Lab 72 in TFFM08

Scanning tunneling microscopy

<table>
<thead>
<tr>
<th>NAME</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PERS. -</td>
<td>NUMBER</td>
</tr>
<tr>
<td>DATE</td>
<td></td>
</tr>
<tr>
<td>APPROVED</td>
<td></td>
</tr>
</tbody>
</table>

Rev. Dec 2006 Ivy Razado
Aug 2014 Tuomas Hänninen
1 Introduction

Before the invention of the scanning tunneling microscope (STM) in the early 1980’s, the possibilities to study the atomic structure of surfaces were mainly limited to diffraction techniques using beams of x-rays, electrons, ions and other particles. Although very accurate surface-structure determinations can be made using these techniques, they have a spatially averaging character, providing little or no information about the surface defects. With the field ion microscope, developed in the 1950’s, the geometrical arrangement of atoms on the surface of sharply pointed tips can be resolved in real space, but the requirements on sample geometry and stability under the high electric fields used in the imaging process make the technique unsuitable for general-purpose microscopy. Also the transmission electron microscopy has the capability to resolve individual atoms, or at least an individual row of atoms, but the applicability for surface studies is limited. Moreover, all the above-mentioned techniques are further restricted by requiring vacuum for their operation. A breakthrough came when Binnig and Rohrer designed the first operating STM. [1] This instrument showed atomic-scale resolution with a capability to use many kinds of samples in
many different environments (e.g. vacuum, air, and liquids). Binnig and Rohrer were awarded the 1986 Nobel prize in physics for their achievement.

2 Operation principles

The central part of the STM is a sharp conductive tip which is moved in a very precise and controlled manner in three dimensions across the surface of the sample, as shown in Fig. 1. A small voltage is applied between tip and sample (typically a few mV to a few V, depending on the sample material) and when the tip is brought close enough to the sample (5-10 Å) a tunneling current flows (10 pA-10 nA) between the tip and the sample. This is a purely quantum mechanical phenomenon (classically there would be no current, since the region between tip and sample is insulating). As will be shown below, the current is exponentially dependent on the distance between the tip and the sample, varying approximately one order of magnitude per ångström. By keeping the current constant, the distance to the sample is held constant and if the tip is scanned over the surface and its movement perpendicular to the sample required to keep the current constant is registered, the result is a topographical image of the sample surface. Alternatively, the tip is scanned across the sample surface at a constant average height and the current variations are registered. This requires a surface that does not contain large protrusions into which the tip would crash. As will be discussed below, the constant-current image is actually not a true topographical image, but an image of the surface electron density that for certain sample materials like metals, agrees fairly well with the true topography. The vertical resolution is limited by the mechanical stability of the instrument and the capability of the electronics to keep the current constant, something that is facilitated by the exponential dependence on the distance between the tip and the sample. Vertical resolution in the 0.01 Å range is readily accomplished. Horizontally, the resolution is limited by the sharpness of the tip, and 10 Å resolution is routinely achieved. Under favorable conditions a lateral resolution as high as 1 Å may be achieved, such that individual atoms can be resolved.

One of the advantages of the STM is the possibility to use varying types of sample materials, the only criterion being that the sample has to be conductive. STM has been used for determination of the surface structure of metals [2] and semiconductors [2] as well as for studies of nucleation
and growth of thin films in vacuum [3]. Other applications include studies of biological materials [4] and in situ studies of electrochemical reactions [2]. There are applications of the STM other than pure topographical measurements, e.g. tunneling spectroscopy where different electronic states of the surface may be mapped with very high spatial resolution [2]. Also emission of secondary particles such as electrons and photons induced by electrons from the tunneling tip have been studied with high spatial resolution using STM [5].

Since the invention of the STM new exciting scanning probe techniques using different probe-sample interactions to control the separation have
appeared. The most notable is the atomic force microscope [6] (AFM) where the force between the tip and the sample is used in the same manner as the tunneling current in the STM. The resolution of the AFM is almost in the range of the STM and the sample materials do not have to be conductive.

2.1 Mechanical considerations

Due to the extremely small distances involved, the mechanical rigidity and vibration isolation are of utmost importance. From the first comparably voluminous STMs which required several stages of vibration isolation, the development has gone towards small and rigid microscopes with little or no vibration isolation at all [7]. It has even been possible to fabricate working miniature STMs on silicon wafers [8].

2.2 Positioning system

In an STM, two functions of the positioning system are required. Besides the need for a three-dimensional fine-positioning device to move the tip in the ångström to micrometer range, a mechanism is needed to bring the tip and sample within the range of the fine-positioning device from millimeters apart. The fine-positioning system has since the first STM been realized with piezoelectric ceramics. A piezoelectric material is a material that deforms in a controlled manner when a voltage is applied across it, with a typical sensitivity in the range of 10-100 Å/V. Basically two types of scanners are used, the tripod and the tube, see Fig. 2.

The tripod scanner consists of three piezo rods orthogonally connected to each other to give a three-dimensional motion. The tube scanner consists of a single piezoelectric tube with one inner electrode and four axial and orthogonal electrodes. The z-motion is a function of the voltage applied between the inner electrode and the outer electrodes and the lateral motion is achieved by applying a voltage between the inner and only one of the outer electrodes. This causes that particular segment to stretch or contract and the tube bends accordingly. Compared to the tripod, the tube scanner is more rigid and thus has a higher mechanical resonance frequency, making it possible to scan at higher speeds. Nowadays the tube scanner is the most common scanner type. A great variety of coarse-positioning devices have been presented and a simple example is to use a screw with some
kind of gear. Another type is utilizing the inertia of a moving object as in the instrument used in this exercise. The sample holder consists of a circular metal plate with a hole in the center where the sample, clamped to the upper face, is exposed to the tip coming up from below, cf. appendix. Parallel to the piezoelectric tube for the movement of the tip are three tubes also made of a piezoelectric material. By applying appropriate voltages to the supporting tubes, the sample holder may be rotated. This rotation is of course very small. However, if the driving voltages are applied in a sequence of slow rotations in one direction alternated by fast rotations in the opposite direction, the inertia of the sample holder will prevent it from moving during the fast part of the sequence resulting in a net rotation. If the procedure is repeated at a high frequency, the net motion is fast enough to be useful for the coarse approach.

### 2.3 Electronics

The most common imaging mode is the constant current mode, which requires a regulator that adjust the $z$ driving voltage to keep the tunneling current at a preset value, as shown in the block diagram in Fig. 3.

The current from the sample is fed to a current-to-voltage converter whose output voltage is fed to a logarithmic amplifier that compensates for the exponential behavior of the tunneling junction. The signal is compared to the set current in a difference amplifier and the error signal is amplified in a proportional and sometimes also in an integrating stage. Finally, the
Figure 3: The basic controller for the tunneling current.

signal is fed to the high voltage amplifier that drives the piezoelement for
the vertical motion of the tip, thus closing the feedback loop such that for
example a too high current causes a retraction of the tip.

2.4 Tip

The performance of the STM is much dependent on the condition of the
tip as it determines the resolution of the instrument. The tip consists of a
mechanically or electrochemically sharpened wire of e.g. tungsten, gold,
or platinum. Ideally it has a monoatomic point, but the apex continuously
rearranges and sample atoms adsorb during operation. Since the image
actually is a convolution of the tip and the sample, the symmetry of the tip
is reflected in the recorded image and several different tips must be used for
a given sample before conclusions can be drawn about the surface structure.
Sometimes tunneling current flows simultaneously from several parts of
the tip and the resulting image is a superposition of more than one images.
The problem with a blunt, double tip is illustrated in Fig. 4, where it can be
seen that scanning the single protrusion on the sample with the double tip
results in an image showing two “bumps”. When scanning with the sharp
tip, the only distortion of the image is a slight broadening of the “bump”.

6
Figure 4: The paths followed by a sharp tip (left) and a blunt, double tip (right).

3 Theoretical background

A full treatment of the tunneling between tip and sample in an STM requires three-dimensional tunneling theory, well beyond the scope of this text. Instead, a one-dimensional treatment is presented, which gives results in qualitative agreement with three-dimensional theory. A simple approach when modeling tunneling in one dimension is to assume that only elastic tunneling occurs, that the two (metallic) electrodes are semi-infinite potential wells with depth $E_F + \phi$, the Fermi energy and the work function, respectively, each as in Fig. 5.

The Schrödinger equation for one of the metal electrodes can be written as:

$$-\hbar^2 \frac{\partial^2}{2m \partial z^2} \psi(z) + V(z)\psi(z) = E\psi(z),$$

with the potential given by

$$V(z) = \begin{cases} 0, & z < 0 \\ E_F + \phi, & z \geq 0. \end{cases}$$

Inside the metal, where $z < 0$ and $V(z) = 0$, the Schrödinger equation can be rewritten as:

$$-\hbar^2 \frac{\partial^2}{2m \partial z^2} \psi(z) = E\psi(z).$$

This can be solved by assuming a plane-wave solution for the wave function:

$$\psi(z) = Ae^{ixz} + Be^{-ixz}.$$
When the solution is inserted into (1), we get:

$$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial z^2} (Ae^{i\kappa z} + Be^{-i\kappa z}) = E (Ae^{i\kappa z} + Be^{-i\kappa z})$$

(4)

$$\Rightarrow \kappa(E) = \sqrt{\frac{2mE}{\hbar^2}}.\tag{5}$$

Outside the metal, where $z \geq 0$ and $V(z) = E_F + \phi$, the Schrödinger equation can be rewritten as:

$$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \psi(z) + (E_F + \phi) \psi(z) = E \psi(z).\tag{6}$$

Since the values of wave function must approach zero when far away from the metal, we assume a solution of the form

$$\psi(z) = Ce^{-\kappa z}.$$ 

This inserted to (1) yields

$$\frac{-\hbar^2}{2m} \kappa^2 Ce^{-\kappa z} = (E - (E_F + \phi)) Ce^{-\kappa z}$$

(7)

$$\Rightarrow \kappa(E) = \sqrt{\frac{2mE}{\hbar^2} - (E_F + \phi - E)},\tag{8}$$
where $\kappa$ is the so-called inverse decay length and $\left((E_F + \phi) - E\right)$ is the effective barrier height.

To obtain the full solution to the Schrödinger equation (1) for the assumed potential (2) we require the solutions for the regimes $z < 0$ and $z \geq 0$ to equal at $z = 0$ as the wave function and its derivative have to be continuous. The result is a function that is periodic inside the metal and exponentially decaying outside.

To get a numerical value for the inverse decay length $\kappa$ we set $E = E_F$ and $\phi = 4.5$ eV, a typical value for a metal. This yields:

$$\kappa(E) = \sqrt{\frac{2mE}{\hbar^2}} \left((E_F + \phi) - E\right) = \sqrt{\frac{2m\phi}{\hbar^2}} \approx 1.1 \text{ Å}^{-1}. \quad (9)$$

The probability to find an electron with energy $E$ at location $z$ is given by the probability distribution:

$$\rho(E, z) = |\psi(E, z)|^2, \quad (10)$$

and outside the electrode we get:

$$\rho(E, z) \sim e^{-2\kappa(E)z}. \quad (11)$$

From this we can see that:

- The probability distribution decays approximately one order of magnitude when $z$ is increased by 1 Å.
- Lower energy results in larger $\kappa$, which implies more rapid decay.

For a real metal with a more complex potential $V(z)$ and a density of states $g(E)$, the total probability of finding an electron with energy $E$ at location $z$ is given by the probability distribution (11) weighted by the density of states, and the situation may look like one depicted in Fig. 6.

Two planar electrodes (modeled as potential wells as described above) brought close to each other may be seen as an STM with an extremely blunt tip. This is depicted in Fig. 7 for a negative bias on the tip, i.e., the electrons tunnel from the tip to the sample.

On the tip side there are no electrons that can contribute to a tunneling current for energies above the Fermi level, $E_{FT}$ (region I in Fig. 7). For the region below the Fermi level of the sample, $E_{FS}$, (region III) electrons are...
available for tunneling on both sides of the junction but the net contribution to the tunneling is zero due to the fact that the tunneling probability is equal in both directions. Therefore the net tunneling current comes from the region between $E_{FT}$ and $E_{FS}$ (region II). As can be seen in Fig. 7, these electrons experience an average barrier height given by:

$$\bar{\phi} = \frac{\phi_T + \phi_S}{2} + \frac{eV}{2} - E, \quad (12)$$

resulting in an inverse decay length equal to:

$$\kappa(E) = \sqrt{\frac{2m\bar{\phi}}{\hbar^2}}. \quad (13)$$

We can now express the net tunneling current as given by the overlap between the wave functions of the tip and the sample weighted by the corresponding density of states:

$$I(V) \sim \int_{E_{FT}}^{E_{FS}} g_T(E)e^{-\kappa(E)T} g_S(E - eV)e^{-\kappa(E)S} dE. \quad (14)$$
Figure 7: Two potential wells brought close to each other which may be regarded as a one-dimensional STM.

If we assume that these principles also hold for real samples and sharper tips, i.e., a smaller probe area and thus an increased lateral resolution, we obtain an expression for the tunneling current in the STM:

\[ I = I(\vec{r}, E) g_s(\vec{r}, E - eV) e^{-2\kappa(E)s} dE. \]  

Although several simplifying assumptions have been made in the derivation of this equation, the qualitative features are in agreement with results from more elaborate three-dimensional calculations [2]. The exponential dependence of the current on the tip-sample separation is evident from the equation. Moreover, it is seen that the tip and the sample are equivalent in the theory, and that the tunneling current is proportional to the convolution of the density of states. Ideally one would like to relate the STM image directly to the properties of the sample, which would require an ideal, infinitesimal tip with a constant density of states. This is not possible to achieve in practice, so the properties of the tip must always be taken into account when interpreting STM images. Even for an ideal tip, a constant-current STM image is not a true image of the topography of the sample surface, but rather a map of the surface electronic states.
4 Exercises

4.1 Graphite

1. Get acquainted with the program. Take some images of different sizes.

2. What is the magnification of the printed images? Compare with the optical microscope (< 2000 x) and the scanning electron microscope (< 500 000 x).

3. What kind of resolution do you get? That is, how close can two points come to each other and still be resolved as two distinct points? (The order of magnitude is sufficient.)

4. Given the resolution, is it possible to figure out the physical size of the tunneling current, i.e. the diameter of the tunneling electron beam? What power density does that imply? Express in W/cm². (The order of magnitude is sufficient here too.)

5. Compare the taken images with the supplied model of graphite Fig. 8.
   (a) There is a difference between the model and the captured image. In what way are they different?
   (b) How does the side of the hexagonal unit cell in the model match the cell in the captured images?
   (c) Why is there a difference? Try to explain it. (Hint: Count the number of bonds each C atom has at different lattice positions. Are all lattice sites equivalent?)

6. Given the result in (e), the recorded image data is a mix of two types of information. Which?

7. Change the current step-wise from 0.2 nA to 2 nA and take images.
   (a) How does the current affect the image and its quality?
   (b) What other parameter changes (indirectly) when the current is changed?
(c) What are the disadvantages of having a high and a low current, respectively?

8. Change the voltage step-wise from 0.05 V to 2 V and record some images.
   
   (a) How does the voltage affect the quality of the image?
   (b) Describe with the aid of Fig. 7 in the lab introduction, what happens when the voltage increases.
   (c) Is the current monotonically increasing with increasing voltage?
   (d) From theory, is $dI/dU$ monotonically increasing with increasing voltage?
   (e) Is it possible to somehow interpret $dI/dU$ from theory?

4.2 Gold

1. How does the structure of the film look like?

2. Can we get atomic resolution? If not, why?

4.3 Tip-related questions

1. How is it possible to get atomic resolution with a 0.4 mm Pt wire?

2. Give some other possible methods on how to make better tips.

3. What happens to the STM image when the sample features are sharper than the tip apex?
References


Appendix

Excerpt from the manual for the Besocke STM
Setting up the microscope:

The Scanning Tunneling Microscope is mounted on a NW 35 UHV flange with feedthroughs and with all the necessary electrical connections provided. For transportation purposes it is covered with an outer and an inner protective cap.

Before removing the protective caps, please prepare a stable place for installation. The flange plane has to be aligned horizontally. For testing and for use under normal air pressure the STM should be mounted on a stable installation board. Provide sufficient room for the connecting plug. Possible ways of dampening vibration are rubber buffers, air cushions, or suspending the instrument from elastic bands; with the installation flange, or rather the surface plane, aligned horizontally. For installation in a vacuum chamber, the above rules also apply. Before installing in the chamber remove the outer protective cap carefully.

Attention!

Before removing the inner protective cap by unscrewing the three locking screws, please take note of the following:

1. The four piezo-tubes are fragile and brittle. They are likely to snap, if not treated with the utmost care. It is essential to prevent impacts of any kind.

2. The STM base plate rests only on the Viton-dampers, in order to prevent high-frequency vibrations. The locking screws hold the base plate with its piezo-tubes tightly in place on to the STM platform. Having loosened the locking screws, the base plate rests on top of the Viton-dampers. If not handled with the utmost care or if tilted to an angle acuter than 20 degrees off the horizontal plane the base plate could detach itself from the STM platform, fall down and the delicate electrical connections could be destroyed. While working with the microscope, the locking screws should always be put in place, with or without the protective cap, depending on the kind of work you perform. In order to maintain the elasticity of the
Viton-dampers, the screws should not be tightened to the extreme. The distance between the base plate and the STM platform should be in the range of 1 mm.

3. On changing the tunneling tip, apply only vertical forces very carefully (Z-direction). Avoid horizontal forces, in order not to snap the piezo-tubes. On removing the tunnel tip, screw in the locking screws, so that the base plate is prevented from moving.
The Tunneling Tip:

The Beetle STM requires tunneling tips made of 0.25mm diameter wire. The tunneling tips can be obtained from specialist retailers, or you, yourself can manufacture them following the usual procedures of etching (W), grinding or cutting with scissors (Pt). Having prepared the tip, the wires should be shortened to a length of approximately 6mm. To ensure a smooth insertion of the tip, even out the wire's blunt end and round it off. (Grind through the wires, rather than simply cutting them, as they tend to split on being cut.) Provide tension in the wires by bending them lightly and insert them into the metal tube of the Z-piezo by means of tweezers. The wire must have enough tension to sit tightly in the tube, while at the same time remaining flexible enough to be manipulated. By moving the tunneling-tip wire back and forth in the metal tube, the protruding length (L) can be adjusted. The value (L) is dependant upon the exact size of the tunneling microscope, the Triple-helix sample holder and the position of the sample's surface. The length (L) should correspond as accurately as possible to the Z-variation of the Triple-helix sample holder (approx. 0.5mm).

To ensure that the tips are placed in their optimum position, please use the clamp-tweezers provided to insert them; the tweezers are ready-made with tips that have been measured under microscope and clamped in accordingly, as well as provided with the necessary tension. Insert the tunneling tip into the Z-piezo until the tweezers touch the tube rim, unscrew the clamping-screw and withdraw the tweezers carefully sideways without touching the tip.
The Triple-Helix Sample Holder:

The sample holder is made of Mo and its gliding-surfaces are coated with a special material to enhance its gliding property and to prevent a welding together of the surface with the bearings that it rests upon. Put the sample into place from the back and press it down with the W-clamping-spring. Under UHV conditions the sample holder and sample can be subjected to a temperature up to 1200 degrees Celsius. The tunneling microscope itself, however, must not exceed 200 degrees Celsius. Make sure that the gliding-surfaces and bearings are always kept clean, since dirt particles can reduce gliding efficiency considerably.

The utmost care should be taken when placing the sample holder on to the STM. In vacuum an adequate manipulator is needed. A sufficient supervision is essential, so please carry out the installation process accordingly! Before putting the sample holder into place, it should be rotated in such a way that the distance between the sample and the tip is the furthest possible, so that contact between them is avoided. Once in its place, the electronic approach procedure can be activated by pressing the APPROACH key. The sample rotates down slowly and stops automatically when the tunneling current is sensed. Before installing it in a vacuum chamber, it is advisable to practise the STM operation under normal air pressure. Suggested suitable samples for testing are: pyrolytic graphite (HOPG) or Au layers on smooth substrates (glass, Si-Wafers). The distance between the sample and the tip and its manoeuvering can be supervised by means of a telescope, a microscope or a magnifying glass. The tip and its reflection can be observed directly or via the STM's base plate, which serves as a mirror. Using the TRANSPORT mode the sample area that is to be tested can be manoeuvred over the tip and then be approached using the APPROACH mode.

The motion properties of the Tripel-helix sample holder are dependant on the mass, the moment of inertia, the gliding properties and the gradient to be dealt with. (The sample holder moves easier downwards than upwards.)
Supervision of the tip position

Sample
Sample holder

Direct observation

Observer

Using STM baseplate as a mirror

Observed image of the tunneling tip