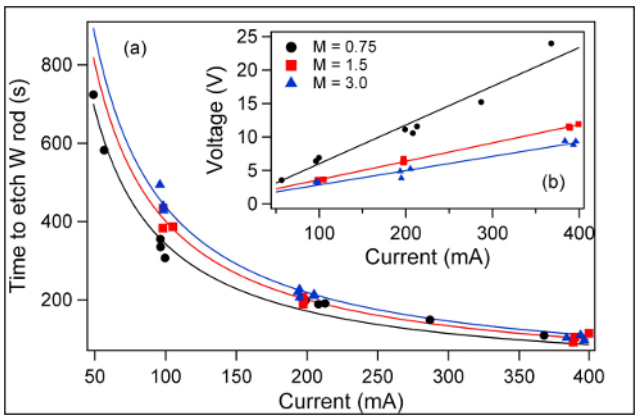

Figure 7. Etching time and voltage vs current and molarity. (**a**) Main: Time required to etch through 0.5 mm diameter tungsten rods as a function of etching current for NaOH solution molarities of 0.75, 1.5, and 3.0. (**b**) Inset: Average voltage supplied by the constant-current power supply during the etching process. Please click here to view a larger version of this figure.
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SEM imaging:

SEM imaging can be used to reveal the structure of the tip. **Figure 8** shows SEM images of (a) top and (b) bottom tips. In (i), the bottom tips can be seen to have a larger aspect ratio than the top tips. This is due to the fact that some etching solution runs down the tungsten rod, etching or polishing the surface. The images in (ii) and (iii) show that the bottom tips generally have an acute cone angle and in many cases have a large bulb at the tip, increasing the effective radius of curvature. The upper tips on the other hand generally taper to a fine point.

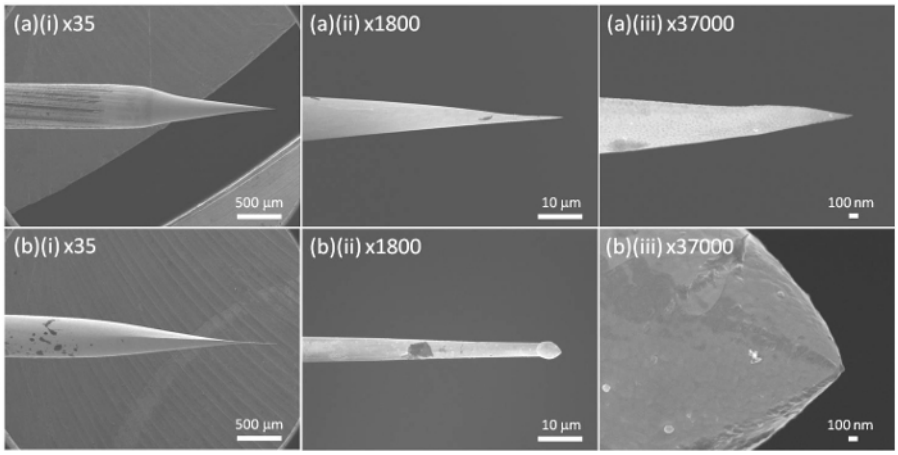

Figure 8. SEM images of field emission tips. SEM images of (a) top and (b) bottom tips etched from a 0.5 mm diameter tungsten rod using 0.75 M NaOH solution and a nominally 200 mA etching current, shown with magnifications of (i) 35X, (ii) 1,800X, and (iii) 37,000X. Please click here to view a larger version of this figure.
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The bulb structure seen on the lower tips has been observed by other researchers, *e.g.,* Ibe *et al.*[15], and is attributed to the recoil force on the tip as it fractures and the bottom piece drops off. In this scenario, the energy released during fracturing can cause local melting, deforming the tip. The upper tips do not show a corresponding bulb. We attribute this to the post-drop off etching period after the lower tips drops off, but before the current is completely switched off (the current decreases significantly after the lower tip falls off, but does not go completely to zero since the upper tip is still in contact with the etching solution).

Field emission tests:

The FEPs were operated in field emission mode by applying a negative bias of between a few hundred volts and a few kilovolts between the FEP and ground. The field emission electrons struck a Faraday cup and the current was recorded. The field emission current as a function of bias voltage was investigated. A plot of $\ln(I/V^2)$ vs $1/V$ shows a linearly decreasing dependence. This relationship is well described by the Fowler-Nordheim equation. Using this equation and the slope of the data in the Fowler-Nordheim (FN) plot, the effective radius of the tip can be extracted. These measurements were consistent with results obtained from the SEM images[14]. The tips were conditioned for ~1 hr by operating them in field emission mode with a constant current of ~5 nA. After this time, the measurement of field emission current vs bias voltage was repeated. In general, the location of the data on the FN plot and the slope changed. In **Figure 9**, it can be seen that after the conditioning process the tip fires at a lower voltage and the slope has decreased. This indicates that the effective radius of the tip has decreased and hence the electric field required to remove electrons from the tip can be attained at a lower bias potential.

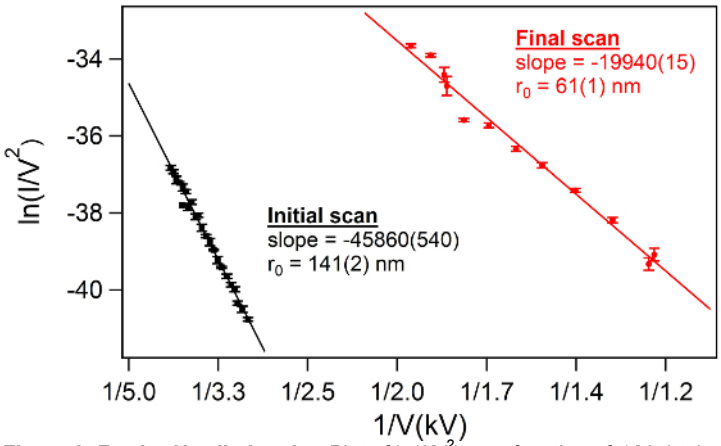

Figure 9. Fowler-Nordheim plot. Plot of $\ln(I/V^2)$ as a function of $1/V$ obtained by scanning the bias voltage, V, applied to the FEP and recording the average field emission current, I, produced by the tip. The two data sets correspond to measurements taken after the FEP first fired and after conditioning it for 1 hr. The straight lines are linear least-squares fits to the data, the slope of which is proportional to the effective radius of the tip. Please click here to view a larger version of this figure.
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The conditioning of the FEPs, inferred from the data shown in **Figure 9**, suggests that the field emission process can reduce the effective radius of the tip of the FEP. This behavior has been observed by other researchers and is attributed to heating of the tip by the electron current, and sputtering by atoms and molecules in the background gas of the vacuum that are ionized by the electron beam and accelerated toward the tip of the FEP[16,17]. In our apparatus, the main background gas (determined with a residual gas analyzer) was H_2O, and the most abundant ion species produced was H_3O^+ (determined via the cyclotron frequency of ions in a Penning trap[14]). Heating can clean the end of the FEP and also melt the tip. The results of melting range from a rearrangement of the atoms at the apex, which can sharpen the tip, to producing a molten blob of material at the end of the tip, blunting it. Sputtering can remove material from the tip, hence sharpening it, and can also decapitate the tip of the FEP. Significant changes in the field emission current were often observed during the conditioning process and SEM images of FEPs after field emission showed significant changes in the geometry of the tip, including the formation of blobs of melted metal at the tip, bent tips, and tips that had been decapitated-see Redshaw *et al*. for further details[14].

Discussion

We have described straightforward procedures to electrochemically etch sharp field emission points (FEPs) in a NaOH solution, and to test the FEPs by operating them in field emission mode. The etching procedure described is a variation of existing techniques-the lamella drop-off technique[7,8] and the floating layer technique[9,10]. However, we found it to be more convenient and reliable to implement than the aforementioned methods.

Before starting the etching procedure, to minimize the likelihood of producing tips with gross deformations, *e.g.,* a bent tip, as shown in **Figure 2**, the tungsten rod must be aligned through the hole in the copper cathode as vertically as possible. During etching, the NaOH drip rate from the separatory funnel should be monitored to ensure that the level of NaOH in the small reservoir in the copper cathode plate remains approximately constant. At the end of the etching procedure, the bottom tip will drop off, and the etching current will be greatly reduced. Shortly after this drop-off, the etching current should be switched off completely to avoid blunting the tip by continued etching. However, some etching/polishing of the tip at this stage is beneficial to the production of FEPs to be used as electron beam sources, since it appears that this polishing stage can smooth the tip and remove irregularities[14]. In our set-up a cut-off time of ~100 msec after the bottom tip drops off was used to produce tips with radii of ~100 nm. Other researchers have used fast transistor-based cut-off circuits to stop the etching process in as little as 500 nsec after the drop-off of the lower part of the tip, resulting in tips with radii down to ~10 nm to be used for STM applications[12,15]. Such a circuit was also tested in our set-up, and enabled tips with <100 nm radii to be produced. However, we found that these tips were less uniform at the tip and did not perform so well in field emission mode because, we believe, the smaller tips made them more susceptible to being melted by the electron beam current.

Field emission was initiated by applying a negative HV to the FEP, which was gradually increased until the FEP fired. The voltage required to initiate field emission depends on the geometry of the tip, and is typically lower for sharper tips[14]. While firing the FEP for the first time, the HV should not be scanned too quickly (~250 V/sec) to avoid a sudden current spike. We generally kept the electron beam current below 1 μA to avoid melting the tip. After the tip had fired, we conditioned it for 1 hr by operating it in field emission mode with an electron beam current of ~5 nA. We found that this procedure made the tip more stable, *i.e.,* the HV required to produce a given electron beam current (typically 1 nA or less in our application) remained fairly constant.

In summary, we have presented a straight-forward technique for electrochemically etching sharp FEPs from tungsten rods. These FEPs have been successfully operated in field emission mode with voltages ranging from a few hundred volts to a few kilovolts to produce an emission current on the order of nA. These FEP tips have also been implemented in a Penning trap mass spectrometry application[14].

Disclosures

The authors have nothing to disclose.

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