Ni and W nanotips: Fabrication and characterisation

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Abstract. Etching techniques are used to fabricate nickel and tungsten tips suitable as probes for in-situ SEM and TEM experiments. The smallest tip radius achieved is 10nm for Ni and 1.5nm for W. Depending on the electrolyte concentration and speed of tip movement during etching, the macroscopic morphology can be changed between conical and concave shapes and the tip end can be modified. HREM and EELS characterisation is used to determine oxide layer thickness. For Ni the oxide layer is found to be extremely thin, while for W various thicknesses can be achieved. The particular amorphous WO₃ layer is imaged by plasmon resonance mapping in EELS, which turns out to be a sensitive and discriminative technique exploiting the much larger plasmon peak width of the oxide compared to the pure metal.

1. Introduction
Metal nanoprobes have multiple applications in nanotechnology, most notably for mechanical and electrical testing. For the latter, hardness and stiffness of the tip are most important while conductivity and a minimum of ductility are often added as further criteria. This leads to W-metal as first choice for such applications as nanoindentation and for STM tip materials. A second group of applications takes advantage of the combined properties of ferromagnetism, easy plastic flow, high surface oxidation resistance and high conductivity, which are all shared by Ni as tip materials. Ni has therefore developed into a common material for studies of point contact ballistic magnetoresistance, but also serves as a standard for fcc-nanopillar deformation in extreme nanoscale mechanical deformation studies. In the present work, fabrication of Ni and W nanotips are compared and TEM characterization of the tip morphology and chemistry is presented including high resolution studies of possible oxidation layers.

2. Tip fabrication and SEM Imaging
Tungsten (W) tips were fabricated using the well known electrochemical etching method based on simple electronics and an electrochemical cell as described in [1] and with our local details as in [2]. We adapted this method, but with slight modifications [3-5] to produce sharp Ni tips with good tip-apex. Ni tips were prepared from 0.125 mm diameter Ni wire (Advent Research Materials, UK, 99.98%) by electrochemical etching. A 1M NaCl (Fisher, UK, 99.97%) aqueous solution was used as the electrolyte at 2–2.5V dc voltage supplied using a normal power supply. The etching apparatus is a simple one arranged in our Laboratory, the anode electrode of the Ni wire, which was clamped in a tweezer passed through a NaCl thin membrane captured on an Au cathode ring of diameter 10 mm.

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The initial etching current is relatively high, around 12mA. As the nickel necks off, electrolyte loses some of its conductivity, the current gradually falls and drops almost to zero at the end of the etching process. When etching is completed, the lower part of the wire is separated from the upper part and moves downwards due to gravity, but sometime it hangs from the film, if the weight of the lower part is less than the upward force due to surface tension acting on it. In order to detach it from the film we attached a small weight sphere of clay at the lower end of the wire. This lower part is then collected in a small plastic beaker of 4mm in diameter, placed just below the wire.

For a 0.125 mm diameter Ni wire, the etching lasts only a couple of minutes. By this method we obtained two tips at one attempt, the lower one with high aspect ratio (Fig 1a) and the upper one with low aspect ratio (Fig 1b) with reproducibility of around 80%.

We used two slightly different experimental techniques to produce tips with different shape. To produce a sharper tip, but shorter in length as shown in Fig 1a and b, the ring was first dipped into NaCl solution while gently trapping a membrane on it. A length of Ni wire was then inserted vertically at the centre of the membrane and allowed to etch. On the other hand, when we immersed the ring system with Ni wire at the centre as a whole into the beaker with NaCl solution and then removed the beaker we captured a membrane of NaCl on the ring. A greater length of the wire would wet resulting in more length being etched. This yields sharper tips longer in length as shown in Fig 1c.

**Figure 1.** SEM image of Ni tips (a) Lower tip of etching couple: Scale bar 30\(\mu\)m, (b) Upper tip of etching couple: Scale bar 30\(\mu\)m, (c) Longer tip (see text for details): Scale bar 300\(\mu\)m.

**Figure 2.** TEM images of (a) Ni tip, (b) Another Ni tip with neck-formation formed at the moment of break-off, (c) Detail of the tip of (a) with diagonal fault lines (composition from 2 micrographs)
3. TEM and EELS Analysis

TEM and HREM imaging can reveal the polycrystalline structure of the metal as well as the detailed tip-shape, such as deviations from roundness, surface roughness and oxide layers. A 3D tomographic reconstruction of a W tip has been presented in [6]. In this work we use a JEM 2010F FEGTEM at 200kV with Gatan GIF EELS spectrometer.

**Ni tips:**

Nickel tips with different cone angle are shown in Fig 2a,b. The magnified image (Fig 2c) of the tip of Fig 2a shows a series of parallel slip bands indicating a single grain at this front end of the tip, as also confirmed by selected area diffraction. Shortly before break-off the tip experiences significant stress under gravity during fabrication. Two magnified images of the tip of Fig 2b are shown in Fig 3a,b emphasizing the very thin (2-3nm) oxide layer and a neck-formation formed at the moment of break-off. Such necks are generally undesirable for mechanical testing, but do not necessarily compromise electric testing performance, especially as extremely small tip curvature can be achieved in this way. Two EELS spectra of the O-K-edge and Ni-L-edge region complement our analysis (Fig 3c,d).

**W tips:**

An annular dark field STEM image of a tungsten tip is shown in Fig 4a, highlighting the core-shell structure with a bright core (higher average atomic number Z). Previous analysis [6] has identified the core as metallic W and the oxide as amorphous WO$_3$. The separation of the metal tungsten from its oxide is a wide spread problem, and has extensive importance throughout nanotechnology applications, including STM imaging and nanoindentation. Apart from oxygen mapping using energy filtered imaging [6], application of EELS is complicated by the fact that W has no high contrast edges in energy regions with good signal-to-noise ratio. It is therefore desirable to explore how low-loss EELS with its very high contrast can be used to map the distribution of metal and oxide. A low-loss EELS spectrum recorded from the centre of the tip is presented as Fig 4b, indicating a major resonance near 25eV and a minor excitation near 50eV. The former is the primary plasmon resonance while the latter constitutes a superposition of inner shell losses with onset energies of 37 (W-N6) and 47 (W-O2) eV [7] and possible double excitation of the 25eV peak. A line scan has been acquired with Gatan Digiscan and Spectrum Imaging software along a cross-section through the W wire near the tip (see Fig 4a). The magnified region around the 25eV plasmon resonance (Fig 4c) shows primarily distinct absorption effects, as the plasmon intensity inside the W core drops by a factor of 2 compared to the oxide shell. Unlike for the system Al-Al$_2$O$_3$ [8], however, the resonance maxima for W metal and WO$_3$ are found to be almost coincident. We therefore postprocess the spectrum image of Fig 4a into a 2nd derivative map (Fig 4d) to quantify the width of the peaks. In this case the metallic core now appears with bright contrast due to its sharpness of resonance compared with the oxide, which shows a very wide resonance maximum. Further discrimination between the two phases can be gained from the
40-50 eV region, where W contributes N- and O-shell peaks, and again the pure W metal sticks out by the sharpness of the peak.

Figure 4. (a) Shows the cross-section along with the line scan is acquired (b) Low-loss EELS spectrum recorded from the centre of the tip (c) Line scan acquired along a cross-section through the W wire near the tip (d) 2nd derivative map.

4. Conclusions
Using carefully selected etching conditions, we have shown that nickel tips with ultra-thin oxide layer can be produced at least as sharp as the more common procedure for tungsten tips. EELS Line scan spectrum imaging in the low-loss region is demonstrated in combination with 2nd derivative mapping to separate W and WO₃ phases in spite of nearly coinciding plasmon resonance.

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