Scanning Tunneling Microscopy (STM) (II)

Instrumentation:

The following figure shows essential elements of STM. A probe tip, usually made of W or Pt-Ir alloy, is attached to a piezo drive, which consists of three mutually perpendicular piezoelectric transducers: x piezo, y piezo, and z piezo. Upon applying a voltage, a piezoelectric transducer expands or contracts. One controls x-y piezo to scan in xy plane and uses coarse positioner and z piezo to bring the tip and the sample within a few angstroms. The electron functions in the tip overlap electron functions in the sample surface. A bias voltage, applied between the tip and the sample, causes an electrical current to flow. Such a current is a quantum-mechanical phenomenon, tunneling.

The tunneling current is amplified by the current amplifier to become a voltage, which is compared with a reference value. The difference is then amplified to drive the z peizo. The phase of the amplifier is chosen to provide negative feedback: If the tunneling current is larger than the reference value, then the voltage applied to the z piezo tends to withdraw the tip from the sample surface, and vice versa. Therefore, an equilibrium z position is established through the feedback loop. As the tip scans over the xy plane, a two-dimensional array of equilibrium z positions, representing a contour plot of the equal tunneling-current surface, is obtained and stored.

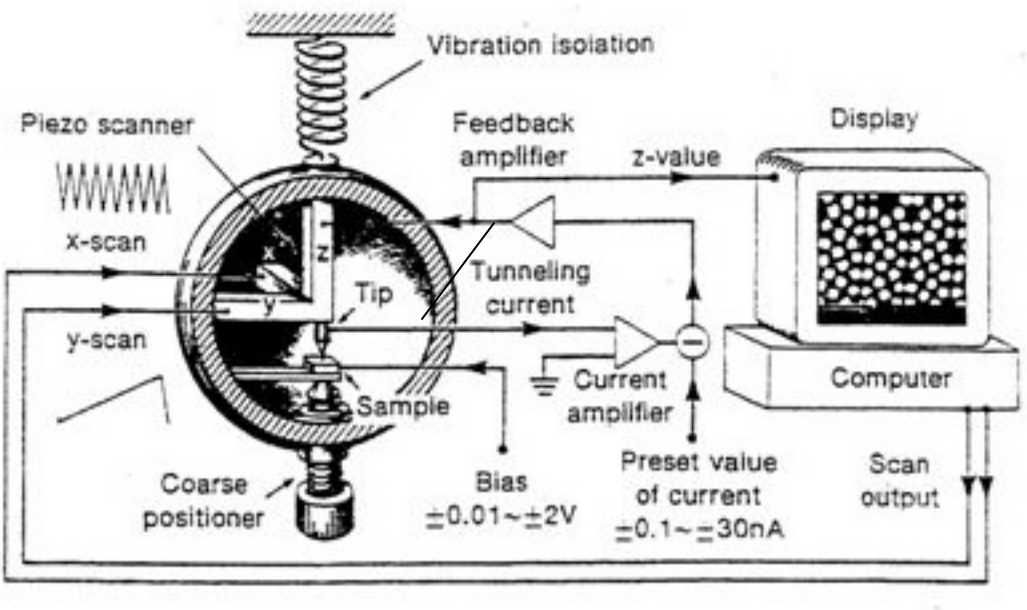
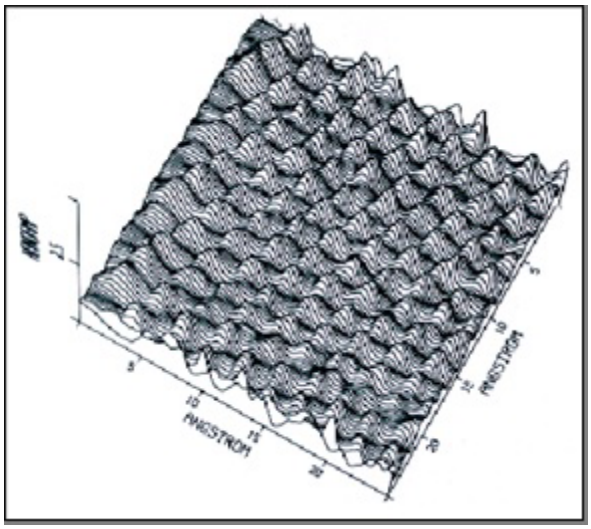
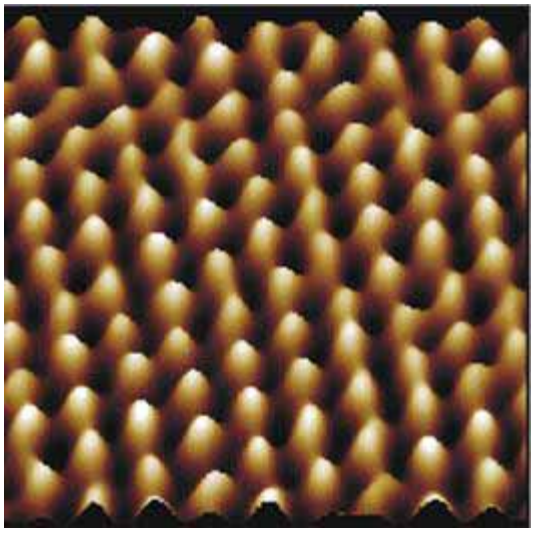


Figure. Schematic diagram of the scanning tunneling microscope

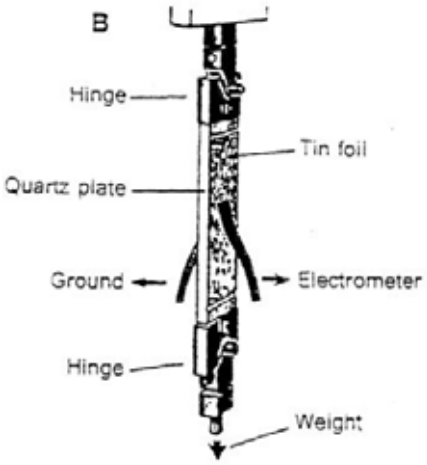
The contour plot is displayed on a computer screen, either as a line-scan image or as a gray-scale image (color-scale). The line-scale image is a sequence of curves, each of which represents a contour along the x direction with constant y. The gray-scale image is similar to a black-and-white television picture. The bright spots represent high z values (protrusions), and the dark spots represent low z values. The following figures are line scan image and color-scale image of graphite surface.



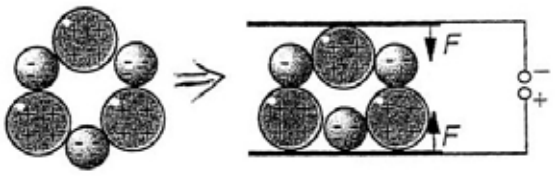


Now we shall look into a little bit more details on individual component of the STM and we start with the Piezoelectric Scanner.

Piezoelectric effect was discovered by Pierre Curie in about 1880.



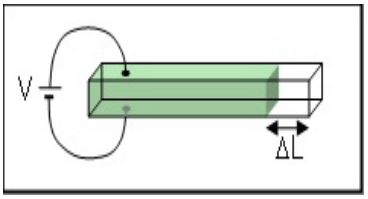
By stressing the quartz plate
an electrical charge is generated.



Quartz crystal: (Si positive, O negative)
The pressure put on the crystal causes a displacement of the charge inside the crystal. Opposite charge are collected at the opposite sides of the crystal.

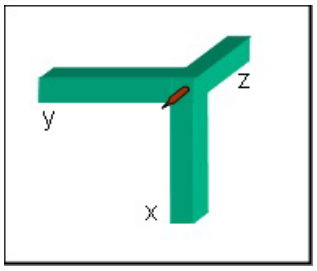
STM use inverse piezoelectric effect, i.e., by applying voltage on the material and the material deforms. The piezoelectric materials used in STM are various kinds of lead zirconate (PbZrO3) or lead titanate ceramics (PbTiO3) since these would have a larger piezoelectric coefficient (unit: Å/V) and other advantages.

Definition: $E = \frac{V}{L}$, strain tensor: $S = \frac{\Delta L}{L}$, piezoelectric C: $C = \frac{S}{E} = \frac{\Delta L}{V}$



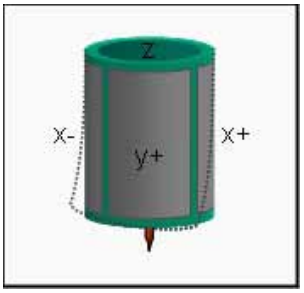
Principle of piezo element. The applied voltage makes the element longer or shorter.

$5x10^{-7}$-$5x10^{-12}$m,i.e.,a fraction of one micrometer to atomic resolution



The combination of three piezo elements makes it possible to move the STM tip in the X-, Y-, and Z-directions.

Tripod Scanner



In most modern scanning probe microscopes, one uses a tube geometry.

Tube Scanner

Principles of the tube scanner:

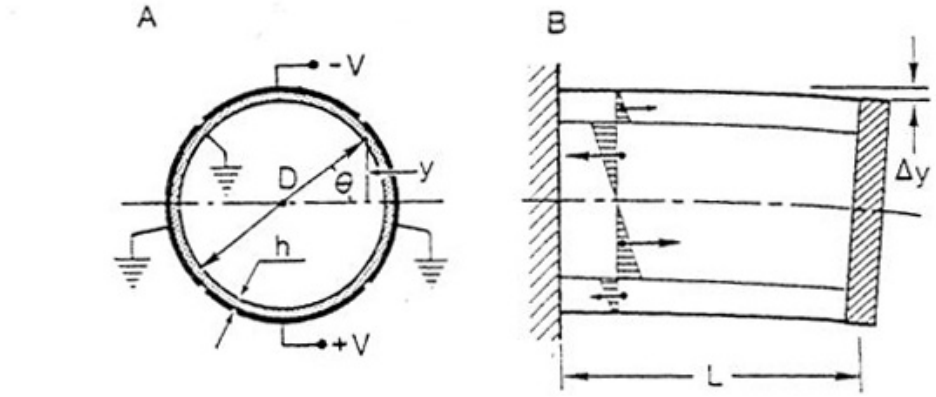


Figure Deflection of a tube scanner. (A) Opposite and equal voltages are applied to the y electrodes of a tube scanner. The x, z electrodes are grounded. A positive stress (pressure) is generated in the upper quadrant, and a negative stress (tension) is generated in the lower quadrant. (B) At equilibrium, a distribution of stress and strain is established such that the total torque at each cross section is zero. This condition determines the deflection of the tube scanner in the y direction.

Using elementary geometry, you will get:

$$\Delta y = \frac{2\sqrt{2}dVL^2}{\pi Dh}$$

and a piezo constant for tube scanner is $K_{tube} = \frac{dy}{dV} = \frac{2\sqrt{2}dL^2}{\pi Dh}$, h: thickness of piezo; d: piezoelectric coefficient for the piezo.

Vibration Isolation

Effective vibration isolation is one of the critical elements in achieving atomic resolution by STM. The typical resolution in the z-direction (normal to sample surface) is about 0.01nm. Therefore, the disturbance from external vibration must be reduced to less than 0.001nm. This is done by introduction of Vibration Isolation System in STM.

Much of the physics of vibration isolation can be illustrated as single-stage suspension-spring isolation system in the following figure and understood easily.

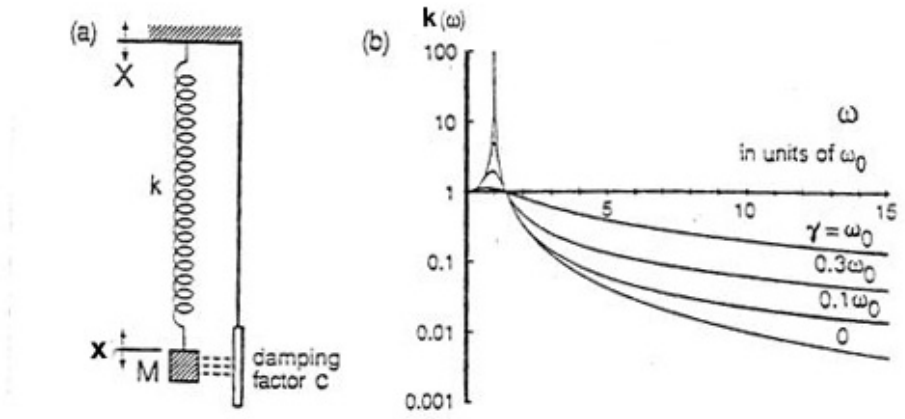


Fig. A vibrating system with one degree of freedom and its transfer function. (a) The vibrating system. A mass M is connected to the frame through a spring and a viscous damper. Regarding STM, the frame represents the floor, and the mass represents the STM. (b) The transfer function, which is the ratio of the vibration amplitude of the mass to that of the frame at different frequencies.

The restoring force of the spring acting on the mass is:

$f=-k(x-X)$, k is the stiffness of the spring

A viscous (damping) force is acting between the frame and the mass:

$$f' = -c(x' - X')$$

Newton's law: $F = Mx'' \Rightarrow -k(x - X) - c(x' - X') = Mx''$

$$\Rightarrow x'' + \frac{k}{M}x + \frac{c}{M}x' = \frac{k}{M}X + \frac{c}{M}X'$$

$$\Rightarrow x'' + 2\gamma x' + \omega_0^2 x = 2\gamma X' + \omega_0^2 X$$

here, ω_0 is natural circular frequency $\omega_0 = 2\pi f_0 = \sqrt{\frac{k}{M}}$

γ: damping constant: $\gamma = \frac{c}{2M}$

Assume a sinusoidal vibration: $X(t) = X_0 e^{i\omega t}$

at the steady state, the motion of the mass should also be sinusoidal:

$$x(t) = x_0 e^{i\omega t}$$

Substitute these two into previous equation, we obtain

$$\frac{x_0}{X_0} = \frac{{\omega_0}^2 + 2i\gamma\omega}{{\omega_0}^2 - \omega^2 + 2i\gamma\omega}$$

The ratio of the amplitudes is the transfer function or the response function of the vibration isolation system:

$$k(\omega) \equiv \left|\frac{x_0}{X_0}\right| = \sqrt{\frac{{\omega_0}^2 + 4\gamma^2\omega^2}{({\omega_0}^2 - \omega^2)^2 + 4\gamma^2\omega^2}}$$

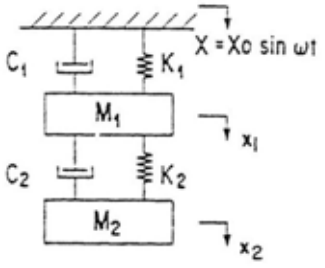
In the engineering literature, the decibel (db) unit is frequently used:

$$Z = 20\log_{10} k(\omega) \quad \text{(db)}$$

k(ω) ~ ω figure shown in previous page. An efficient vibration isolation means a small k(ω).

<u>Two-stage suspension spring vibration isolation system</u>:

Fig. A two-stage suspension-spring vibration isolation system. Two masses are hung from the frame via two springs and tow damping mechanisms. The ratio between the vibration amplitudes of the frame and of the second mass (the transfer function) is calculated. The efficiency of its vibration isolation is much better than the single-stage system.



For two masses:

$$M_1 x_1'' + c_1 x_1' + k_1 x_1 + c_2(x_1' - x_2') + k_2(x_1 - x_2) = c_1 X' + k_1 X$$

$$M_2 x_2'' + c_2(x_2' - x_1') + k_2(x_2 - x_1) = 0$$

For a sinusoidal external excitation,

$$X = X_0 e^{i\omega t} \Rightarrow$$

$$[A]\vec{x} = \vec{X}, \vec{x} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}, \vec{X} = \begin{pmatrix} X \\ 0 \end{pmatrix}$$

$$[A] = \begin{bmatrix} k_1 + k_2 - M_1\omega^2 & -k_2 \\ -k_2 & k_2 - M_2\omega^2 \end{bmatrix} + i\omega \begin{bmatrix} c_1 + c_2 & -c_2 \\ -c_2 & c_2 \end{bmatrix}$$

and transfer function is: $Z \equiv 20\log_{10}\left|\frac{x_2}{X}\right|$

Stacked plate-elastomer system

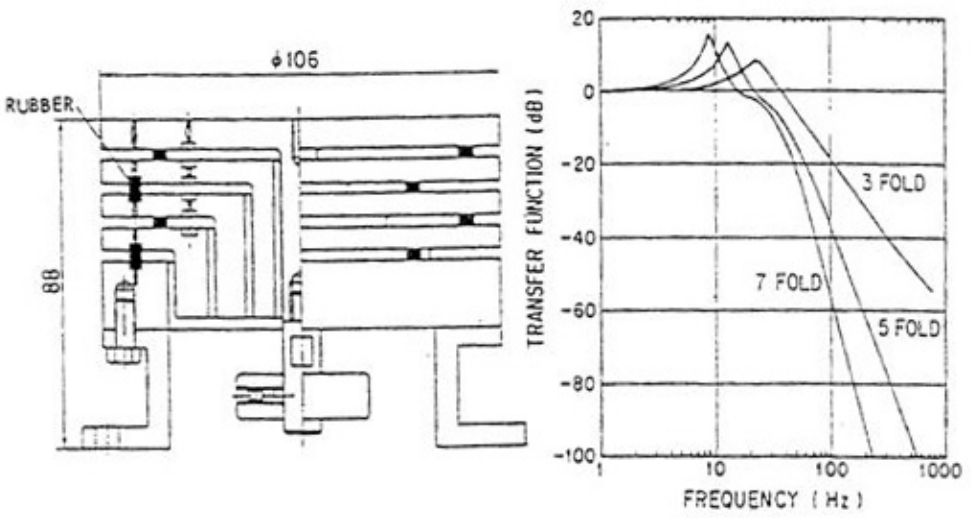


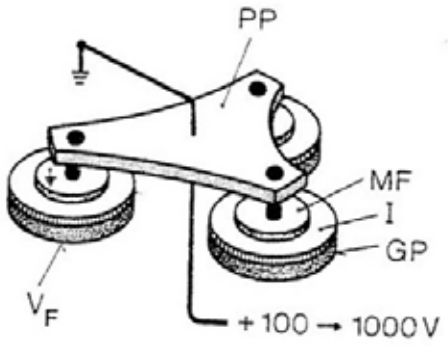
Fig. Stacked plate system and its transfer function. (a) A fivefold stacked-plate vibration system, with four sets of viton pieces between metal plates. (b) Transfer function for 3, 5, and 7 fold stacked-plate vibration system.

Easyscan STM uses such approach. The STM is placed on a soft rubber mattress, which in turn lies on a two-kilogram heavy granite piece whose base is made of foam material. The rubber mattress damps the high frequency vibrations, while the base damps the low frequency vibrations.

Coarse Positioner

Coarse positioner is another important element, which moves the relative position of the tip versus the sample in steps exceeding the range of the piezodrive.

Fig. The piezoelectric stepper – the louse. It consists of a piezoelectric plate (PP), standing on three metal feet (MF), separated by high – dielectric-constant insulators (I) from three metal ground plates (GP). The feet can be clamped electrostatically to the ground plate by applying a voltage V_F. By alternatively activating the clamping voltage and the voltage on the piezo plate, the louse crawls like a creature with three legs.



The above piezoelectric stepper is somewhat complicated device. In many surface-science experiments, the actual location on the sample surface does not matter. A one-dimensional stepper is sufficient. In its simplest form, a fine-pitch lead screw can make controlled steps of a few micrometers. One typical design is shown as Single-tube STM in the following:

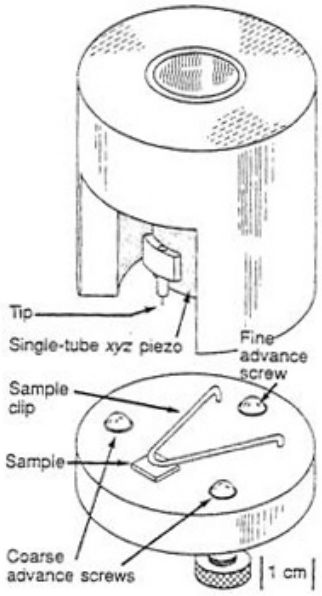
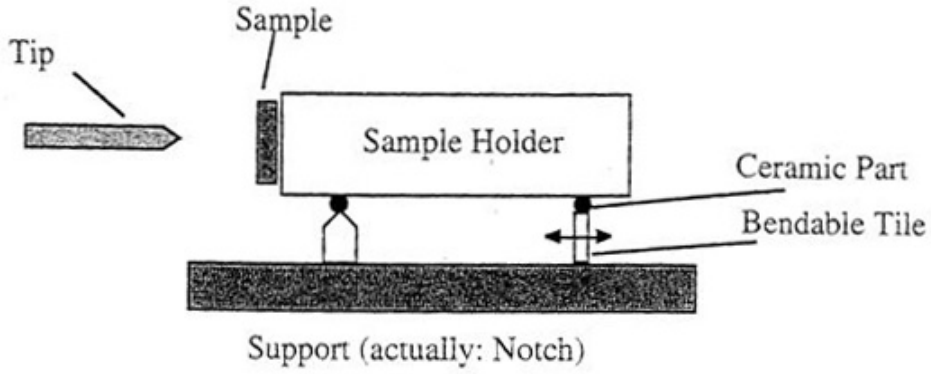


Fig. Single-tube STM. The tube piezo scanner is adhered inside a sturdy metal cylinder, which sits on three screws on the base plates. The two front screws make the coarse approaching. The rear screw makes fine approaching by using the two front screw as the pivot axis. The rear screw is actuated by a stepping motor for automatic approaching. The entire unit is rigid enough that a mediocre vibration isolation device can provide atomic resolution.

In our STM used for LAB, we have so-called Inertial Coarse Positioner.



Bendable tile is a piezo crystal, by using a "saw tooth" voltage (rises slowly, drops quickly), the sample holder is moving ahead.

Electronics and Control

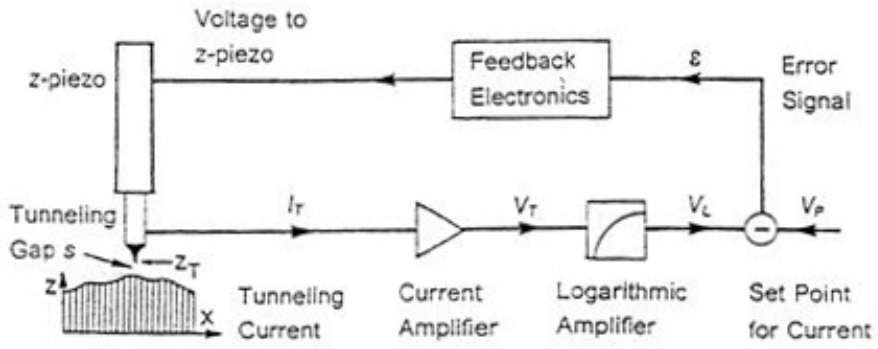
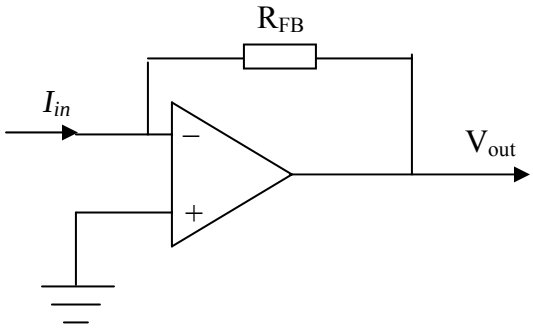


Fig. A schematic of the feedback loop in an STM. The tunneling current, after the current amplifier and the logarithmic amplifier, is compared with a predetermined voltage, which represents the current setpoint. The error signal is processed by the feedback electronics, which typically contains an amplifier and an integration circuit. The output of the feedback electronics is applied to the z piezo, to keep the error between the actual tunneling current and the reference current very small. The voltage applied to the z piezo is recorded as the topographic image.

Tunneling current occurring in STM is very small, typically from 0.01nA to 100nA. Such small current has to be amplified by Current amplifier:

$$V_{out} = -I_{in} R_{FB}$$

The minus sign indicate that the phase is reversed. Typically the feedback resistance is 100MΩ in STM. Estimate: If you have one nA of input current, what is the output?

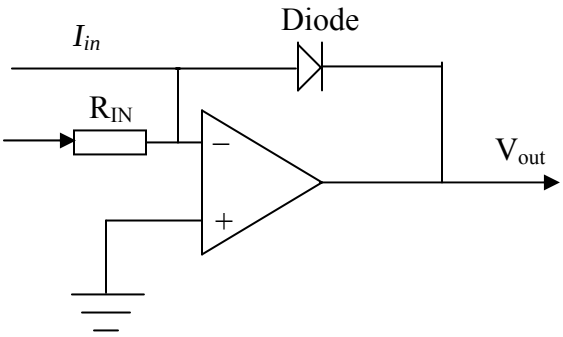


Logarithmic amplifier:

Since the tunneling current: $I_T \propto e^{-2ks}$,

logarithmic amplifier is to make the entire electronic response linear with respect to tunneling gas s.

Diode I-V: $I = I_0(\exp(\frac{eV}{kT}) - 1) \approx I_0 \exp(\frac{eV}{kT})$



By using an input resistor, the logarithmic amplifier accepts voltage input:

$$V_{out} = const. + \frac{kT}{e} \ln I_{IN}$$

So for every decade of input, the output changes about 60mV.

After that, the V_L is compared to reference V_P, the difference is sent to feedback electronics, and amplified to become a voltage and control z-piezo.

Making STM tips:

Materials: W, Pt-Ir, etc.
Procedures: 1) Electrochemical tip etching: For W: Cathode: $6H_2O+6e^-=3H_2(g)+6OH^-$.
Anode: $W(s)+8OH^-=WO_4+4H_2O+6e^-$. Etching occurs at the air-electrolyte (NaOH) interface. The etching takes a few minutes. When the neck of the wire near the interface becomes thin enough, it ruptures, making two tips at the same time.

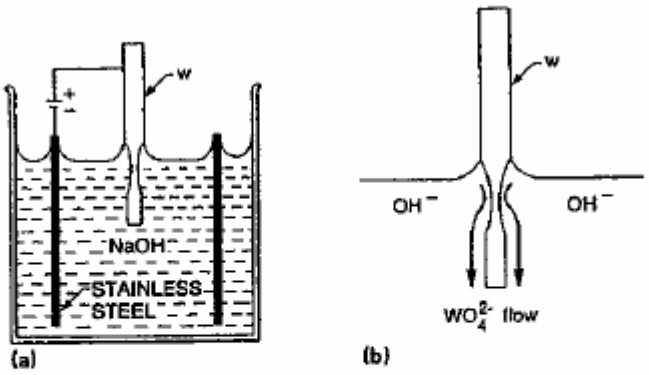


Fig. 13.1. Electrochemical etching of tungsten tips. (a) A tungsten wire, typically 0.5 mm in diameter, is vertically inserted in a solution of 1N NaOH. A counterelectrode, usually a piece of platinum or stainless steel, is kept at a negative potential relative to the tungsten wire. (b) A schematic illustration of the etching mechanism, showing the "flow" of the tungstate anion down the sides of the wire in solution. (Reproduced from Ibe et al., 1990, with permission.)

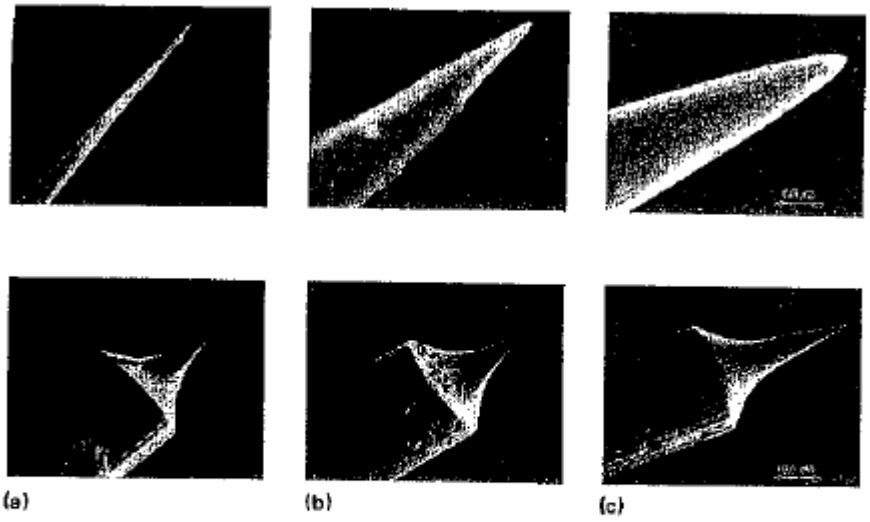


Fig. 13.2. Dependence of tip radius of curvature with cutoff time. Scanning electron micrographs of tips with different etching-current cutoff time. (a) 600 ns, with an average radius of curvature 32 nm. (b) 140 ms, with an average radius of curvature 58 nm. (c) 640 ms, with an average radius of curvature 100nm. (reproduced from Ibe et al., 1990, with permission.)

To etch Pt-Ir tips, a solution containing 3 M NaCN and 1 M NaOH is used. A circular Ni foil is used as the cathode.

The tips (for example W) generated by electrochemical etching are seldom applicable immediately as the tip surfaces is covered with oxide, contaminations as well as organic molecules, etc.

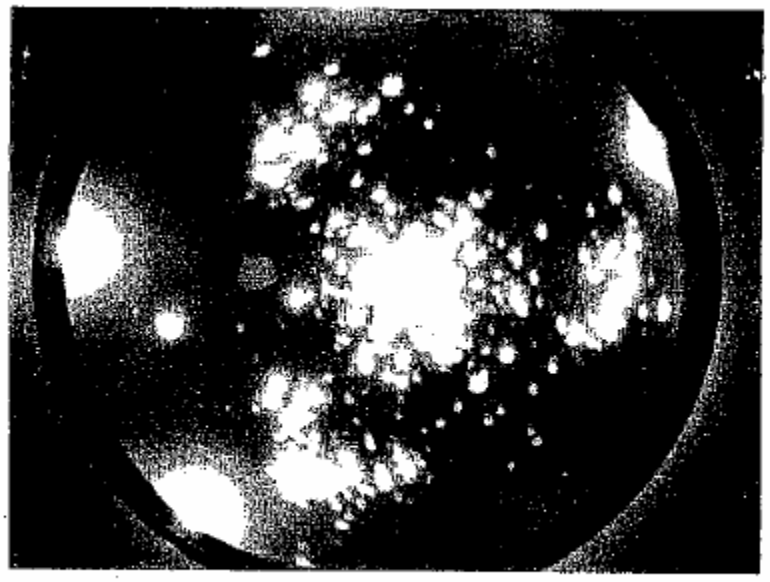


Fig. 13.3. FIM image of a W tip immediately after etching. The tip is etched from a single-crystal W wire with (111) orientation. The threefold symmetry is visible on a large scale. Locally, severe dislocations are observed. (Courtesy of U. Staufer.)

Procedure 2: Annealing the tip. The purpose of the tip annealing is to remove the contamination and oxides without cause tip blunting. The removal of tungsten oxide is based on the following mechanism: On tungsten surfaces, the stable oxide is WO3. At high temperature, the following reaction takes place: $2WO_3+W=3WO_2$ (g). Several methods for annealing are shown here.

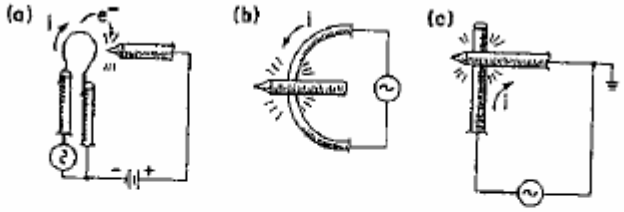


Fig. 13.5. Tip annealing methods. (a) Electron bombardment. A filament, biased negatively with regard to the tip, emits electrons to heat up the tip. (b) Resistive heating by a W filament. The tip is spotwelded to the filament. After heating, the tip is removed from the chamber and detached from the filament, and put into the vacuum chamber quickly. (c) Using the tip shank as the heating element. The tip is made in touch with a thicker W wire, which is connected to a power supply. Current flows through the tip shank to the ground.

Procedure 3: Field evaporation and controlled deposition: By controlling the field intensity at the tip apex, the most protruding W atoms are stripped off, leaving a well-defined tip apex. (see figure, with one atom, tree atoms and 7 atoms.

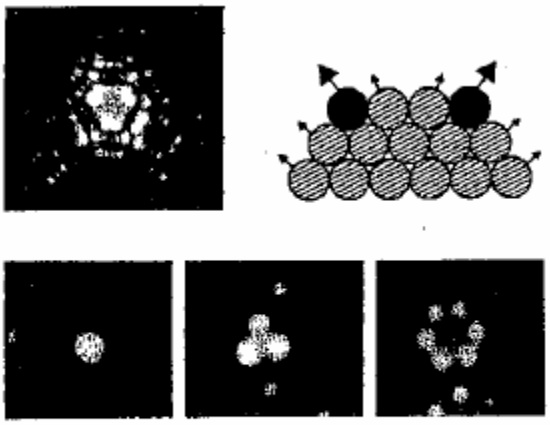


Fig. 13.6. Tip formation by field evaporation. Top left, FIM image of a (111)-oriented W tip; the (111) apex plane contains 18 atoms. Top right, the field evaporation process. Bottom, tip with pyramidal apex with one, three, and seven W atoms at the apex plane. (Reproduced from Fink, 1986, with permission.)

Some people do annealing and field deposition at the same time:

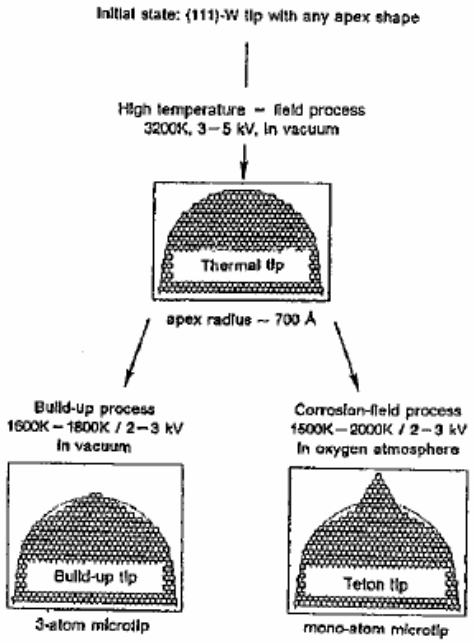


Fig. 13.7. Tip treatment by annealing in a field. Top: At a temperature close to the melting point of tungsten, the shape of the tip is basically determined by diffusion process. A rather round-shaped thermal tip is formed. Bottom left, at lower temperature, the directional effect of the field dominates. A built-up tip is formed. Bottom right, in an oxygen atmosphere, the corrosion process further generates a nanotip. After Binh (1988a).

Atomic metallic ion emission: Binh and Garcia reported in 1992 that at temperatures around one third of the bulk melting temperature (for W: 3410°C), by applying an even higher electric field to the tip, the metal ions move to the protrusions and emit from the ends. These tips may contain multi mini-tips at the tip end, and you know this is fine for STM measurements to resolve atomic resolution.

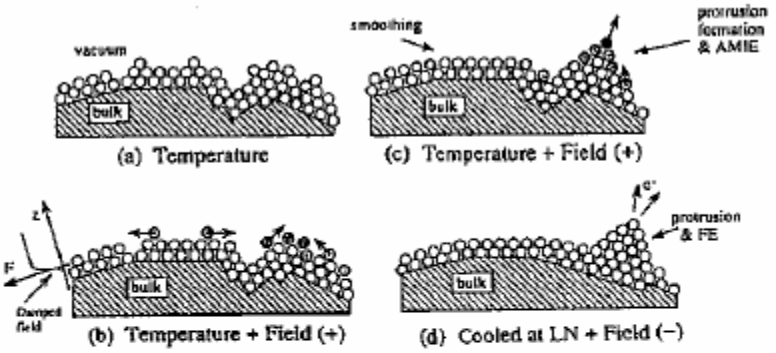


Fig. 13.8. Atomic metallic ion emission and nanotip formation. (a) At high temperature, the atoms on a W tip becomes mobile. The tip surface is macroscopically flat but microscopically rough. (b) By applying a high field (1.2–1.8 V/Å,), the W atoms move to the protrusions. (c) The apex atom has the highest probability to be ionized and leave the tip. The W ions form an image of the tip on the fluorescence screen. (d) A well-defined pyramidal protrusion, often ended with a single atom, is formed. By cooling down the tip and reversing the bias, a field-emission image is observed on the fluorescence screen. The patterns are almost identical. (Reproduced from Binh and Garcia, 1992, with permission.)

In situ tip treatments: The tips treated by the above procedures may still not resolve atomic images of your sample. Now you may try a couple of method during the measurements.

1) High field treatment: Atomic resolution is supposed to be obtained at a smaller gap voltage, but is not obtained, try to increase the gap voltage to increase the field at the tip for some time and reduce the gap voltage back to the original again.

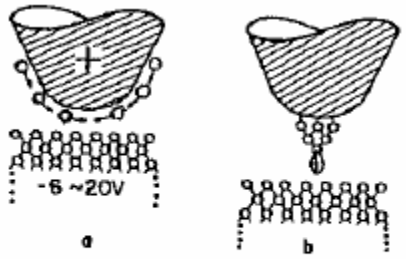


Fig. 13.10. Mechanism of tip sharpening by an electrical field. (a) W atoms on the tip shank walk to the tip apex due to the nonuniform electrical field. (b) A nanotip is formed. (Reproduced from Chen, 1991, with permission.)

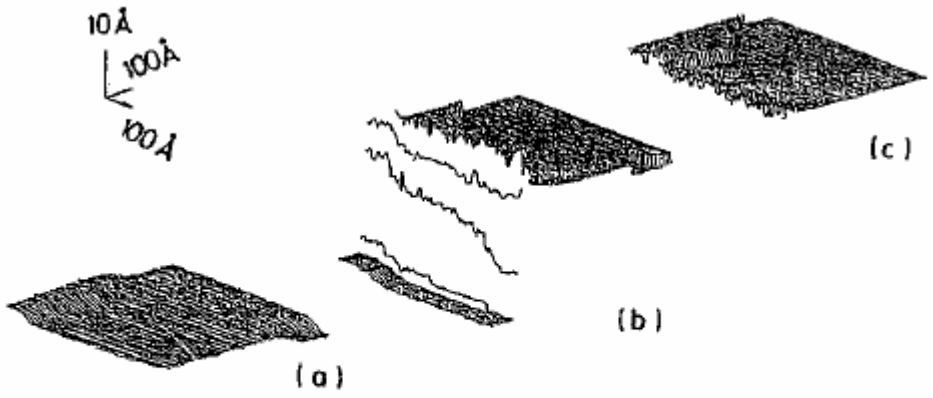


Fig. 13.9. In situ tip sharpening by electrical field. (a) Tunneling at −500 mV and 1 nA with no atomic resolution. (b) By suddenly raising the bias to −7.5 V for several scan lines, the tip end is elongated. (c) A tip with atomic resolution is formed. (Reproduced from Wintterlin et al., 1989, with permission.)

2) Controlled collision:

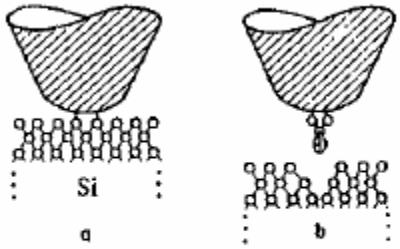


Fig. 13.11. Mechanism of tip sharpening by controlled collision. (a) The W tip picks up a Si cluster from the Si surface. (b) A Si cap forms at the apex of the tip, providing a p_z dangling bond. (Reproduced from Chen, 1991, with permission.)