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Short Communication

The electrochemical etching of tungsten STM tips

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INTRODUCTION

The achievement of high resolution in scanning tunnelling microscopy (STM) relies on the use of sharp, high-aspect ratio tips which are usually produced from electrochemical etching of metals such as tungsten or platinum/platinum–iridium alloys under *dc* or *ac* conditions. A few general reviews on tip fabrication methods have appeared in the literature [1–5], but many STM publications omit crucial details on the tip preparation method for their studies. Where they are reported, very little attention is given to optimizing the methods used to produce tips of high aspect ratio and small radii of curvature. Recently, much effort has focused on the use of two-step fabrication techniques; the first step to produce a fine point using electrochemical etching, followed by a second process, usually ion-milling, to obtain the sharp tip apex [6]. For many applications, including those where atomic resolution is not required, two-step fabrication methods are often unnecessary and electrochemical etching alone will produce sufficiently sharp tips. This short communication reports the findings of a systematic study to address the relative importance of various factors affecting one-step electrochemical etching of tungsten wire to produce sharp tips under steady-state *dc* conditions. The aim was to define conditions where the etching rate was high while achieving acceptably sharp tips.

EXPERIMENTAL

STM tips were prepared from electrochemically etched, high-purity tungsten wire (0.25 mm diameter, 99.95% purity; Goodfellow, Cambridge, U.K.). Sodium hydroxide and potassium hydroxide pellets (BDH, microselect) were used as received. Double-distilled water was used to dilute alkali metal hydroxides.

The well-known "loop" technique was used to anodically fabricate tungsten STM tips [5]; a drop of the etchant solution (typically, 2 M NaOH) was placed on a platinum wire ring cathode (wire thickness, 0.4 mm) so as to produce a thin film (Fig. 1). The wire to be etched was then placed through this film and a potential applied between the ring electrode and the wire (inter-electrode gap, 4 mm). After a few minutes, etching was complete. The lower section of the wire fell away from the ring and was carefully collected in a narrow-walled glass cylinder, shorter than the length of the lower tip so that the side walls did not touch the tip apex. Experiments were performed at room temperature, 22°C. Both upper and lower sections of the etched surfaces of the tungsten wires were examined using an optical microscope and a JEOL JSM-35C SEM.

STM measurements were performed in air under normal atmospheric conditions using a Discoverer TopoMetrix TMX2000 Scanning Probe Microscope (TopoMetrix Corporation, Essex, U.K.). A scanner

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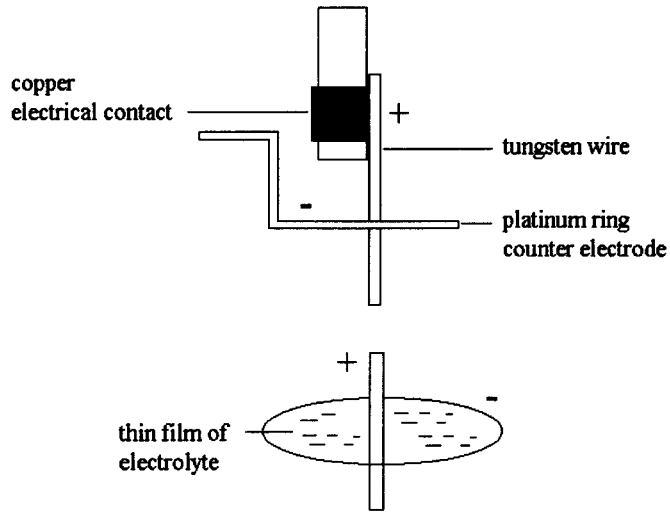

Fig. 1. Typical apparatus used for the "loop" etching technique.

capable of a maximum *X-Y* translation of $25 \times 25\ \mu m$ was used and images were obtained using a tip bias potential of 10 mV (sample at 0 V). Tip sharpness and performance were assessed by imaging an aluminum-coated, silicon grid sample.

RESULTS AND DISCUSSION

Effect of cell potential on etch rate and tip geometry

For classification purposes, it is convenient to define two parameters, *viz.* the "tip angle", θ and "etch length", a (Fig. 2). The former is simply a measure of the sharpness of the tip, while the etch length is the distance from where the wire begins to dissolve due to the surface tension of the electrolyte to the apex of the tip.

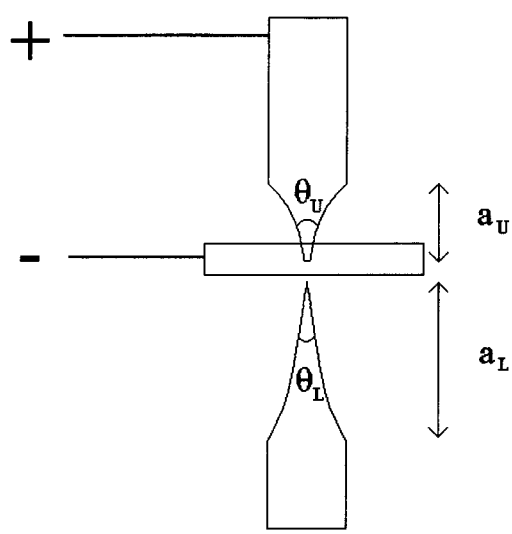

Fig. 2. Schematic defining "tip angle", θ, and "etch length", a. Subscripts "U" and "L" denote upper and lower tips, respectively.

To investigate the effect of cell potential on etch rate, potentiostatic polarisation curves [7] of tungsten in alkali media using the electrochemical apparatus described were obtained (Fig. 3). Etching typically commenced at an applied cell potential of *ca.* +1.4 V. The current reached a plateau at *ca.* 2 V, but on increasing the potential further, the current density did not change significantly up until the onset of oxygen evolution at a cell potential of *ca.* 9 V. Above 5 V, a thick black oxide film was sometimes produced, rendering the tip non-conducting [1].

Figure 4 shows some typical tip-profiles obtained from etching at constant cell voltages of 4, 5, 10, 15 and 20 V in 2 M KOH. In all cases, distinct differences in tip-shape between upper tips, *ie* those remaining above the platinum ring after the etching process, and lower-tips, the "drop-off" sections, were observed. The upper tips generally had a conical profile which would be expected from surface tension considerations [5]. The lower tips possessed a tapered profile and were much sharper as a result of the increased force per unit area on the reducing diameter of the wire as etching proceeded. In the final stages of etching, the high current density acting at the very apex of the lower tip produced a very fine, high aspect ratio tip.

In all cases, the etching time was inversely proportional to the cell voltage. The effect of cell potentials less than 4 V on tip sharpness were not investigated due to an impractically long etching time. At potentials of 4 and 5 V, there were no significant differences in profiles for upper tips. This was also the case for lower tips, although these had a longer etch length than upper tips since the weight

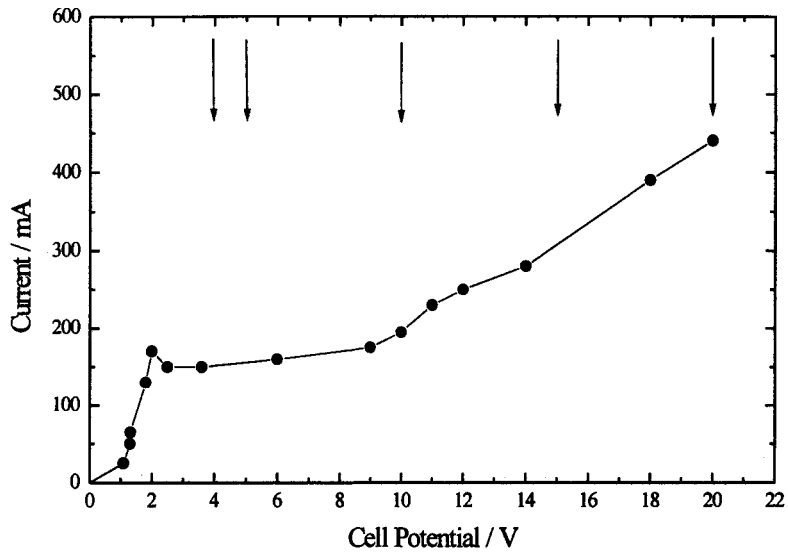

Fig. 3. Current *vs* cell potential curve for tungsten in 2 M aq KOH at 22°C (Pt wire ring cathode). Vertical arrows show cell potentials used.

of the wire pulled it through the etching region. The upper tips were also affected by the time taken to switch off the potential after etching had completed. Although this time was only about 1 s, a significant amount of etching at the apex could occur resulting in tip broadening. For cell potentials of 10 V and above, very irreproducible behaviour was observed. Some tips appeared to be covered in dark oxide layers, most probably WO_3, while others were clean, but very sharp and often possessed recoiled ends [Fig. 4(e)]. "Ball-shaped" features were occasionally observed at the apex of upper-tips when using very positive cell voltages. These were probably formed as a result of the rapid etching causing a sudden release of energy dissipated as heat to the end of the tip resulting in localised melting, as observed elsewhere [1].

Effect of different alkali metal hydroxide electrolytes

The literature reports the use of both KOH and NaOH as etchants for tungsten etching. After performing many etching experiments using 2 M solutions of these two etchants, we conclude that the use of a sodium rather than a potassium cation had no direct influence on the rate of reaction, tip angles or etch lengths.

Effect of etchant concentration

The etch rate was significantly reduced when the concentration of NaOH was changed from 2 to 0.5 M. For potentials of 4 and 5 V, there were no obvious changes in tip profiles for the upper or lower tips. At potentials above 5 V, oxide layers were more frequently observed on tips compared with those obtained from etching in more concentrated electrolytes. Concentration effects can be rationalized by considering the decrease in pH during etching. The lower pH of the 0.5 M electrolyte will mean that the system lies closer to the zone of passivity (on the Pourbaix diagram of the tungsten–water system) than the higher concentration electrolyte [8]. Therefore, more oxide would be expected from lower alkali concentrations.

Effect of applied force on etch-rates and tip-profiles

The length of the wire protruding below the platinum ring cathode was inversely proportional to the etch time (Table 1). This would suggest that very small forces ($< ca.$ 0.2 mN) have a direct influence on the etching reaction. While there does not appear to be any significant effect of applied force on etch length, sharper lower tips (θ_L) were favoured with increased wire tension. Tips corresponding to wire lengths of 5 and 10 cm possessed broken ends due to the weight of the wire exceeding the mechanical strength of the fine, necked region during etching.

Microscopic characterization of tips by SEM

While optical microscopy studies are useful for screening fabricated tips, it may be that tips which appear sharp have large radii of curvature or that blunt tips may, in fact, possess sub-micrometre protrusions which would make them ideal tunnelling tips. SEM studies of a large number of tips which were considered "sharp" from optical microscopy studies were found to possess defects at the apex. In addition, many possessed large radii of curvature, typically in the range 300–400 nm. Figure 5 shows

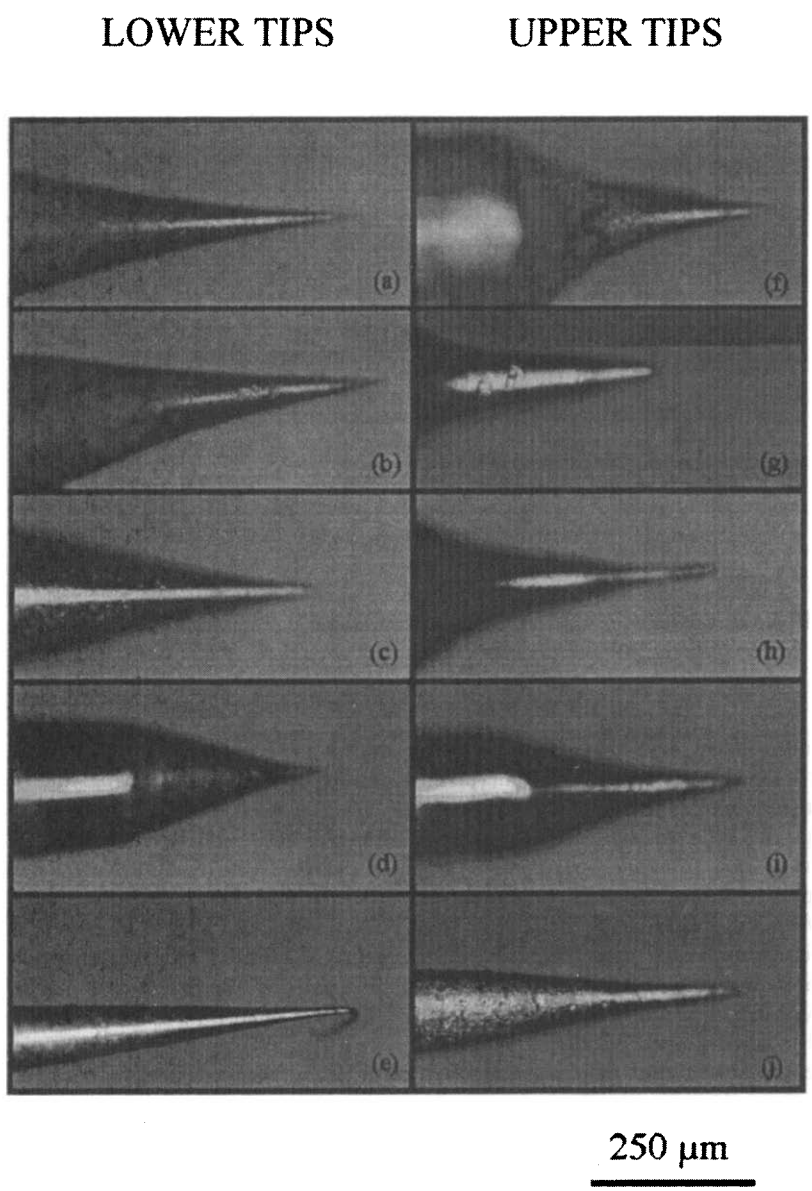

Fig. 4. Optical micrographs of tungsten tips obtained from electrochemical etching using 2 M aq KOH; cell potential: (a) 4, (b) 5, (c) 10, (d) 15 and (e) 20 V; (a)–(e) lower "drop off" tips, (f)–(j) corresponding upper tips.

Table 1.
Effect of applied force on etch-rate and tip-profiles of electrochemically etched tungsten tips

Length of wire (cm)	Mass of wire (mg)	Upper-tip angle, θ_U (°)	Lower-tip angle, θ_L (°)	Upper-tip etch length a_U (μ m)	Lower tip etch length a_L (μ m)	Etch time (s)
1	9.5	20	33	62	39	690
2	19.0	22	22	44	76	680
3	28.4	24	18	41	77	671
4	37.9	25	12	45	77	660
5[a]	47.4	—	—	—	—	649
6	56.9	41	16	36	80	640
7	66.4	61	15	41	78	638
8	75.8	24	11	39	66	630
9	85.3	—	10	39	74	620
10[a]	94.8	—	—	—	—	608

[a]Wire snapped under applied load.

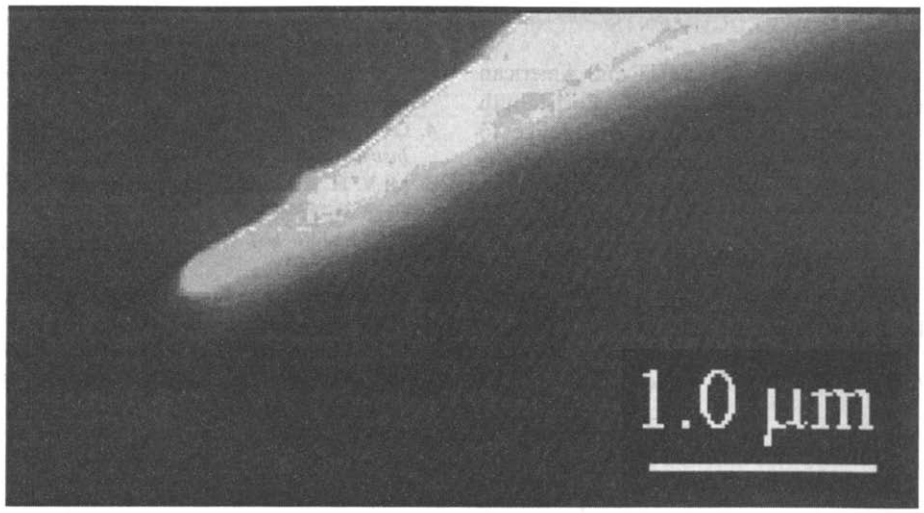

Fig. 5. SEM micrograph of a "sharp" tip; radius of curvature = 80 nm.

one of the sharpest lower tips produced, having a radius of curvature of 80 nm.

Tip characterization using STM

To examine the performance of various tips, an aluminum-coated silicon wafer sample possessing a regular grid pattern of 2 μm pitch was imaged. Tips of large radii of curvature (> 500 nm) gave noisy images of low resolution [Fig. 6(a)]. With an intermediate range of curvature (*ca.* 300–400 nm) image resolution was improved, but "ghost" images could be seen resulting from broad tunnelling away from the apex tip [Fig. 6(b)]. The best image was obtained using a tip possessing a radius of curvature of 80 nm [Fig. 6(c)]. Radii of curvature, rather than tip aspect ratio, influence tunnelling in the images presented in Fig. 6. However, imaging steep side walls of features would result in artifacts when using tips of low aspect ratio.

CONCLUSIONS

Factors influencing the electrochemical etching of tungsten under *dc* conditions using a one-step process to produce sharp, high aspect-ratio STM tips have been investigated. The optimum conditions for tip fabrication were:

(a) use of a relatively low value of cell potential (< 5 V);
(b) use of KOH or NaOH electrolyte concentrations of 2 M;
(c) applying tension to the wire during etching, but making sure that the wire did not snap under the applied load.

Tips should be initially screened using optical microscopy and then imaged by SEM to calculate the radius of curvature, a fundamental parameter for effective STM tips.

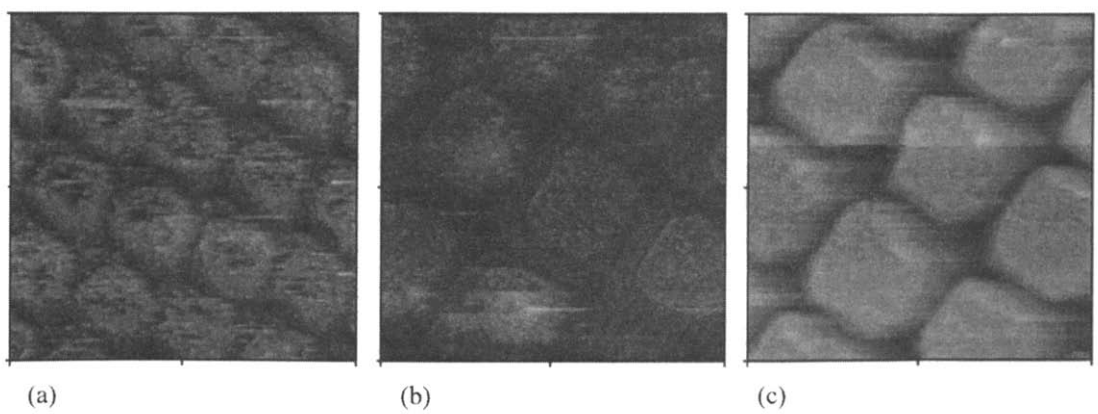

Fig. 6. STM micrographs of aluminum-coated, silicon grids obtained using tungsten tips of radii of curvature (a) > 500, (b) 300–400 and (c) 80 nm; bias potential = 10 mV, tunnelling current = 1.0 nA; scan rate = 20 μm s^{-1}; dimensions: $X = Y = 7.95$ μm, Z = (a) 296, (b) 215 and (c) 250 nm.

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