Mono-atomic tips for scanning tunneling microscopy

by Hans-Werner Fink

By field-ion microscopy techniques, we have been able to create stable tips whose very ends are made up of just one individual atom, deposited from the gas phase onto an upper terrace of a pyramidal (111)-oriented tungsten tip. The first three layers of the tip consist of one, three, and seven atoms, respectively. Consequences of these observations for the understanding of energy transfer between gas-phase atoms and a solid surface are also discussed.

1. Introduction

The power of the scanning tunneling microscope is based on the strong distance dependence of the tunneling current. This causes the sensitivity of this instrument to the local atomic arrangement of the sample when the tip is scanned over its surface [1]. However, at the same time, current changes are also related to the structure of the tip. In order to separate these two contributions, it is essential to know the detailed atomic arrangement of the tip prior to its use in STM. With such an effort, the following achievements are to be expected.

The creation of mono-atomic tips should give the ultimate lateral resolution inasmuch as the spatial limitation of the tunneling current can be associated with the electronic structure above "one" single atom. The known atomic arrangement of the tip and its electronic structure predefines the lateral resolution of the STM. Investigations of nonperiodic structures should then be routinely possible with defined resolution.

The long time stability of the tip allows experiments that require statistical treatment and, therefore, data collection over an extended period of time.

Last but not least, a more detailed understanding of tunneling between two microscopic objects may be expected since the tip as well as the sample will eventually be known in atomic detail.

A first step in the direction outlined above will be to create single-atom tips where we deposit an additional W atom on top of a pyramidal W(111) tip. These procedures are described in Section 3 after a brief introduction to the technique of field-ion microscopy. Ultimately, the chemical specificity of the additional atom to be put onto the tip has to be chosen to give the "best" suitable electronic configuration and with this the narrowest filament to probe the surface of the sample.

Apart from the benefits to be expected for STM, the physics of such tips is of interest in its own right since their ends constitute small three-dimensional clusters which are likely to show unique physical properties; some of these properties are discussed in Section 4.

2. Field-ion microscopy

In the 1950s, Erwin W. Mueller invented the field-ion microscope (FIM), an instrument that provides atomic resolution and works with tips and only with tips [2]. We take advantage of the FIM technique to prepare tips with the

desired properties for tunneling, as outlined in the Introduction.

The image in the field-ion microscope is formed by the ionization of neutral gases in the presence of high electric fields of the order of 4 V/Å. As suggested in **Figure 1**, a sharp tip is put at some kV-high positive potential with respect to an ion detector, usually a micro-channel plate assembly. Most of the potential difference drops in front of the tip surface, creating a highly inhomogeneous electric field. An image gas atom (usually helium or neon) is attracted towards the tip surface owing to its field-induced dipole. Close to the tip, the potential for the electron in the image-gas atom will be disturbed by the high field, and this enables the electron to tunnel from the gas atom to the tip surface, leaving a positively charged ion behind. The image-gas ions are accelerated along the electric field lines and strike the detector, where they create a highly magnified picture of those locations of the surface where ionization took place. The rate of ionization, which provides the image contrast, is determined (neglecting changes in image-gas supply and variations in the tunneling rate caused by different electronic properties) by the local electric field at the surface that is highest above protrusions such as steps or adsorbed atoms. As is evident from a comparison of the ball model of a (110)-oriented bcc tip **[Figure 2(a)]** with the field-ion image of a W tip with (110) orientation **[Figure 2(b)]**, steps can readily be seen, as well as the atomic arrangement of relatively small open faces of the (bcc) lattice.

The structure of the dense-packed (110) apex plane cannot be resolved; however, individual adatoms deposited onto the surface from the gas phase can be visualized with a resolution between 2 and 3 Å. This has made field-ion microscopy a powerful tool for investigating individual atomic events on surfaces [3, 4].

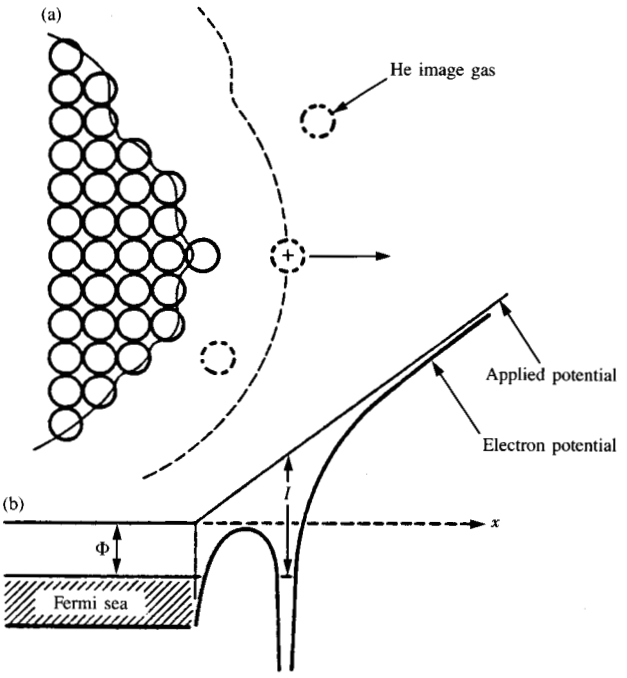
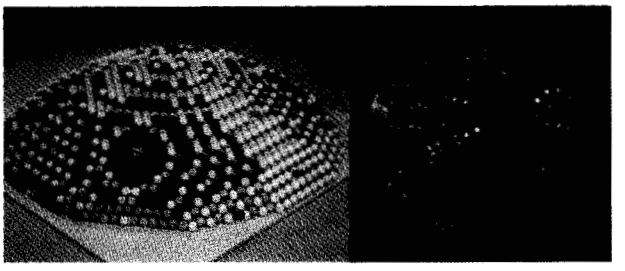


Figure 1

Field ionization of helium at a metal surface. (a) Cross section of tip. Dashed line indicates critical distance which must be exceeded for ionization to occur. (b) Electron potential at distance x from the surface for the ion core at the critical distance. I = ionization potential of free atom; Φ = work function of the surface. From [3]. Diagram courtesy R. S. Chambers. ©Asociación Española del Vacío y Sus Aplicaciónes (ASEVA); reprinted with permission.



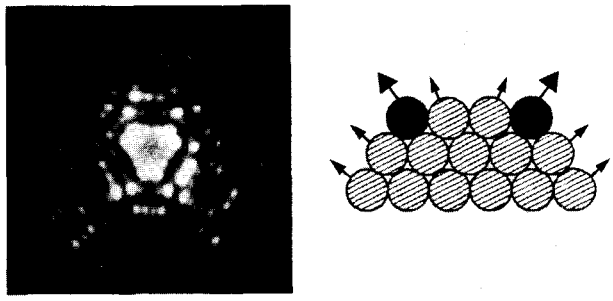
(a) (b)

Figure 2

(a) Hard-sphere model of bcc (110)-oriented tip. (b) Helium field-ion micrograph of (110)-oriented tungsten tip. Ball model picture courtesy G. Ehrlich.

3. Preparation of mono-atomic tips

The criteria of obtaining tips as sharp as possible and stable led us to choose the (111) tungsten surface to be the apex plane of our STM-probe tips. In contrast to the densely packed (110) plane of tungsten (see Figure 2), the (111) plane is smaller in size because of its relatively high surface free energy. The structure of the (111) face can be directly visualized in the FIM, as is apparent from **Figure 3(a)**. Combined with the open atomic arrangement is the fact that single-atom self-diffusion on this plane proceeds over a large barrier of 1.8 eV [5]. As a consequence of the deep potential wall around adsorption sites on this plane, there are no displacements of adatoms below 600 K. This ensures thermal stability with respect to adatom diffusion on the tip apex plane, a desirable point for STM operation. The plane in Figure 3(a) was shaped by a process called field evaporation, which is a way to create defect-free surfaces. As indicated in the schematic in **Figure 3(b)**, removal of atoms by the electric field starts where the field is highest; that is, at the plane edges. By carefully adjusting the tip potential, one layer after the other can be removed by field evaporation. A number of models have been considered, and quite some effort devoted to the experimental side to understand the



(a) (b)

Figure 3

(a) FIM picture of (111)-oriented W tip; the (111) apex plane contains 18 atoms. (b) Cross section through tip showing qualitatively the electric-field distribution. The enhanced field at the edge causes atoms to be removed first by field evaporation.

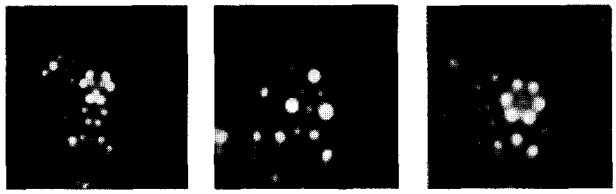


Figure 4

Different shapes of apex planes on (111)-oriented W tips.

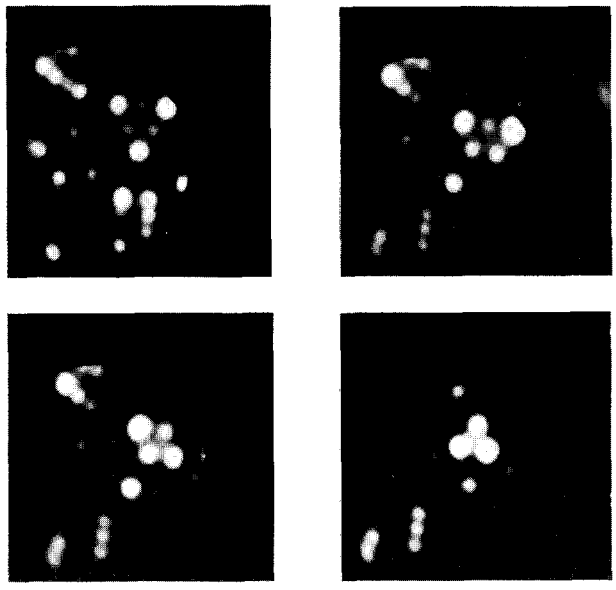


Figure 5

Decrease of upper (111) terrace of W tip by successive field evaporation one atom at a time. The original layer made up of six atoms has been shrunk down to just three.

physical processes involved in field evaporation [6]. The number of atoms contained in the apex (111) plane depends on the overall diameter of the tip and the moment at which the evaporation process is stopped by reducing the electric field.

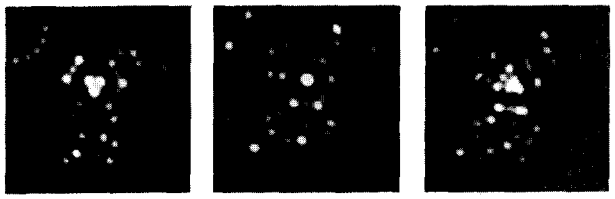
Important for STM operation are the electron current densities. By pumping out the image gas and inverting the polarity on the tip, we measured the total field-emission current from a tip like the one shown in Figure 3. It evolved that currents of 10 μA did not cause any changes in the atomic arrangement of the tip, which had been checked by re-imaging the tip in the field-ion mode.

Various geometries of W(111) apex planes are shown in **Figure 4.** The individual stages in the successive field evaporation of a (111) plane, made up of six atoms, are demonstrated in **Figure 5.** Here, the apex plane was evaporated atom by atom in a controlled way until only three atoms remained.

The trimer itself, however, field-evaporates as a unit at quite elevated fields compared to those needed for the removal of edge atoms from a more extended plane. Keeping in mind our original goal of creating mono-atomic tips, we then filled this one site on top of the trimer with an extra atom from the gas phase. For this purpose, a rotatable tungsten evaporator was placed in front of the tip for depositing additional W atoms. The FIM pictures in **Figure 6** demonstrate such a trial. First [Figure 6(a)], the creation of the trimer was achieved by careful field evaporation of the upper (111) terrace.

After the evaporation of W atoms, the field-ion picture in Figure 6(b) shows that an atom has actually been adsorbed in this one site on top of the trimer. Apparently, owing to the local high protrusion constituted by this additional atom on top of the trimer, field ionization occurs mainly above the extra atom and at the plane edge and vicinal planes. Only after the extra atom has been removed by field desorption (in contrast to field "evaporation," field "desorption" names the process that removes an adsorbed atom, not a substrate atom, by means of the electric field) does the underlying trimer again become visible. Figure 6(c) is a superposition of the FIM picture with the single atom on the trimer, and shows the situation after the additional atom has been removed by field desorption. From this it is apparent not only that the site on top of the trimer had been occupied by an atom from the gas phase, but that another three atoms had stuck to the (111) surface next to the trimer.

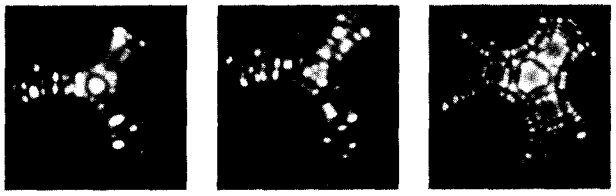
It should be noted that there are also ways to prepare single-atom tips by just heating, as shown in **Figure 7.** The tip in Figure 7(a) was subject to annealing at roughly 1500 K for a few seconds. At this temperature, self-diffusion is quite rapid and the tip evolves towards its equilibrium shape; note the large size of the three (110), (101), and (011) planes around the apex plane that exhibit dense packing and low surface free energy. In this particular example, heating was



(a) (b) (c)

Figure 6

Deposition of extra W atom from the gas phase onto a trimer on the (111) apex plane. (a) Trimer created by field evaporation; (b) after deposition of W atoms onto the tip. On the (111) plane, only the extra atom adsorbed on the trimer is visible. (c) Superposition of micrograph in (b) and the FIM pattern after removal of the extra atom. Additional atoms adsorbed on the (111) terrace next to the trimer are now apparent.



(a) (b) (c)

Figure 7

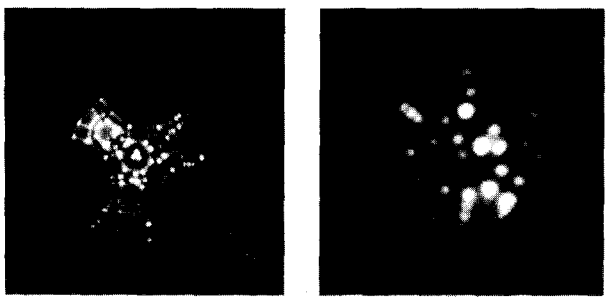
Creation of a mono-atomic tip by heating. (a) Single-atom tip after annealing at about 1500 K; (b) underlying terrace is visible after field evaporation of single atom; (c) tip after further field evaporation.

stopped at the right moment in the evolution of the tip towards its equilibrium shape, and finally there was just one atom at the apex of the tip. However, this method does not work in a routine way, and therefore was not further considered and explored as a practical tip-preparation procedure.

Although tips like the one prepared in Figure 6 might prove to be useful for tunneling, the next step was to make sure that the layer underneath the trimer was minimal so as not to offer extra binding sites of (111) geometry that could be occupied by atoms evaporated onto the tip. This can be achieved by decreasing the overall radius of curvature of the tip by bombarding it with Ne ions. They are produced from Ne atoms by collisions with field electrons from the tip [7]. The electric field focuses the Ne ions onto the tip, where they sputter away substrate material. The reduction of the overall radius of curvature by applying this procedure is evident from **Figure 8(a)**, where a relatively blunt tip is shown with a trimer that was the result of careful field evaporation.

After sputtering with Ne ions and annealing the tip to heal out defects, followed by field evaporation of a few layers, the FIM pattern of **Figure 8(b)** is obtained, imaged here at about 2.5-kV tip voltage compared to the 15 kV necessary to create the same field strength for helium ionization prior to sputtering the blunt tip. Since the magnification of the FIM is mainly given by the ratio of the tip-detector distance and the curvature radius of the tip, the increased magnification apparent in Figure 8(b) also indicates the sharpness of the tip.

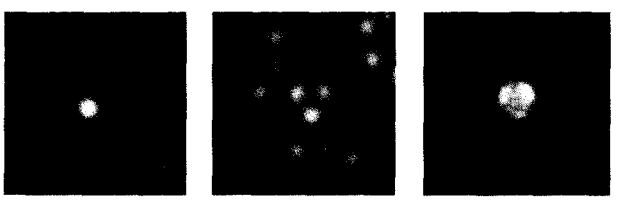
If one now deposits an extra atom onto such an ultrasharp tip, the resulting field-ion micrograph, shown in **Figure 9(a)**, consists mainly of a one-atom spot, since a sufficient electric field for ionization of helium is only present above the high local protrusion constituted by the single W atom on top of the trimer forming the very end of the tip.



(a) (b)

Figure 8

The effect of sputtering on the overall radius of curvature of the tip. (a) W(111) tip with trimer at top imaged at 15 kV. (b) Same tip, imaged at 2.5 kV, after sputtering with Ne ions, annealing, and field evaporation of upper terrace to the size of a trimer. Note: Change in magnification is due to decreased tip radius.



(a) (b) (c)

Figure 9

Single-atom tip. (a) FIM pattern of single-atom tip, created by evaporation of additional W atom onto very sharp tip. (b) Field desorption of the single atom reveals trimer. (c) Color superposition of (a) and (b) shows adsorption site of the extra atom on the trimer.

Only after the individual atom has been taken away by field desorption does the trimer again become visible **[Figure 9(b)]**. A color superposition of the two pictures, the single

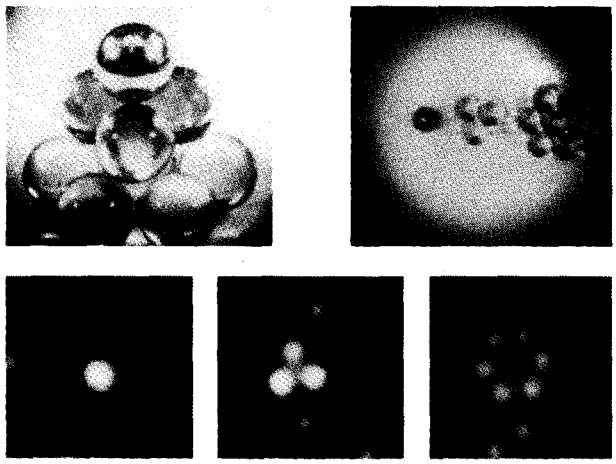


Figure 10

First three layers of mono-atomic tip are made up of one, three, and seven atoms. Top: ball model of mono-atomic tip. Bottom: successive removal by the field shows field-ion pattern of first three layers of the tip.

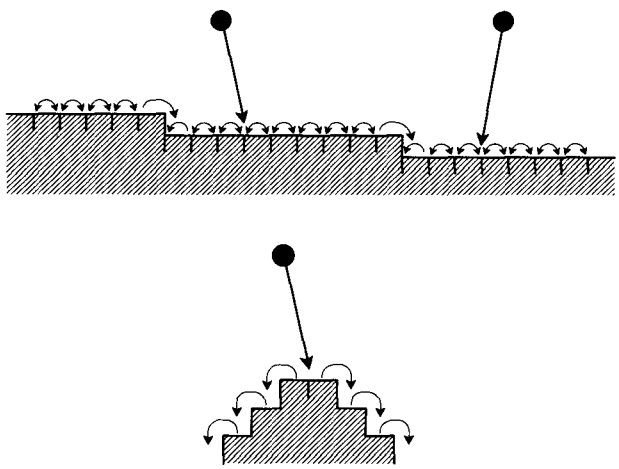


Figure 11

Schematic diagrams indicating probable atomic events in the equilibrium of a gas-phase atom striking a crystal surface. Top: macroscopic crystal surface. Bottom: tip with only one adsorption site at its end.

atom in red and the trimer in green, shows the adsorption site of the extra atom on the trimer [**Figure 9(c)**].

Further field evaporation also reveals the third layer of the tip which supports the trimer; this layer contains seven atoms, as is evident from **Figure 10**. The top part of Figure 10 shows a ball model of the first three layers of the tip.

4. Some remarks on the physics of mono-atomic tips

This paper describes a straightforward way to create and characterize single-atom tips. This procedure works so well because of the interesting physics it contains, which will now be briefly discussed.

Our experiments show that an atom from the gas phase can readily be adsorbed onto the very end of the tip. This has important consequences for the understanding of energy transfer between gas-phase atoms and the surface of a solid, one of the fundamental atomic events in crystal-growth phenomena.

Apart from the translational energy, a rather small quantity (in the case of tungsten roughly a quarter of an eV), the binding energy of the atom to the surface, has to be transferred to the solid. However, this is roughly 6 eV for tungsten on the W(111) plane [8]. One way of visualizing this is that the atom undergoes several jumps at the surface in order to lose this large amount of energy in several collisions with the substrate surface atoms, as indicated schematically in the top part of **Figure 11**. In this process, once a descending step has been reached, the atom moves down the step but it is very unlikely to move back up again, since this would involve a much larger barrier. If this were the process that actually takes place in our experiments on creating single-atom tips, there would be no chance to adsorb an atom onto this one site on the trimer. Atoms that strike this site would have to jump over the surface in order to transfer energy by collisions with substrate atoms. Since there are no neighboring sites on the apex plane, the atom has to move down the steps; there are only descending steps around the very end of the tip (see lower part of Figure 11).

The fact that we can routinely (with a flux, corresponding to roughly one monolayer coverage) deposit an individual atom onto the trimer contradicts this view. In other words, the atom sticks on this one site on first impact, and therefore manages immediately to transfer to the tip enough energy to localize itself. This energy of localization amounts to the difference between the binding energy (~6 eV) and the activation energy for diffusion (1.8 eV). Bearing in mind that the activation barrier for diffusion and the binding energy are probably slightly different on this extremely small plane, roughly some 4 eV have to be transferred to the solid, a surprisingly large quantity.

The distribution of adatoms evaporated from the site onto a tip showed small deviations from the geometrical shadow line as observed in the field-ion microscope after deposition. From this, it was concluded that the atoms need not perform more than 100 jumps before equilibration with the cold tip surface is obtained [3].

Our observations show that in our particular case not even a single jump must be undertaken to reach equilibrium with the tip surface. However, the interesting question remains how this energy transfer actually proceeds and in what way phonons or electrons are involved to absorb so much energy.

5. Conclusion

The procedures outlined in this paper describe a straightforward way to build up stable single-atom tips *in situ*. It is now just a matter of actually using them for tunneling. For the future, it might be desirable to take advantage of the possibility of choosing the chemical nature of the additional atom to be put onto the trimer by using different evaporators. This provides a way to vary the electronic structure above the mono-atomic tip and select the most suitable electronic configuration depending on the sample to be investigated with the STM.

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