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A method for production of cheap, reliable Pt–Ir tips

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A new method of producing Pt–Ir tips for use in scanning tunneling microscopy is described. This reproducible method is simple, cheap, fast, and avoids the use of hazardous chemicals common in many other methods. Scanning electron microscopy, time of flight–secondary ion mass spectroscopy, and x-ray photoelectron spectroscopy have been applied to understand both the chemical and morphological changes that occur as a result of the etching. The method has been demonstrated on both stock Pt–Ir wire and commercial tips and has been found to dramatically enhance image quality. It is also reusable on the same tip extending the lifetime of a single tip indefinitely. © *2000 American Institute of Physics.* [S0034-6748(00)00904-7]

I. INTRODUCTION

The growth of scanning tunneling microscopy (STM) as a surface science tool has been extremely rapid since its initial development.[1] A vital element in the operation of the STM is the structure and characteristics of the STM tip.[2] It has repeatedly been shown that the chemical and electronic nature of the tip material is directly related to the quality of the images produced.[3,4] It is vital that the STM tip is atomically sharp in order to obtain atomically resolved images.[5] In addition, a low aspect ratio (tip length/shank diameter) is desirable in order to prevent tip vibration during the raster of the tip.[6]

Tungsten tips have been widely used due to the ease of their construction through electrochemical etching, the atomically sharp nature of the tip, the low aspect ratio commonly attainable, and the comparatively cheap cost of tungsten wire.[7,8] However, it has been shown that a tungsten tip created through a typical electrochemical etching process has a contamination layer consisting of carbonaceous deposits and tungsten oxide at least 10 nm thick at the tip apex.[9] In addition, tungsten tips will react further with oxygen in air-operated STMs creating further oxide layers.[10] This contamination layer reduces image quality and eventually causes the tip to stop conducting. In particular, the imaging of poorly conducting biological samples with contaminated tungsten tips may present problems as the combination of the insulating properties of the tip contamination layer and the biological sample may result in the tip colliding with the sample.[9]

Inert materials such as platinum or platinum–iridium alloys are better materials to use for the construction of STM tips as they are known to remain free of contamination layers for periods up to several weeks, even under continual use in a STM at atmospheric pressure.[11] The longevity and improved image quality exhibited by tips made of such materials offsets to some extent the expense of platinum and platinum alloy wire, particularly when examining biological specimens.

A number of methods for producing Pt–Ir tips have been cited in the literature. Gorbunov *et al.* have experimented with Pt–Ir tips formed through direct mechanical cutting.[11] This method was found to produce tips of poor, nonreproducible quality, lacking the durability and stability necessary for exact STM measurements. Weinstein *et al.* developed a method of forming Pt–Ir tips through etching in a solution of NaOH and NaOCN using a current of 30–40 mA at a frequency of 400 Hz.[12] This process was very time consuming, typically requiring 40 min of etching in order to produce a sharp tip. Nagahara *et al.* propose etching Pt–Ir tips in a solution of NaOH and NaCN using a current of 0.5 A at 20 V A C.[13] Efforts to reproduce this method in our laboratory repeatedly failed; producing blunt tips of very high curvature radius, and typically involved etching times greater than 1 h. Without exception, these methods involve lengthy procedures or hazardous chemicals and the quality of the resulting tips does not appear to be reproducible.

The production of Pt–Ir tips through mechanical action (cutting, shearing, filing, etc.) is known to produce tips exhibiting a large number of small microtips which can result in confused, noisy STM images.[11,14] Electrochemical etching of Pt–Ir tips avoids this problem but the inert nature of the alloy necessitates lengthy etching procedures or hazardous chemicals.

This article describes a quick procedure for producing

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Pt–Ir tips exhibiting a single atomically sharp apex and a low aspect ratio without the use of hazardous etching chemicals. A method of re-etching tips following periods of use is also introduced. This allows tips to be reused repeatedly, dramatically lowering the effective cost of these tips.

II. EXPERIMENT

Tips were prepared from either stock 0.5 mm diameter $Pt_{80}Ir_{20}$ wire or 0.25 mm diameter $Pt_{80}Ir_{20}$ wire that initially was obtained as commercial tips from Digital Instruments. In the case of the commercial tips, the nontip end of the wire was used for these experiments to avoid inconsistencies resulting from the previous processing of the wire. Results obtained were identical regardless of the wire used. The wire was cut using ordinary pincer-type wire cutters at an angle of approximately 15° from the axis of the wire, in order to produce a sharp tip. The tips were then immersed to a depth of 1–2 cm in an etching solution of $CaCl_2 \cdot 2H_2O$ (35 g), de-ionized water (200 mL), and acetone (10 ml). A circular platinum ring counter electrode was immersed to the same depth as the tip to position the tip in the center of the ring. An etching current of 1 A at 15 V A C was then applied across the tip wire and the counter electrode for periods of 0.25, 1, 3, and 10 s. The tips were removed from the etching solution and then washed initially in de-ionized water with a final rinse in 95% ethanol.

Tips produced in this fashion were examined via scanning electron microscopy (SEM), time of flight–secondary ion mass spectroscopy (TOF–SIMS), and x-ray photoelectron spectroscopy (XPS). The SEM used was an ETEC Autoscan operated at 20 kV in secondary electron mode. XPS was performed with a Physical Electronics PHI 5600 hemispherical spectrometer with Mg $K\alpha$ excitation and small spot facility. Analyses were taken of 120 μm areas near the tip point. A Physical Electronics TRIFT II TOF–SIMS system with a Ga liquid metal ion gun (LMIG) (15 kV, 600 pA) source was used to collect static SIMS mass spectra of untreated and treated tips.

III. RESULTS

SEM images of Pt–Ir tips produced by cutting the wire at an acute angle confirms the presence of microtips and whiskers as shown in Fig. 1. However, a dominant, larger tip can be seen, which appears quite sharp. Assuming that electrochemical etching takes place at a uniform rate over the surface exposed to the etchant and considering that the dominant tip is significantly larger than the microtips, it was hypothesized that etching could be performed for a sufficiently small amount of time such that the microtips could be removed leaving a single, sharp tip.

Examination of mechanically cut tips using SEM repeatedly indicates the presence of a pair of large microtips as seen in Fig. 1(b). These microtips are thought to result from a shattering effect as the tip wire is cut at an acute angle to form the tip. Electrochemical etching would result in the removal of material from all available surface area and, hence, this crack would be enlarged during the subsequent etching process. After etching, these microtips appear to be of different lengths with one microtip being significantly larger than the other as seen in Fig. 2.

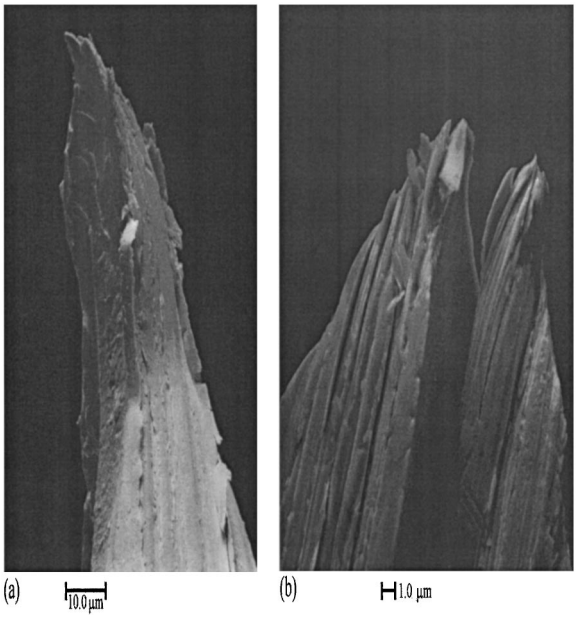

FIG. 1. (a) SEM image of a Pt–Ir tip formed by mechanically cutting Pt–Ir wire at an acute angle. The scale bar represents 10 μm. (b) Higher resolution SEM image of a mechanically cut Pt–Ir tip. Scale bar represents 1 μm.

Figure 3 shows a series of SEM images of tips etched for 0.25, 1, 3, and 10 s, respectively. SEM examination of the tip etched for 0.25 s reveals a reasonably sharp apex. The tip surface, however, appears jagged and rough with numerous whiskers. These whiskers are of comparable length and, hence, may easily form multiple simultaneous tunneling points. Tips etched for 1 s appear significantly smoother un-

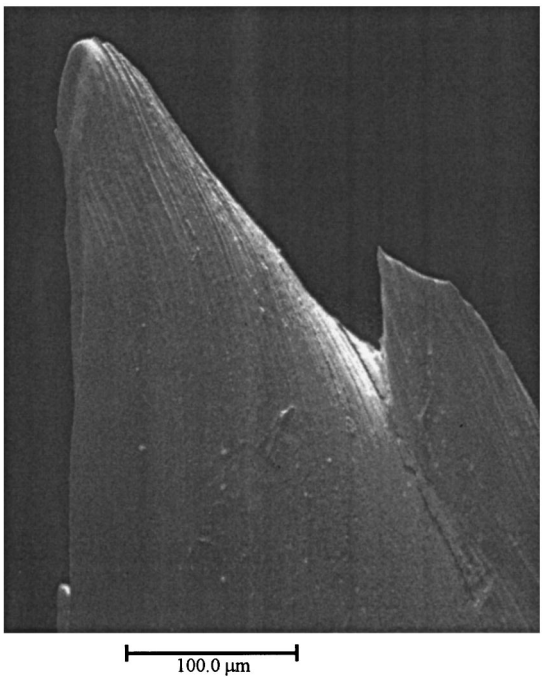

FIG. 2. SEM image of a mechanically cut Pt–Ir tip after electrochemical etching. Scale bar represents 100 μm.

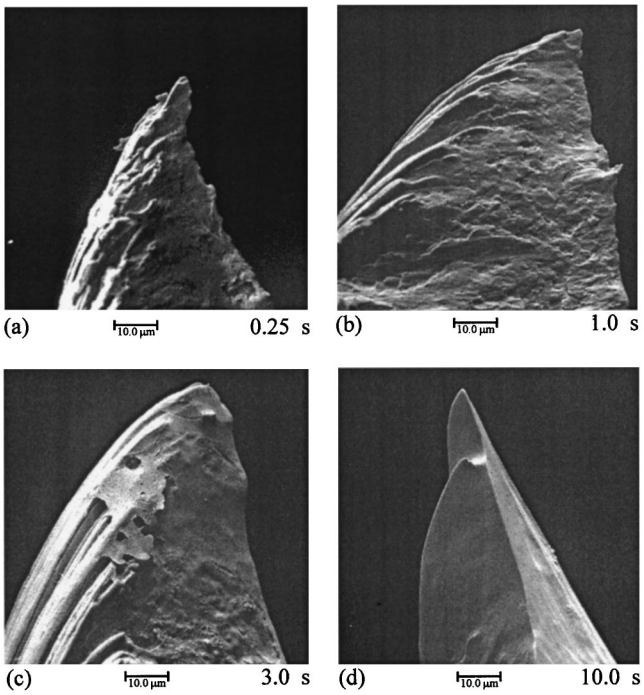

FIG. 3. SEM images of mechanically cut Pt–Ir tips following electrochemical etching. Etching times are as indicated, i.e., (a) 0.25, (b) 1, (c) 3, and (d) 10 s. Scale bar represents 10 μm in all images.

der SEM examination. Most of the whiskers have been etched away, leaving only smooth, rounded protrusions on the tip surface. In addition, the tip appears to be very sharp. The tip etched for 3 s yields a similar result although the surface does appear slightly smoother. SEM examination of the tip etched for 10 s reveals a very smooth, very sharp tip. All of the whiskers and rounded protrusions seen on the other tips have been etched away leaving only a single dominant tip.

Etching for longer periods of time was not attempted. Other work in our lab has shown that longer etching times lead to dramatic reductions in the aspect ratio of the tip and quite blunt tips. The tips etched for long periods rarely give good STM results.

TOF–SIMS spectra of the Pt–Ir tips before and after etching are shown in Fig. 4. XPS experiments using the same samples were also performed. Analysis of the Pt–Ir tips by both TOF–SIMS and XPS prior to electrochemical etching indicates the presence of high levels of carbon and oxygen. In addition, signals from platinum and iridium are lower in intensity than would be otherwise predicted. Following 10 s of electrochemical etching, TOF–SIMS and XPS spectra of the same tips show improved signals for platinum and iridium, and dramatically reduced signals for oxygen.

The relative amounts of various elements are given in Table I. Of special note is the dramatic rise in the amounts of observable Pt and Ir. This suggests that nonconductive oxides of platinum and iridium have been removed from the surface during the electrochemical etching procedure. Removal of these oxide layers improves tip performance in STM studies. TOF–SIMS and XPS signals for carbon did not change significantly. The carbon signal is obtained from material present in the vacuum chamber used to perform

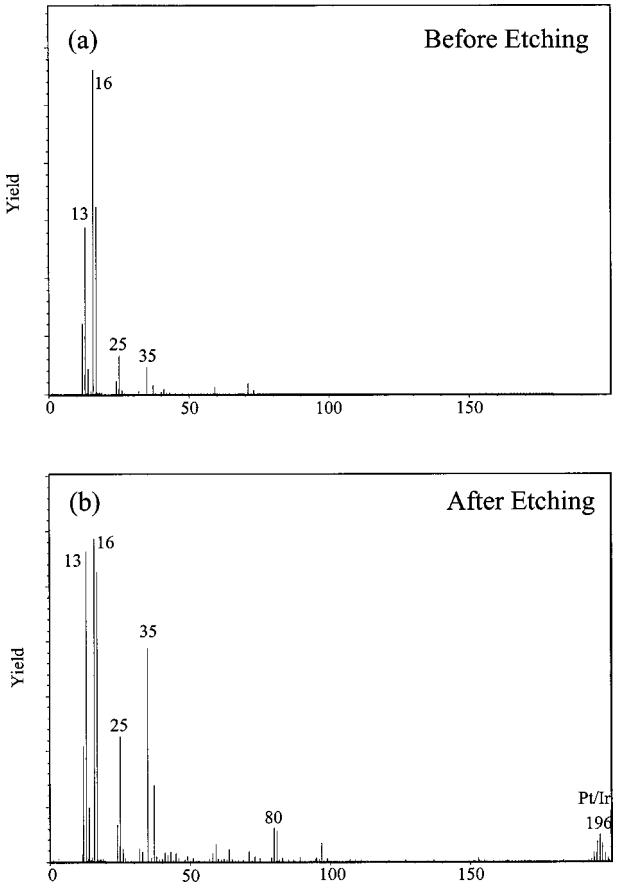

FIG. 4. TOF–SIMS yields for Pt–Ir tips (a) before etching and (b) after etching.

these studies. It should be noted that the XPS Cl signal has changed little after etching indicating that the etchant is very effectively removed in the washing step.

The etching part of the technique described in this article has also been applied to ''as-received'' commercial tips (Digital Instruments) when their performance was deemed to be unsatisfactory. This treatment invariably improved the tip characteristics and better STM imaging was possible. TOF–SIMS and XPS examination of the tips before and after this treatment gives identical results to those obtained when starting with unprocessed wire with the exception that a nitrogen signal is observed in the XPS spectrum. The amount of nitrogen is unaffected by the etching treatment. The nitrogen residues are thought to have remained following cyanide etching procedures often used in Pt–Ir tip production.

Attempts to image highly oriented pyrolytic graphite

TABLE I. (a) TOF–SIMS secondary ion yields of Pt and Ir (normalized to total yield) for control (unetched) and etched Pt–Ir tips and (b) parallel XPS surface atomic concentrations (at. %).

	(a) TOF–SIMS		(b) XPS	
	Control ($\times 10^3$)	Etched ($\times 10^3$)	Control	Etched
C			68.4	62.8
O			25.7	11.9
Pt	0.6	2.8	1.0	20.1
Ir	0.6	1.3	0.3	3.7
Cl			1.9	1.4

(HOPG) were carried out initially using tips prepared by cutting the tip wire at an acute angle. 30 Å square images were obtained using a 3 nA reference current at 20 mV bias. Images obtained using these tips appear noisy and distorted and the atomic detail of the HOPG is often difficult to distinguish. The same tips were then etched for 10 s using the technique described. Attempts to image HOPG under identical conditions then yielded images relatively free of noise or distortion and clearly show the atomic detail of the HOPG surface. This clearly indicates the improvement in image quality that is obtained through a short etching procedure.

STM image quality often deteriorates over extended periods of operation with a single tip due to contamination of the tip surface and atomic rearrangement at the tip apex. It has been found that such tips can be etched for a further 10 s using the techniques described to remove any surface contamination present. Such treatment may extend the lifetime of the tip indefinitely. Tips treated in this fashion have been found to produce images of identical or improved quality to those obtained using commercially available Pt–Ir tips. Implementation of such etching procedures could therefore be expected to result in quite significant savings when the expensive nature of Pt–Ir tips is considered.

A method for safe and rapid production of Pt–Ir tips for use in STM experiments is described. While the experiments described are for $Pt_{80}Ir_{20}$ wire, this etching technique should be equally applicable to Pt–Ir alloys of any composition. The method can be used to initially create the tip and subsequently to regenerate the tips after they have ceased to behave properly. This improvement in performance is related to both morphological and chemical changes of the tip as a result of the etching. This procedure allows the long-term use of these otherwise costly tips.

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[1] G. A. Fried, X. D. Wang, and K. W. Hipps, Rev. Sci. Instrum. **64**, 1495 (1993).
[2] E. I. Givargizov, A. N. Kiselev, L. N. Obolenskaya, and A. N. Stepanova, Appl. Surf. Sci. **67**, 73 (1993).
[3] T. Klitsner, R. S. Becker, and J. S. Vickers, Phys. Rev. B **41**, 3837 (1990).
[4] S. Watanabe, M. Aono, and M. Tsukada, Jpn. J. Appl. Phys., Part 1 **32**, 2911 (1993).
[5] M. Klein and G. Schwitzgebel, Rev. Sci. Instrum. **68**, 3099 (1997).
[6] H. Bourque and R. M. Leblanc, Rev. Sci. Instrum. **66**, 2695 (1995).
[7] J. Mèndez, M. Luna, and A. M. Barû, Surf. Sci. **266**, 294 (1992).
[8] H. Bourque and R. M. Leblanc, Rev. Sci. Instrum. **66**, 2695 (1995).
[9] A. Cricenti, E. Paparazzo, M. A. Scarselli, L. Moretto, and S. Selci, Rev. Sci. Instrum. **65**, 1558 (1994).
[10] L. Libioulle, Y. Houbion, and J. M. Gilles, Rev. Sci. Instrum. **66**, 97 (1995).
[11] A. A. Gorbunov, B. Wolf, and J. Edelmann, Rev. Sci. Instrum. **64**, 2393 (1993).
[12] V. Weinstein, M. Slutzky, A. Arenshtam, and E. Ben-Jacob, Rev. Sci. Instrum. **66**, 3075 (1995).
[13] L. A. Nagahara, T. Thundat, and S. M. Lindsay, Rev. Sci. Instrum. **60**, 3128 (1989).
[14] M. Fotino, Rev. Sci. Instrum. **64**, 159 (1993).