One Nanometer Radius of Curvature Metallic Probes Created by Field-Directed Sputter Sharpening

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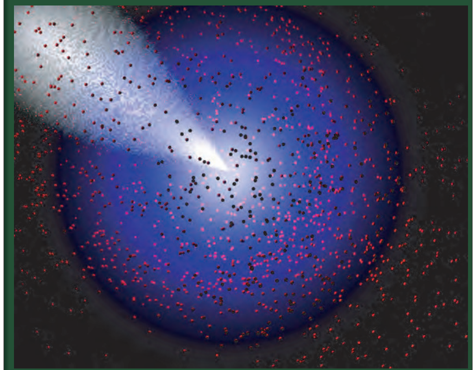
Introduction

We have developed a new field-directed sputter sharpening (FDSS) technique for producing sub-nanometer radius of curvature probes for scanned probe and field emission applications. In FDSS a positive bias is applied to a dull probe while it is subjected to on-axis ion sputtering. The field enhancement near the probe apex deflects some of the ions resulting in preferential sputtering away from the apex. This sharpens the apex, which enhances the selectivity of this process. Ultimately, FDSS is self-limiting and final tip radii of curvature <1 nm are routinely achieved.

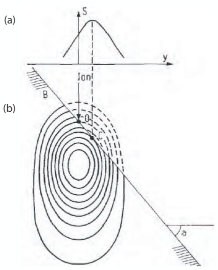
It is well known that the sputtering of a probe by energetic ions can effect its apex form. Efforts spanning several decades have repeatedly verified this effect, including the fundamental theoretical works of Sigmund [1] and the experimental efforts of Kubby and Siegel [2], among others. Results of these attempts have demonstrated an ability to construct probes on a scale of 5 to 10 nanometers.

Simulation suggests that roughness in probe surfaces may result in sharper probes for FDSS cases. Experimental observations in the Transmission Electron Microscope and Field Ion Microscope indicate that unbiased tips offer an expected radius of curvature of approximately 5 nanometers while the FDSS procedure reliably and reproducibly generates single nanometer or sub-nanometer radii with a single atom apex.



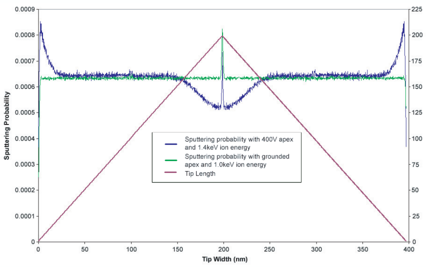
Above: Computer generated representation of the Field-Directed Sputter Sharpening process.

Sputtering Theory and Simulation



Left: Diagram from reference [3] demonstrating a second-order approach to sputter erosion as defined by the Sigmund theory of sputtering [1,3]. Sputtering probability (a) is shown along an angled surface (b), where the region of highest sputter probability is offset from the location of ion impact due to ion penetration of the surface.

Right: Two-dimensional computer simulation of sputtering probability along the length of a sharp tungsten probe given a uniform random distribution of incoming ions. The red curve provides the probe length along its width, the green curve represents the probability of atomic removal at each point for a random sputtering event by 1.0keV ions and the blue curve demonstrates probability of atomic removal when a bias of 400V is applied uniformly to the probe and the ion energy is increased to 1.4keV.

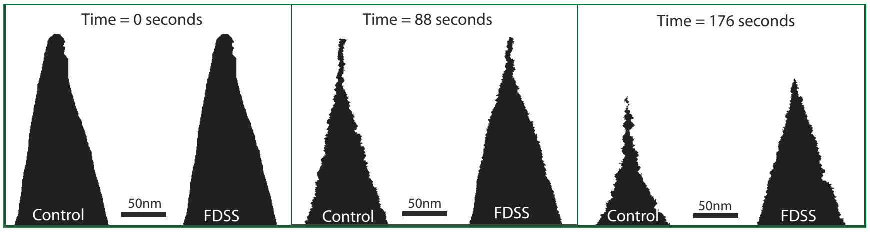


Upon impact of energetic ions at a solid surface, where the ion energies are sufficiently high to excite the removal of surface atoms, but not sufficiently high as to fall under the category of ion implantation, sputtering of atoms from the surface layer can occur. Removal of atoms from the crystal lattice leads to modification of the surface structure, which proceeds in a predictable manner. Within the Sigmund theory of sputtering, surface modification can be approximated on the large scale by introducing an angular dependence to the sputter yield. At scales small relative to the ion penetration depth, one can apply a second-order erosion theory. Sputtering probability for surface atoms is computed by allowing impinging ions to enter the surface to their penetration depth, before dissipating stored energy over a region elongated along the axis of ion trajectory.

For analysis of the FDSS technique, a simulation engine based upon this sputtering model was developed[1]. In addition to duplicating these traditional sputtering simulations, our software performs an iterative solution of the Poisson equation in the vacuum region surrounding a probe, reproducing the electrical potential surrounding any apex and allowing for simulation of each ion trajectory.

With this simulation we observe a decrease in sputtering propensity for atoms near a sharp surface asperity, as seen in the above right. Such behavior results from the selective repulsion of ions from regions of high electric field, allowing for reproducible and self-limiting sputter sharpening of metallic tips. By comparison no such effect is observed in the unbiased control case. As expected, boundary condition fluctuations are observed near the tip edge in our biased case. A single abrupt peak is observed for both cases immediately at the probe apex, but this is suspected to be an artifact of the simulation without physical significance.

In an effort to understand the progression of an FDSS procedure simulation was performed at voltages beyond experimental reach. The application of high ion energies allows for small surface features, which may otherwise be overwhelmed by limitations in the surface migration algorithm, to become distinct. In the unbiased control case we observe development of rough surface features, consistent with prevailing theory, while this roughening is strikingly absent from the FDSS tip. The unbiased control tip is seen to oscillate regularly between superior radii of curvature and significantly larger apices, while our experimental apex maintains its form with superb reliability throughout the sputtering process.



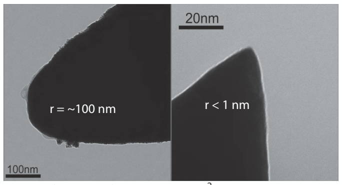
Above: Simulation results for both FDSS processed probes and unbiased control tips over a period of 176 seconds. A bias of 50kV was applied to the FDSS probe, while ions with energies of 150keV were injected for sputtering of the control probe, and 200keV for the FDSS probe. As a result of the high voltages applied in this simulation, surface features of interest are visible despite limitations in simulated surface atom migration. As our simulator disregards any effects beyond Sigmund's sputtering theory, no additional mechanics exist in this high bias simulation.

[1]Computation of ion range and energy dissipation parameters was performed by SRIM 2003 software package and results provided to our simulator

Characterization by Transmission Electron Microscopy

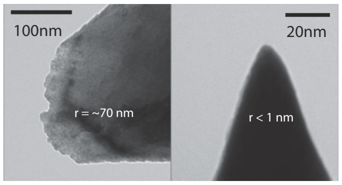
Transmission Electron Microscopy (TEM) provides an ideal technique for the verification of nanometer-scale probe formation. Typical apices resulting from FDSS provide single nanometer or sub-nanometer radii of curvature with half cone angles between 20° and 35°. Given sufficient sputtering activity and a sub-micron single-apex probe, such tips can be reliably produced. Under our present configuration sputtering times ranging from 20 to 40 minutes are commonly required to achieve atomic-scale sharpening of a 100 nm metallic probe, though additional sputtering does not adversely effect the tip apex.

As compared to most existing methods for the construction of atomically sharp probes, FDSS allows for the sputter sharpening of probes from a variety of materials, as the technique is not chemically restricted. In practice, any metallic compound can be sharpened by FDSS, as demonstrated herein by the sharpening of both tungsten and of a platinum-iridium alloy. Of significant interest are those materials resistant to oxidation which can be freely removed from the ultra-high vacuum environment, such as noble metals, or materials more resistant to physical damage, such as titanium nitride or diamond-like carbon coatings applied to existing metal tips.

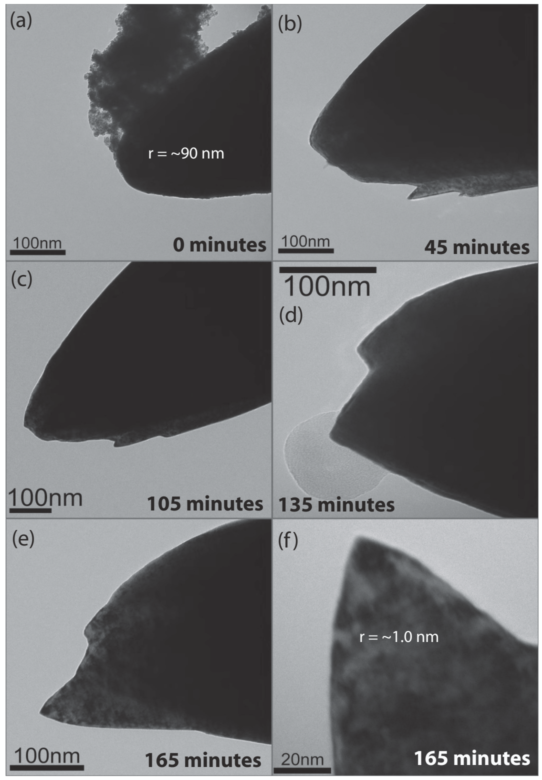


Above: Initial and final images of platinum-iridium alloy[2] sharpened to a sub-nanometer radius of curvature by FDSS. We applied a bias of 400V to the probe while sputtering was induced by 2.00keV Neon ions for 35 minutes.

[2]Platinum-Iridium STM tips purchased from Materials Analytical Services, Inc, Raleigh, NC



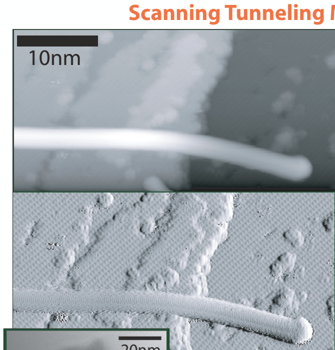
Above: Electrochemically etched polycrystalline tungsten sharpened to a nanometer-scale radius of curvature by FDSS. We applied a bias of 200V to the probe while sputtering was accomplished by 1.20keV neon ions for 62 minutes.

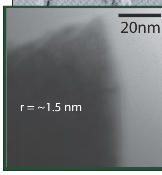


Incremental Sharpening of a Platinum-Iridium Probe by FDSS

For the effect observed in the above image series, sputtering was performed under reduced ion density to limit the rate of modification. This reduction was accomplished by alignment of the tip only partially with the ion beam. A tip voltage of 400V was applied with sputtering induced by 2.00keV neon ions.

Scanning Tunneling Microscopy





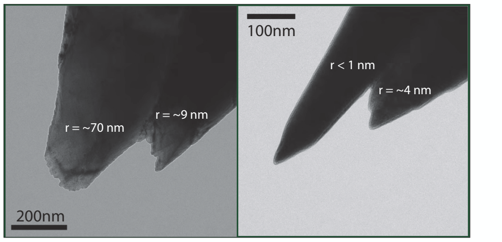
Left: TEM micrograph of tungsten STM probe following a 35 minute FDSS procedure with a tip bias of 400V and ion energies of 2.00keV.
Far Above: Topographic cross-sectional STM image (-1.8V, 7pA) of a SWNT crossing a terrace edge on an undoped cleaved InAs wafer.
Above: Current buffer image of the above SWNT and surface in which surface structure and nanotube chirality can be seen in greater detail.

Nanoscale metallic probes generated by FDSS offer distinct benefits in Scanning Tunneling Microscopy (STM). FDSS tips contain a single atomically precise apex, thus avoiding multiple-tip shadow effects in STM images. By dramatic reduction in the probe radius of curvature as well as cone angle, the effects of tip-surface convolution on the resulting STM image are minimized, allowing abrupt features such as the single-walled carbon nanotube (SWNT) seen here to appear clearly. Measured height of the SWNT is 1.15 nm with an observed full width at half maximum of 2.25 nm, results indicative of a sharp tip apex.

The polycrystalline tungsten tip used for this scan was electrochemically etched to a radius of 90 nanometers, then sputtered to an approximate single nanometer radius, as shown.

The sputtered probe was found to endure extensive use in the STM, including a three hour Current Image Tunneling Spectroscopy (CITS) data collection cycle.

Simultaneous Sharpening of Parallel Probes



Multiple tips can be sharpened in parallel, as long as reasonable spacing of at least 100-200 nanometers exists between apices. If tips are closely packed, or one is significantly more prominent, secondary apices may experience limited sharpening.

Apices separated by lengths of microns are theoretically unaffected by this interference, and the feasibility of simultaneous parallel FDSS on dozens or hundreds of probes is reasonably expected.

Above: Electrochemically etched tungsten wire with multiple tips, sputtered by FDSS for 62 minutes with a tip bias of 200V and ion energies of 1.20keV. Both tips experience sharpening, but the secondary peak sharpened to a lesser extent, falling within the ion shadow of the primary apex.

References
[1] Sigmund *Phys. Rev.* **184**, 383 (1969).
[2] Kubby and Siegel *J. Vac. Sci. Technol. B* **4**, 120 (1986)
[3] Sigmund *J. Mat. Sci.* **8**, 1545 (1973).

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