

Note: Electrochemical etching of sharp iridium tips

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(Received 19 October 2011; accepted 28 October 2011; published online 11 November 2011)

We describe an etching procedure for the production of sharp iridium tips with apex radii of 15–70 nm, as determined by scanning electron microscopy, field ion microscopy, and field emission measurements. A coarse electrochemical etch followed by zone electropolishing is performed in a relatively harmless calcium chloride solution with high success rate. © 2011 American Institute of Physics. [doi:10.1063/1.3662473]

Iridium (Ir) has a very high Young's modulus (528 GPa) and is chemically inert, being the most corrosion-resistant metal.¹ It is thus a material of choice to prepare sharp tips for scanning probe microscopy and nanoindentation experiments.

However, the chemical stability of Ir necessarily implies a laborious sharpening process, as opposed to that of tungsten for example. As an illustration, molten salt electrochemical etching, a dangerous technique requiring a dedicated apparatus, is still being used to prepare sharp Ir tips.²

We present an electrochemical method to prepare Ir tips, based on Melmed's two-step procedure,^{3,4} that uses relatively harmless chemicals. Though not automated, the process is reproducible (~80% success rate) and yields tip with apex radius ranging from 15 to 70 nm, as evidenced by scanning electron microscopy (SEM), field ion microscopy (FIM), and field emission measurements. This note is concerned with the technical details of the etching process.

The first stage of etching, the coarse etch, aims to reduce the diameter of a 0.25 mm polycrystalline Ir wire (Alfa Aeser, 99.8% purity) to ~2 μm .

The wire is thoroughly cleaned with ethanol and acetone in an ultrasonic bath. It is then immersed to a depth of 0.7 mm using a micrometer stage in a chemical solution of one part saturated CaCl_2 (Alfa Aeser, >85% purity) solution and two parts deionized water.⁵ A carbon counter electrode (Alfa Aeser, 99.9995% purity) is used.

Then, an AC bias of 35 V_{RMS} is applied between the wire and counter electrode. The reversing polarity of the AC voltage helps to remove a non-reactive layer which would otherwise build up and halt the reaction under DC bias. The AC etching results in the formation of bubbles at the air-liquid interface, as well as black particulates in solution. In order to avoid condensation on the wire and to minimize bubble accumulation, the etching station should be properly ventilated. A small computer fan is used for this purpose. Corrosion-sensitive parts (such as tip holders made of stainless steel) can be protected from splashing and condensation by coating them with nail polish which is removed by thorough ultrasonic cleaning in acetone after the coarse etch.

After 2 min, the bias is turned off and the wire examined under a microscope. Evidence of etching should be visible. The wire is then re-immersed to the same depth in the solution and the bias applied for an additional minute. Looking at

the wire again should reveal a noticeable tapering of the shank in a "teardrop" shape. At this point, the etching should be interrupted every 20–30 s to monitor progress. This is best done with a stereomicroscope directed toward the etching station.

Once the diameter of the thinned shank is about one quarter of the Ir wire's diameter, the bias should be decreased to 20 V_{RMS} . This lowers the etching speed to provide better control for the delicate task of further reducing the shank's width.

Etching can be resumed, but the process must be stopped frequently to monitor progress at 3–5 s intervals. Note that sparks under the air-solution interface can be seen at this stage. As the shank gets very thin, the etching time must be correspondingly reduced. The aim is to stop etching as soon as the lower part of the wire has fallen. Bubble formation during the AC etching of iridium leads to significant fluctuations in the measured current, hindering automatic "drop-off" detection similar to methods implemented for DC tungsten etching,⁶ so the etching must be interrupted manually. Leaving the bias applied for too long after drop-off can completely etch away the fine point. A tip with an apex radius of ~2 μm should remain. Figure 1 demonstrates a typical wire shape evolution.

Due to the mechanical instability introduced by the bubbles generated by the reaction, there is a limit to the fineness of the point that can be obtained with this step. A few microns is usually the best that can be achieved. It is preferable to have a successful coarse etching before moving on to the second stage. Figure 2 displays a typical poor and optimal coarse etching result.

The second stage is zone electropolishing.^{3,4} Here, the fine point obtained in the previous step is sharpened further using the same solution, but with a thin film as etchant retained in a loop of wire of a few millimeters in size



FIG. 1. (Color online) 0.25 mm Ir wire during the coarse etching at roughly 30 s intervals.

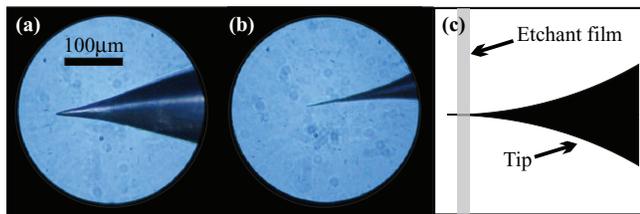


FIG. 2. (Color online) (a) Unsuccessful coarse etching. (b) Successful coarse etching. (c) Approximate position of the etchant relative to the tip in the zone electropolishing stage.

(tungsten, 0.1 mm diameter). This provides additional control for the etching. The process is monitored using an optical microscope with at least $500\times$ magnification. A micrometer stage is used to control the position of the tip with respect to the loop. A glass slide mounted to a plexiglass enclosure provides high-quality optical access with the microscope while protecting it from the etchant.

One must be careful as the fine point obtained from the coarse etching step is very fragile. Simply dipping the point in the film of solution and applying a bias will not sharpen the point, but will either etch it away or dull it. After thorough experimentation, one method stood out as providing reproducible sharpening.

First, the thickness of the solution film must be minimized. Using mm^2 size pieces of tissue paper torn with tweezers to absorb a controlled amount of etchant, the thickness of the film could be reduced to about $5\text{--}10\ \mu\text{m}$. Then the tip is inserted so that the fine point emerges by a few microns on the other side of the film as shown in Figure 2(c). Turning on the bias to $1\ V_{\text{RMS}}$ for about $2\text{--}3\ \text{s}$ slowly etches the shank. Turning off the bias and retracting the tip, a teardrop shape should be observed, as in the coarse etching stage, but on a much smaller scale. This step is repeated and the etching time and bias voltage are diminished in proportion to the thinning of the shank. The end should eventually fall, leaving a very fine point. As before, the bias must be turned off as soon as this occurs.

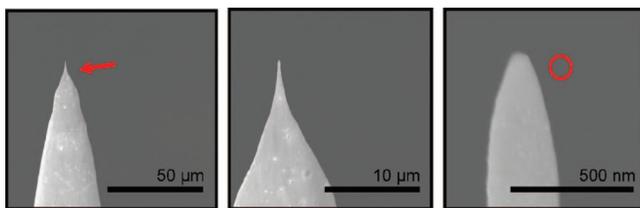


FIG. 3. (Color online) SEM images of a successfully prepared Ir tip. The local thinning of the zone electropolishing is clearly visible in the left frame (arrow). The circle in the right frame serves as a guide to the eye (50 nm radius).

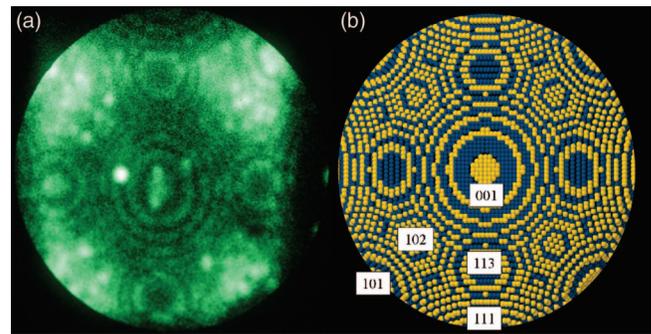


FIG. 4. (Color online) (a) FIM image. Bias voltage: 8.5 kV, Neon pressure: 1×10^{-5} mbar. (b) FCC ball model of the (100) oriented tip.

Patience is key in the final step. It is preferable to start with very low biases and immersion times and to increase slowly than to lose a fine point because of excessive starting parameters.

Several prepared tips were imaged under SEM. Figure 3 shows a typical tip, which has final apex radius of roughly 50 nm. The other tip apex radii ranged from 40 to 70 nm. These values are however limited by the SEM resolution ($\sim 30\ \text{nm}$) and therefore constitute an upper bound. The SEM micrographs are mainly used to determine the mesoscopic structure of the tip. To gain information on the atomic structure of the apex, we turn to FIM.

Figure 4 displays a FIM image of an Ir tip taken at room temperature. Neon is used as an imaging gas. The crystallographic planes are clearly identified and the direction of the apex is determined to be (100). An apex radius of $16 \pm 2\ \text{nm}$ is deduced using the ring counting method and by comparison with a ball model. Moreover, Fowler-Nordheim field emission analysis of the tip yields apex radius of $12 \pm 3\ \text{nm}$.⁷

To conclude, a detailed reproducible method for preparing Ir tips suitable for scanning probe microscopy was presented. The tips are shown to have apex radii in the range of $15\text{--}70\ \text{nm}$. Tip quality, both in the mesoscopic and microscopic structure, was demonstrated with SEM and FIM imaging, respectively.

We thank Robert Gagnon for the acquisition of the SEM images. Funding from NSERC is gratefully acknowledged.

¹F. Cardarelli, *Materials Handbook* (Springer, London, 2008).

²H.-S. Kuo, I.-S. Hwang, T.-Y. Fu, Y.-S. Hwang, Y.-H. Lu, C.-Y. Lin, T. T. Tsong, and J.-L. Hou, *Nanotechnology* **20**, 335701 (2009).

³A. J. Melmed, *J. Vac. Sci. Technol. B* **9**, 601 (1991).

⁴A. J. Melmed and J. J. Carroll, *J. Vac. Sci. Technol. A* **2**, 1388 (1984).

⁵A. J. Nam, A. Teren, T. A. Lusby, and A. J. Melmed, *J. Vac. Sci. Technol. B* **13**, 1556 (1995).

⁶J. P. Ibe, P. P. Bey, S. L. Brandow, R. A. Brizzolara, N. A. Burnham, D. P. DiLella, K. P. Lee, Richard J Colton, and C. R. K. Marrian, *J. Vac. Sci. Technol. A* **8**, 3570 (1990).

⁷A.-S. Lucier, H. Mortensen, Y. Sun, and P. Grütter, *Phys. Rev. B* **72**, 1 (2005).