Tip preparation for usage in an ultra-low temperature UHV scanning tunneling microscope

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Abstract

This work deals with the preparation and characterization of tungsten tips for the use in UHV low-temperature scanning tunneling microscopy and spectroscopy (STM and STS, respectively). These specific environments require in situ facilities for tip conditioning, for further sharpening of the tips, as well as for reliable tip characterization. The implemented conditioning methods include direct resistive annealing, annealing by electron bombardment, and self-sputtering with noble gas ions. Moreover, results from in situ tip characterization by field emission and STM experiments were compared to ex situ scanning electron microscopy. Using the so-prepared tips, high resolution STM images and tunneling spectra were obtained in a temperature range from ambient down to 350 mK, partially with applied magnetic field, on a variety of materials.

Keywords: Scanning tunneling microscopy (STM); STM tip preparation; Au(1 1 1); NbSe2; Superconductor

1. Introduction

Scanning tunneling microscopy (STM) has matured into a very powerful tool for the characterization of surfaces. Its capability of conducting local spectroscopy, i.e., the local $I–V$ measurement, can provide valuable information on the local electronic properties of the given material (or, more precisely, its surface), specifically the local density of states (DOS). In many cases, however, experimental conditions highly demanding in several respects (e.g. low temperature, high magnetic field, ultra-high vacuum (UHV)) are advantageous or even required. As an example, low temperatures operation may improve the energy resolution of STM but is certainly a requirement for the investigation of superconductors if the superconducting (SC) energy gap is to be resolved. Moreover, many applications call for operation at UHV conditions and/or at applied magnetic fields. All these requirements make sample and tip handling quite involved, often cumbersome and exceedingly time consuming.

Therefore, in situ tip preparation and characterization routines become essential. The properties of the probe tip have severe influence on the performance of STM. The shape and chemical composition of the tip apex are important factors that influence the quality of the obtained data, such as resolution. Sharp tungsten (W) tips can easily be prepared ex situ by electrochemical etching but are naturally covered by a dense oxide layer. The latter may drastically change the properties of the tip: as the tip is not metallic, it may be difficult to establish a stable tunneling current, such that the resolution can be reduced, or the tip might crash into the sample. Even more severe are the consequences for tunneling spectroscopy: the tunneling characteristics no longer correspond to vacuum junctions, and the additional barrier may alter the quantum states involved into tunneling. Numerous techniques have been suggested to clean electrochemically etched W tips.

Here, we present the implementation of two different methods for in situ tip treatment into our UHV STM setups: firstly, annealing of the tips, either resistive or by electron bombardment, and secondly, self-sputtering by...
noble gas ions. The so-treated tips are characterized, comparing results from STM, field emission (FE), and \textit{ex situ} scanning electron microscopy (SEM) experiments. With these capabilities, the probability of obtaining high quality tips could be drastically increased. Specifically, more than 2 out of 3 tips that showed nice FE behavior of treatment could be used for tunneling.

2. Experimental

The tips were prepared [1] from polycrystalline tungsten wire [2] by the commonly used electrochemical etching method. As a first step of cleaning, the end of the wire was etched for few seconds, in order to obtain a clean and smooth surface. In the actual etching step, we used voltages of 6–7 V for 4 M NaOH solution. The immersion depth was varied between 1–2 mm, but no significant influence on the resulting tip has been observed. The etching process was observed through an optical microscope. As a byproduct of the etching reaction, H$_2$ gas evolve at both electrodes, which may lead to turbulences in the etchant. These disturbances could be reduced by placing the counter electrode such that it only just touches the surface of the etchant. During etching, the wire was lowered by 0.1–0.2 mm. The readily etched tips were rinsed in deionized water, and either mounted directly into the STM chamber or stored in ethanol.

Most experiments were carried out using a Cryogenic STM [3] inside a $^3$He cryostat. This STM is operated under UHV conditions and a magnetic field of up to 12 T perpendicular to the sample surface can be applied.

In order to study the efficiency of conditioning methods, it was necessary to characterize tips in a reproducible way. FE from the tip was conducted with the tip situated in a specially constructed stage, Fig. 1, inside the load lock chamber of the STM (base pressure $< 2 \times 10^{-8}$ mbar). For FE experiments, the tip (fixed inside the appropriate holder) was placed into position 1 shown in Fig. 1, a few millimeters below the looped tungsten counter electrode and a negative high voltage $V_e$ was applied to the tip. The electron emission current $I_e$ from a tip-shaped conductor under the influence of $V_e$ obeys the Fowler-Nordheim relation [4–6]:

$$I_e \propto \left(\frac{V_e}{r}\right)^2 \exp\left\{-6.8 \times 10^9 \phi^{3/2} \frac{\xi kr}{V_e}\right\}, \quad (1)$$

where $\Phi$ is the work function of the emitting surface, $\xi$ is a correction factor [5], and $r$ is the radius of curvature of the tip apex. If $\ln(I_e/V_e^2)$ is plotted as a function of the inverse voltage, Eq. (1) predicts a linear dependence. The latter was used to verify that FE is working properly. However, it is difficult to extract $r$ from the slope of this plot, since the constants involved are generally unknown, especially the exact $\Phi$ of the tip. Nonetheless, FE can be used as a quick check on tip quality: the threshold voltage $V_e^{\text{th}}$ required to achieve a fixed $I_e = 1$ nA at a given work function is proportional to $r$, i.e., a lower value $V_e^{\text{th}}$ indicates a sharper tip apex. Assuming an average work function of 4.5 eV for tungsten, comparison with SEM data revealed $r \approx 4(\pm 1) V_e^{\text{th}}$ for $r$ in Å and $V_e^{\text{th}}$ in V. Here, the rather large uncertainty of $r$ results from the finite resolution of SEM. We note that changes to the tip during the conditioning processes can easily be monitored by FE. Atomically resolved STM images and stable tunneling spectra (more specifically, an exponential dependence of the tunneling current $I$ on the relative distance $z$ between tip and sample) could be achieved with tips exhibiting a range of $150 \leq V_e^{\text{th}} \leq 430$ V, best results were obtained between 150 and 300 V. Interestingly, a number of tips with very low $V_e^{\text{th}} \leq 150$ V did not show any decent tunneling at all. One reason for this might be that very sharp tips are mechanically unstable. On the other hand, these tips may have had multiple sharp tips or sharp edges at the apex which led to high $I_e$ but were unfavorable for STM. In principle, certain specific contamination atoms located at the very tip apex may also result in enhanced FE but inhibit decent tunneling. Above $V_e^{\text{th}} = 400$ V, we rarely obtained good STM results.

For STM, the dense oxide layer covering an as-etched tip [7] has to be removed while retaining the tip sharpness. We studied two different ways of \textit{in situ} tip conditioning: annealing and self-sputtering with noble gas ions. If an as-etched tip is heated to about 800 °C, then WO$_3$ is reduced to WO$_2$ which is volatile. Tip annealing was conducted by either resistive heating or by electron bombardment. For the former, the tip shank was brought into mechanical contact with a tungsten filament (position 3 in Fig. 1) which itself was resistively heated. This simple process is, however, difficult to control. Tips may accidentally be molten, or even crashed when brought into contact with the filament. Nonetheless, in our experience it is advantageous to use gentle resistive annealing as a first cleaning step, in combination with other methods.

![Fig. 1. Stage for \textit{in situ} tip conditioning. 1—tip, 2—looped electrode/filament, 3—wire for direct heating; B is at ground potential, a high voltage can be applied to tip via D (positive for annealing, negative for FE/sputtering), power to the respective filaments is supplied via A and C.](image-url)
For more subtle tip heating, electron bombardment is applied [8]. To this end, the tip was situated close to a looped filament (position 1 in Fig. 1 as for FE experiments) and a positive high voltage \( V_{HV} \) with respect to the filament was applied to the tip. As the filament was resistively heated, thermally emitted electrons were accelerated towards the tip and heated up its apex very locally due to the high field gradient. We applied annealing powers between 10 \( \mu \text{W} \) and 10 mW for 30–60 s, with \( V_{HV} \) ranging from 0.2 to 2.0 kV. Fig. 2 illustrates the effect of electron heating on the tip shape. The tip was annealed repeatedly with gradually increased power and FE was probed after each annealing step. \( V^\text{th}_e \) reduces linearly with increasing power up to some minimum indicating tip sharpening. One possible explanation is that annealing first enhances diffusion of surface atoms towards the tip apex until an energetically favorable state is reached [9]. For further increasing annealing power, \( V^\text{th}_e \) increases gradually resulting in a more blunt tip. In the latter case, SEM investigations indicated a local melting of the tip apex. Typically, blunting started between 0.5 and 1.5 mW, in some cases at even lower power. Optimal annealing powers were 20–100 \( \mu \text{W} \) at \( V_{HV} = 200 \text{ V} \). We note, however, that only about one-third of the tips exclusively treated by electron beam annealing showed excellent results in STM.

The second tip conditioning method studied was self-sputtering by noble gas ions [8,10–13]. The same setup as in case of FE was utilized. Clean noble gas was introduced into the vacuum chamber. A high voltage \( V_s \) was applied between tip and counter electrode such that electrons were field-emitted from the tip producing the current \( I_s \) and, in turn, ionize noble gas atoms (the noble gas ion current is about three orders of magnitude smaller than \( I_s \) [13]). The high electric field accelerated the positively charged ions towards the tip and sputtered its surface. During sputtering, \( V_s \) as well as \( I_s \) were monitored. The latter was maintained constant by controlling \( V_s \) to ensure a constant sputter rate and to avoid damages to the tip. Since \( I_s \) depends on the tip’s apex radius, a decrease of \( V_s \) over time indicates a tip sharpening, cf. Fig. 3. The insets show SEM micrographs of two tips for which sputtering was terminated at different states of the process. The formation of a neck is clearly visible at a distance of a few hundred nanometers away from the apex. This neck occurs due to the higher density of impinging ions at the tip shank as compared to the very apex, and due to the higher sputter yield of the ions at the shank [13,14]. As sputtering proceeds, the neck deepens until decapitation which manifests itself in a sudden drop of \( V_s \) [12]. Detecting this drop allows to automatically terminate the sputter process immediately after decapitation resulting in very sharp and clean tips with apex radii of few nanometers [8,11,12]. Notably, the decapitation of the tip is typically preceded by a faster decrease of \( V_s(t) \) along with a reduction of its noise, cf. Fig. 3.

Our experiments confirmed that neon is preferable to argon as sputter gas [13], likely due to the high atomic mass of Ar. More than half of all tips prepared by Ne sputtering showed excellent atomic resolution on graphite. These tips showed FE of \( I_s = 1 \text{ nA} \) at \( V_s \) between 180 and 250 V. The success rate of the sputter process was even further increased by subsequent annealing of the tips which cures damages entailed by the sputter treatment, and brings the tip into a more stable state [8,11]. No good STM was obtained with tips that were sputtered without the occurrence of a decapitation.

The pressure \( p_s \) of the sputter gas was varied between 2 and 5 \( \times 10^{-3} \) mbar, and \( I_s \) ranged from 5 to 16 \( \mu \text{A} \). Within the given range, no influence of \( p_s \) on the tip performance was found. However, the cleanliness of the sputter gas turned out to be crucial for the sputter process. For high residual gas pressure in the recipient before introducing the sputter gas, we often observed sudden breakdows of the sputter process. SEM and FE indicated that the respective tips were blunt, probably due to discharges between tip and

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**Fig. 2.** The effect of tip annealing by electron bombardment. The tip was annealed with gradually increasing power. After each heating cycle, field emission was measured.

**Fig. 3.** Typical evolution of the sputter voltage \( V_s \) with time. The gradual decrease of \( V_s \) indicates a sharpening of the tip, the sudden drop is related to a decapitation process. The insets show SEM micrographs of tips for which the sputter process has been terminated before, and immediately after decapitation, respectively. The scale bars indicate a length of 500 nm.
counter electrode. To avoid this the base pressure in the chamber needed to be at least three orders of magnitude smaller than $p_{\text{th}}$.

We utilized a homemade power supply for DC voltages of up to 1 kV that can be operated in two modes: for FE, the high voltage is tuned and the current is measured with a sensitivity of 0.1 nA. In order to conduct self-sputtering the applied voltage is controlled to maintain a preset constant current. Moreover, jumps in the current or, equivalently, in the controlled voltage can be detected and shut down the voltage immediately. Voltage and current can be monitored via a computer interface.

3. Results

Undoubtedly, the ultimate benchmark test for a tip is by STM and tunneling spectroscopy. Therefore, any judgment on the quality of tips prepared in the above ways refers to its performance in STM. Tunneling experiments were conducted on several samples: graphite (HOPG), single crystalline gold and NbSe$_2$. The former two materials were typically used for tip characterization and to calibrate our STM, whereas the latter material (which turns into a superconductor at sufficiently low temperature $T$) can provide information about energy resolution and is, in addition, of more scientific interest.

We first discuss results obtained on the (1 1 1) surface of a gold single crystal. The surface was cleaned in situ by repeated cycles of Ar ion sputtering and consecutive heating up to 1073 K, and then kept under UHV conditions. For the results shown in Fig. 4, a W tip was used which was heated by electron bombardment ($\approx 40 \mu$W) and self-sputtered ($p_{\text{th}} = 3.5 \times 10^{-2}$ mbar, $I_s = 10\text{--}12 \mu$A). FE resulted in $V_{\text{th}}^{\text{diff}} = 350$ V. A good vacuum tunnel junction is evidenced by the exponential dependence of $I$ on $z$, Fig. 4(a), holding for almost three decades in $I$. The work function derived from this plot is $\Phi \approx 1$ eV. The reduced value of $\Phi$ compared to the plain surface value is commonly attributed to the small tip radius [15] and the close proximity of tip and sample [16]. Fig. 4(b) shows an atomically resolved STM image of $6.5 \times 6.5$ nm$^2$ at 350 mK ($V = -0.32$ V, $I = 0.7$ nA). The three-fold rotational symmetry of the (1 1 1) plane of the fcc crystal is clearly resolved. In addition, Au exhibits a surface reconstruction commonly referred to as $(22 \times \sqrt{3})$ reconstruction that results in the well-known “herringbone” pattern at larger scales [17–19]. The superstructure resulting from the surface reconstruction is visible as a corrugation of magnitude 0.8–1.0 Å in Fig. 4(b) but is more obvious as a regular pattern in the larger scan image of $35 \times 35$ nm$^2$, Fig. 4(c).

In Fig. 5 some results obtained after successful tip preparation on NbSe$_2$ are presented. The sample was cleaved ex situ. Inset (b) shows an atomically resolved topographic image acquired at 385 mK. The periodic modulations caused by the formation of a charge density wave (CDW) below about 33 K are clearly visible [20]. What’s more, NbSe$_2$ is a type II superconductor with a SC transition temperature $T_c \approx 7.2$ K. In Fig. 5(a), differential conductance spectra, $dI/dV$, are plotted which were obtained at 385 mK and with magnetic field $\mu_0 H = 0.6$ T applied perpendicular to the sample surface. The curves were acquired at different locations along a line with equal spacing of 3.2 nm (right axis); this line is indicated by the arrow in Fig. 5(c). All curves are normalized with respect to their normal-state conductance (obtained at 5 mV). In addition, the individual $dI/dV$-curves were shifted vertically by 0.1 unit for clarity. The topmost curve shows a

![Fig. 4. Tunneling microscopy on a Au(1 1 1) single crystal utilizing a treated W tip. (a) Tunneling current $I$ in dependence on the relative distance $z$ between tip and sample surface on a semi-logarithmic plot. (b) Atomically resolved topographic image ($6.5 \times 6.5$ nm$^2$, $V = -0.32$ V, $I = 0.7$ nA) obtained at $T = 350$ mK. (c) Similar image over an area of $35 \times 35$ nm$^2$ clearly showing the modification resulting from the surface reconstruction.](image1)

![Fig. 5. Tunneling spectroscopy on NbSe$_2$ at $T = 385$ mK and $\mu_0 H = 0.6$ T. (a) Differential conductance curves acquired along a line with a mutual distance of 3.2 nm between the points at which spectroscopy was conducted. This line extends from a vortex center into the superconducting region, as indicated by the arrow in inset (c). For clarity, the individual curves are vertically offset. Inset (b) presents a topographic image ($8 \times 8$ nm$^2$, $V = 0.1$ V, $I = 1$ nA) exemplifying atomic resolution as well as a CDW pattern. Inset (c) shows an $80 \times 80$ nm$^2$ map of $dI/dV|_{V=\text{ref}}$ revealing the triangular vortex lattice.](image2)
maximum in conductance at zero bias, and minima at around ±1 mV. The zero bias peak corresponds to quasiparticle bound states in the core of a vortex [21,22]. Following the arrow, the zero bias peak and the minima disappear, and eventually develop into a SC gap structure. Inset (c) presents a scanning tunneling spectroscopy (STS) image in which local values \( dI/dV|_{V=0} \) are plotted: the brighter spots reflect the enhanced zero bias conductance inside of vortices, whereas the dark regions originate from low values of \( dI/dV|_{V=0} \) in SC regions. A threefold symmetry of the vortex lattice can be recognized. The measured average spacing of two vortices is \( 67 ± 5 \) nm which is in reasonable agreement with the theoretical value of \( 48.9 \text{ (nm)} / \sqrt{B(T)} = 63.1 \text{ (nm)} \) [21,23].

4. Conclusions

In situ tip conditioning and characterization for complex STM setups was reported. FE was established as a quick tool for tip characterization, specifically to monitor changes resulting from tip conditioning. Gentle direct annealing of a tip helped improve the outcome of subsequent treatments. Best results were obtained by sputtering utilizing Ne. Here, the cleanliness of the sputter gas appears to be crucial. Gentle annealing after sputtering by electron bombardment seemed useful. STM of the so-prepared tips was checked on HOPG and gold. Examples of high resolution STM and STS—the latter with energy resolution down to ~70 \( \mu \)eV—on Au(1 1 1) and NbSe\(_2\) have been presented.

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