Note: Fabrication and Characterization of Molybdenum Tips for Scanning Tunneling Microscopy and Spectroscopy

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We present a method for the preparation of bulk molybdenum tips for Scanning Tunneling Microscopy and Spectroscopy (STM-STS) and we assess their potential in performing high resolution imaging and local spectroscopy by measurements on different single crystal surfaces in UHV, namely Au(111), Si(111)-7x7 and titanium oxide 2D ordered nanostructures supported on Au(111). The fabrication method is versatile and can be extended to other metals, e.g. cobalt.

Scanning tunneling microscopy (STM) is a widely employed technique for the study of surfaces, since it allows imaging of surface features with nm-scale or even atomic resolution, but also the investigation of surface local electronic properties via Scanning Tunneling Spectroscopy (STS). A wide variety of materials for tip fabrication have been so far proposed and used. STM-STS measurements in UHV are usually performed with chemically etched tips, typically made of W, even though for specific applications other metals are sometimes employed. Magnetic tips are for instance adopted for spin polarized (SP) measurements, either by fabricating bulk tips (e.g. Fe[1], Cr[2,3], Co[4], Ni[5]) or by coating W tips[6], and use of superconducting Nb tips[7] has been proposed to perform high resolution low-temperature STS measurements. Even a simple 1D modeling of the tip-surface tunneling current[8,9,10] shows that the tip electronic properties play a fundamental role in determining STM/STS data. Tip electronic states influence not only STM topographical measurements by changing the apparent corrugation of the investigated surface, but also differential conductivity (STS) spectra that are characterized by a term that contains the tip LDOS. Tips with non-constant LDOS can generate extra features in STS spectra that can make the extraction (through proper so-called 'normalization methods[8]) of the 'true' surface LDOS difficult[11]. A method to avoid this problem is to use tips made of different materials for acquiring dI/dV signals, in order to identify possible tip contributions to the differential conductivity data.

Electrochemical etching of a metal wire is the routine technique to generate good STM tips, by dipping a small diameter metal wire into an electrolyte solution in which a counter electrode is placed and applying an AC or DC voltage between the electrodes to perform electrochemical etching of the tip until a sharp tip shape is achieved.
Among the reasons why tungsten is such a popular material for the production of STM tips is that an extremely sharp tip can be obtained in a single electrochemical step using fairly mild chemicals. The drawback is that, due to its poor resistance to oxidation, the W tip will most likely undergo surface modifications or contamination that can affect the quality of STM measurements; hence the application of various post-etching treatments (e.g. tip annealing, ion sputtering, HF cleaning) is usually necessary in order to remove the oxide contamination layer from the tip surface. Other metals, such as Au and Pt (or Pt/Ir alloy), can be used to avoid this drawback, thanks to their high resistance to oxidation; however, due to chemical inertness, electrochemical etching procedures are more complex[12,13], while mechanical cutting is known to produce tips of poorer quality. In this framework, molybdenum represents a good option thanks to its inertness and ease of handling, but up to now, even though fabrication and characterization (mainly limited to level of contaminations) of Mo tips was reported[14,15] back in 1991-1992, a characterization of their potential for achieving high resolution imaging or spectroscopy measurements is lacking, and Mo tips have not been routinely used for STM imaging or STS measurements afterwards.

In this Note we present a simple and versatile electrochemical etching method for the production of Mo tips. The potential of Mo tips to achieve high resolution imaging, down to atomic resolution, on different ordered surfaces of metal and semiconducting materials, even with a very complex unit cell, is shown by testing their performance and spatial sensitivity on the Au(111) and Si(111)-7x7 reconstructed surfaces, and on 2D titanium oxide supported nanostructures with structure different from bulk TiO_2. The potential for performing STS measurements for the investigation of surface DOS is demonstrated by the observation of the Shockley peak of the Au(111) surface in differential conductivity (dI/dV) data. The preparation method can be extended to other materials, such as cobalt.

Mo tips are made from 0.3 mm diameter polycrystalline Mo wires (purity 99.95%). The etching procedure is very similar to the one we developed for bulk Cr tips[2]; it consists in two successive steps; first, we

perform a 'lamella' preetching, with a ring-shaped gold cathode, applying a DC voltage in the 4-5 V range. To obtain the lamella (i.e. a circular liquid plate held by the ring cathode thanks to the solution surface tension) we dip the cathode into the solution by lifting the filled glass beaker (Fig.1 left). The lamella can break rather often during etching; by wetting the ring with the solution, we can restore it and proceed in this way in order to reduce as much as possible the wire cross-section. The second etching step is performed using a reduced DC voltage in the 3-4 V range by wire immersion until the drop off of the dipped part of the tip occurs (Fig.1 right). We tested both NaOH and KOH 2 M solutions with good results. The overall electrochemical reaction is

$$Mo + 2OH^- + 2H_2O \rightarrow MoO_4^{2-} + 3H_2$$

and during the etching we observe formation of Na/K and Mo compounds (e.g. K_2MoO_4) on the surface of the wire; a lower voltage is used in the second step to limit the accumulation of the compounds on the rod.

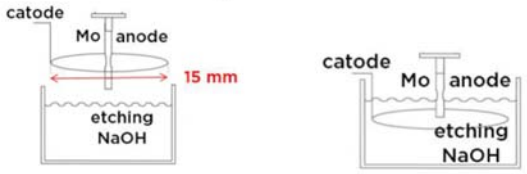

Figure 1: Schematic set up of the tip-etching unit: (left) the lamella pre-etching and (right) the immersion etching.

To test the quality of the manufactured tips we used an optical microscope, which can highlight the major defects, followed by Scanning Electron Microscopy (SEM) analysis using a Zeiss Supra 40 FE-SEM. In Fig.2 an example of a produced Mo tip is shown. For the majority of tips we observed that even though the overall shape on a micron scale is in some cases not regular, the tip apex is usually sharp at the scale of a few tens of nm, with a curvature radius less than 50 nm, and even down to 15 nm. Energy Dispersive Spectroscopy (EDS) analysis indicates that a negligible amount of oxygen is detected at the tip surface. The suitable tips are subjected to a preliminary cleaning procedure in an ultrasonic bath of deionized water for 15 minutes to release the residuals of the electrochemical solution. Then they are introduced in the UHV chamber where they undergo a standard degassing procedure at 200 °C for some hours.

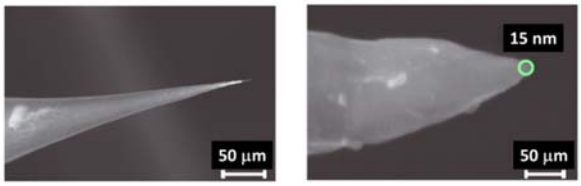

Figure 2: SEM images of a bulk Mo tip obtained with the described procedure. A curvature radius of 15 nm can be estimated for this tip.

Room temperature (RT), constant current STM measurements with Mo tips have been performed using an Omicron UHV VT-SPM. The Si(111)-7x7 surface was chosen as a benchmark as a semiconductor surface. In Fig.3A a topographic image acquired with a Mo tip at positive bias shows atomic resolution, clear separation among atoms as well as the characteristic superstructure of this surface. Si(111)-7x7 is one of the most investigated surfaces with STM, and the complex structure of its 7x7 unit cell[16] makes it a good to test of the capability of resolving spatial details with high resolution. Usually, at positive sample-tip bias the STM image shows the 12 adatoms[17]. On the other hand, the so-called rest atoms of the reconstructed cell, which lie about 0.7 Å below the nearest corner adatom, are observed only in very particular conditions, e.g. with tips presenting peculiar electronic properties (and only at selected negative bias)[2,18], or with W tips with a very high aspect ratio. While Fig.3A reports a representative image of the Si(111)-7x7 surface at positive bias, showing the cell adatoms, in Figs.3B and 3C the same surface is imaged at negative bias (-1.4 V), showing the unfaulted and faulted half-cells, and all the rest atoms, as evident in the line profile of Fig.3d. This result was obtained routinely when using bulk Mo tips, generally for sample bias < -1.2 V, similarly to what observed with bulk Cr tips[2].

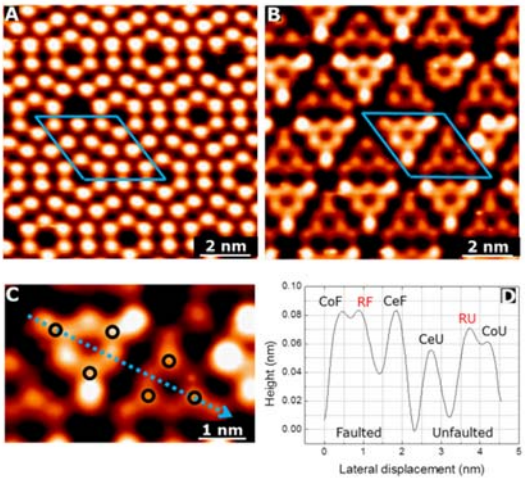

Figure 3: STM images of Si(111) acquired at 300 K with bulk Mo tips. (A) and (B): Respectively positive and negative bias images showing the 7x7 unit cell (A: V = 1 V, I = 0.3 nA; B: V = –1.4 V, I = 0.3 nA). (C) Higher magnification of (B) showing the faulted and unfaulted regions of the unit cell. Rest atom positions are indicated by black dots. (D) Line profile along the dashed blue line in (C) (Co=Corner atom, Ce=Center atom, R=Rest atom).

As for other kind of tips (e.g. Cr) we can guess that the capability of routinely achieving high resolution and detection of the rest atoms may be related to the electronic properties of the tip and to the spatial distribution of the apex atom electronic orbitals, rather than to a peculiar geometrical configuration (aspect ratio).

Mo tips were tested also on the Au(111) surface, as a typical example of a metallic surface. In Fig.4A a topographic image of the surface is shown; the characteristic herringbone reconstruction[19] is easily imaged. The Au(111) surface has also been used as a benchmark for the capability of Mo tips to perform stable and reliable STS measurements. The Au(111) surface is characterized by a nearly-free-electron Shockley state

having a parabolic dispersion with electron momentum, and giving rise to a 'step' in the surface DOS with the onset at about -0.5 eV, typically observed in differential conductivity (dI/dV) curves as superimposed over a decreasing background due to the energy dependence of the transmission coefficient[20]. STS measurements were acquired by means of a lock-in amplifier applying a modulation of 20 mV at the frequency of 8 kHz, keeping the sample at low temperature (about 100 K) to reduce tip and sample instability and thermal drift. dI/dV measurements acquired on different sites of Au(111) reconstruction using a bulk Mo tip do not show significant differences; therefore, we report in Fig.4B an average of several spectra, revealing a decreasing background starting at negative bias in addition to the well-known onset at about -0.5 eV.

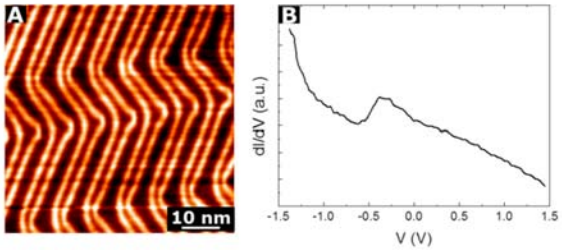

Figure 4: (A) STM image of Au(111) surface acquired at 300 K with bulk Mo tips showing the herringbone reconstruction (V = –1 V, I = 1 nA). (B) STS conductivity curve of Au(111) acquired at 100 K using a Mo tip.

The appearance of STS spectra for the Au(111) surface is very similar to what observed when using standard W tips; this could be an indication that our tips may be characterized by an almost constant LDOS or at least a LDOS not presenting relevant features at specific energies (while other tips, e.g. bulk Cr, show a different behavior ascribable to a non constant tip DOS[11]. Of course Mo tips may present different possible electronic configurations of the tip apex; however we did not observe relevant differences repeating STS measurements on the Au(111) surface with the same or other Mo tips.

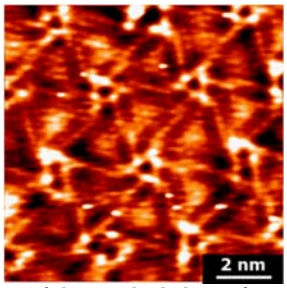

Figure 5: STM image of the *pinwheel* phase of TiO_x on Au(111). The image was acquired at 300 K and shows the atomically resolved surface structure of this phase (V = 0.1 V, I = 1.5 nA).

As a concluding example, Mo tips have been employed to achieve high resolution imaging also on 2-dimensional oxide nanostructures with complex unit cell, namely peculiar TiOx phases supported on the Au(111) surface and obtained by oxidation of the Ti/Au(111) system at low (< 1ML) coverage. The structure reported in Fig. 5 is called 'pinwheel' or 'wagonwheel', and has been interpreted as due to a Moiré pattern formed by the superposition of a rotated hexagonal Ti monolayer on the underlying Au(111) surface[21], while no conclusion has been reached so far concerning the position of O atoms.

In conclusion, we have reported a simple method to produce bulk Mo tips and we have investigated their potentiality as STM/STS probes capable of atomic resolution on a number of test surfaces. The sensitivity of these tips allowed us to image the Si(111)-7x7 surface with atomic resolution routinely resolving the rest atoms of the surface unit cell, contrary to what usually observed with W tips. Mo tips have also proved to be capable of performing STS measurements, showing the detection of the Shockley surface state of the Au(111) surface, which is compatible with an almost constant tip DOS. Finally Mo tips have been successfully employed for high resolution imaging of complex oxide surface nanostructures, namely peculiar TiO_x ordered phases grown on Au(111). The method used for the fabrication of Mo tips is versatile and can be easily extended to the preparation of bulk tips of other metals, e.g. Fe and Ta; we have already verified that it can be employed to fabricate bulk Co tips, which were tested on the Si(111)7x7 surface showing atomic resolution and sensitivity to rest atoms (not shown).

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