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FIM tips in SPM: Apex orientation and temperature considerations on atom transfer and diffusion

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ABSTRACT

Atoms transferred to W(1 1 1) and W(1 1 0) tip apices from the Au(1 1 1) surface during tunneling and approach to mechanical contact experiments in STM are characterized in FIM at room temperature and at 158 K. The different activation energies for diffusion on the (1 1 1) and (1 1 0) tip planes and the experiment temperature are shown to be important factors controlling the extent of changes to the atomic structure of the tip. W(1 1 1) tips are much better suited to scanning probe studies which require the characterization of an atomically defined tip and subsequent verification of its integrity in FIM. The statistics of the observed spikes in the tunneling current when the tips are approached to Au(1 1 1) are interpreted using a simple model of adatoms diffusing through the STM junction.

1. Introduction

The use of tips defined by field ion microscopy (FIM) in scanning probe microscopy (SPM) has several notable advantages [1]: an atomically defined tip will pre-define the lateral imaging resolution, the chemical nature of the apex is guaranteed, and the electronic structure is calculable based on the known geometry. FIM tips offer great potential for the understanding of contrast mechanisms in scanning tunneling microscopy (STM) and atomic force microscopy (AFM) where the atomic configuration of the tip is expected to be of great importance [2], but is usually experimentally uncharacterizable. These tips are also well suited for atomic-scale nanoindentation where the tip geometry is needed to understand the initiation of plasticity as well as the electronic conductance of the junction [3,4]. With the recent developments of the qPlus [5] and length extension resonators [6] in AFM which often employ tungsten tips appropriate for FIM [7,8], we expect the number of instruments using atomically characterized FIM tips to grow in the near future.

The implementation of an atomically defined FIM tip in simultaneous AFM and STM opens up the possibility of performing force and current characterization of an atomically defined nanojunction, perhaps connecting to a single molecule, where the positions of all relevant atoms are controlled. In a single molecule junction, the exact atomic arrangement of the metallic contacts affects metal-molecule coupling, energy-level lineup, and the electrostatic potential profile across the junction resulting in considerable changes to *I–V* curves [9,10]. To rigorously test and contribute to the refinement of theoretical modeling of nanoscale structures, one needs data from experiments in which the atomic-scale contact geometry is known and controllable.

In such atomically-defined SPM experiments, tip integrity is of paramount importance – one must be able to characterize a probe apex in FIM and transfer it to the SPM experiment with certainty that the atomic arrangement at the end of the tip is unchanged. Tungsten tips are highly reactive and will readily dissociate and chemically bind with gases. Even in ultra-high vacuum conditions, one must be careful to keep impurity gases at bay especially during and after admission of the FIM imaging gas (usually helium). The transfer between imaging modes must also be relatively prompt in order to maintain statistical confidence that no rest gases have adsorbed. This has been a subject of a previous investigation, in which we developed the 'force-field' method of preserving the atomic integrity of the tip using a large electric field to ionize and repel any impinging rest gas molecules [11]. This method allowed us to controllably approach an atomically-defined FIM tip to a cleaved silicon surface in STM and demonstrate its return to FIM with an unchanged apex.

After taking care that the FIM tip does not react with impurity gases in the vacuum chamber, one must carefully approach

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it to the sample surface without overshoot of the feedback controller [12]. Finally, tip changes (due to tip-sample interactions, for example) must be absent from an atomically-defined experiment to be assured that the apex structure remains intact. We have noted that scanning Au(1 1 1) and HOPG surfaces at low tunneling current conditions (6 pA) at room temperature leads to completely altered FIM tips, while scanning cleaved Si(1 1 1) can be carried out for few minutes with no detectable tip alterations. The absence of tip alterations in FIM is also correlated with the absence of any tunneling current instabilities (spikes) during the experiment.

Here, we explore tip integrity and the resolvability of tip changes in FIM in greater detail by approaching tips of differing apex orientations (W(1 1 1) and W(1 1 0)) to tunneling proximity with Au(1 1 1) surfaces at temperatures of 298 K and 158 K. The tips are additionally approached to mechanical contact to induce changes to their atomic structure and are subsequently characterized by FIM. At both of these temperatures, gold is uncontrollably transferred to the tip.

In the case of the W(1 1 1) tip, the transferred atoms can diffuse readily on the tip surface at room temperature, but do not diffuse when the system is cooled to 158 K. The smooth close-packed planes of the W(1 1 0) surface, however, still allow the surface diffusion of transferred adatoms at 158 K. In contrast to W(1 1 0) tips, W(1 1 1) tips are better suited to SPM studies with atomically defined probes because their large surface corrugation hampers the diffusion of transferred atoms and also permits atomic resolution at the apex region in FIM.

The experimental results presented in this paper are separated into two main sections: Section 3 presents FIM characterization of W(1 1 1) and W(1 1 0) tips after tunneling and mechanical contact experiments with Au(1 1 1) surfaces. In Section 4, the statistics of tunneling current spikes are interpreted by invoking a simple model of a diffusing adatom momentarily altering the conductance of the STM junction, and we comment on the prospects and challenges of using this method for the study of surface diffusion.

2. Experimental methods

Experiments were carried out in ultra-high vacuum (UHV) at room temperature and at 158 K (temperature of the tip and sample during both FIM and STM). Au(1 1 1) substrates were prepared by epitaxial growth of Au on mica to a thickness of 100 nm (these samples were rigidly anchored in order to minimize tip-sample mechanical noise – they were not mounted in the cantilevered geometry used elsewhere [3,4]). The Au(1 1 1) surfaces were cleaned by repeated 1 keV Ne^+ ion sputtering and annealing cycles in UHV to several cycles beyond the disappearance of carbon in Auger electron spectroscopy. A STM topograph of a clean Au(1 1 1) surface is shown in Fig. 1(c).

Tips were electrochemically etched from polycrystalline tungsten or single-crystalline W(1 1 1) wire and prepared by flash annealing and degassing cycles in UHV [13,14]. Tips fabricated from polycrystalline tungsten wire nearly always terminate with a (1 1 0) oriented grain at the apex (to within several degrees) due to the crystallographic texture arising from the cold drawing process used to fabricate the wire [15,16]. Field evaporation was used to prepare a clean tip surface by raising the imaging field by ~10–20% during FIM relative to the field required for He^+ ion imaging of the apex. The FIM image of a 6.7 ± 0.8 nm radius W(1 1 1) tip apex is shown in Fig. 1(a) with the low-index planes labeled. The radius is determined by the ring counting method [11,17–19]. The apices of the W(1 1 1) tips end in three individually resolved atoms (trimer), similar to the tips described in Ref. [11].

After preserving the atomic integrity of the tips using the 'force field' protocol while UHV conditions recovered following FIM [11],

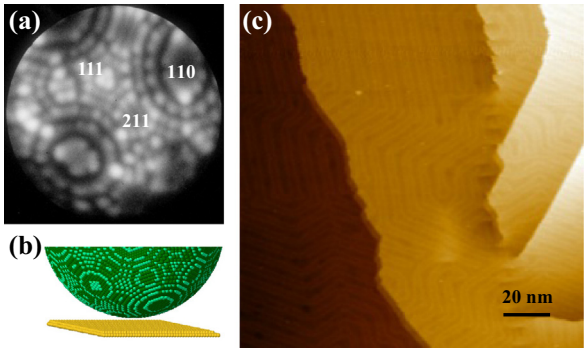

Fig. 1. (a) Typical W(1 1 1) trimer tip prepared by field evaporation having a radius of 6.7 ± 0.8 nm, imaged at 7.3 kV in FIM; (b) Ball model (side view) of a W(1 1 1) tip and Au(1 1 1) surface; (c) Room temperature STM image of a clean Au(1 1 1) surface showing the herringbone reconstruction (8 pA, −0.95 V sample bias).

the tips were approached to tunneling interaction with Au(1 1 1) samples at a setpoint of 6 pA at −0.08 V sample bias without overshoot of the tunneling setpoint. The initial coarse approach was monitored optically: the tip can be brought to 5–10 μm from the surface by observing its reflection off the sample, allowing the sample surface to be found less than 30 min after removing the 'force field' voltage from the tip. Upon finding the sample surface, the tunneling current was recorded at low feedback gain for later analysis. In the case of the W(1 1 0) tips made from polycrystalline wire, soft mechanical indentations were carried out as described in the results section. FIM was then performed again on the tip apices to examine modification caused during the tunneling or mechanical contacts experiments. The FIM and STM microscopes are combined into the same unit which enables the switching of modes without any transfer of the tip.

3. Atom transfer to W(1 1 1) and W(1 1 0) tips

3.1. W(1 1 1) tip/Au(1 1 1) surface at 298 K and 158 K

When clean FIM tips are approached to tunneling proximity with Au(1 1 1) surfaces, spikes are always observed in the tunneling current. At room temperature, the spikes reach a maximum of ~40 pA, and lead to a completely changed tip structure after remaining within tunneling proximity of the sample for a few minutes, as illustrated in Fig. 2(a). The same type of tunneling experiment was again performed with the Au(1 1 1) surface but at a temperature of 158 K, as shown in Fig. 2(b). A representative snapshot of the current trace during tunneling and FIM images of the tip structure before and after tunneling are shown. The vertical axes of the current traces have the same limits, emphasizing that the current spikes in the lower-temperature data are much larger, reaching ~130 pA (the larger spike amplitude reflects the longer residency time of adatoms under the tip at low temperature, discussed in Section 4). The FIM tip retracted from the tunneling junction at 158 K appears to have a nearly identical apex, with the exception of an additional atom appearing very brightly next to the original trimer apex. The lower-right atom in the trimer also appears brighter.

The minor modification of the tip apex near the (111) plane provides two encouraging results: Firstly, the minor tip changes located only at the tip apex confirm that the adatoms we observe on the FIM tips after tunneling originate from the sample, not from the tip shank. This supports our previous supposition based on the absence of tip changes when approaching the reactive cleaved Si surface [11]. Secondly, the localized modification demonstrates that the tip's (1 1 1) apex is indeed the part of the tip which interacts with the sample – it confirms that the apex is oriented in the correct