doi:10.1017/S1431927613004650

Microsc. Microanal. 19 (Suppl 2), 2013

Tungsten Tips as a Sample Platform for Single Atom Resolution S/TEM Tomography of Clusters and Interfaces

Peter Ercius[1] and Wolfgang Theis[2]

[1.] National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, USA
[2.] School of Physics and Astronomy, University of Birmingham, Birmingham, UK

An aberration-corrected (scanning) transmission electron microscope S/TEM can now resolve single atoms in special cases where the background is sufficiently low and the atoms are stable on / within a substrate [1-2]. Tilting such a sample on a slab-like substrate to high angles – for example in electron tomography – increases the sample thickness by >2.8× at tilts >70° such that resolution and the signal to noise ratio may be significantly degraded for single atom counting. Even the thinnest slab-like TEM substrates like ultra-thin carbon have thicknesses of 3 – 5 nm resulting in a much thicker substrate at high tilts. A needle-like geometry is ideal for tomography experiments due to the lack of a background signal from a substrate, and FIB preparation has been previously used for this purpose. However, preparing needles with a sufficiently small radius of curvature at the tip and minimal damage is challenging for many materials. Nanoparticles, for example, can not be prepared this way, and FIB induced damage at the tip can destroy many other types of samples.

We demonstrate ultra-sharp W needles prepared by KOH etching similar to procedures used in the STM community as a substrate for high-resolution tomography [3]. Tips can be mounted in a normal holder for high-tilt, zero-background imaging or in a 360° rotation holder for full rotational access around one axis for a full tomography tilt-series. Further, the tips can be mounted in the TEAM stage in the TEAM I microscope at NCEM with ±20° axial tilt and ±180° rotational tilt without shadowing. Such a large range of motion provides an ideal platform for traditional and zone-axis (discrete) electron tomography.

Figure 1 shows a series of TEM images of a W tip at progressively smaller length scales. W wire is etched in a KOH bath to produce a 5 – 20 nm radius of curvature at the tip. The overall etching shape of the tip is apparent in Figure 1a. An amorphous W oxide layer grows after extended exposure to air, and a tip with a crystalline center and oxide covering is seen in Figure 1b. The amorphous material can be used as the final substrate or removed by a short dip in KOH etchant. Once formed, the tip provides a platform for direct deposition of materials by various growth methods in vacuum (MBE, PVD, etc.) or drop cast from solution. A suite of dedicated equipment has been developed to allow rapid preparation and screening of W tips with deposited clusters. For example, Au islands were grown on a tip by molecular beam epitaxy (MBE) ready for HR-S/TEM imaging from multiple orientations (Figure 1c).

A second geometry with a single-crystalline (110) terrace (see Figure 2) is produced after various post-processing steps including high temperature annealing. This geometry could be used to deposit multilayers under high vacuum and possibly capped for protection against reactions with air. The material can then be directly imaged along multiple zone-axes in a S/TEM without further sample preparation by grinding and ion milling. The tip in Figure 2 has Au nanoparticles attached to the terrace.

In the aberration-corrected TEAM I microscope at the National Center for Electron Microscopy these types of samples provide a unique capability for zero-background HR-S/TEM imaging along multiple zone-axes. Figure 3 shows a Au nanoparticle grown by MBE imagined in high-angle annular dark field

(HAADF) STEM mode along the [!̄ ! !], [! " "], [! ! !] and [! " "] zone-axes of the W tip at 300 keV with a 30 mrad probe convergence semi-angle and 70 pA of beam current. The W tip has an 18 nm radius of curvature allowing for a large range of viewing angles. The interface between the Au and W is visible as is the shape of the particle.

The development of a versatile tomography sample platform described in this work is an important step in our effort to enable atomic resolution electron tomography of nanomaterials such as clusters, catalysts and multilayers.

References

[1] S van Aert, KJ Batenburg, MD Rossell, R Erni, GV Tendeloo, Nature **470** (2011) pp. 374 - 377.
[2] OL Krivanek, MF Chisholm, V Nicolosi, TJ Pennycook, GJ Corbin, N Dellby, MF Murfitt, CS Own, ZS Szilagyi, MP Oxley, ST Pantelides and SJ Pennycook, Nature **464** (2010) pp. 571 - 574.
[3] OL Guise, JW Ahner, MC Jung, PC Goughnour and JT Yates, Jr, Nano Letters **2** (2002) pp. 191-193
[4] NCEM is supported by the Office of Science, Office of Basic Energy Sciences, Scientific User Facilities Division, of the U.S. Department of Energy under Contract No. DE-AC02—05CH11231.

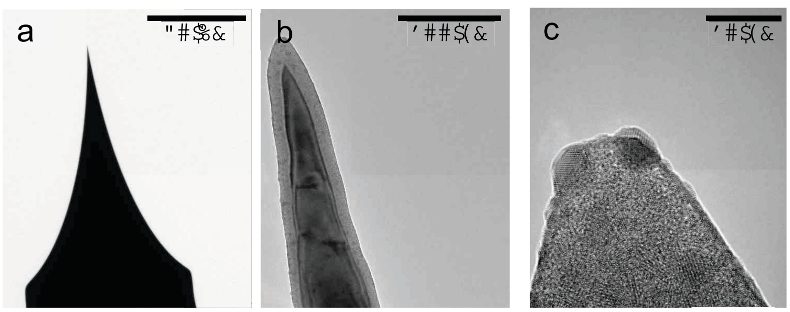

Figure 1. TEM images of an etched W tip at different length scales. The KOH etching creates (a) a tapered surface with (b) a very sharp tip. Materials such as (a) Au can be deposited on the tip for imaging with a large tilt range.

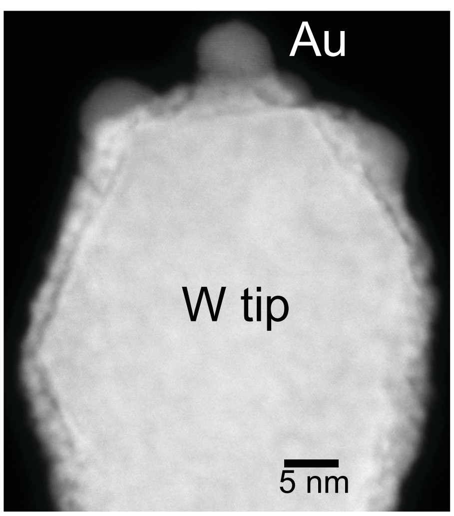

Figure 2. Post-processing the W tip after KOH etching creates a single crystalline, faceted structure with a (011) terrace perpendicular to the tip axis. Materials can be deposited on the terrace and the W tip used to orient on zone. Dark field STEM image of W tip and MBE grown Au clusters.

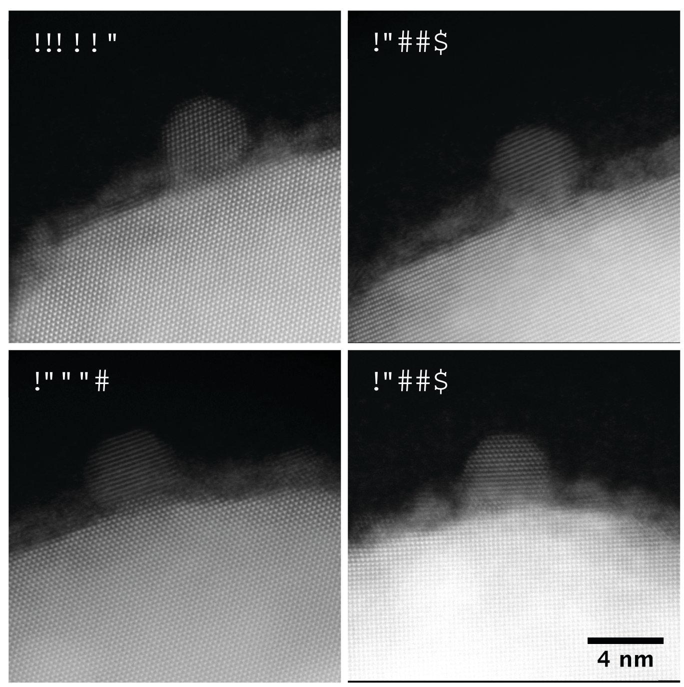

Figure 3. A W tip with a Au particle grown by MBE. The tip is imaged in STEM mode along 4 different zone axes at atomic resolution showing the particle's shape and the Au / W interface. Such a sample is ideal for discrete (zone-axis) 3D tomography.

https://doi.org/10.1017/S1431927613004650 Published online by Cambridge University Press