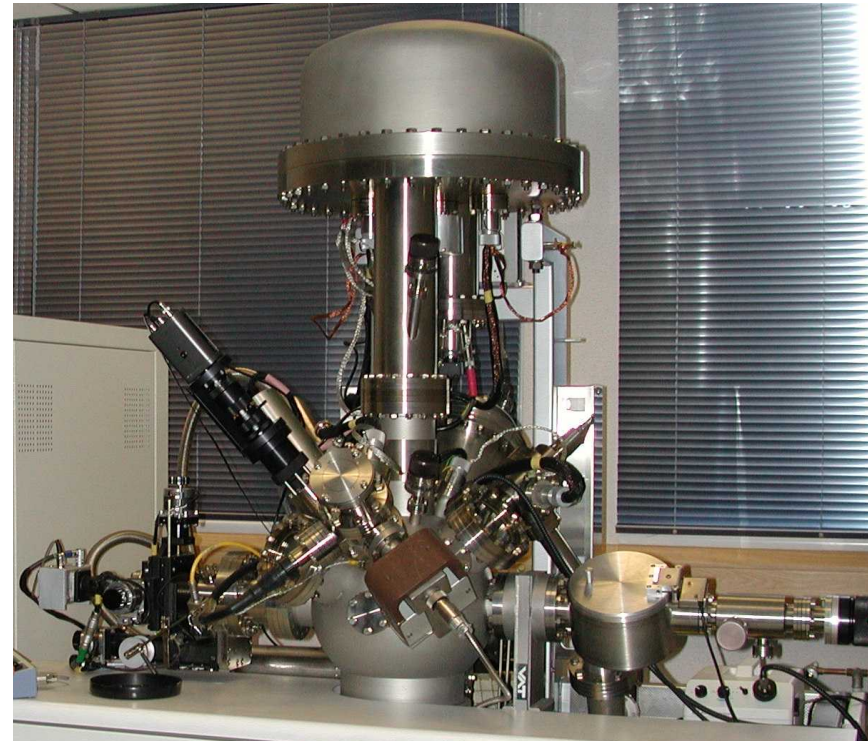


Surface analysis

part I: local probe; part II: beam techniques
techniques



Teachers:

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Surface analysis: planning

Course organization and evaluation

- Part I (4 lectures, in-class exercises)
- Part II (4 lectures, in-class exercises)
- Weeks 9-13 TPs in labs (individual projects in small groups)
- Week 14: TP presentations and evaluation

Final evaluation grade: $\frac{1}{3}$ (part I) + $\frac{1}{3}$ (part II) + $\frac{1}{3}$ (TP)

Surface analysis: part I

local probe techniques

Goals

- Understand the basic concepts behind local probe techniques
- Principal approaches, hardware, methods, advantages and limitations
- Practical aspects, technical solutions, data analysis and interpretation, identification and removal of artifacts
- Applications: use of local probe techniques for solving problems in materials science, physics (also chemistry, biology...) and engineering

Local probe techniques: literature and sources of information

-Lecture handout (contains essentials, usable for exam preparation) - moodle

- Optional reading (cited below + references within the lecture notes)

*Scanning Probe Microscopy, Bert Voigtländer, Springer-Verlag Berlin Heidelberg 2015
(available online through the library)*

Atomic Force Microscopy, Peter Eaton, Paul West, Oxford University Press, 2010

Review papers:

Imaging physical phenomena with local probes: From electrons to photons,
D. Bonnel et al., Review of Modern Physics, Volume 84, pp 1343---1381, 2012

Functional and Spectroscopic Measurements with Scanning Tunneling Microscopy
A Moore and P. Weiss, Annu. Rev. Analyt. Chem. 1, 857, 2008

*further optional reading: papers on modern techniques and youtube resources
- will be indicated for each technique in corresponding chapters*

Local probe techniques:

On-line sources of information

The industry leaders in SPM propose some useful tutorials and application notes on their websites

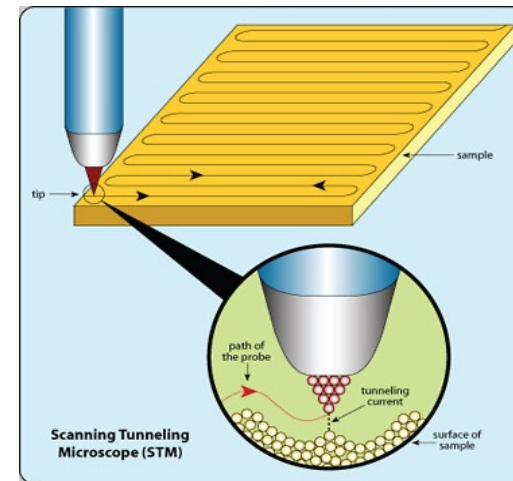
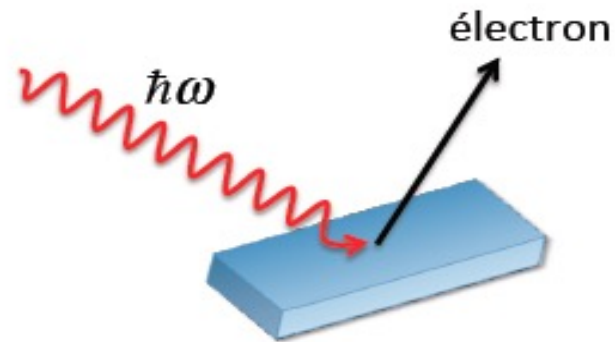
<https://afm.oxinst.com>

<https://www.parksystems.com/>

Many lectures on YouTube on specific SPM topics...
some of them will be recommended within the course

- Be careful, in the real life the things are more complex than in the presentations, try to understand what you (or others) are doing

Global (beam) methods vs. local (probe) methods



- Unlike “global” methods (like XPS, SIMS) the local probe techniques analyze the surface locally, with typical scale of 0.1 – 100nm.

- a limited number of atoms, molecules or nanostructures is concerned.

- Regardless of the method applied the probe techniques measure short-range interactions

- The long-range interactions can also influence the measurements, however their influence is limited since they vary on a much greater scale.



Concept of a scanning probe microscope



Concept of SPM: using the interaction of a small physical probe with a surface to obtain spatially resolved information.

The (small) probe is scanned with respect to the sample, and the interaction is monitored.

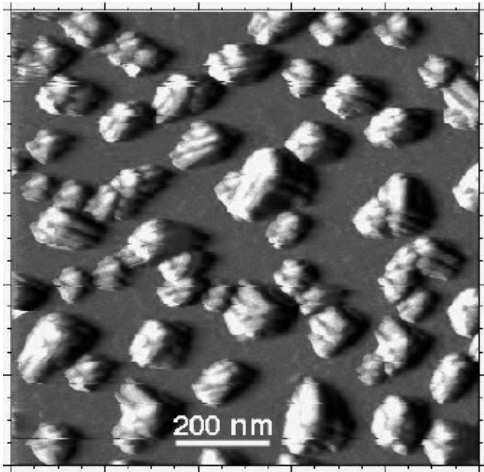
The spatial position (x, y) of the probe is combined with the interaction signal to construct a 3D map of the probe-sample interactions.

Direct (real) space imaging!
Individual objects with nm-pm res.



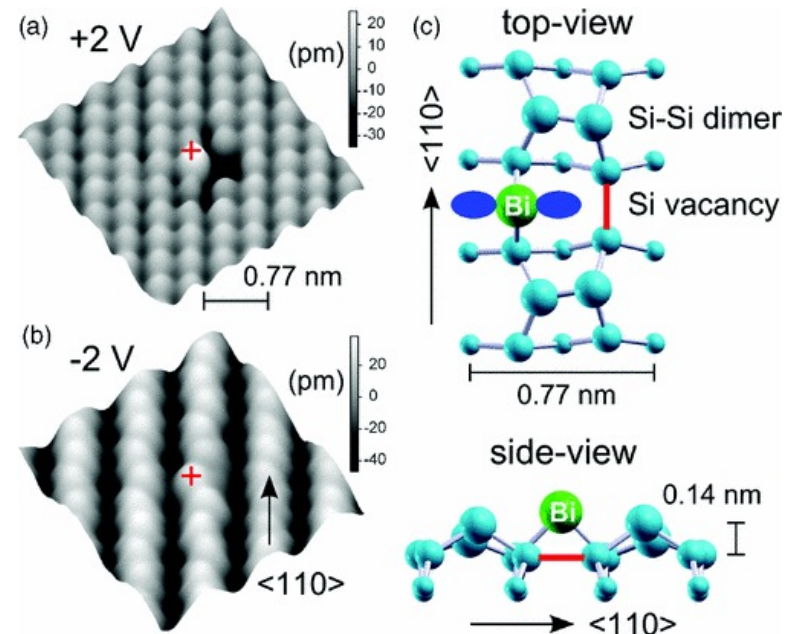
Analysis using SPM: some examples

Topography in sub-micron scale



Example 1:
Surface of island-type
polycrystalline structure
imaged by atomic force
microscopy (AFM)

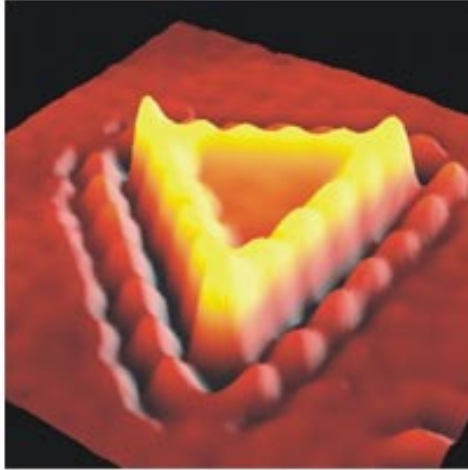
Atomic resolution: dopants and defects



Example 2: atomic resolution scanning tunneling microscopy (STM). Surface of (001) Si with Bi donor (marked with cross). Local structure of electronic orbitals could be explored by analyzing these images.

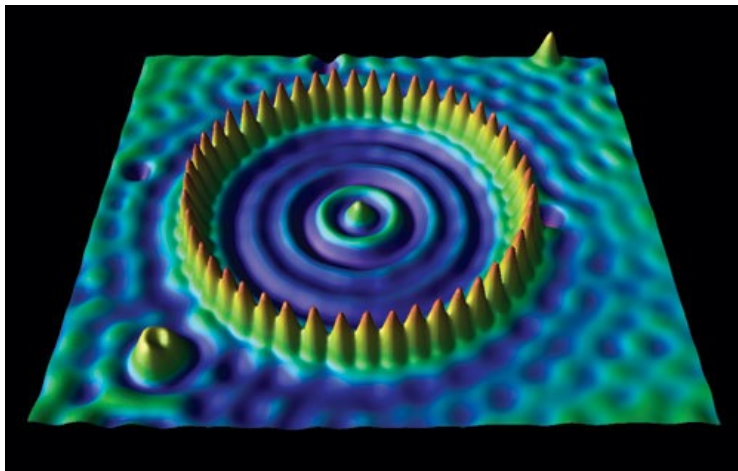
Phys.Rev.B 88, 035440 (2013)

Analysis by scanning probe, examples: beyond surface diagnostics



Molybdenum disulphide nanocrystals are used as catalysts to remove sulphur impurities at oil refineries. Reducing harmful sulphur emissions from the combustion of transport fuel is a major environmental challenge. This STM studies of MoS_2 nanocrystals- which are triangular - on gold surfaces have clarified how these catalysts work and lead to improvement in their performance

Ch. Gerber & H. Lang *Nature Nanotechnology* **1**, 3 - 5 (2006)



"Blue corral" image, published on the cover of *Physics Today* in November 1993. This STM image realized on a ring of iron atoms deposited on the surface of copper displays a contour map of electron density. The electrons confined in the inner area of the ring form a standing wave pattern looking like water waves in a circular pool

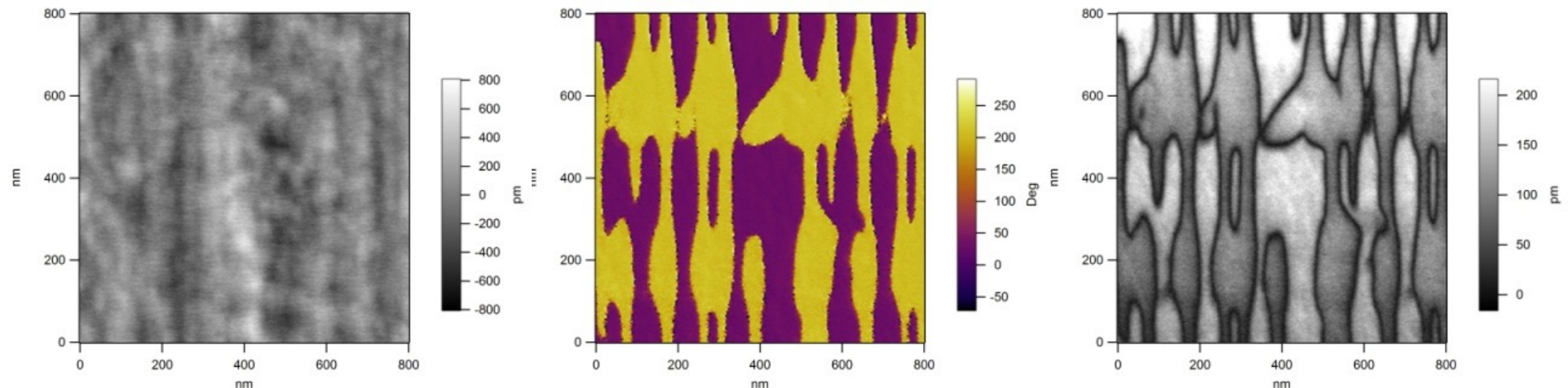
Physics Today 46, **11**, 17 (1993)

Scanning probe techniques beyond topography: how to see polarization domains

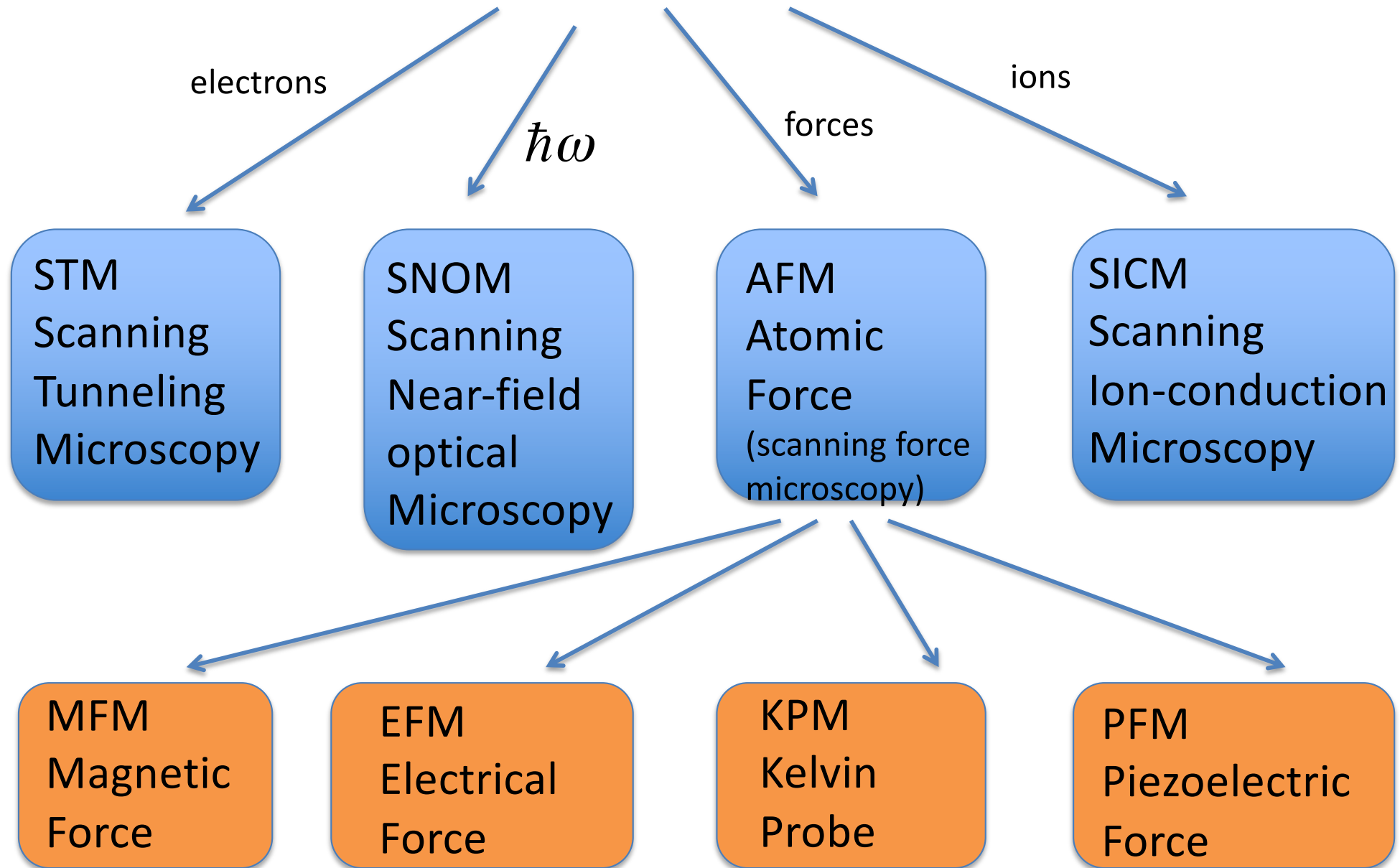
“functional” scanning probe microscopy:

left image : topography measured by atomic force microscopy on a BiFeO_3 thin layer.

If one scans same area while applying to the probe a small ac voltage signal and detect the mechanical vibration of the probe at the same frequency you can map polarization domains. The maps of phase (center) and amplitude (right) of the probe vibration represent the distribution of domains with different spontaneous polarization (oriented “up” or “down”).



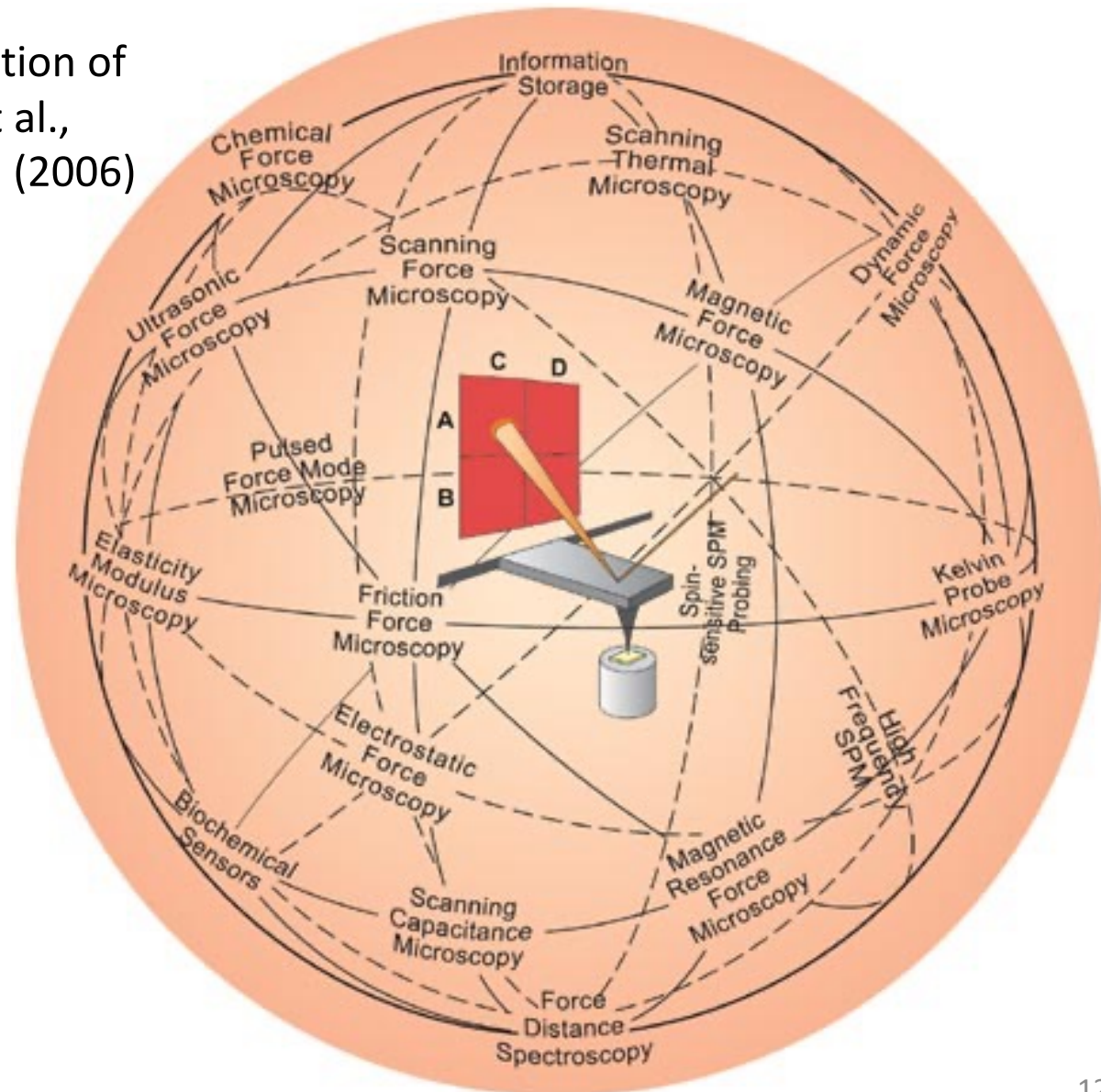
Local probe techniques: some (incomplete) classification



- This is oversimplification, there are modern techniques which exploit hybrid methods e.g. STM probe-enhanced optical spectroscopy methods. More examples will come within the course

Each “family” of scanning probe techniques contains a great variety of approaches.

This is an example of classification of AFM methods from Gerber et al., Nature Nanotechnology 1, 3-5 (2006)



Chapter 1.

Scanning tunneling microscopy (STM)

- First scanning probe technique (first publication in 1982)
- Scanning probe monitors tunneling current
- STM is used only for conductive materials
- STM is a powerful tool for studying surfaces with atomic resolution, analyzing local electronic structure, manipulating atoms and other applications

STM:

<https://www.youtube.com/watch?v=wNEqRq6NyUw>

AFM:

<https://www.youtube.com/watch?v=jRAqhFdwt20>

Revisiting the basics: electron in a quantum well (particle in a box)

The time-independent Schrödinger equation for one particle in one dimension can be written as:

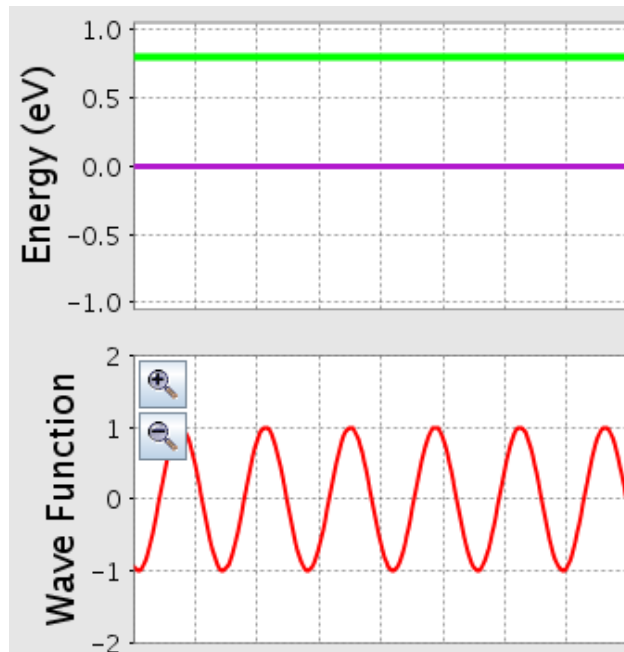
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)}{\partial x^2} + V(x)\Psi(x) = E\Psi(x)$$

where m is the particle's mass, V is potential energy, Ψ is wavefunction

the modulus squared of the wavefunction, $|\psi|^2$, is a real number interpreted as the probability density of finding a particle in a given place

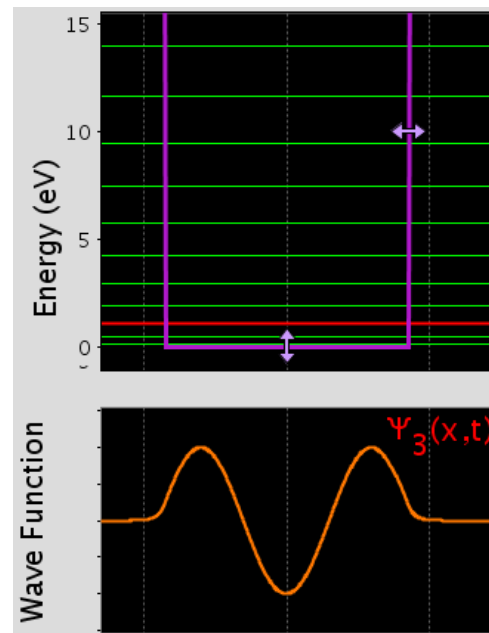
Free Particle

$$\Psi(x) = \Psi_0 e^{ikx} \text{ or } \Psi_0 e^{-ikx}$$



- Infinite Square Well

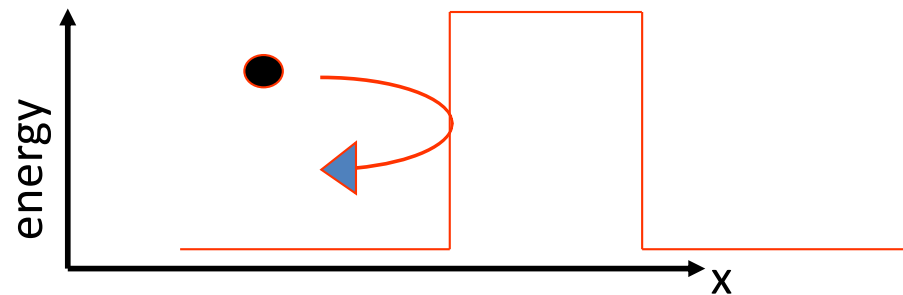
$$\Psi_n(x) \sim \sin(n\pi x/L), \quad E_n = h^2 n^2 / 8mL^2$$



The electron confined between infinitely high barriers behaves like a standing wave that does not penetrate through the barriers

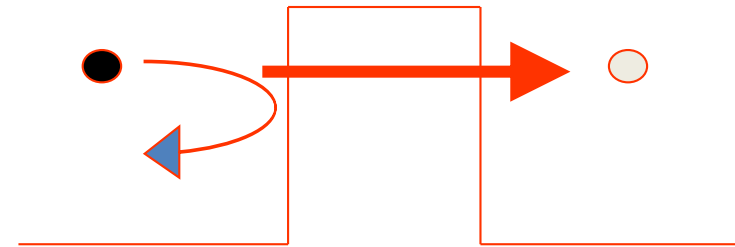
Revisiting the basics: Phenomenon of tunneling

Classical case: there is no chance of the particle being found beyond the barrier.

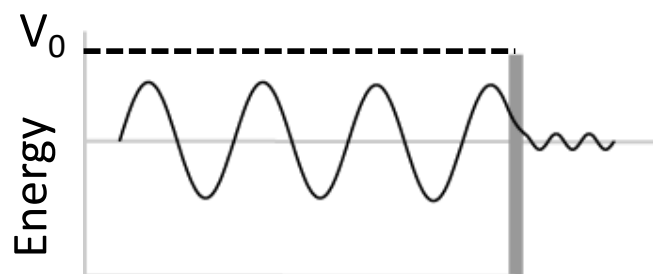


classical barrier – no transmission, only reflection

Quantum mechanics: there is a **probability** that the electron can be found beyond the barrier.



quantum barrier – part transmission, part reflection



General solution: $\Psi(x) = \Psi_0 e^{\pm ikx}$

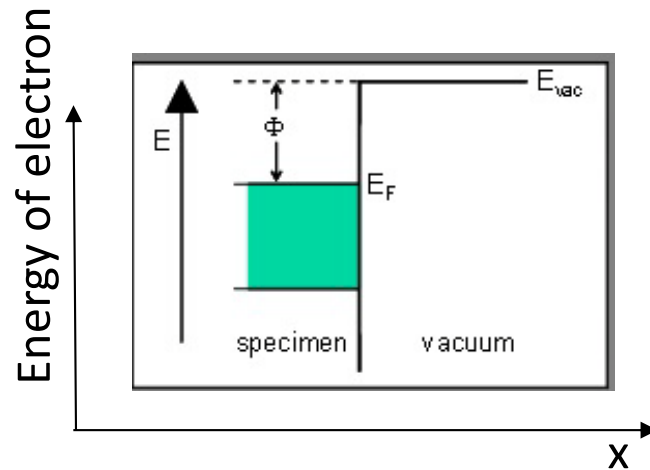
$$k = \sqrt{2mE / \hbar^2}$$

When the wavefunction penetrates the barrier V_0

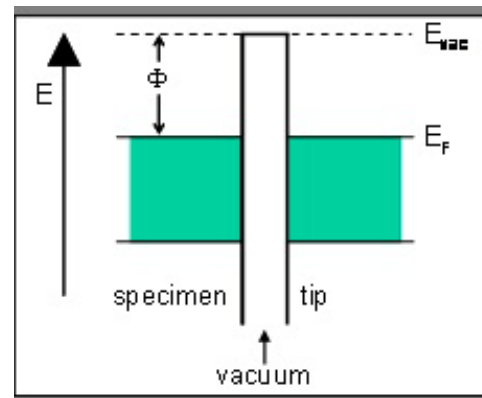
$$k = \sqrt{2m(E - V_0) / \hbar^2}$$

If the energy of the particle is less than the barrier height, the wavenumber k becomes imaginary, hence the amplitude decays exponentially

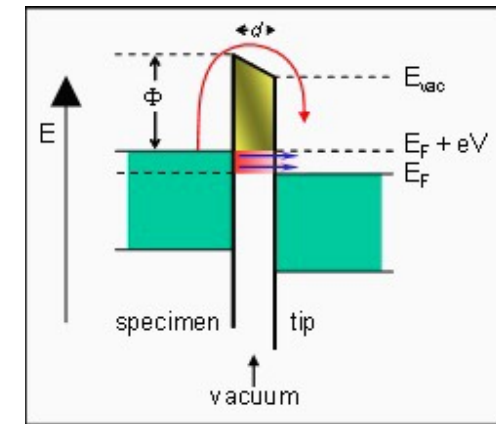
Tunneling effect and Scanning Tunneling Microscopy (STM)



In a metal, the energy levels of the electrons are filled up Fermi energy $-E_F$. In order for an electron to leave the metal, it needs an additional amount of energy Φ , this is so-called 'work function' e.g. work required to remove an electron from material to the vacuum nearby the surface.



When the sample and the tip are brought close to each other, there is only a narrow region of empty space left between them. On either side, the electrons occupy all states up to the Fermi energy. They need to overcome a barrier Φ to travel from tip to sample or vice versa

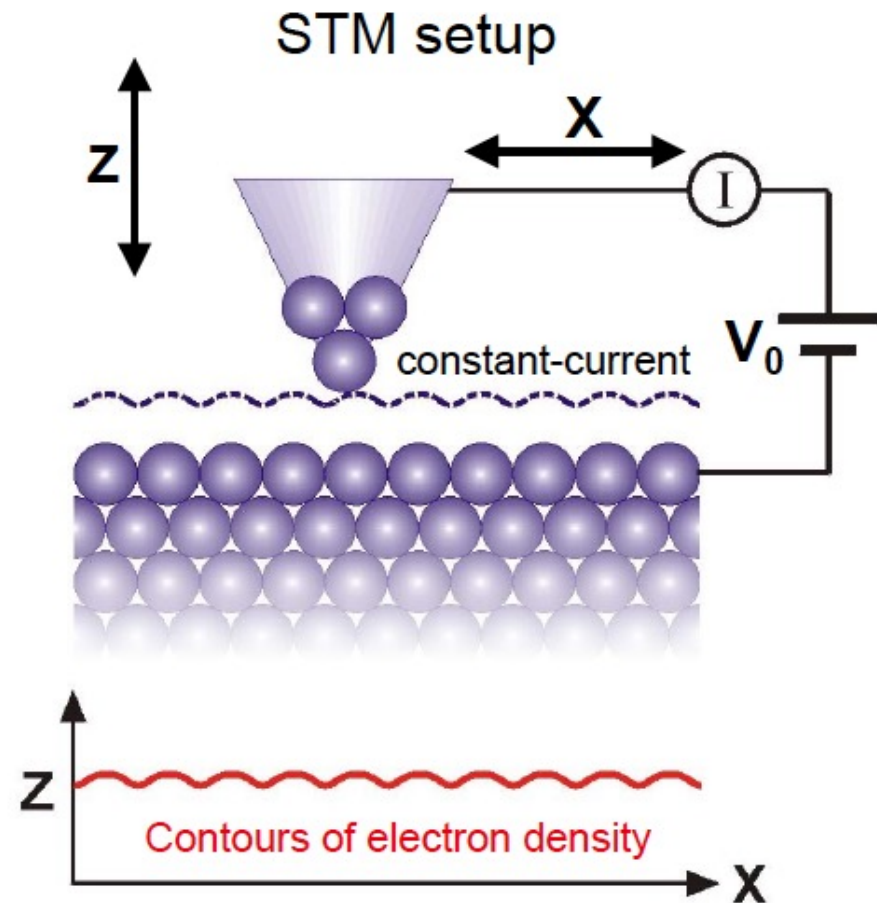
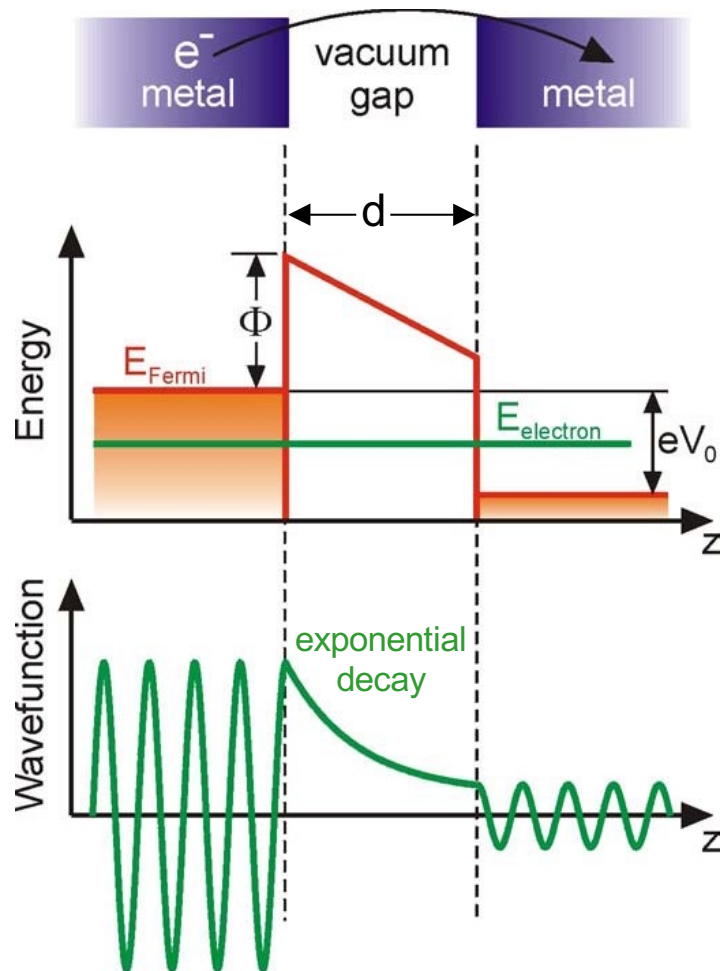


If the distance d between sample and tip is small enough, electrons can 'tunnel' through the vacuum barrier.

The direction of tunneling is determined by applied voltage V , which changes the energy profile as shown above (positive voltage applied to the tip)

Scanning tunneling microscopy (STM): physics of STM, tunneling spectroscopy, applications

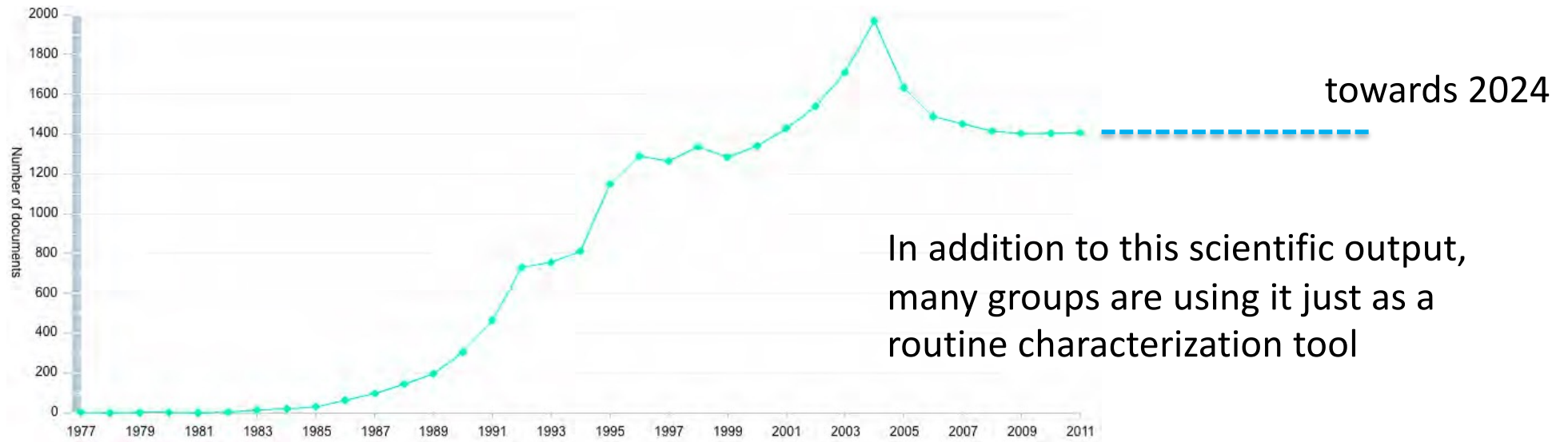
1D tunnel contact



- **Topography information**
(constant-current mode)

$$I(z) \sim e^{-2kz}$$

STM: statistics of publications



Principle fields:

Physics, Appl. Physics
Phys. Chemistry
Material Science
Engineering

Limitations:

- most of applications (beyond low-resolution topography) need vacuum
- Works only for conductive materials

STM relies on detection of tunneling current

- tunneling current: brief overview

- The tunneling current flows across the small gap ($\sim 1-3\text{\AA}$) that separates the tip from the sample, a case that is forbidden in classical physics but that can be described within quantum mechanics framework.
- The tunneling current I has a very important characteristic: it decays exponentially with an increase of the gap d : $I_{\text{tunnel}} \propto \exp(-2Kd)$
- Very small changes in the tip-sample separation induce large changes in the tunneling current!
- This has the consequence : The tip-sample separation can be controlled/measured very exactly (on subangstrom scale) by monitoring tunneling current.
- The tunneling current is only carried by the *outermost* tip atom; the atoms that are second nearest carry only a negligible amount of the current: **The sample surface is scanned by a single atom!**

Invention of STM: probing topography using tunneling

First measurements of tunneling current between two electrodes separated by a gap of vacuum were presented by R. Young, J. Ward and F. Scire (Nat. Bureau of Standards, Washington, 1971)

There was a probe emitting electric field that approaches a metal surface making a metal/vacuum/metal diode

VOLUME 27, NUMBER 14

PHYSICAL REVIEW LETTERS

4 OCTOBER 1971

Observation of Metal-Vacuum-Metal Tunneling, Field Emission, and the Transition Region

Russell Young, John Ward, and Fred Scire

National Bureau of Standards, Washington, D. C. 20234

(Received 26 August 1971)

We report what we believe are the first observations of metal-vacuum-metal tunneling. A field emitter is brought close to a metal surface and the current-voltage characteristic is measured in three regions: the Fowler-Nordheim region, the intermediate region, and the metal-vacuum-metal region.

Further to this experiments Young et al. came up with an idea to create a microscope that measures the current through their diode. This in 1972 they published an article "The Topographiner: An instrument for measuring Surface Microtopography" (Rev. Sci. Instr. 43, 999, (1972))

The resolution of this tool was not overly impressive (3 nm vertical, 400nm lateral), however that was the first local probe.

Invention of STM

About 10 years later Gerd Binnig and Heinrich Rohrer (IBM, Rüschlikon, 1981) proposed a similar system to measure tunneling current between a tungsten probe and a surface of platinum in vacuum. The system was optimized to control the probe movement at atomic scale. The tungsten tip was operated by piezoelements (the vertical displacement was controlled with precision of $0.1\text{\AA}$).

Tunneling through a controllable vacuum gap

G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel

IBM Zurich Research Laboratory, 8803 Rüschlikon-ZH, Switzerland

(Received 30 September 1981; accepted for publication 4 November 1981)

We report on the first successful tunneling experiment with an externally and reproducibly adjustable vacuum gap. The observation of vacuum tunneling is established by the exponential dependence of the tunneling resistance on the width of the gap. The experimental setup allows for simultaneous investigation and treatment of the tunnel electrode surfaces.

PACS numbers: 73.40.Gk

Appl.Phys.Lett. 1982



Nobel Laureates Heinrich Rohrer and Gerd Binnig
The Nobel Prize in Physics 1986

In this work tunnel resistance was measured as a function of displacement of Pt plate with sub-angstrom precision for the first time. This work was followed by presentation of first scanning tunneling microscope next year: ***“Surface studies by scanning probe microscopy”***, Phys. Rev. Lett. 49, 57 (1982).

Invention of STM

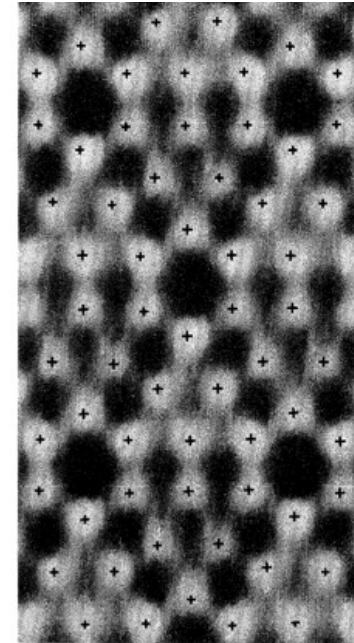
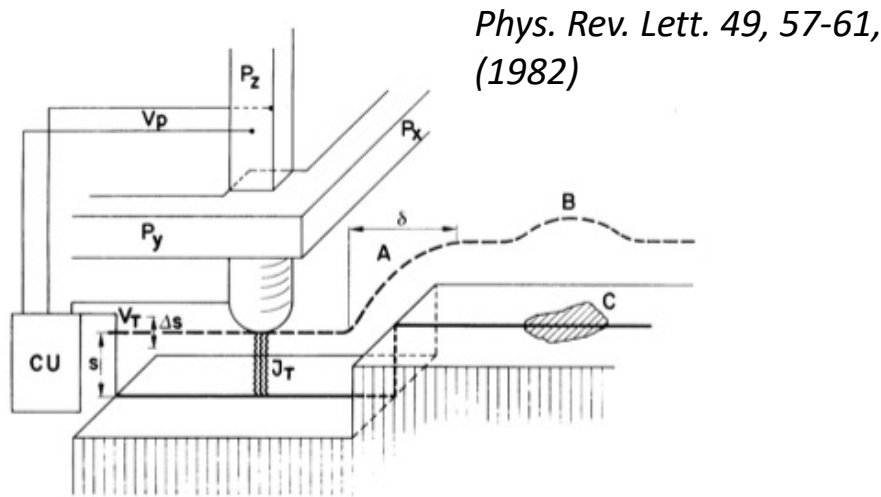
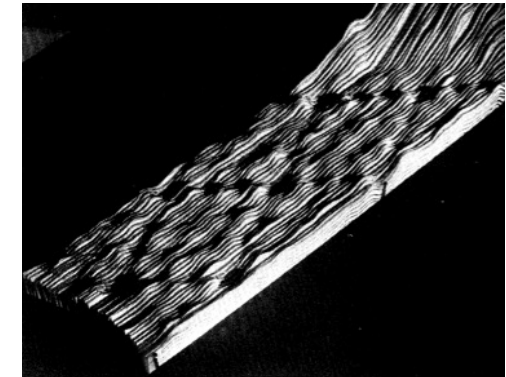


FIG. 2. Top view of the relief shown in Fig. 1 (the hill at the right is not included) clearly exhibiting the sixfold rotational symmetry of the maxima around the rhombohedron corners. Brightness is a measure of the altitude, but is not to scale. The crosses indicate adatom positions of the modified adatom model (see



Phys. Rev. Lett. 50, 120-123, (1983)

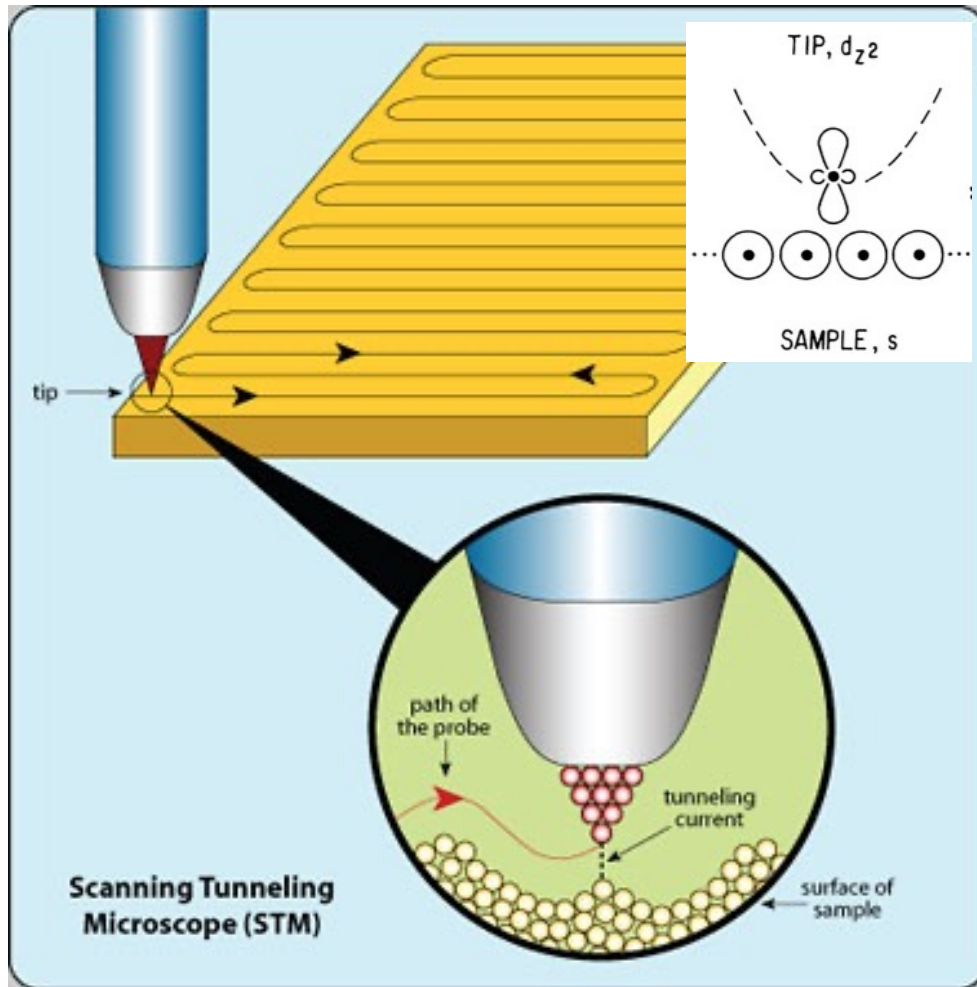
STM topography of Si(111) surface

In the first true STM microscope built by the team of Binnig and Rohrer (IBM, Rüschlikon, 1982) the probe was operated in 3D by three mutually perpendicular piezoelectric actuators (left image). Using a feedback loop that continuously re-adjusts the surface-probe distance in such a way as to keep tunnel current constant Binnig et al. delivered **first atomic resolution images of the surface in real space**.

The example (2 images on the right) shows a surface of monocrystalline silicon. The atoms of the surface are arranged in a special kind of unit cell known as 7x7 reconstruction, which forms after annealing at high vacuum in order to provide an energetically-stable configuration.

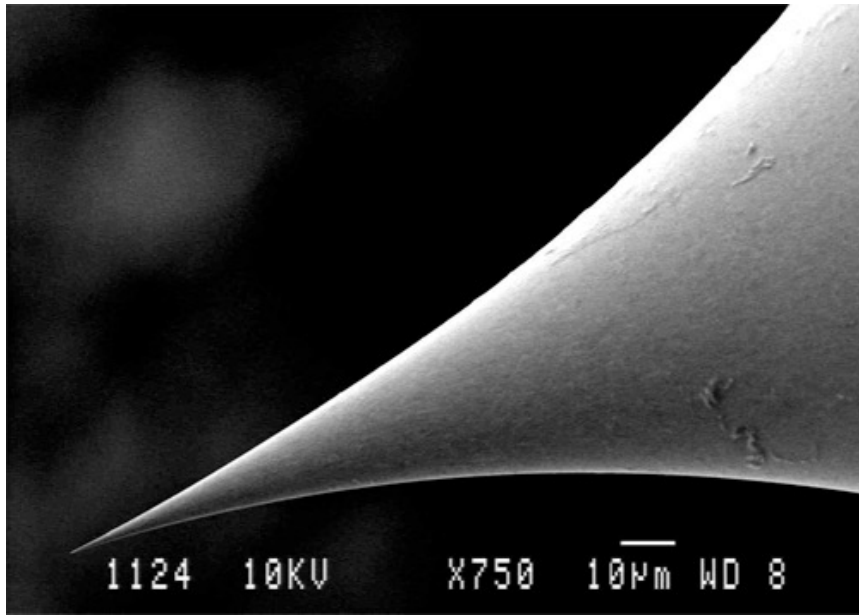
- Vibration control: magnetic levitation in a superconducting bowl of lead (worked only at liquid He temperature)

What is being imaged in an STM? (I)



- In an ideal STM the tip is infinitely sharp
- Tunneling current is proportional to the Local Density of States function (LDOS), at the Fermi energy, E_F , at the tip position
- Hence, a linescan of the tip height above the sample maps a contour of the change in the LDOS at E_{Fermi}

What is being imaged in an STM? (II)



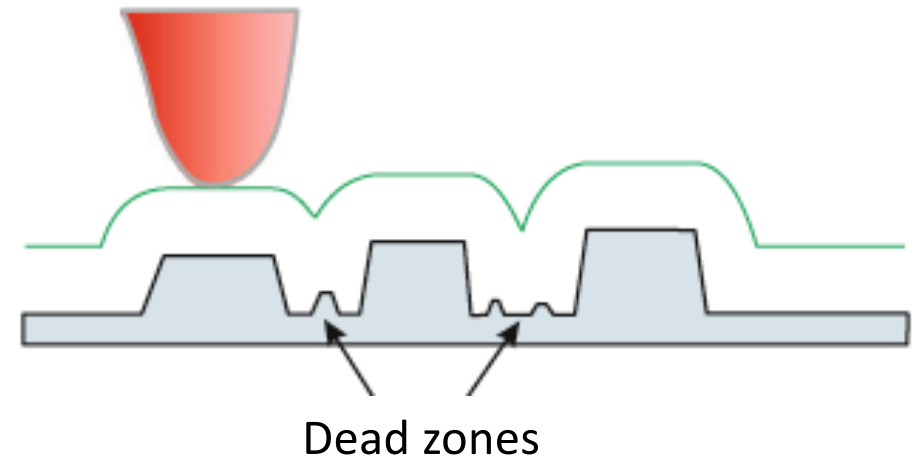
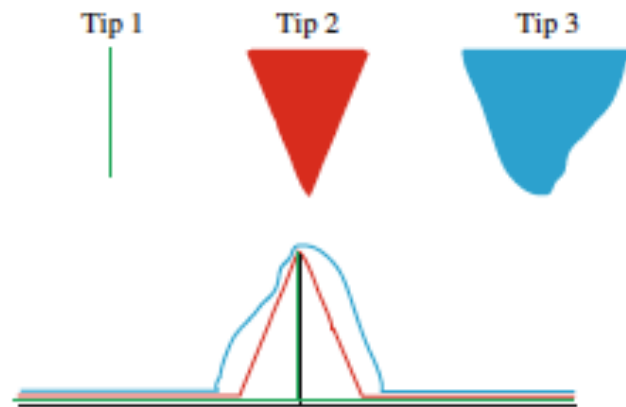
- The real STM tip is not infinitely sharp
- the image of the surface contains an image of the tip.

Therefore:

- Interpretation of images has to include a knowledge of the shape of the tip.
- The sharper the tip the better the possible resolution.
- An image taken with a sharp tip will have less of the image of the tip convoluted with the image of the surface.

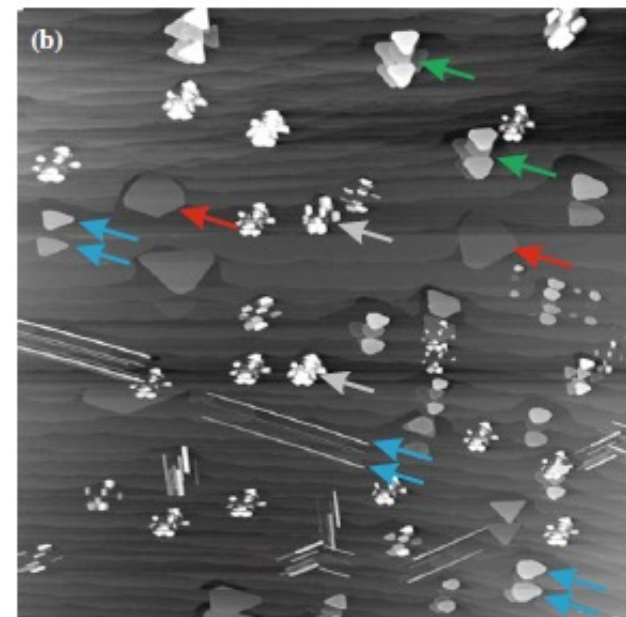
This holds true for all Scanning Probe Microscopes!

Imaging artifacts relating to the tip geometry

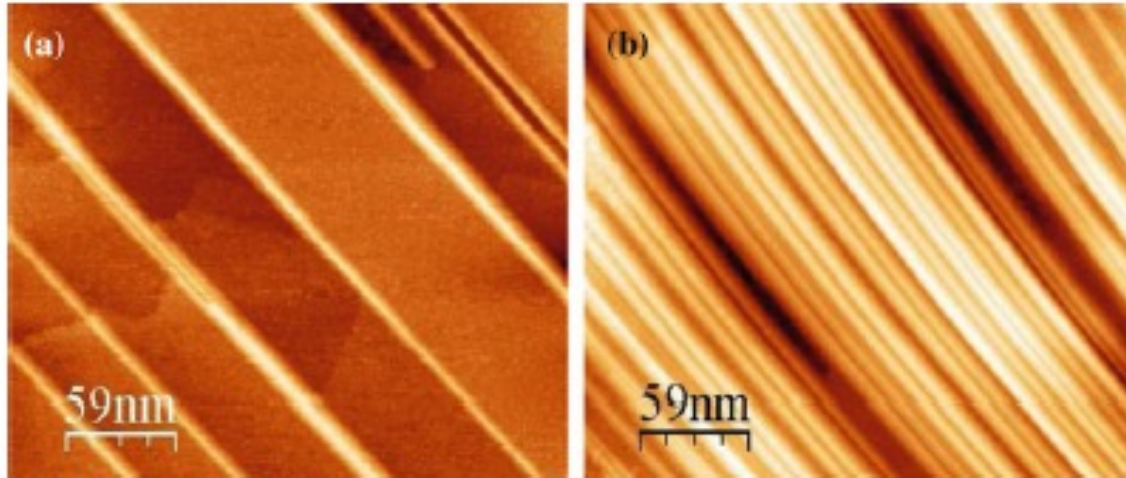


To identify such artifacts:

- change scan direction
- change tip, compare results (must be tip-independent)
- have a reliable reference sample
- use common sense

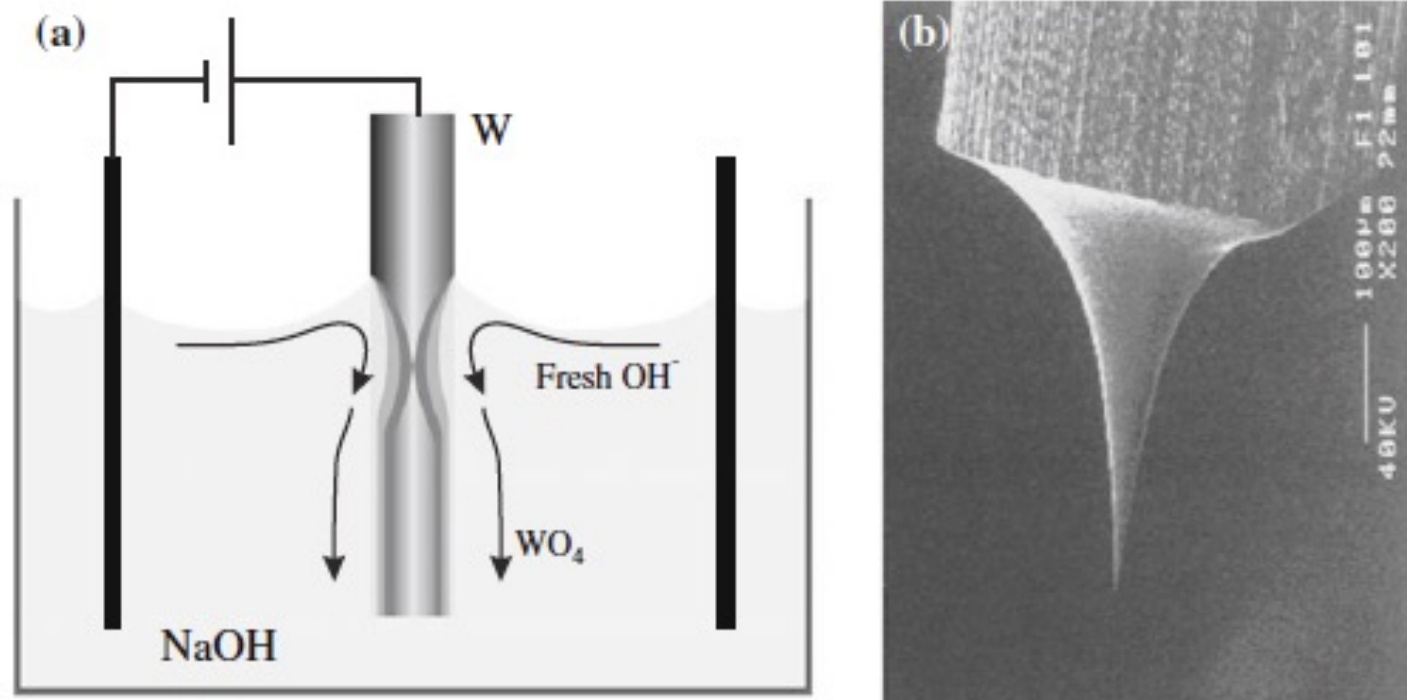


Imaging artifacts relating to the tip geometry



- a) Silicide nanowires imaged with a sharp tip.
- b) The same surface imaged with a blunt tip leads to much higher apparent coverage due to multiple images of the silicide nanowires

Electrochemical tip etching

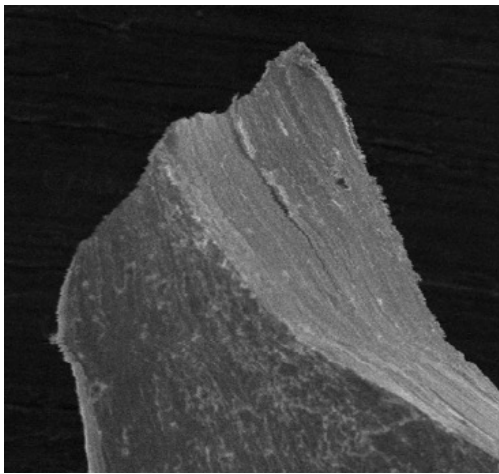


Methods of STM tip fabrication:

- Electrolytic etching
- Ion milling
- Whisker growth
- Mechanical cutting

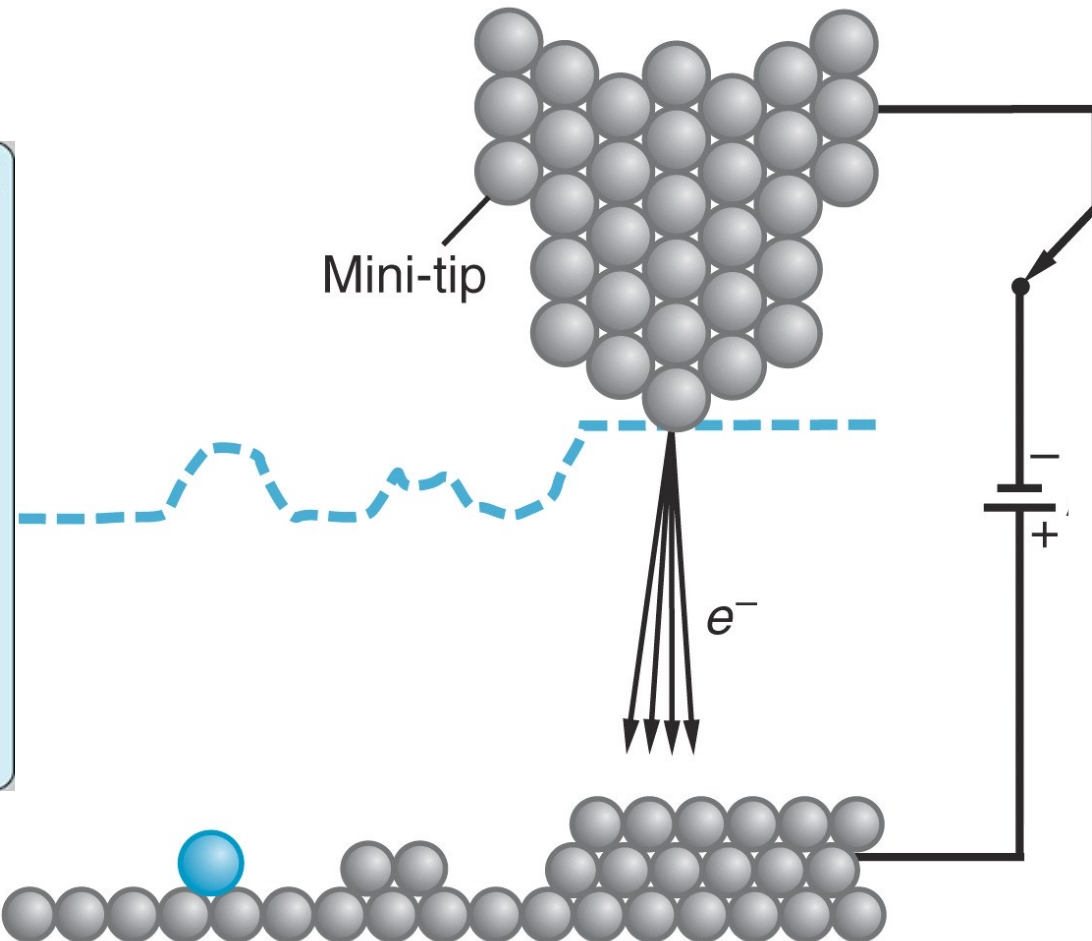
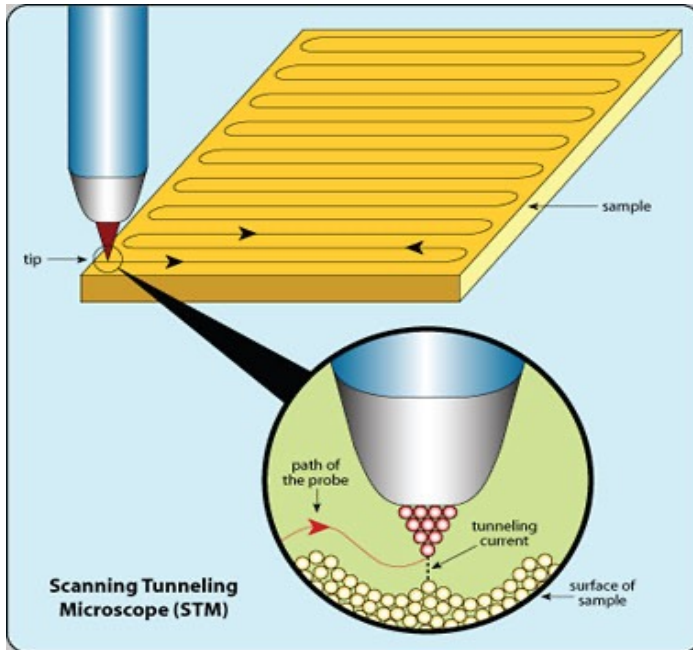
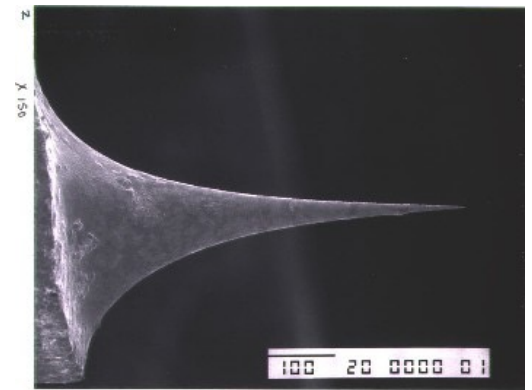
Choice of the tip materials:

- W, Mo, Ir (for UHV studies)
- Pt-Ir (for studies in air)
- CoCr, Fe, Ni, Cr, CrO_2 (for magnetic studies)



STM: imaging with atomically sharp tip

End of tip is atomically sharp.
Various techniques are used for tip conditioning (e.g. voltage pulses)



For true atomic resolution the tip has to be positioned vertically and laterally with accuracy of 1-2 pm (0.01 Å). Hence a good scanner is an essential part of the system

Exercise 1: estimation of STM sensitivity

- In this exercise your goal is to find the characteristic scale or current variation in STM. You are going to show that STM is really suitable for studying atomically-flat surfaces and for detecting individual atoms.

Atomic resolution requires sensitivity at sub-angstrom scale. To estimate the sensitivity limit the problem can be formulated as follows:

Find the variation of distance which is required for tunneling current change by 10%. Use the previously discussed formulae for tunneling current:

$$I_{\text{tunnel}} \propto \exp(-2Kd), \quad K = \sqrt{2m\Phi / \hbar^2}$$

Take as a typical workfunction value $\Phi = 4.5 \text{ eV}$

$$m \approx 9 \times 10^{-28} \text{ g}$$

$$\hbar \approx 1.05 \times 10^{-34} \text{ J} \cdot \text{s}$$

$$\Phi = 4.5 \text{ eV}$$

Technical note 1: piezoelectric scanners

The direct piezoelectric effect:

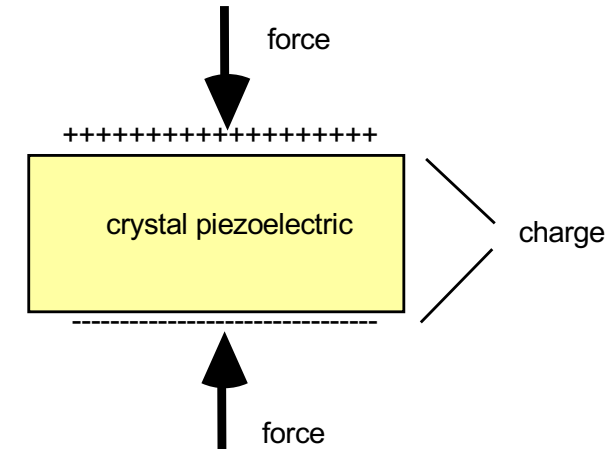
Electrical charges are generated by mechanical pressure

The direct piezoelectric effect:

$$D = d_{\text{direct}} P$$

$$(\text{Coulomb m}^{-2}) = (\text{C N}^{-1}) (\text{N m}^{-2})$$

P- pressure, D- charge density

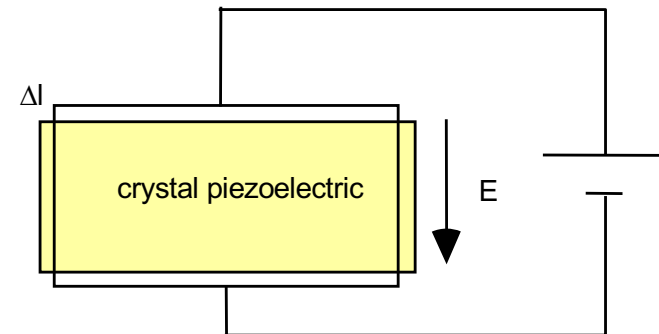


The converse piezoelectric effect:

$$x = d_{\text{converse}} E$$

$$(\text{m m}^{-1}) = (\text{m V}^{-1})(\text{V m}^{-1})$$

E – electric field, x – relative deformation



The piezoelectric effect is linear!

“piezo” is derived from a Greek word for “to press”;
“piezoelectricity”---> electricity produced by pressure

Scanners: Piezoelectric effect, basics

Technical note 1

Very precise control of vertical and lateral position of the tip is essential. How to achieve it? – Using piezoelectric scanners!

Piezoelectric effect: linear electromechanical coupling between the mechanical and electrical state of the material.

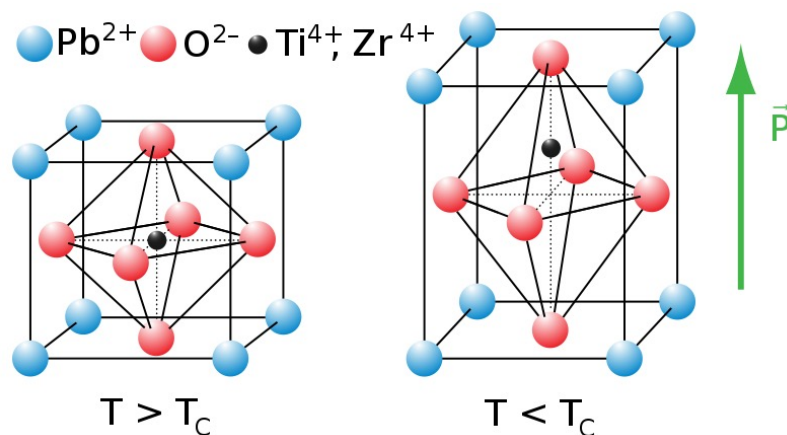
- Electrical response to the mechanical excitation is called direct piezoelectric effect; mechanical response to electrical excitation is called converse piezoelectric effect.

Most of materials with non-centrosymmetric crystalline structure exhibit some piezoelectricity.

For practical applications in piezoelectric actuators (e.g. scanners) the materials with very strong piezoelectric response are required. Suitable piezoelectric properties are found in **ferroelectrics**.

Ferroelectrics are materials characterized by spontaneous electrical polarization, which can be re-oriented by an external electric field (phenomenon of polarization switching). In other words, the material can be represented as an array of electrical dipoles that can be oriented by an external electric field.

One of the very important ferroelectric (and piezoelectric) materials is lead zirconate titanate (PZT), $\text{Pb}(\text{Zr,Ti})\text{O}_3$. This is a perovskite material with cubic structure above $\sim 350^\circ\text{C}$ (Curie temperature) and tetragonal (or rhombohedral) below this temperature.



This low temperature (tetragonal) phase is non-centrosymmetric and polar - the central atom of Zr or Ti is displaced from the central position along one of the axes- this is the direction of spontaneous polarization

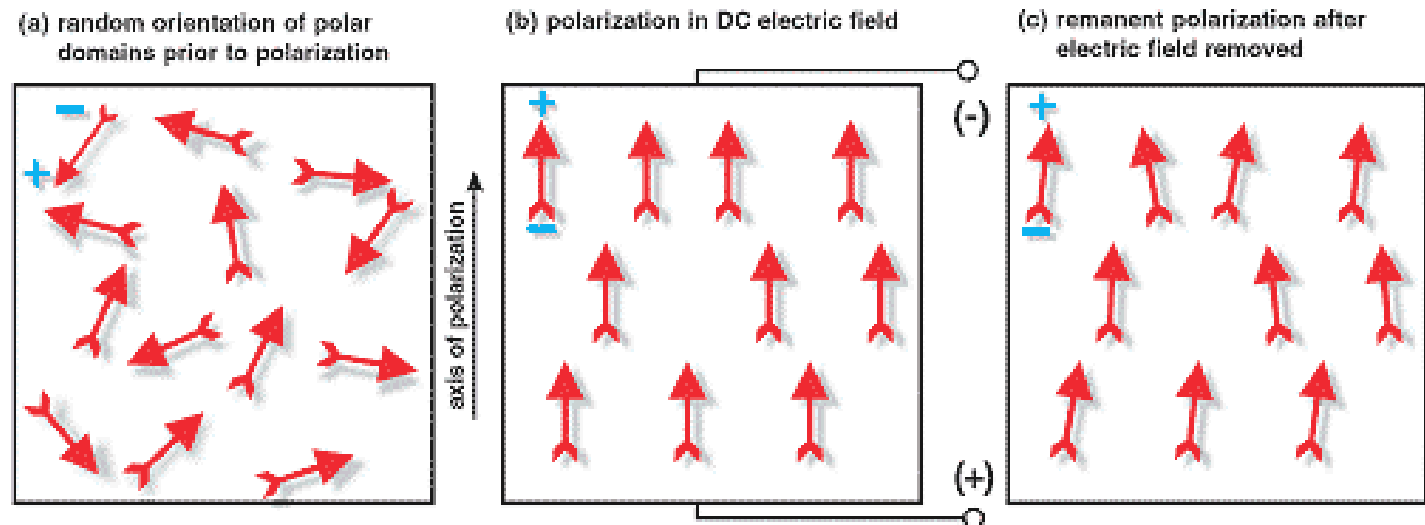
Piezoelectric effect: basics

Technical note 1

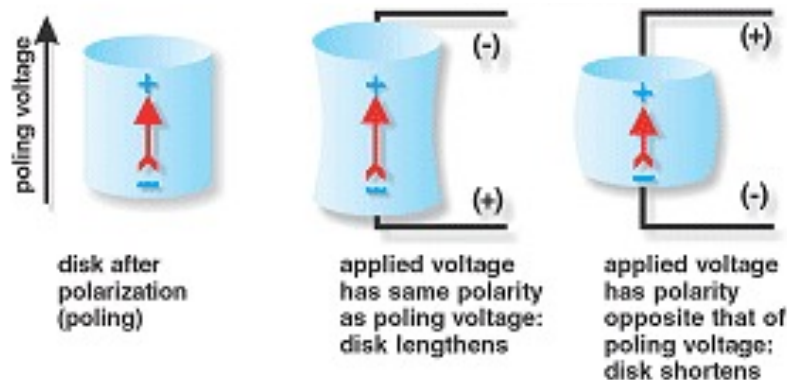
Piezoelectric actuators are typically fabricated from ceramics (polycrystalline material fabricated by high-temperature sintering). In such materials polarization domains are randomly oriented, so there is no macroscopic piezoelectric effect.

Poling

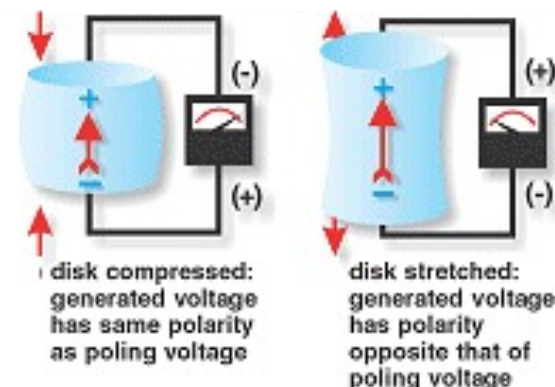
In order to obtain a macroscopic effect, the ferroelectric dipoles need to be aligned.



Converse piezoelectric effect



Direct piezoelectric effect

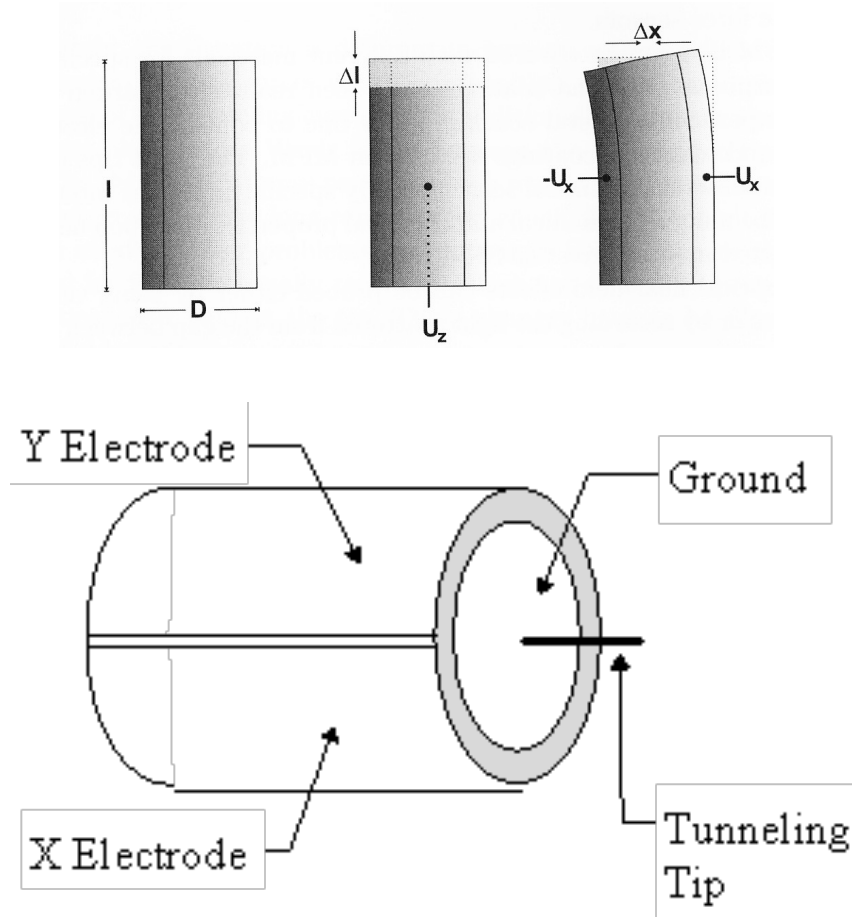


$\Delta d = d_{33}V$, for PZT ceramics $d_{33}=500\text{pm/V}$, e.g. by applying 1V you can get a displacement of 5Å

Piezoelectric scanners used for scanning probe microscopy

Scanners for STM are piezoelectric actuators fabricated from PZT ceramics in the shape of cylindrical tubes. In this configuration the most important characteristic parameter is the transverse piezoelectric coefficient d_{31} : $\Delta l/l = d_{31}E$, where E is electric field applied between the inner and outer electrodes. A typical value for PZT scanners: $d_{31} = 250 \text{ pm/V}$ i.e. to elongate a bar of 1cm by 1 μm one needs to apply 400V (for wall thickness of 1mm).

For tube geometry: $\Delta l = d_{31}l V/h$, where h is the wall thickness of the tube.



- Vertical movement: tube elongation

- Horizontal movement: tube bending

For horizontal movement the outer surface of the tube is contacted by four symmetric electrodes separated along the tube. By applying +/- voltages to opposing electrodes the opposite sides of the tube will experience expansion/contraction, hence the tube will bend.

The inner wall is contacted by a single electrode in order to ensure vertical movement.

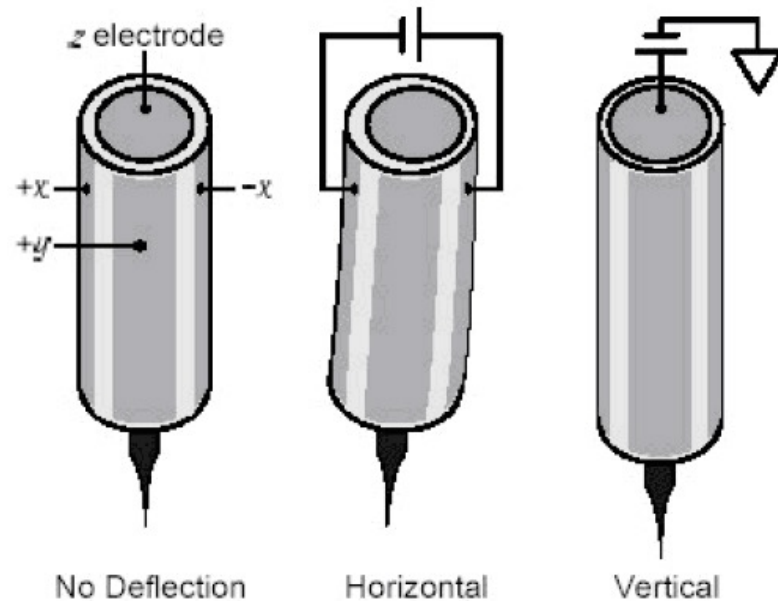
In reality design of piezoactuators involves a lot of complicated solutions to account for many issues:

- non-linearity of the mechanical response
- hysteresis of scanner movement
- creep of the material
- thermal drift

-.....

Piezoelectric Scanners II

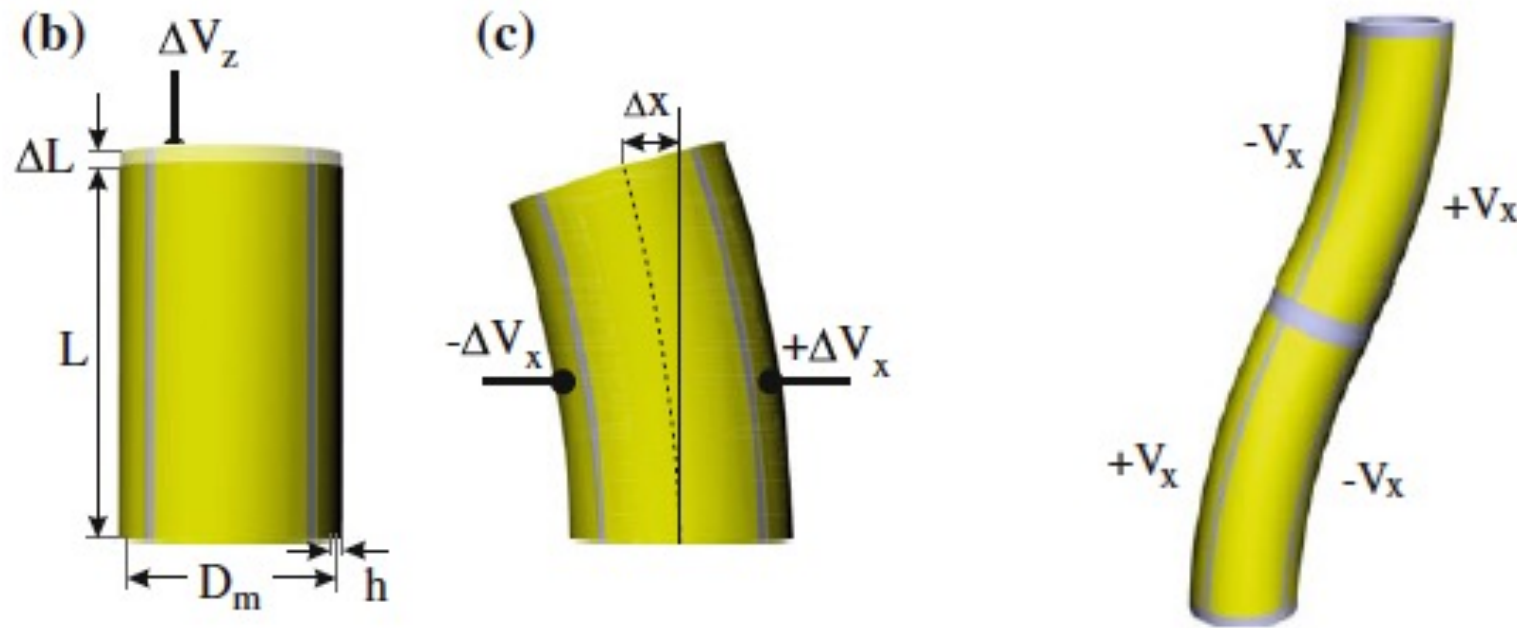
Technical note 1



STM scanner

Piezoelectric tube scanner is not an orthogonal 3-D actuator. Each axis movement is non-linear, the XY-Z crosstalk with non-linearity inevitably results in a significant background curvature.

Different types of cylindrical piezoelectric tubes

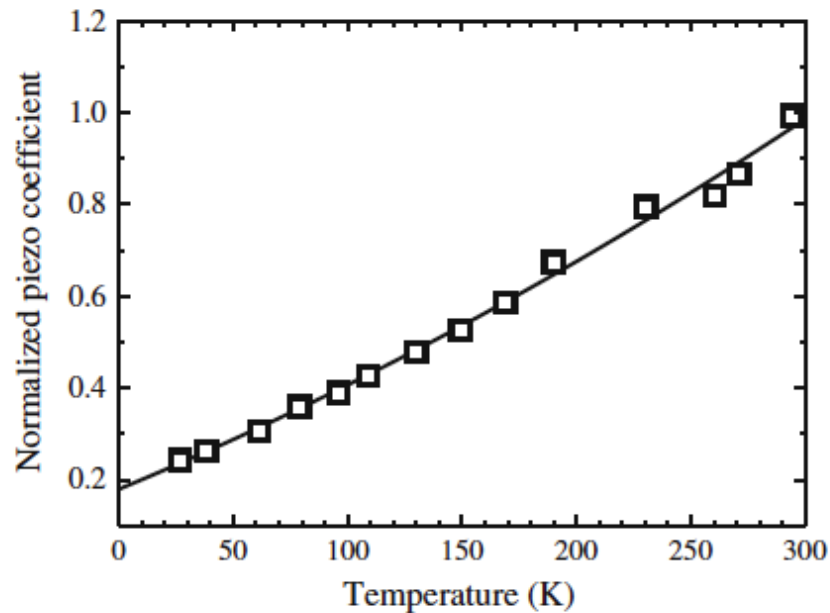


Schematic side view of a tube scanner, and its lateral movement in the x-direction under voltage

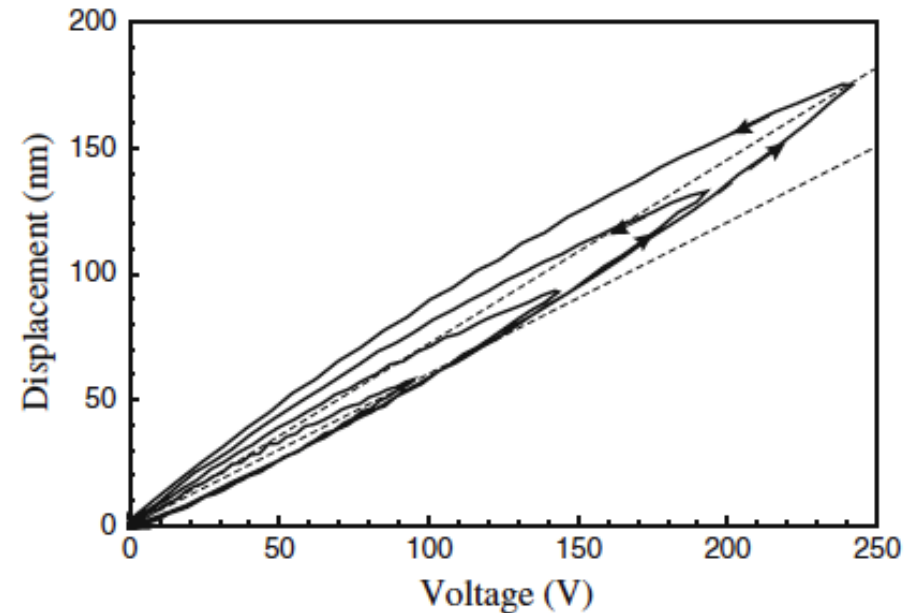
Instead of an outside electrode divided into four segments the outer electrode has eight segments. The upper part of the piezo is bent in the opposite direction to prevent a displacement in the z-direction

Scanner-related artifacts

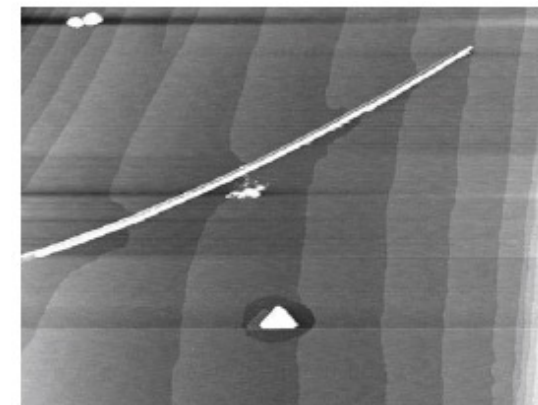
Temperature- dependent
piezoelectric coefficient



Non-linearity of the scanner movement



- Temperature stability is essential
- The scanner movement has to be calibrated for specific temperatures of measurements
- Non-linearity can affect the image (the larger scan – the stronger effect)
- Measurements at varying temperature are challenging!

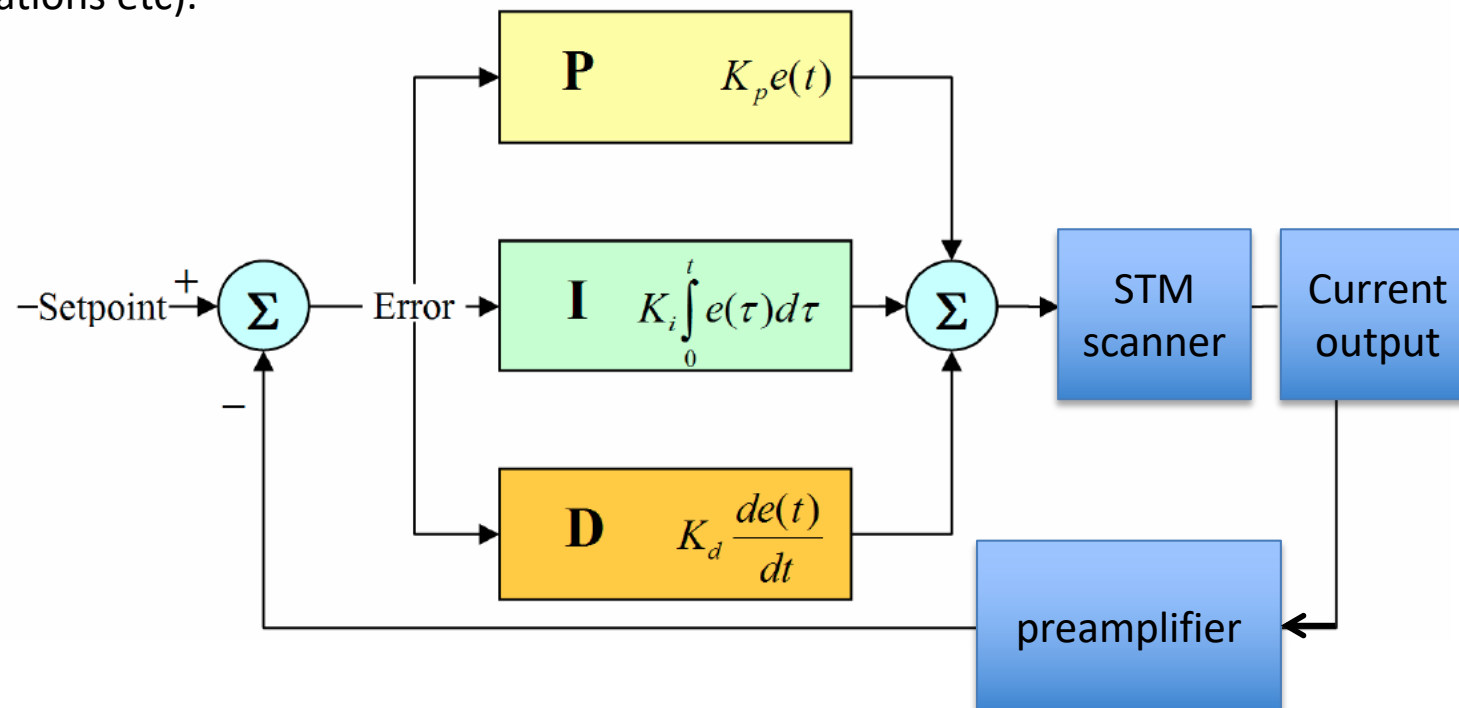


STM imaging in constant-current mode: feedback loop

The most common STM imaging mode is the constant current mode, which requires a regulator that vertically adjust the tip position in such a way as to keep the tunneling current at a preset value.

This adjustment is implemented via feedback loop regulation based on PID (proportional-integral-differential) amplifier. The system constantly measured a selected parameter (Current I_t in our case) and compares it with the reference value (called setpoint, I_{t0} in our case). The difference $e = I_{t0} - I_t$ is so-called error signal that is used as input for for PID controller. This error signal is properly amplified by PID unit and finally transmitted back to the piezoscanner in order to adjust its position in a way to approach desired setpoint current value.

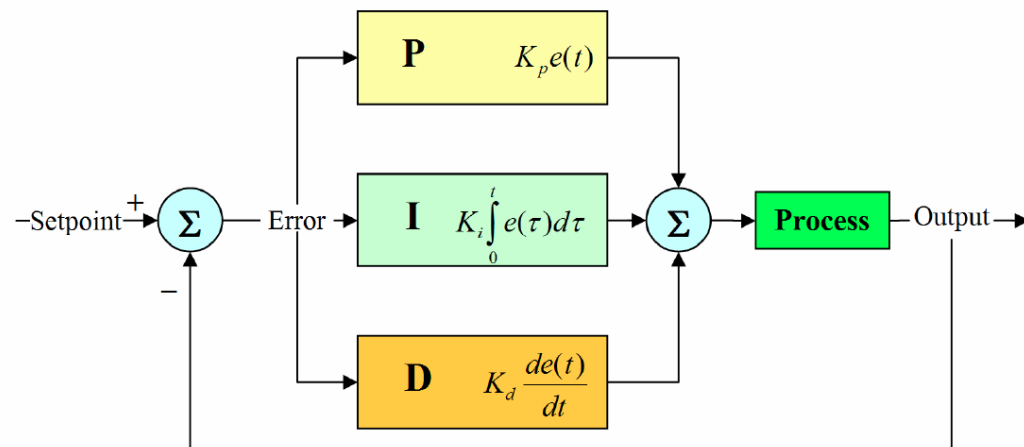
PID generally has 3 amplification gain parameters adjustable by the operator. The goal of adjustment is to find an optimal tradeoff between the speed of reaction and noise (overshoots, oscillations etc).



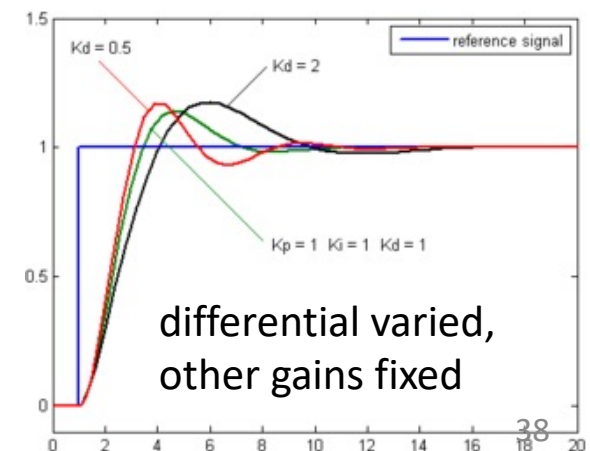
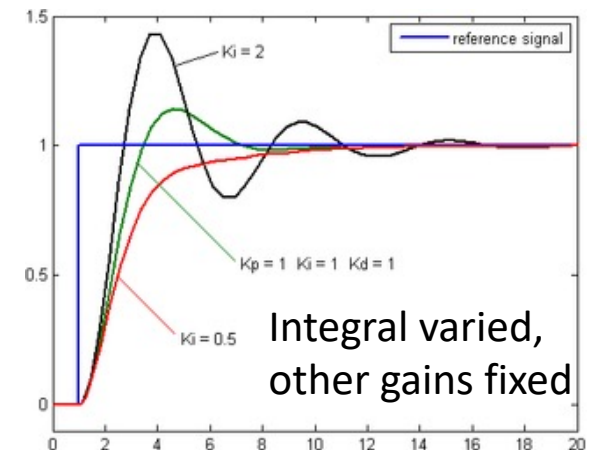
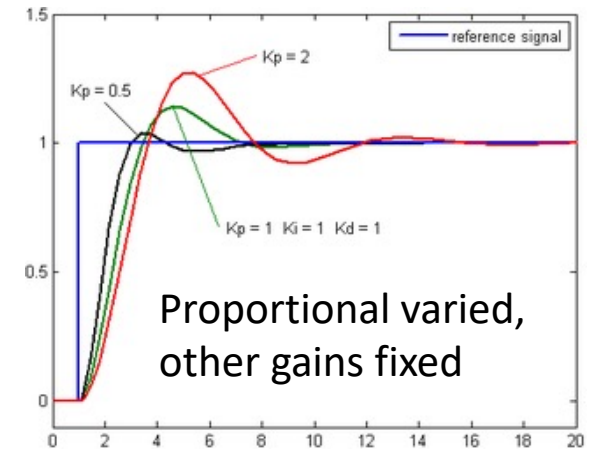
PID controller: sensitivity of the variable to the gain adjustment

PID generally has 3 amplification gain parameters adjustable by operator. Each parameter has its own particular effect the way how the selected variable converges towards setpoint value.

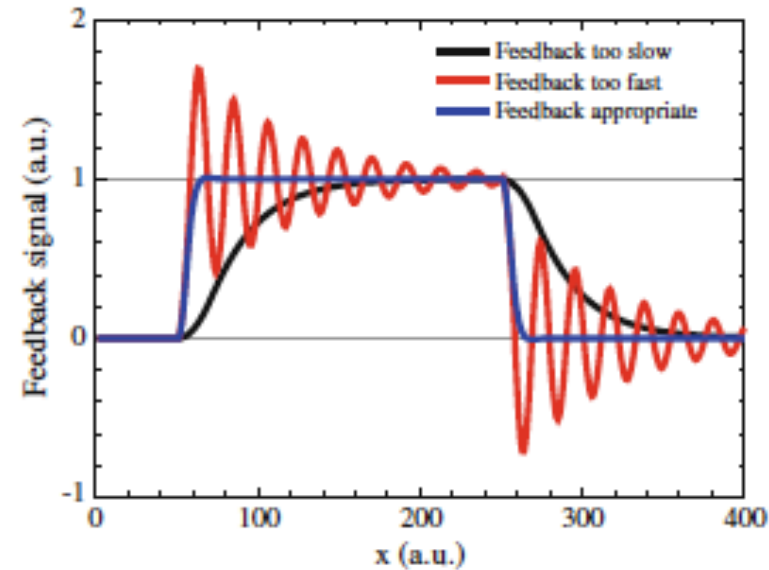
- Proportional gain: reaction proportional to the error value
- Integral gain: changes speed of reaction
- Differential gain: controls convergence toward zero error (setpoint value)



Too high gain: a dangerous source of artifacts!



Feedback-related artifacts



Reaction of the AFM feedback signal to an abrupt change in the topography for too slow feedback settings (black line), too fast feedback settings (red line), and appropriate feedback settings (blue line)

End of technical notes

Exercise 2

- In the first scanning tunneling microscope Binnig and co-workers used some special technique in order to distinguish between the tunnel current variation due to topography change and work function change.

The problem is clearly seen from the tunnel current formulas discussed above:

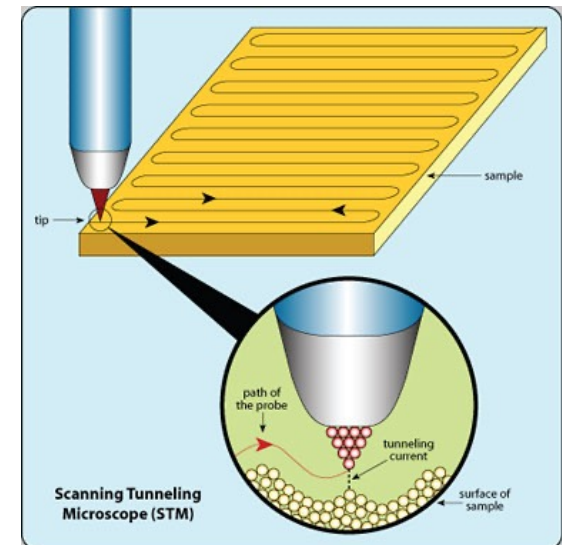
$$I_{\text{tunnel}} \propto \exp(-2Kd), \quad K = \sqrt{2m\Phi / \hbar^2}$$

Thus, any variation of the workfunction along the surface (e.g. due to a composition inhomogeneity) induces a change of tunnel current, which can be easily mistaken for topography change.

How do we know whether we are measuring topography of workfunction gradient?

Try to propose some technical solution to determine whether you measure true surface topography or workfunction profile.

...then during our discussion you will find out how Binnig and Rohrer with coworkers addressed the problem.



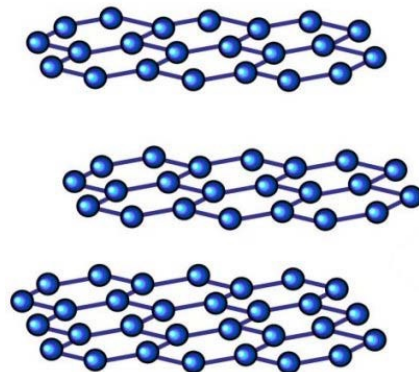
What is measured by STM?

STM is a technique that allows for real-space surface imaging with atomic resolution. As a first approximation, an image of the tunneling current maps the topography of the sample. However, in many cases the STM image interpretation is not that straightforward.

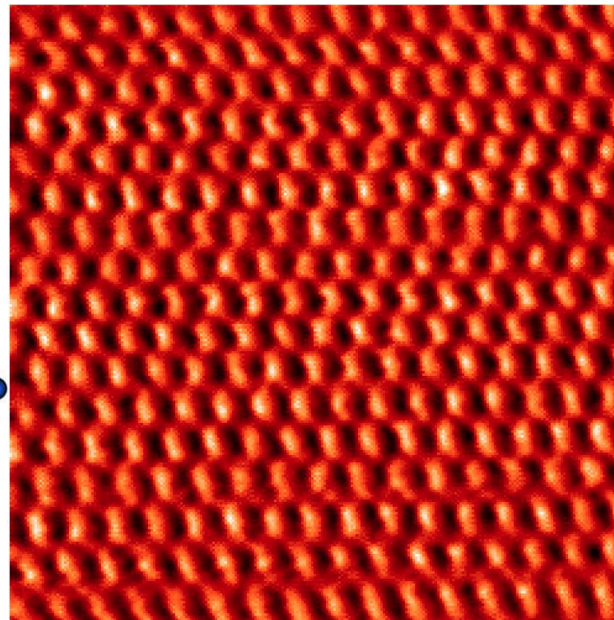
STM does NOT probe the nuclear position directly, but rather it is a probe of the **electron density**, so STM images do not always show the exact position of the atoms.

One of the factors affecting resolution and contrast of image is corrugation, i.e. how much the electron density of surface atoms varies in height.

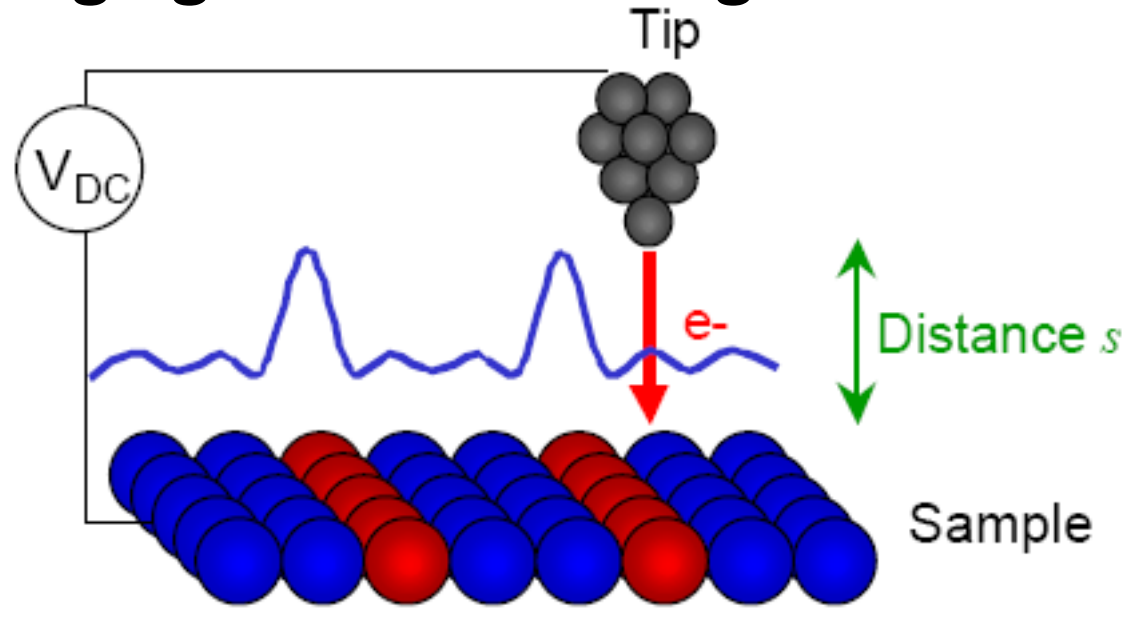
Graphite has a large corrugation, it readily forms atomically flat surfaces that well preserve in different environments (even in air). Thus it is easiest material to image with atomic resolution.



Graphite (0001) 5x5 nm



STM imaging in constant-height mode



There are two common STM operation modes: generally used **Constant Current Mode** where the distance is adjusted via the feedback loop (discussed in previous slides) and **constant-height mode**

Constant-Height Mode is used for some specific applications (e.g. high speed). In this mode the **vertical position of the tip is not changed**. The current as a function of lateral position represents the surface image. It can be convenient for probing defects or surface composition changes on atomically flat surface.

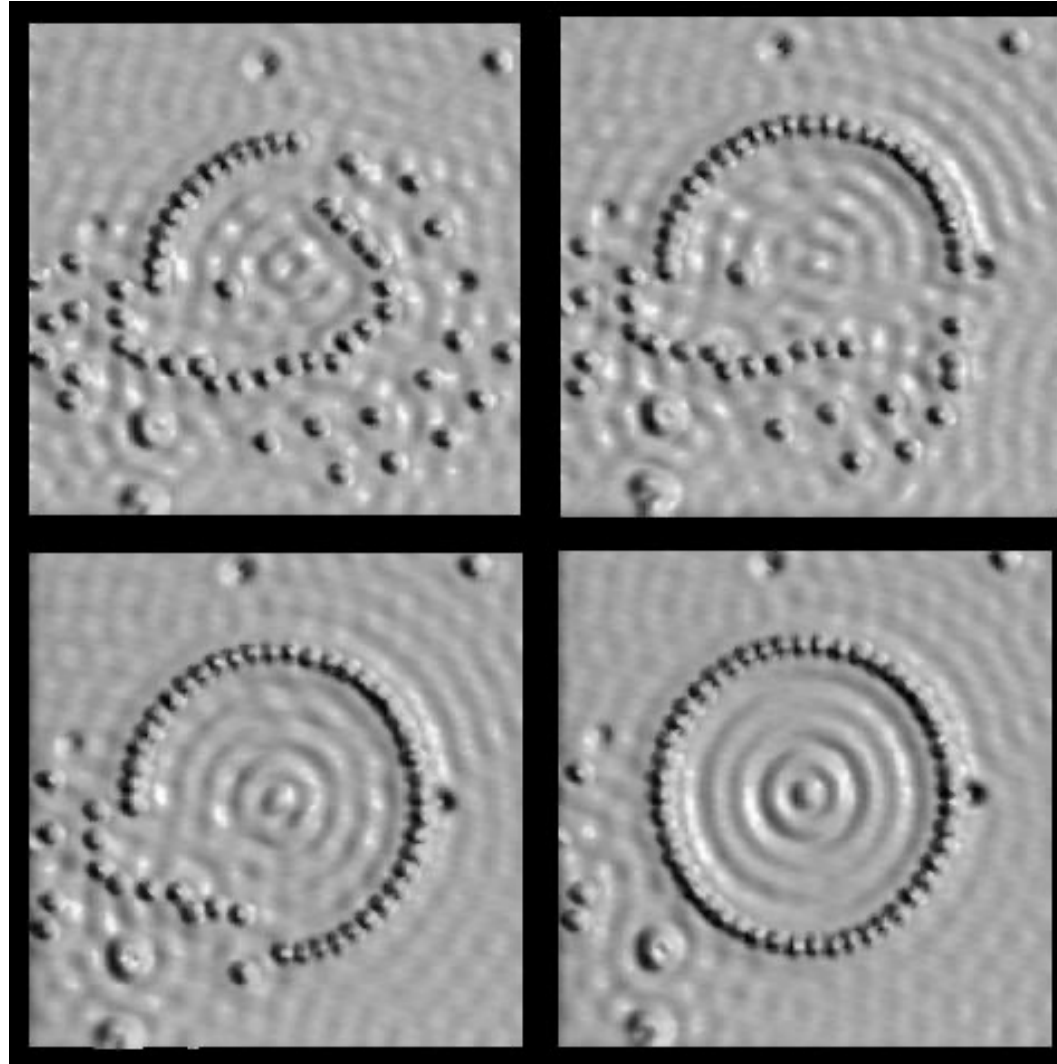
Constant height mode is only appropriate for **atomically flat surfaces** as otherwise a tip crash would be inevitable. One of its advantages is that it can be used at high scanning frequencies (up to 10 kHz). In comparison, the scanning frequency in the constant current mode take from some seconds to several minutes per image.

Some applications of STM

- Topography measurements: quick topo or high resolution (pm vertical resolution!) surface imaging (metals, semiconductors!)
- Manipulation on individual particles (atoms, molecules)
- Electronic structure: scanning tunneling spectroscopy and spatial mapping of local density of states (LDOS)
- Magnetic structures: spin-polarized (SP) STM
- Catalytic activity of the surface, reactions on surface...

Atomic manipulation by STM

STM can be used to manipulate atoms like in the example below showing how the famous “quantum corral” was assembled



Crommie *et al.* Science 262, 218 (1993)

Generally the experiments of this kind are performed at cryogenic temperatures, at ultra-high vacuum

Atomic manipulation by STM

A nice demo: <https://www.youtube.com/watch?v=oSCX78-8-q0>

(for more details: <https://www.youtube.com/watch?v=xA4QWwaweWA>)

1. **Lateral mode** – in which particles (adatoms) are moved along a surface without losing contact to the surface
2. **Vertical mode** – particles attached to a tip are moved and then released from the tip
3. **Tunnel current induced changes** e.g. using the current to excite atoms or to perform chemical reactions

The example in previous slide is accomplished in lateral mode

The 'quantum corral' structure consisting of Fe atoms was assembled on a Cu (111) surface at 4K . The final structure is 14 nm in diameter and consists of 48 Fe atoms.

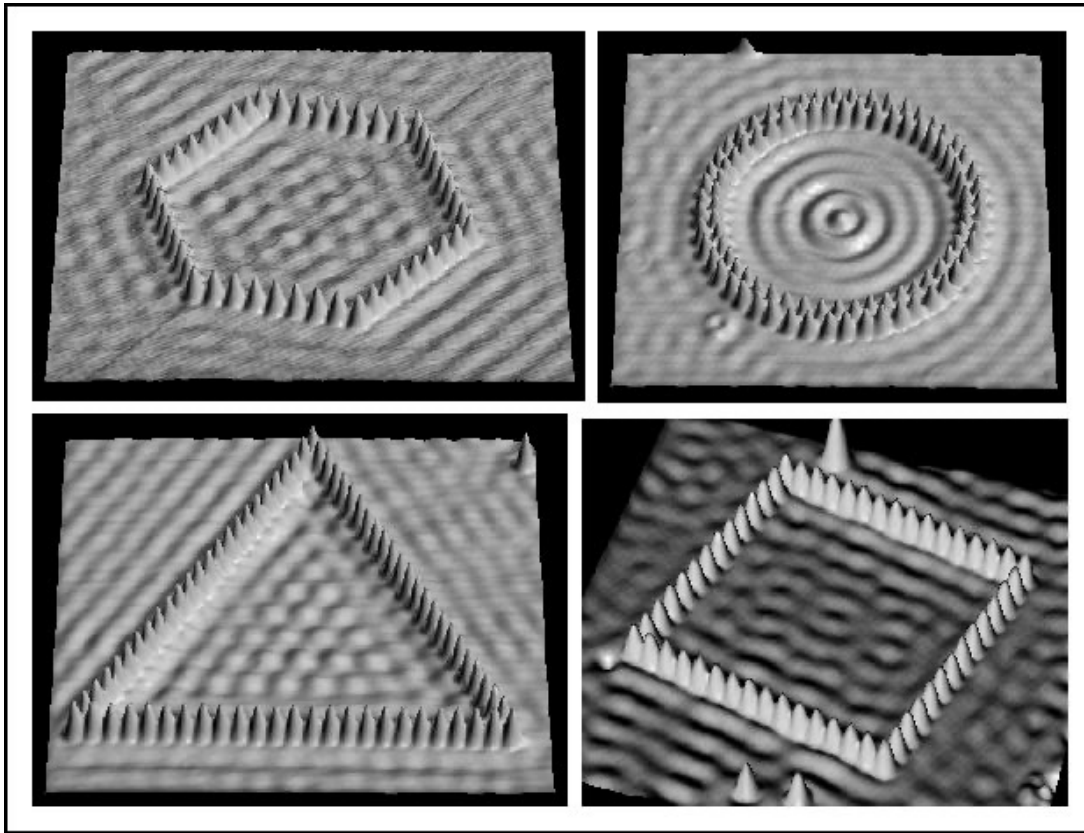
- Fe atoms are evaporated onto a Cu(111) surface at 4K. Initially there will be a random arrangement of atoms which can be examined using STM operating in the normal way.
- In normal operation no atoms are displaced however, if the distance between the tip and an Fe atom is reduced, the tip exerts an attractive force on the Fe atom. As a result the Fe atom can be dragged by the tip.
- Once the Fe atom is at the desired location the tip is retracted, reducing the tip-Fe interaction and the Fe atom remains in its location.

<https://www.youtube.com/watch?v=oSCX78-8-q0>

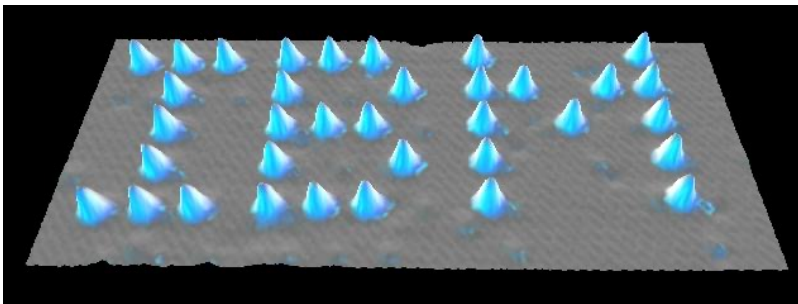
for explanation from IBM reseachers working on this topic check:

<http://www.research.ibm.com/articles/madewithatoms.shtml#fbid=2vPSbbrR37d>

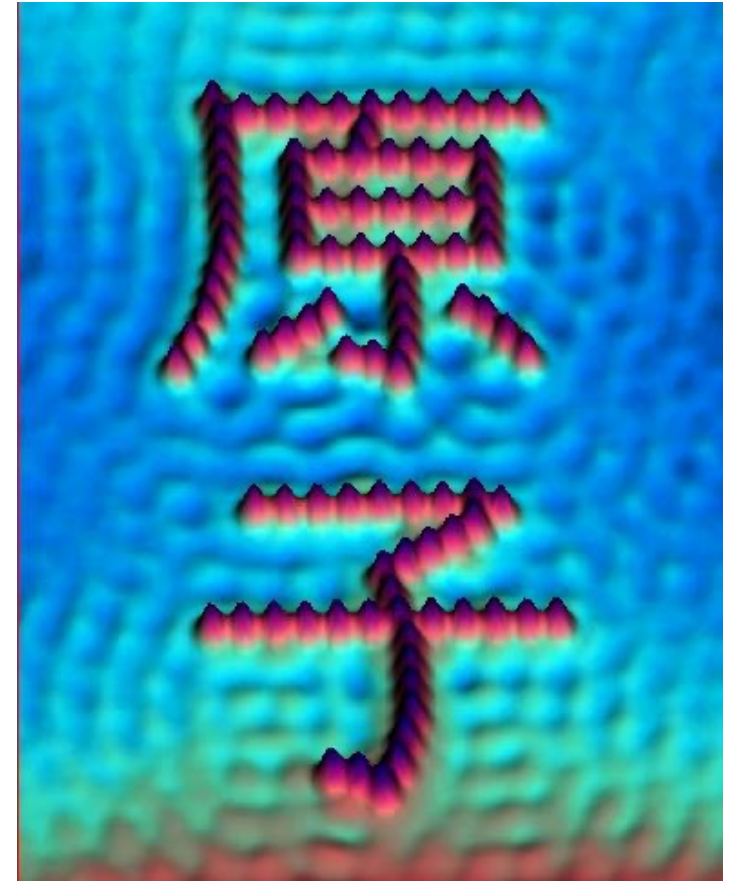
Atomic manipulation by STM: more images from IBM



Iron on Copper (111)



Xenon on Nickel (110)

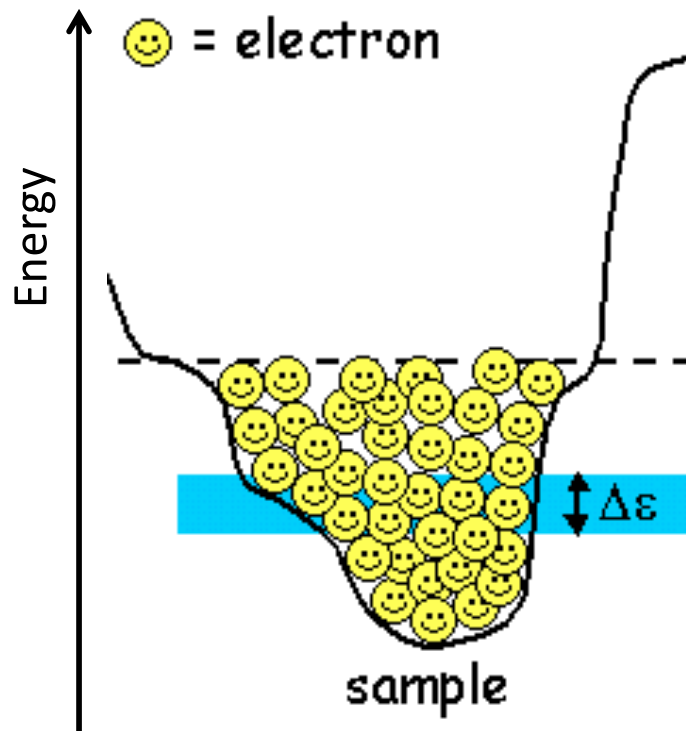


Iron on Copper (111)

What do we measure by STM?

- As a first approximation, an image of the tunneling current maps the topography of the sample. However the real physical picture is more complicated
- **Rather than measuring physical topography, STM measures a surface of constant tunneling probability.**

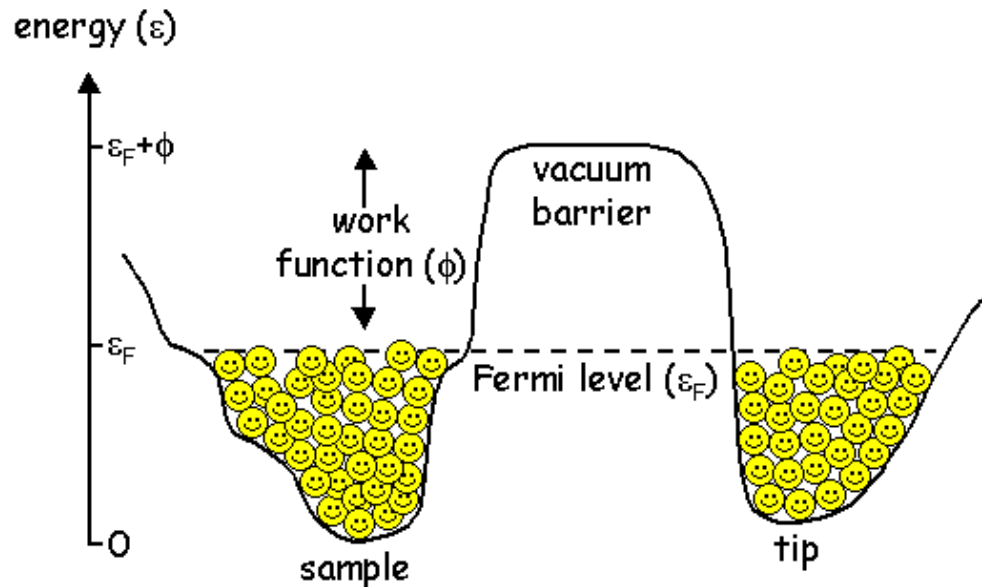
More accurately, the tunneling current corresponds to the electronic density of states at the surface. STM actually senses the number of filled or unfilled electron states near the Fermi level, within an energy range determined by the bias voltage.



Electrons in an isolated atom live at specific discrete energy levels. Likewise in a metal, the electrons must live at specific energy levels, based on the energy landscape of the metal. The difference is, that in a macroscopic piece of metal there are so many electrons that the energy level spacing gets very close and the discrete energy levels merge into energy bands. So, the electron population of the energy bands is characterized by ***density of states***.

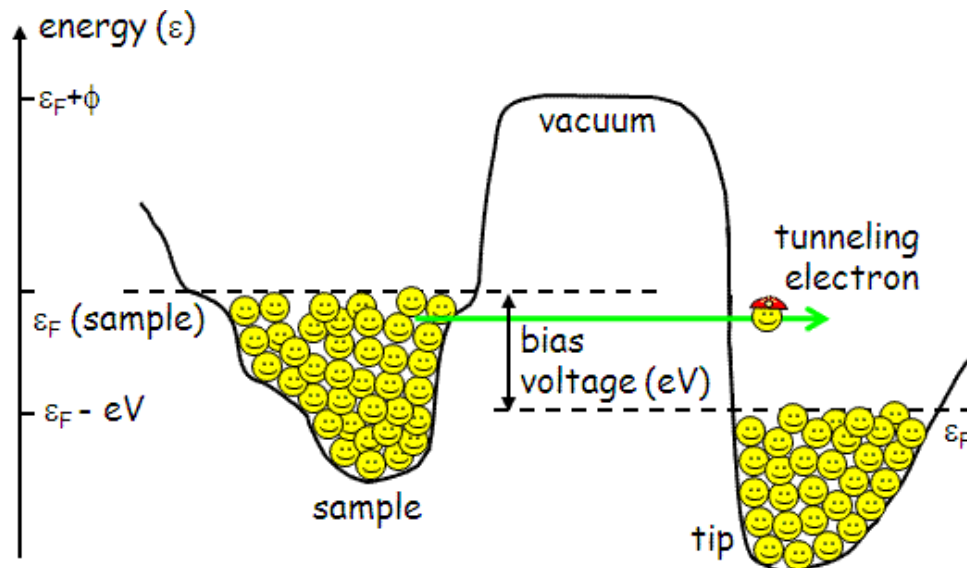
The density of states at energy ϵ , $DOS(\epsilon)$ is the number of electrons sitting in the strip from ϵ to $\epsilon+\Delta\epsilon$ divided by $\Delta\epsilon$

What do we measure by STM: DOS and tunneling current



Now the energy band diagram including the sample and STM tip separated by a gap of vacuum is redrawn with density of states. Without any external voltage applied the Fermi levels on both sides are aligned (upper image) i.e. there are no empty states available for tunneling.

By applying a negative bias voltage to the sample with respect to the tip we raise the Fermi level of the sample with respect to the tip. Electrons will tend to tunnel out of the filled states of the sample, into the empty states of the tip.



The total tunneling current will be proportional to the number of filled states on the left available for tunneling *from*, times the number of empty states on the right available for tunneling *to*. In other words, the tunneling current is proportional to the integral of the density of states of the sample, up to some energy eV . By varying the bias voltage V , we can therefore map out the density of states of the sample, $DOS(\epsilon)$

What do we measure by STM: DOS and tunneling current

Tip-sample tunneling
(filled states are shown in green)

The tunneling current from the sample to the tip for the states of energy ε (with respect to E_F) reads as:

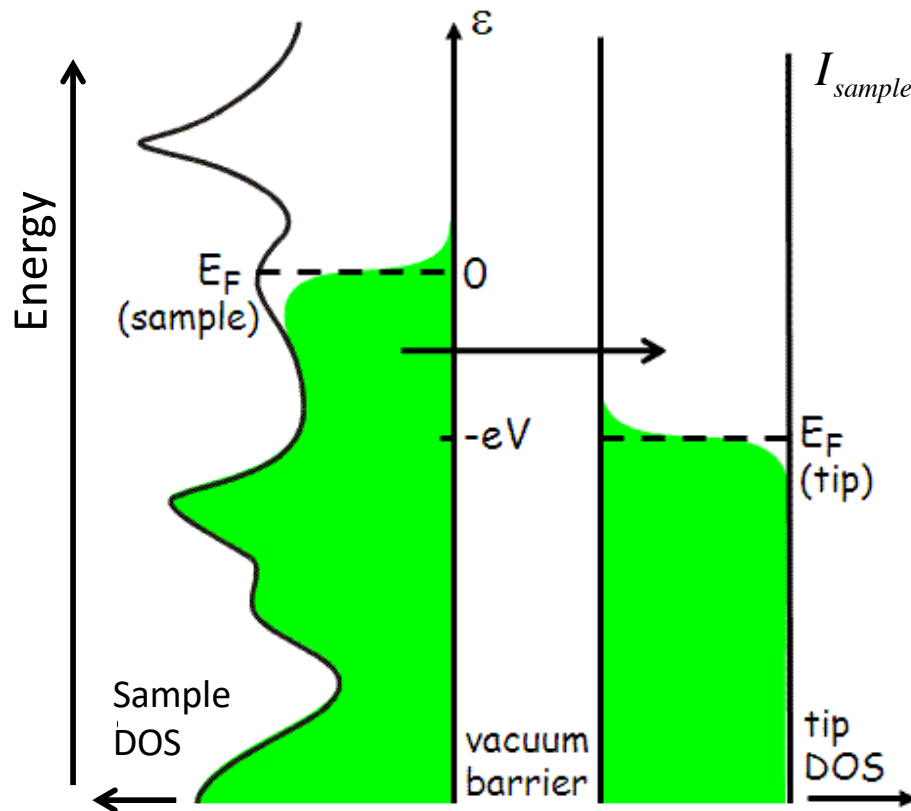
$$I_{\text{sample-tip}} = -2e \cdot \frac{2\pi}{\hbar} |M^2| \cdot (\rho_s(\varepsilon) \cdot f(\varepsilon)) (\rho_t(\varepsilon + eV) \cdot (1 - f(\varepsilon + eV)))$$

Filled sample states
to tunnel from

Empty tip states to
tunnel to

where $f(\varepsilon) = \frac{1}{1 + \exp(\varepsilon / k_B T)}$ - Fermi distribution

ρ_t and ρ_s are densities of
states for the tip and sample



The illustration is barrowed from:
website of Hoffman Lab, Dept. of Physics, Harvard University

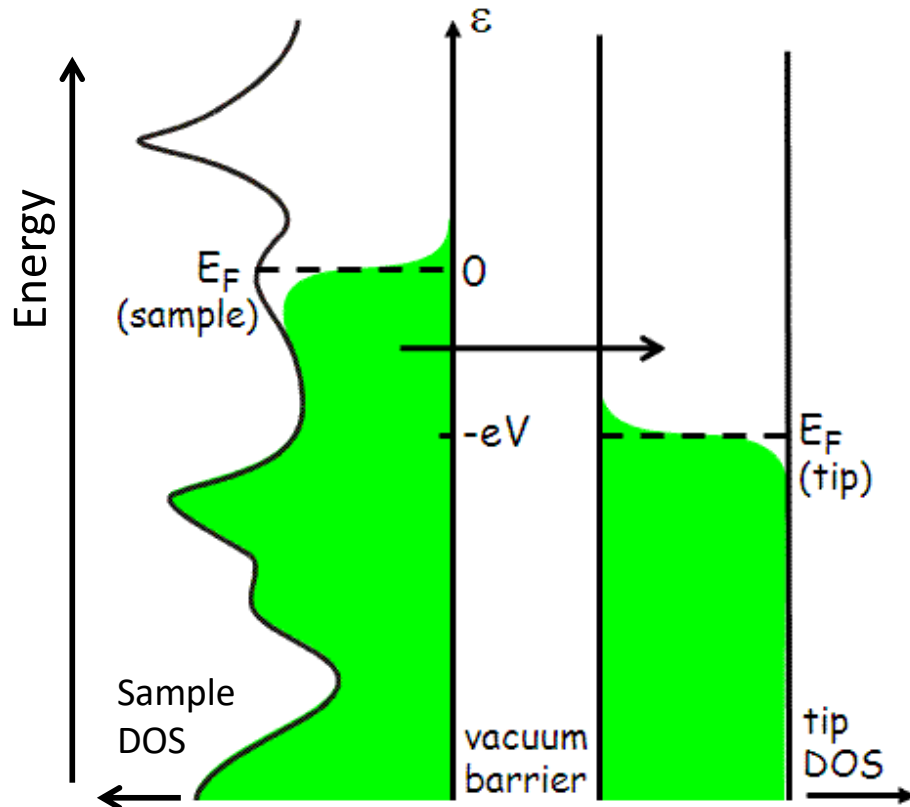
Luckily some simplifications are applicable:

1) Fermi function cuts off very sharply (width of kT i.e. 0.36meV at 4.2K)

To get total current this expression has to be integrated over the energy range approximately from $-eV$ to 0.

2. We pick a tip material which has a flat density of states

What do we measure by STM: DOS and tunneling current



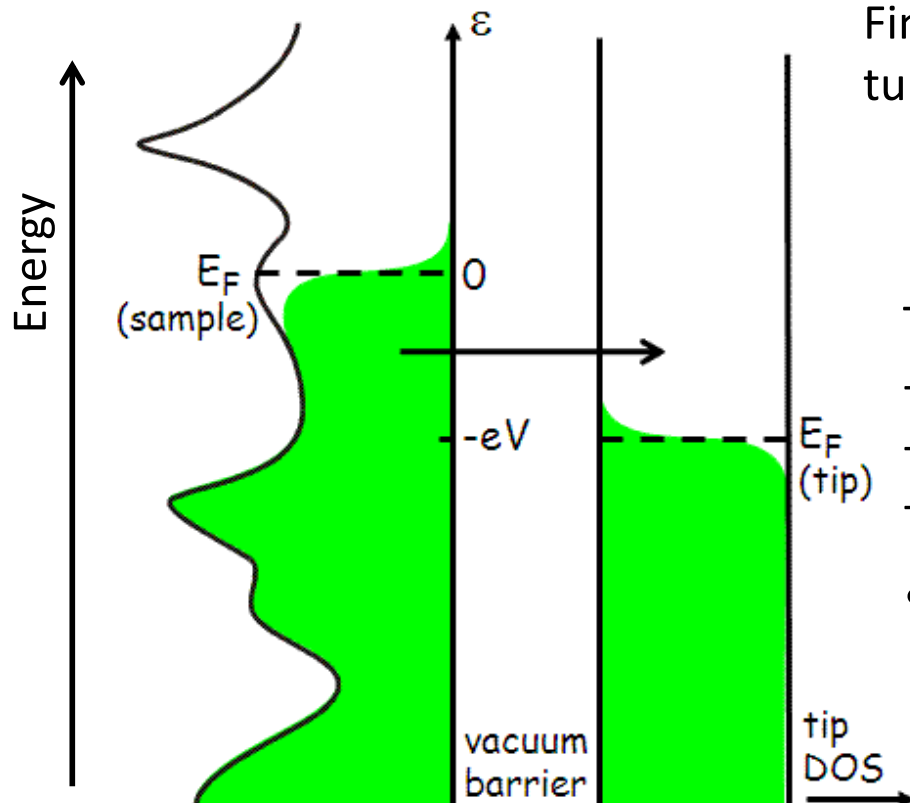
- The measured tunneling current is a convolution of the density of states of the tip and sample in the studied energy range.
- We can choose a tip material which has a flat density of states within this energy range (like W, Ir). Then $\rho_t(\epsilon+eV)$ can be treated as a constant and taken outside the integral

$$I \approx \frac{4\pi e}{\hbar} \rho_t(0) \int_{-eV}^0 |M^2| \rho_s(\epsilon) d\epsilon$$

Further simplification is possible owing to works of Bardeen (1961), who developed a theory of tunneling in vacuum. Briefly, under assumption of sufficiently large vacuum gap (small overlap of the wavefunctions) the matrix element can be taken outside of the integral:

$$|M^2| = \exp\left(-2\frac{d}{\hbar}\sqrt{2m\Phi}\right)$$

What do we measure by STM: DOS and tunneling current



Finally under some reasonable assumptions the tunneling current is approximated as follows:

$$I \approx \frac{4\pi e}{\hbar} \exp(-d\sqrt{8m\Phi/\hbar^2}) \rho_t(0) \int_{-eV}^0 \rho_s(\epsilon) d\epsilon$$

The assumptions include:

- sharp distribution function (Fermi function, 4K)
- flat ρ_t close to E_F — valid e.g. for Ir, W
- sufficiently wide gap (1-3Å is OK)

• Thus STM data contains more than topography!

• STM study of topography relies on on the arbitrary definition of the “height of the surface” as the tip-sample separation for which I_{tunnel} is fixed at some value. Generally this works!

• From the tunneling equation above, we see that if we hold the tip-sample separation constant, at a given (x, y) location, and put a negative bias voltage $-V$ on the sample, we have

$$I = I_0 \int_{-eV}^0 \rho_s(\epsilon) d\epsilon$$

Hence, we probe the **integral of the density of states**, down to any energy $-eV$, by varying $-V$

Density of states (DOS) measured by STM

The DOS is a very useful quantity to be able to measure since it can be used to derive a wealth of information about the crystal's properties.

The DOS can vary as a function of position in the crystal which means that one can define a local density of states (LDOS). LDOS is then a quantity which depends on both energy and on position, $\text{LDOS}(x, y, E)$.

$$I = I_0 \int_{-eV}^0 \rho_s(\epsilon) d\epsilon$$

For a negative bias voltage on the sample, the electrons are tunneling from sample to tip, and we are measuring the integrated density of full states below the Fermi level in the sample.

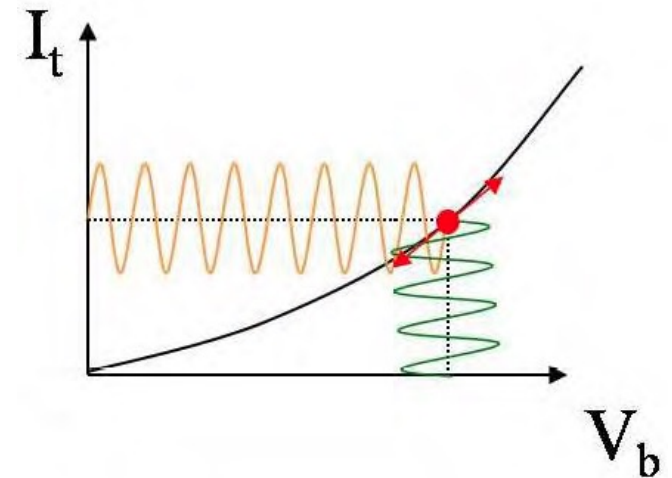
How to get DOS (rather than integrated DOS)? By taking derivative numerically one gets a lot of noise. However derivative can be measured directly by modulating bias voltage.

$$\frac{dI}{dV} \propto \text{DOS}$$

To measure DOS one has to modulate the bias voltage by dV and measure current modulation dI

Technically this is done using **lock-in amplifier**, which is a very sensitive tool that permits to extract a signal at a given frequency and filter out noise that can be much (orders of magnitude) stronger than the signal.

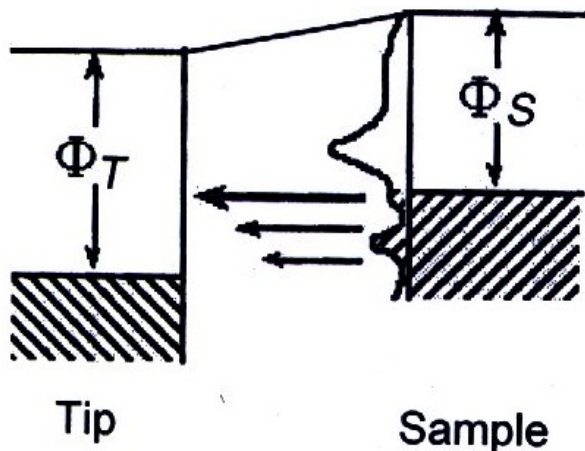
The resolution of DOS measurements is determined by dV . The resolution limit is imposed by the amplitude of thermal wiggle (when the modulation becomes less than $k_B T = 0.36$ meV at $T = 4.2$ K). However in real experiments the modulation can be as small as 2-3mV



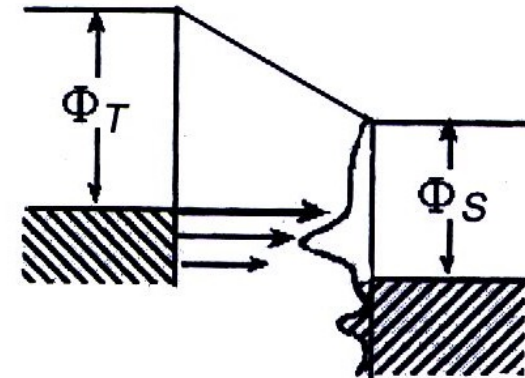
Density of states (DOS) measured by STM

- From the previous discussion it is clear that STM measurements using the bias voltage of different polarities are not equal.
- For a positive bias voltage on the sample, we are tunneling electrons from tip to sample, and we are measuring the integrated density of empty states above the Fermi level in the sample.

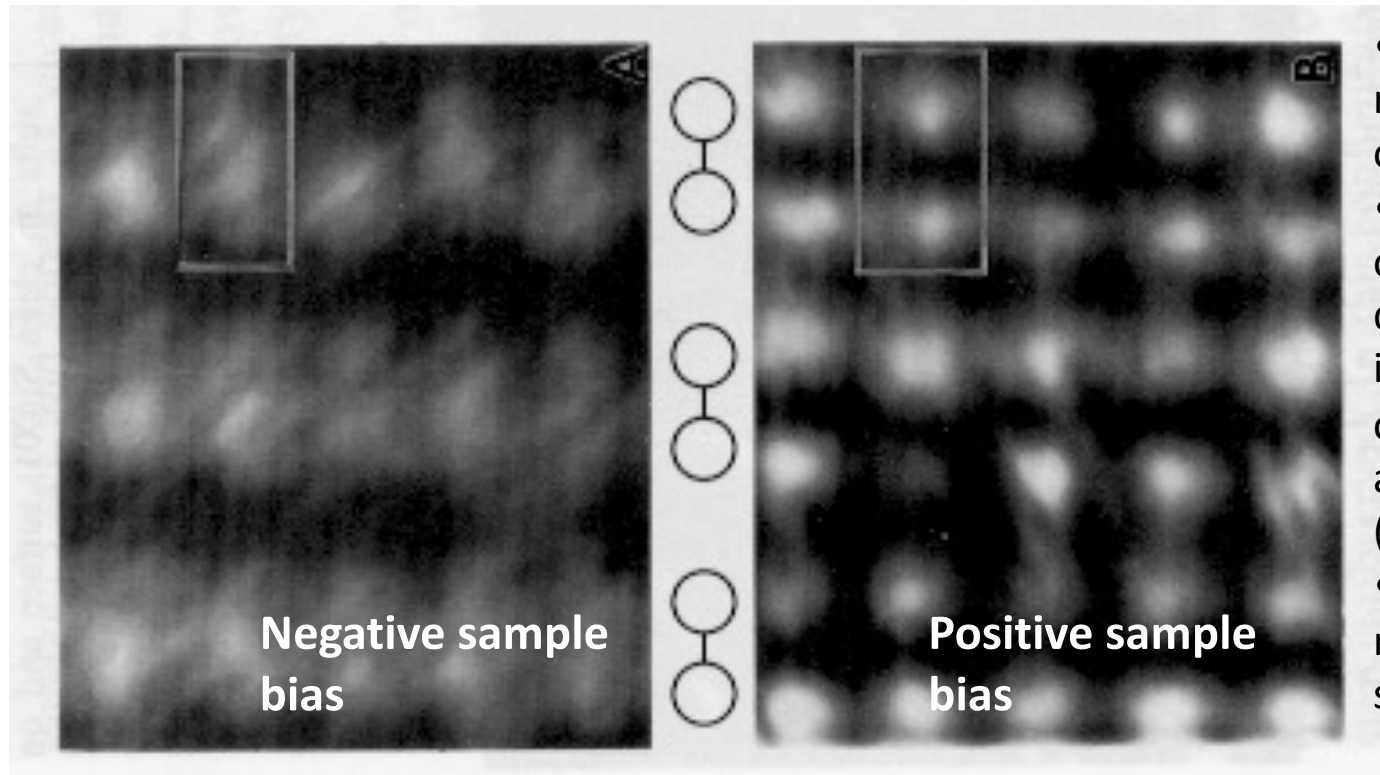
A negative sample bias – probing the filled or occupied states



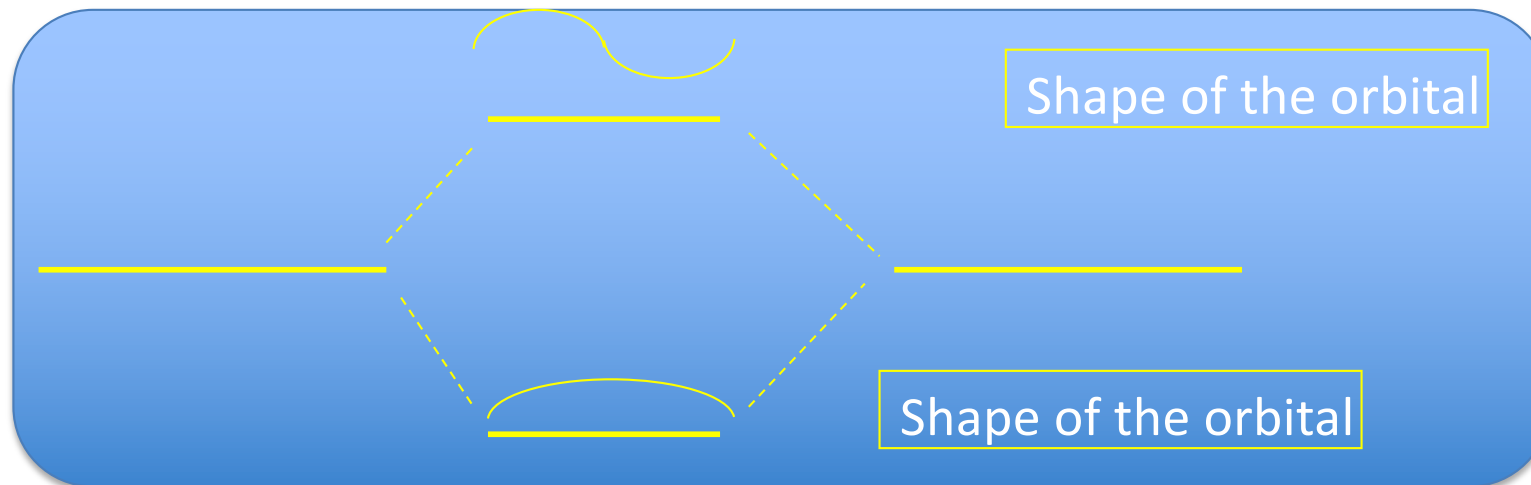
A positive sample bias – probing the empty or unoccupied states



Example: high-resolution STM with positive and negative bias

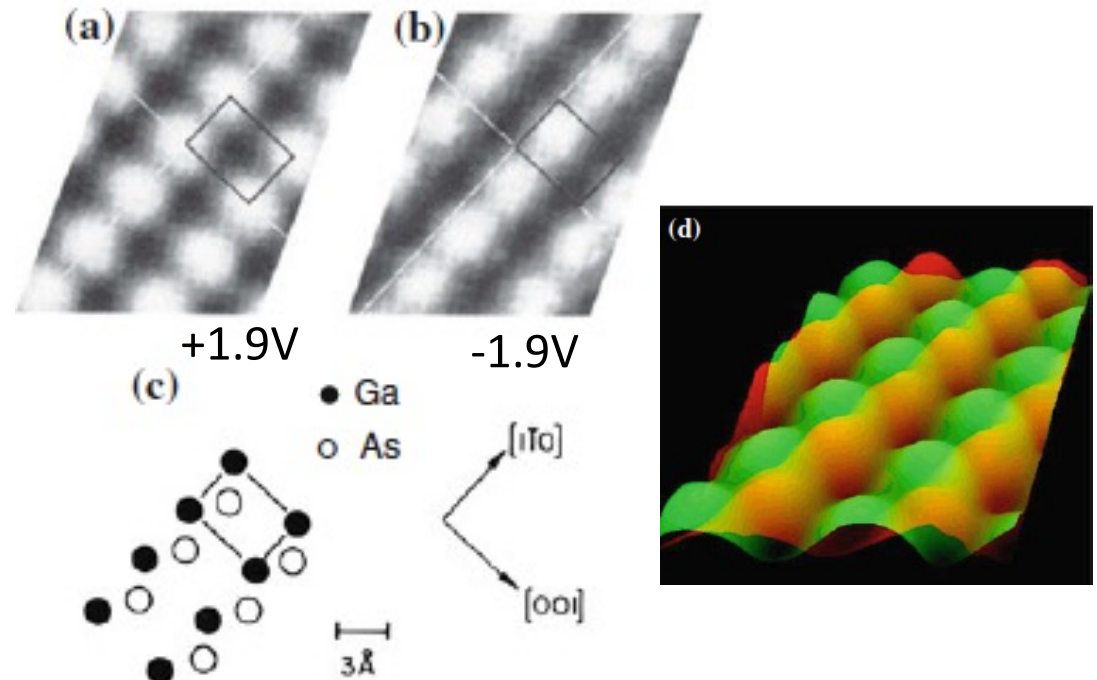
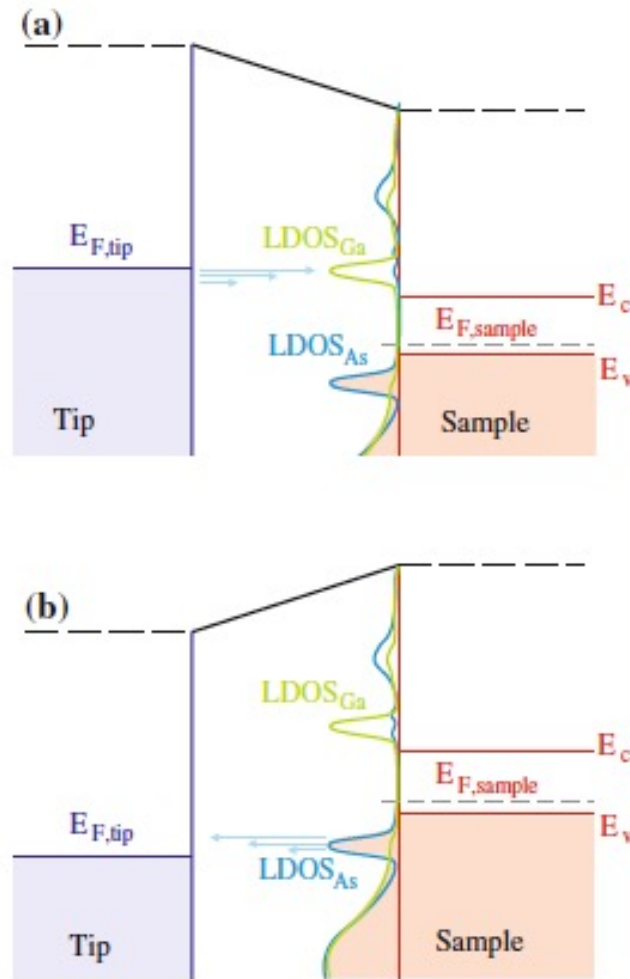


- Si (100) surface reconstructs by the formation of surface dimers
- The scheme of electronic orbital re-arrangement in the dimer is shown below. It includes a symmetric bonding orbital (occupied, below E_F) and antisymmetric orbital (empty, above E_F)
- Tunnel current will be related to the square of the shape of the orbital



- negative bias: one maximum (occupied states)
- positive bias: Two maxima at the sides (non-occupied states)

STM images of a GaAs(110) surface: positive/negative bias



The empty states image in (a) shows the Ga atoms, while the filled states image in (b) shows the As atoms

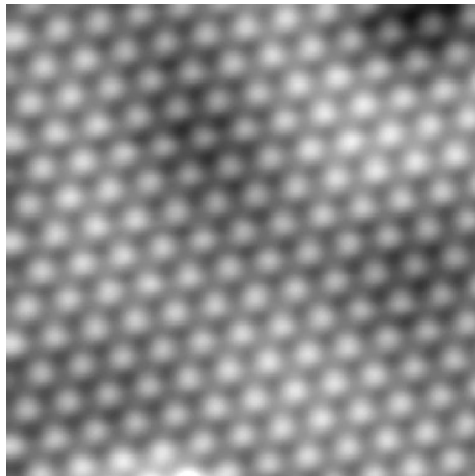
Energy levels involved in tunneling at GaAs surface.

a) At positive sample bias, current flows from occupied tip states to unoccupied Ga sample states.

b) At negative sample bias, current flows from occupied As sample states to unoccupied tip states

Example: scanning tunneling spectroscopy and spatial mapping of local density of states (LDOS)

Cu(111) surface

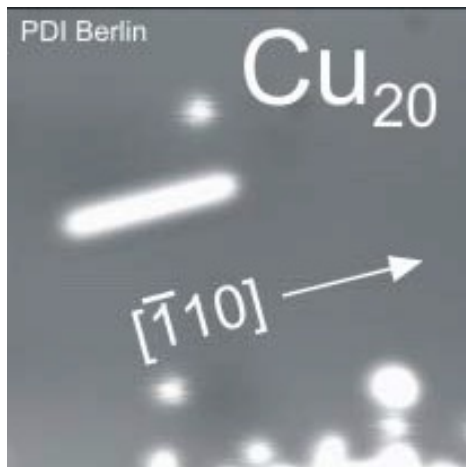


0.1 μ A, 100 mV 29 $\text{\AA}$ x 29 $\text{\AA}$

Analysis of local density of state (LDOS) by measuring I - V curves, dI/dV and space mapping of these characteristics is known as scanning tunneling spectroscopy (STS)

In the example presented below chains of Cu atoms was assembled on Cu (111) surface and spectra of localized electronic states were probed by STS

Building a chain of Cu atoms on Cu(111)



1 nA, 1 V, 135 $\text{\AA}$ x 135 $\text{\AA}$

VOLUME 92, NUMBER 5

PHYSICAL REVIEW LETTERS

week ending
6 FEBRUARY 2004

Quantum Confinement in Monatomic Cu Chains on Cu(111)

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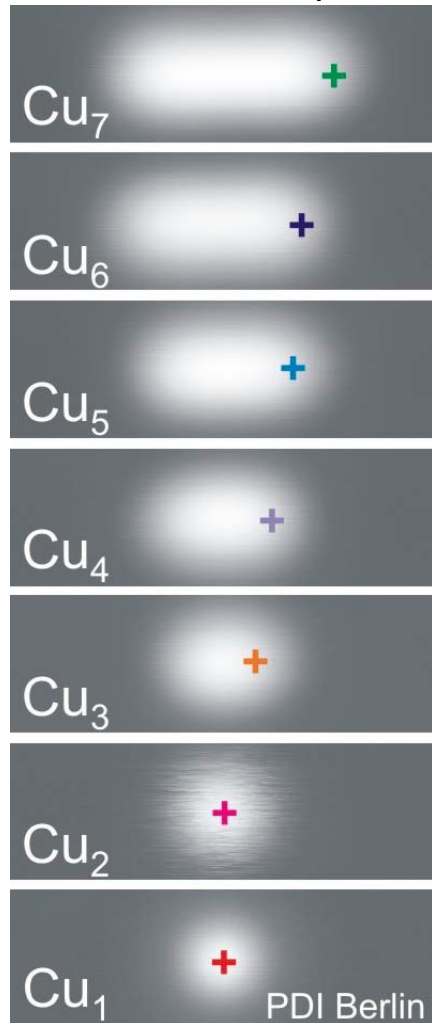
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²Department of Applied Physics, Chalmers University of Technology and Göteborgs University, SE-41296, Göteborg, Sweden
(Received 26 August 2003; published 5 February 2004)

The existence of one-dimensional (1D) electronic states in Cu/Cu(111) chains assembled by atomic manipulation is revealed by low-temperature scanning tunneling spectroscopy and density functional theory (DFT) calculations. Our experimental analysis of the chain-localized electron dynamics shows that the dispersion is fully described within a 1D tight-binding approach. DFT calculations confirm the confinement of unoccupied states to the chain in the relevant energy range, along with a significant extension of these states into the vacuum region.

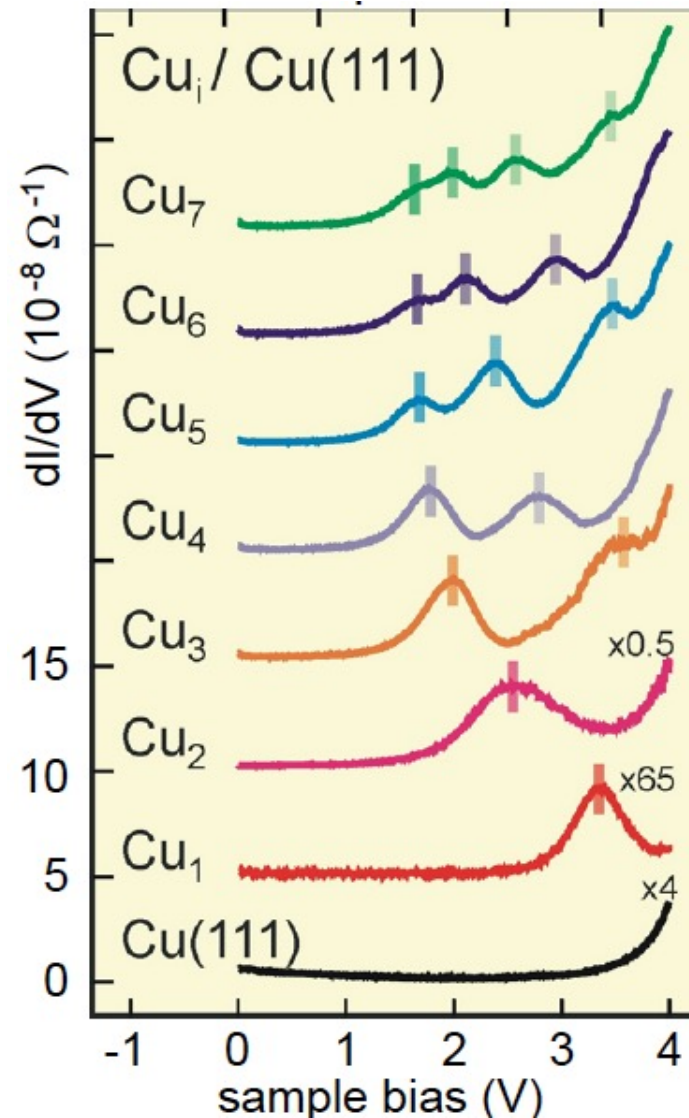
Example 2: single spot spectroscopy of the atom chains

Topography (number of atoms is marked with lower index)



35 Å x 11 Å, 7 K

STS data for different chains and bare
Cu surface – Cu(111)

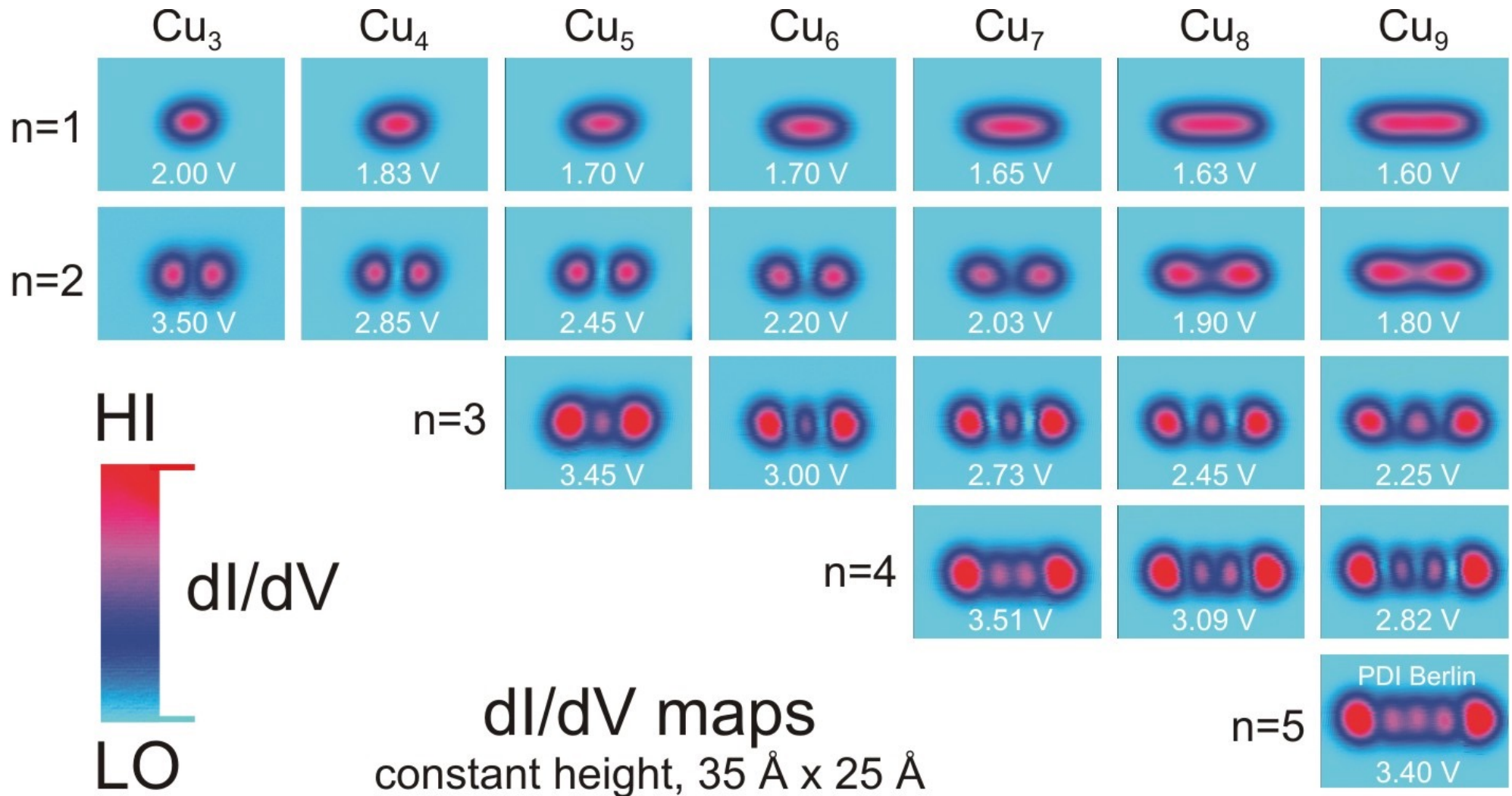


Topography of Cu adatom chains is visualized by STM. Then the tip is positioned as marked with crosses and dI/dV vs. V was measured. Positive sample bias probes unoccupied quantum states.

1D quantum well behavior is observed

Example 2: Cu/Cu(111) chains dI/dV imaging of DOS

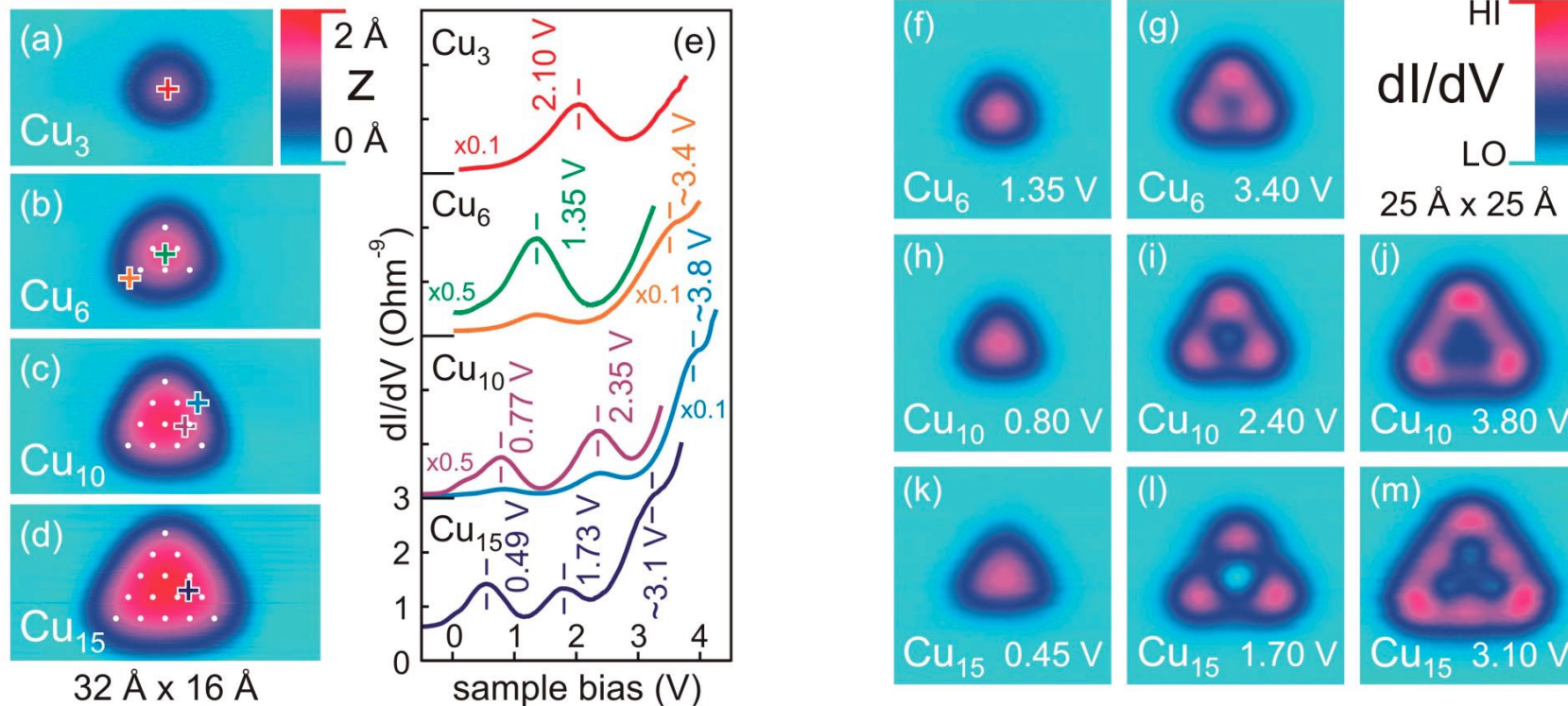
The maps are collected in constant height mode (feedback is switched off)



Chain-localized electronic states characterized by squared wave functions with n lobes and $n-1$ nodes (n : order)

1D quantum well is realized by artificially assembled atom chain

Example 2: Cu islands on Cu(111) : dI/dV imaging of LDOS



PR 95, 136801 (2005)

PHYSICAL REVIEW LETTERS

week ending
23 SEPTEMBER 2005

Link between Adatom Resonances and the Cu(111) Shockley Surface State

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(Received 28 June 2005; published 19 September 2005)

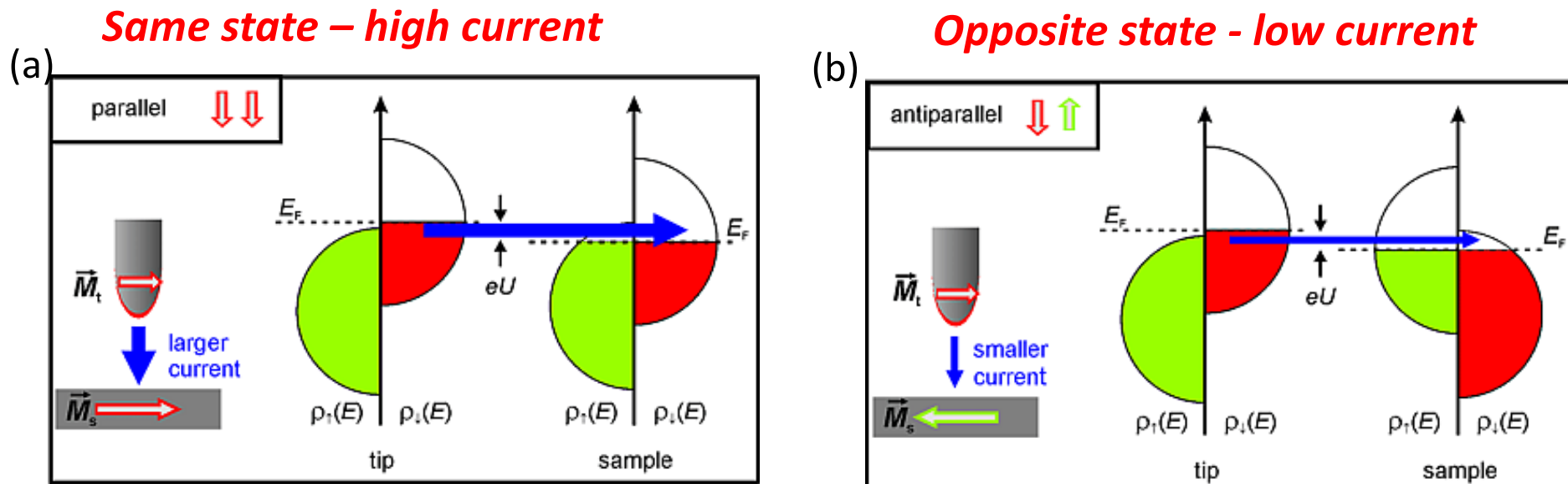
Low-temperature scanning tunneling microscopy and spectroscopy at 7 K was used to assemble and characterize native adatom islands of successive size on the Cu(111) surface. Starting from the single adatom we observe the formation of a series of quantum states which merge into the well known two-

- Ground states – single lobe
- First excited state – maxima close to the corners

Then the structure becomes more complicated

Tunneling magnetoresistance and spin-polarized (SP) STM

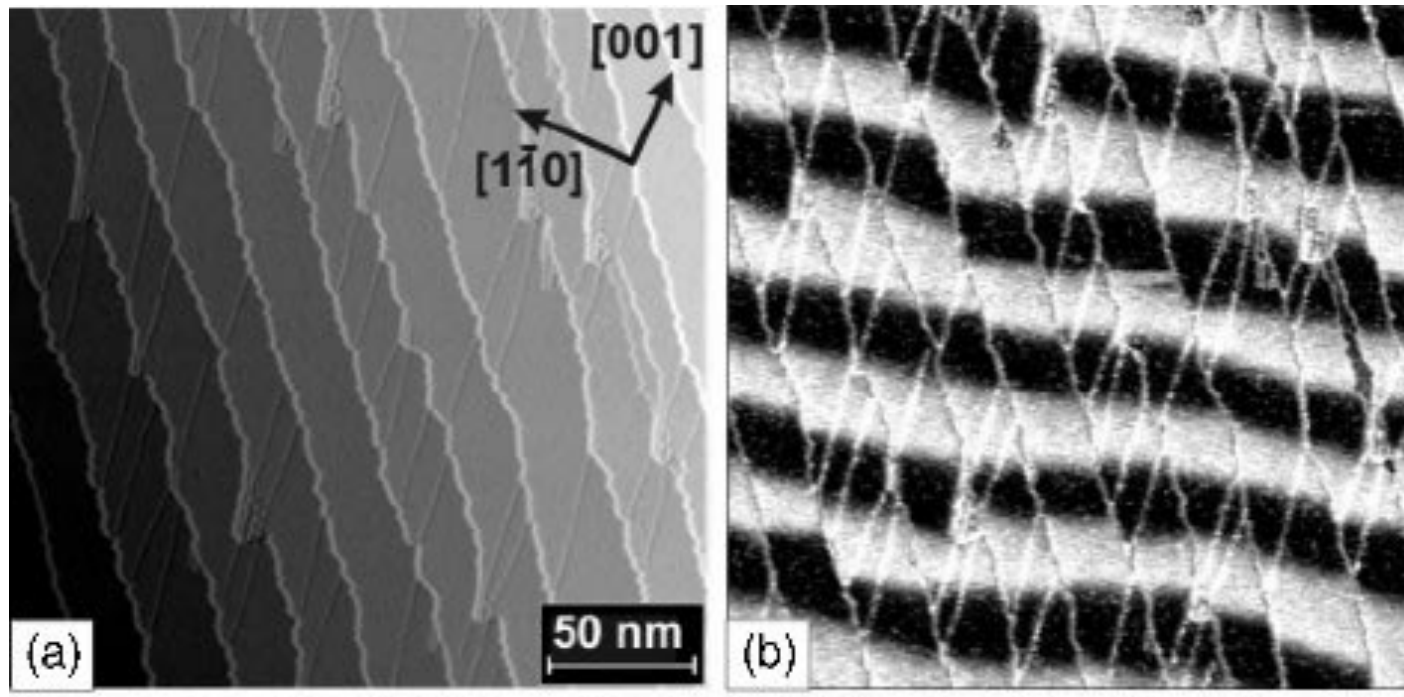
- The principle of operation of SP-STM is based on a fundamental property of ferromagnets—that their magnetic moment is related to an imbalance in occupation of electrons with different spins. Due to the spin-sensitive exchange interaction, the density of states splits up into minority and majority densities. This imbalance causes a spin polarization.
- The tunneling current from a spin-polarized tip is spin-polarized
- The tunneling current depends on the relative orientation of the magnetization of the sample and tip.



For parallel orientation, current is higher than for antiparallel orientation

- The drawing shows tunneling between two identical ferromagnetic electrodes that show spin split density of states. In (a) and (b) the magnetization of the two electrodes is parallel and antiparallel, respectively.

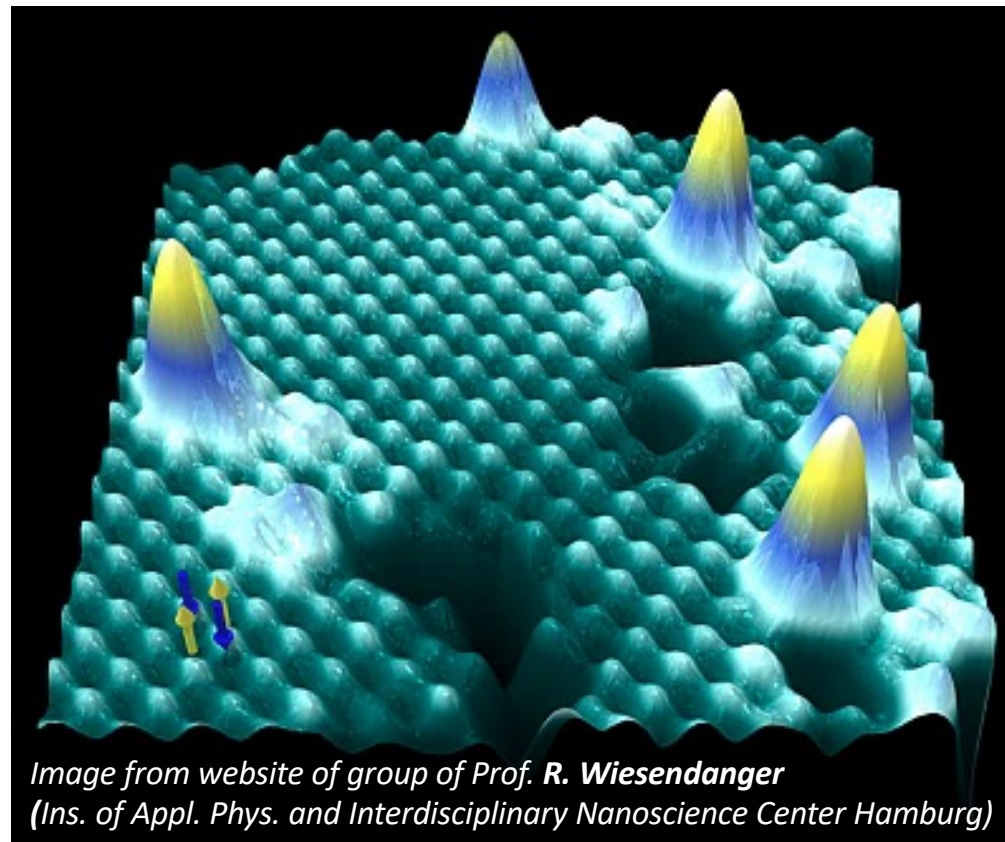
SP STM: viewing ferromagnetic domains



- (a) Topographic image of ≈ 1.75 monolayers of Fe on W(110) surface. The image reveals an atomically flat surface with monolayer terraces of W(110) surface
- (b) SP-STC maps of the local differential conductivity shows stripe magnetic domains which are not visible in topography images

SP STM: probing spin arrangements with high resolution

The SP-STM images can be collected in constant current mode (like the image below). Then the images contain mixed topography and spin information. Because of difficulties with separation of topography and spin information some reference measurements with non-magnetic tip are useful

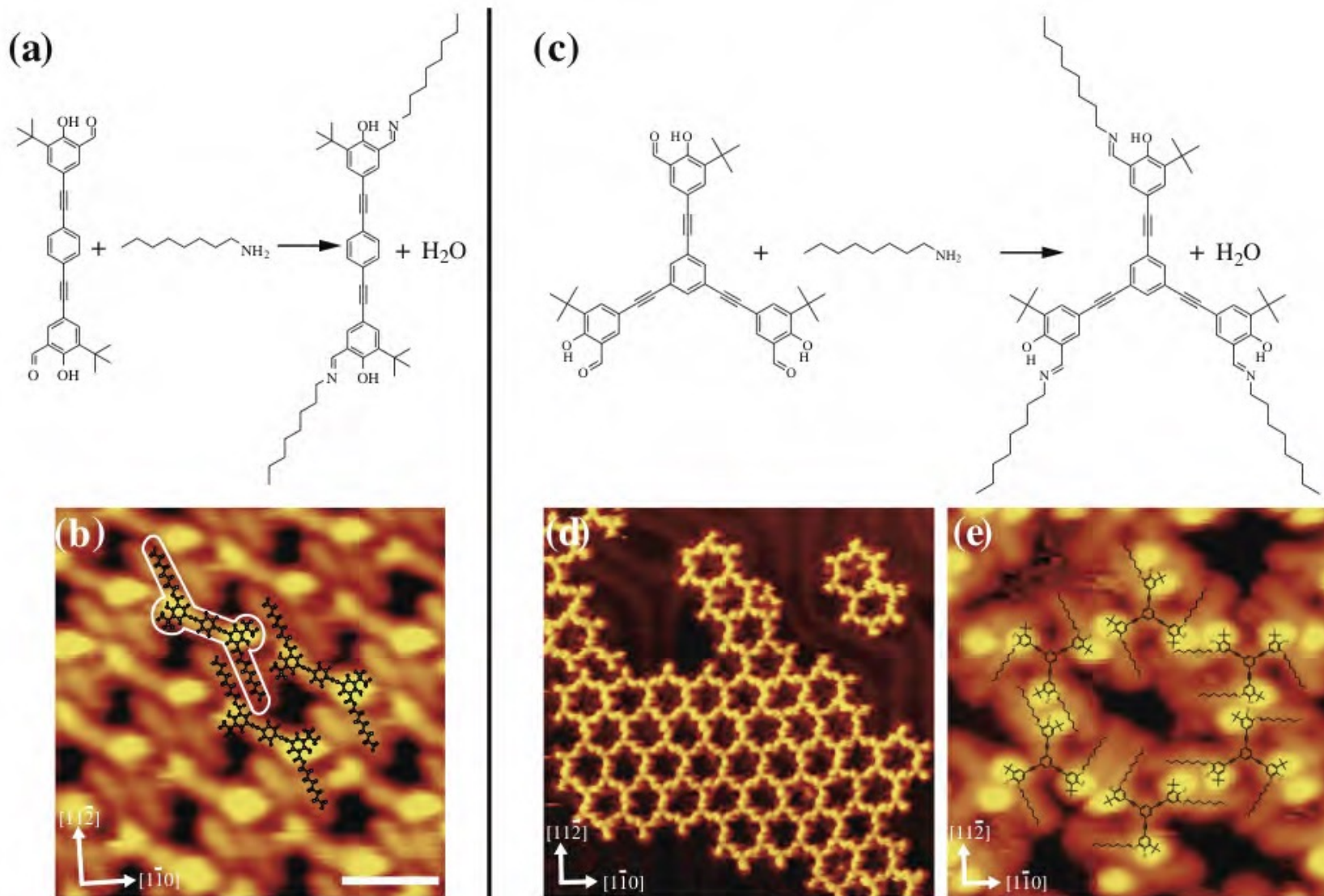


The image above represents SP STM scan of an antiferromagnetic atomic layer of iron on W(001) with defects and adatoms. Depending on their spin direction (up or down, see arrows in image), the Fe atoms appear as protrusion or indentation in constant current images (measurement parameters: $T = 8 \text{ K}$, $I = 1 \text{ nA}$, $U = -50 \text{ mV}$, image size: $10 \times 10 \text{ nm}^2$)

STM analysis of organic molecular assembling

Organic molecular arrangements on the surface like self-arranged monolayers (SAM) or more complicated structures like “DNA origami” are studied for various nanotechnological applications. STM offers a tool to directly observe these structures and test their electronic properties.

F. Besenbacher et al. / Surface Science 603 (2009) 1315–1327

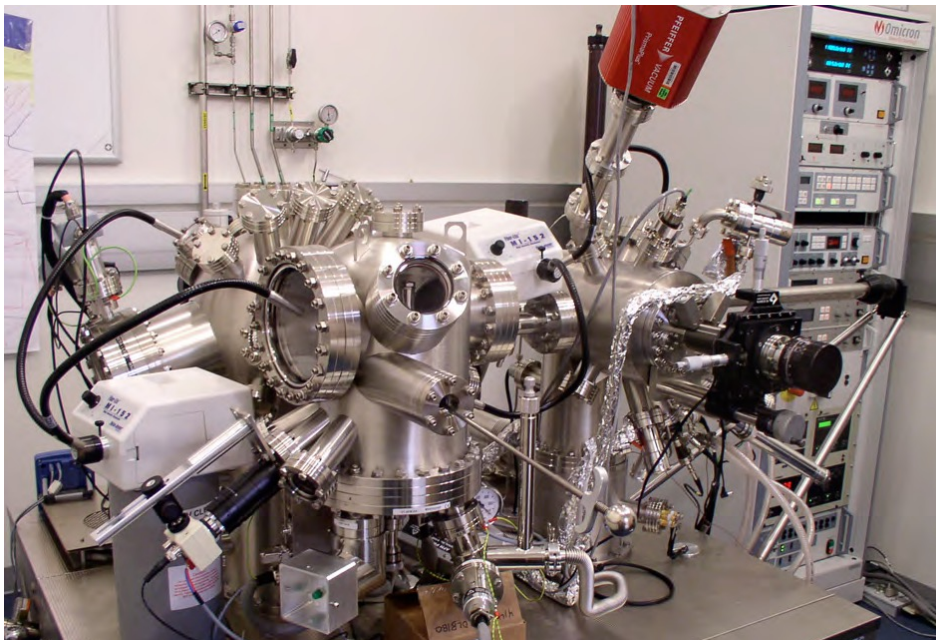


Different types of STM



STMs for ambient conditions are rather compact and relatively inexpensive tools (in the picture you see STM from **Nanosurf** for approximately 20 000 CHF.

They can be used for rapid surface diagnostics (for conductive materials) or for studying stable surfaces that do not change in air.



Ultra-high vacuum STM is a rather complicated system that may incorporate several modules for sample and tip preparation.

Such systems are often equipped for operation at cryogenic temperatures. For magnetotransport measurements the system is often placed in a cryostat with superconductive magnetic coil

Summary of essential points:

STM – operation principles and some applications

- STM is a scanning probe technique that relies on detection of tunnel current that flows across a small gap ($\sim 1\text{-}3\text{\AA}$) between the probe tip and sample No need for mechanical contact!
- tunnel current decays exponentially with an increase of the gap
- The tip-sample separation can be controlled/measured very exactly (on picometer scale) by monitoring tunneling current – delivers very high vertical resolution topography images
- The tunneling current is only carried by the *outermost* tip atom; **the sample surface is scanned by a single atom – high lateral resolution**
- Operation modes: constant current mode (most commonly used , employs feedback loop); constant-height mode – used for some special applications
- Technical aspects discussed: piezo scanner, feedback loop regulator – ***important for all scanning probe techniques!***

Summary of essential points :

STM –operation principles and some applications

- Rather than measuring physical topography, STM measures a surface of constant tunneling probability
- STM actually senses the number of filled or unfilled electron states near the Fermi level, within an energy range determined by the bias voltage
- STM spectroscopy can be used to probe the density of filled or unfilled states

$$\frac{dI}{dV} \propto DOS$$

- Applications:
 - atomic resolution topography, sensing electronic orbitals
 - local density of states mapping, spectra of low-dimensional nanostructures
 - spin-polarized STM: probing ferromagnetic domain structure; probing spin arrangements on atomic scale
 - atomic manipulation by STM
 - surface analysis: organic molecular assembling, catalytic activity

Atomic force microscopy (AFM) vs STM

Both are scanning probe techniques (local probes + scanners with feedback loops)

- STM is usable only for conductive
- STM measures electronic properties of the surface
- STM measures tunnel current
- AFM can be used for any materials
- AFM measures short-range atomic forces
- AFM measures mechanical deflection of a flexible cantilever (atomic forces are sufficient to induce a measurable deflection of a macroscopic cantilever)

