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AFM/STM methods

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Dept. of Materials Physics

Lecture in the ELTE course of
Experimental methods of condensed materials
23 Nov 2021.

Contents

AFM/STM methods

- Introduction to scanning probe microscopy
- Scanning tunneling microscopy (STM)
    - Technical details, tips and some examples
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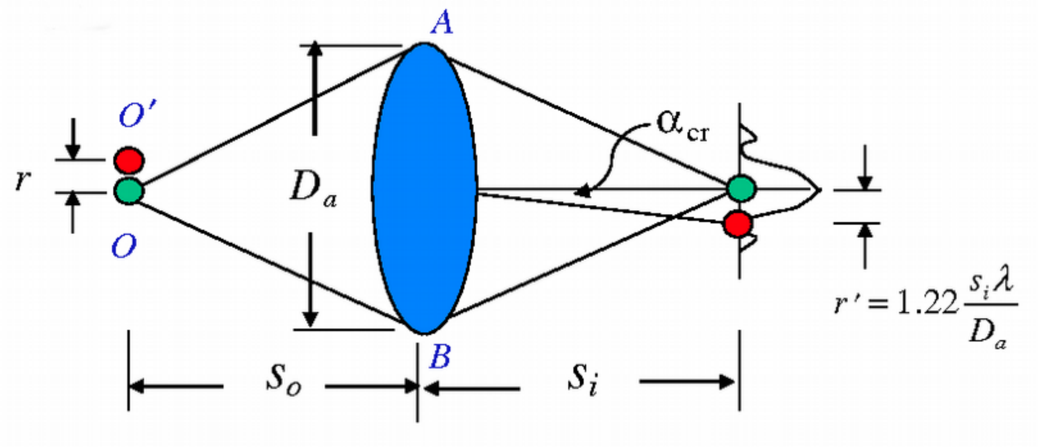
- Atomic force microscopy (AFM)
    - Technical details, tips and some examples
    - AFM methods (contact vs. non-contact method)
- Electronic force microscopy (EFM)
- Magnetic force microscopy (MFM)

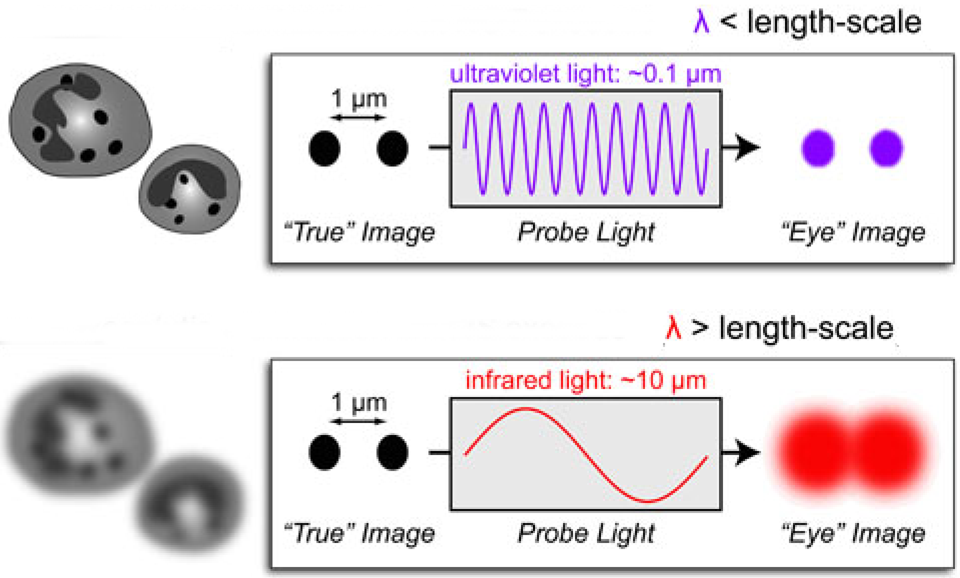
Introduction to scanning probe microscopy

Problem of the limited resolution in imaging methods due to finite wavelength



diffraction limit

C.D. Meinhart and S.T. Wereley.
Meas. Sci. and Technol. 2003.



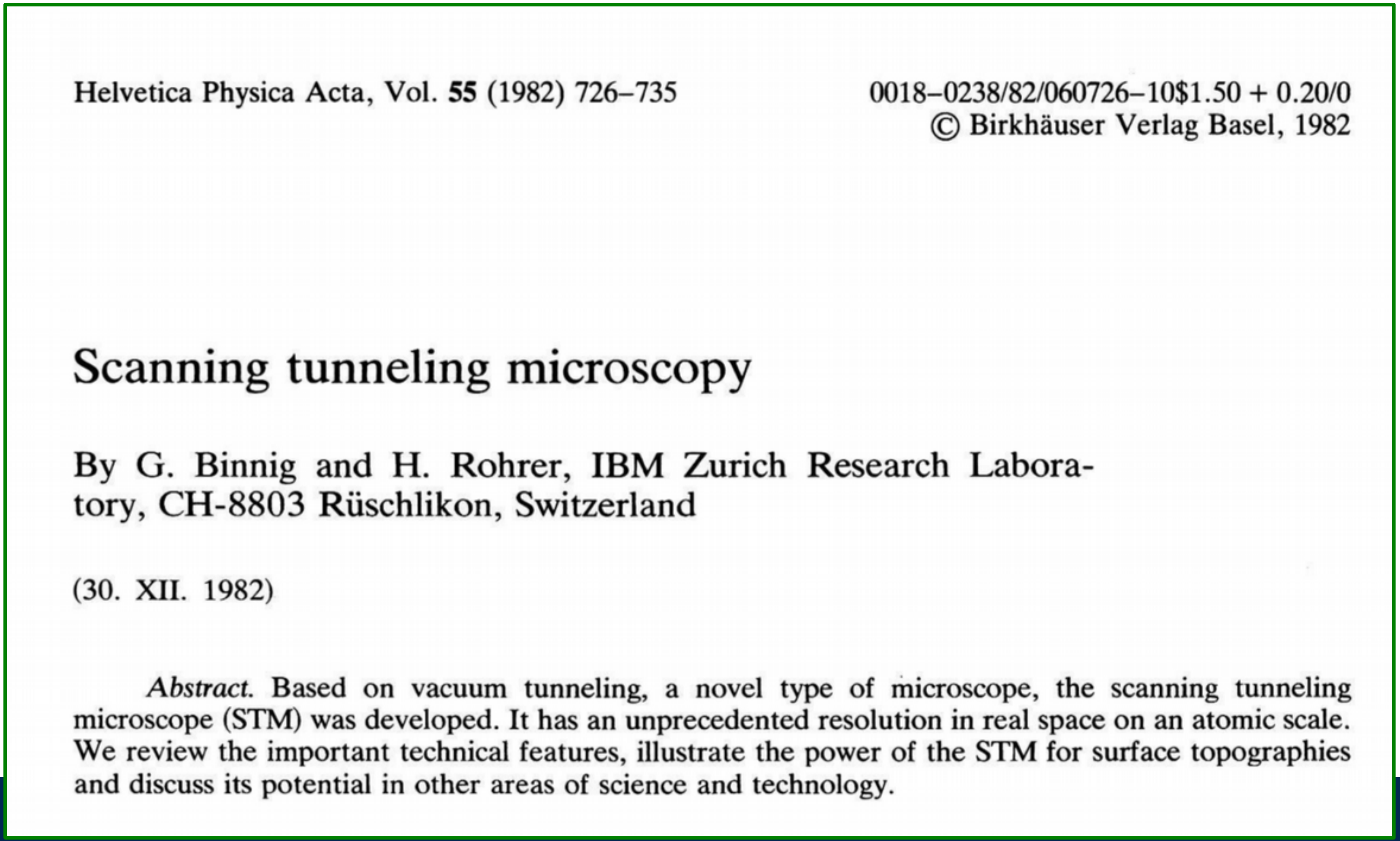
https://www.cherrybiotech.com

Solutions

1) shorter lambda (X-ray microscopy or electron microscopy)
2) local interaction with a sharp tip (probe) + scan with atomic resolution

Introduction to scanning probe microscopy

In 1981, Gerd Binnig and Heinrich Rohrer published results on the visualization of the atomic structure of Si surface using a scanning probe microscope.



Helvetica Physica Acta, Vol. **55** (1982) 726–735

0018–0238/82/060726–10$1.50 + 0.20/0

Scanning tunneling microscopy

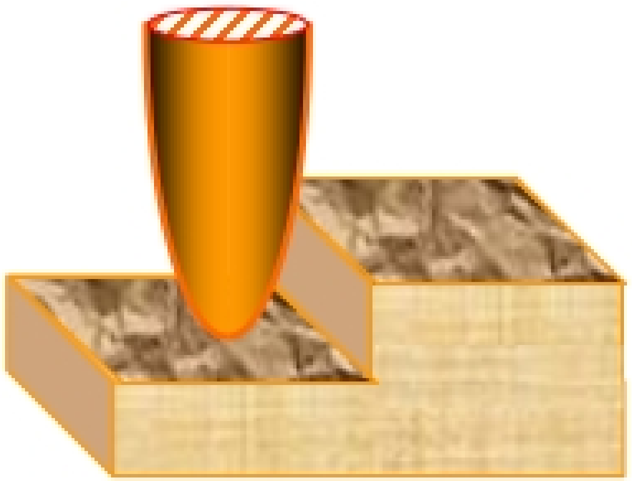
By G. Binnig and H. Rohrer, IBM Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

(30. XII. 1982)

Abstract. Based on vacuum tunneling, a novel type of microscope, the scanning tunneling microscope (STM) was developed. It has an unprecedented resolution in real space on an atomic scale. We review the important technical features, illustrate the power of the STM for surface topographies and discuss its potential in other areas of science and technology.

Introduction to scanning probe microscopy

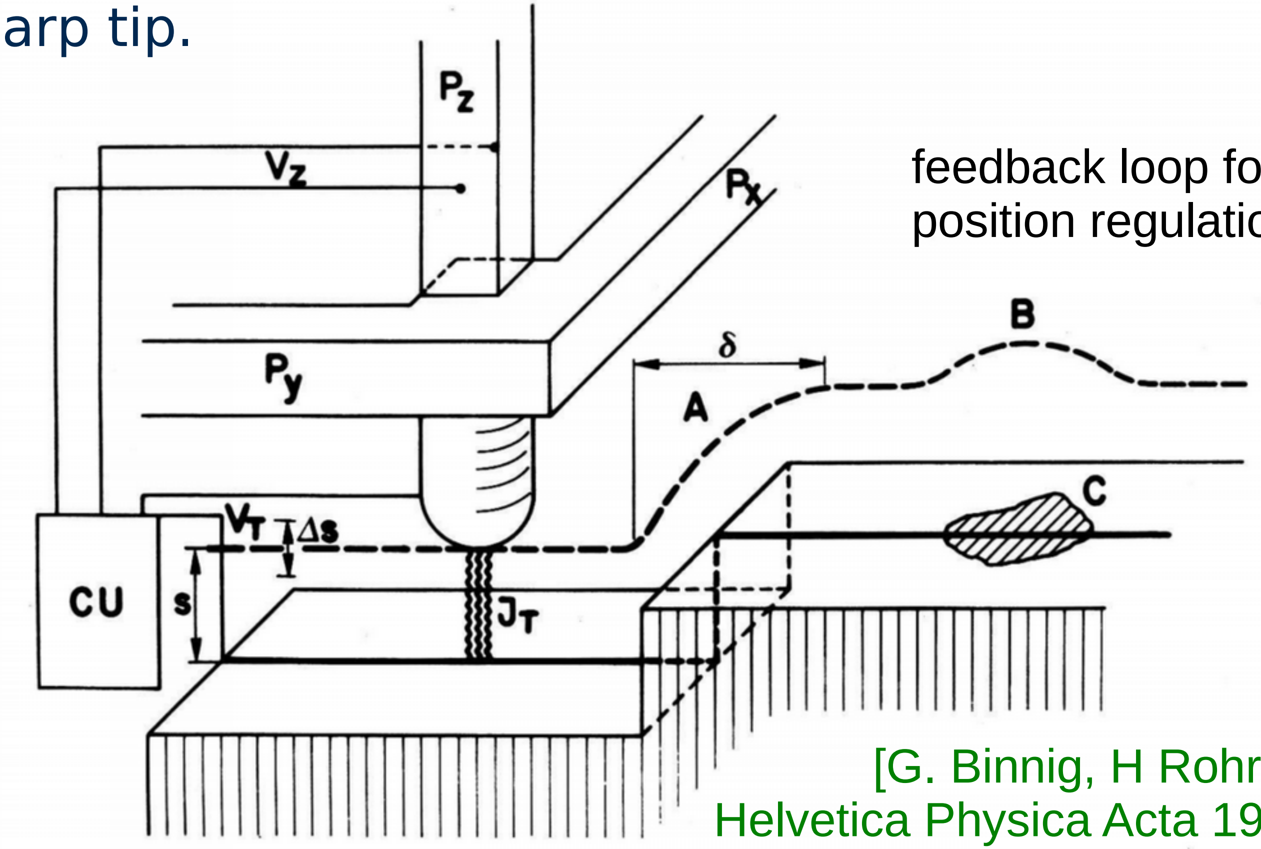
Basic idea: scan a surface with piezo actuators and measure surface properties locally with a sharp tip.



sharp tip

sample surface

[V. L. Mironov: Fundamentals of scanning probe microscopy]

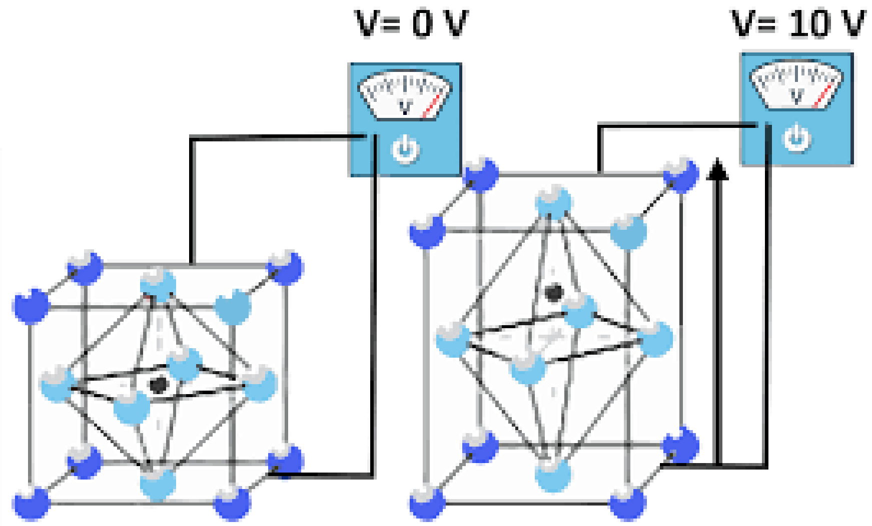


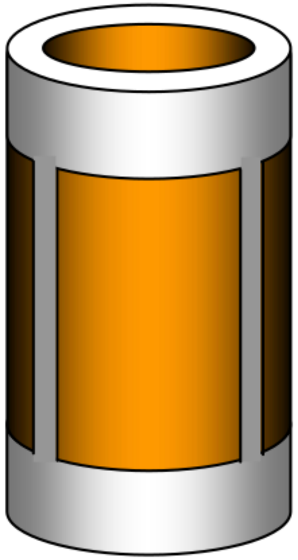
feedback loop for position regulation

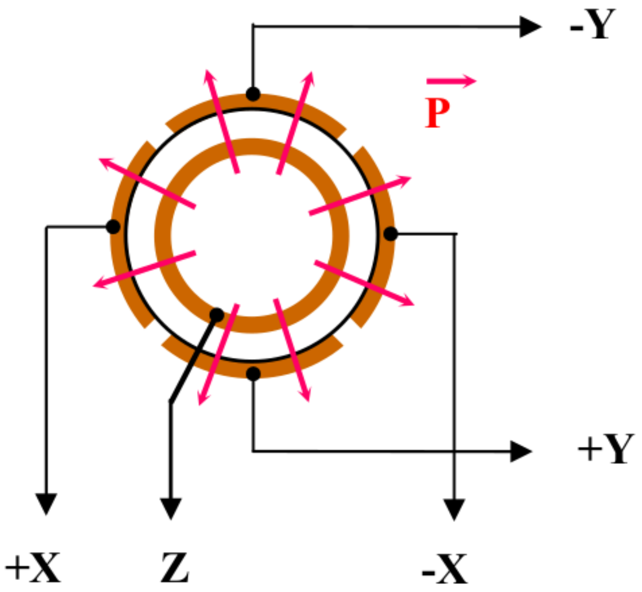
[G. Binnig, H Rohrer: Helvetica Physica Acta 1982]

Introduction to scanning probe microscopy

Fine movement of the tip requires subatomic resolution in scanner positioning
→ use piezo materials







For example from Lead Zirconate Titanate

Typical piezo crystal expand about 1 nm/V

[V. L. Mironov: Fundamentals of scanning probe microscopy]

Introduction to scanning probe microscopy

[G. Binnig, H Rohrer: Helvetica Physica Acta 1982]

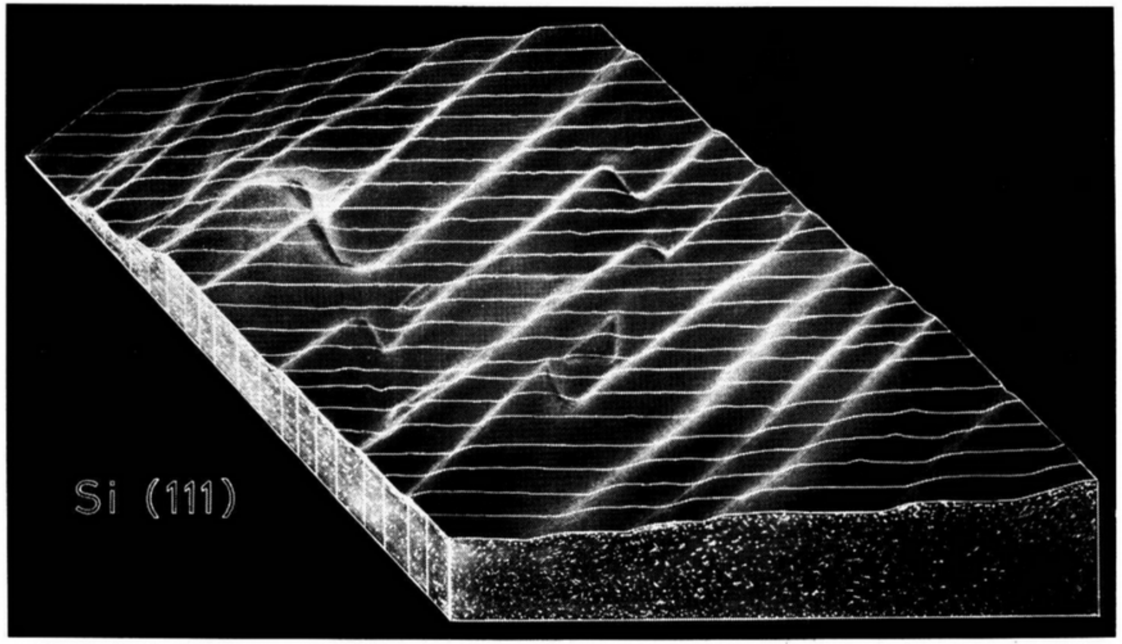


Figure 4
STM picture of a Si(111) surface exhibiting lines of mono-atomic step. © 1983 North-Holland.

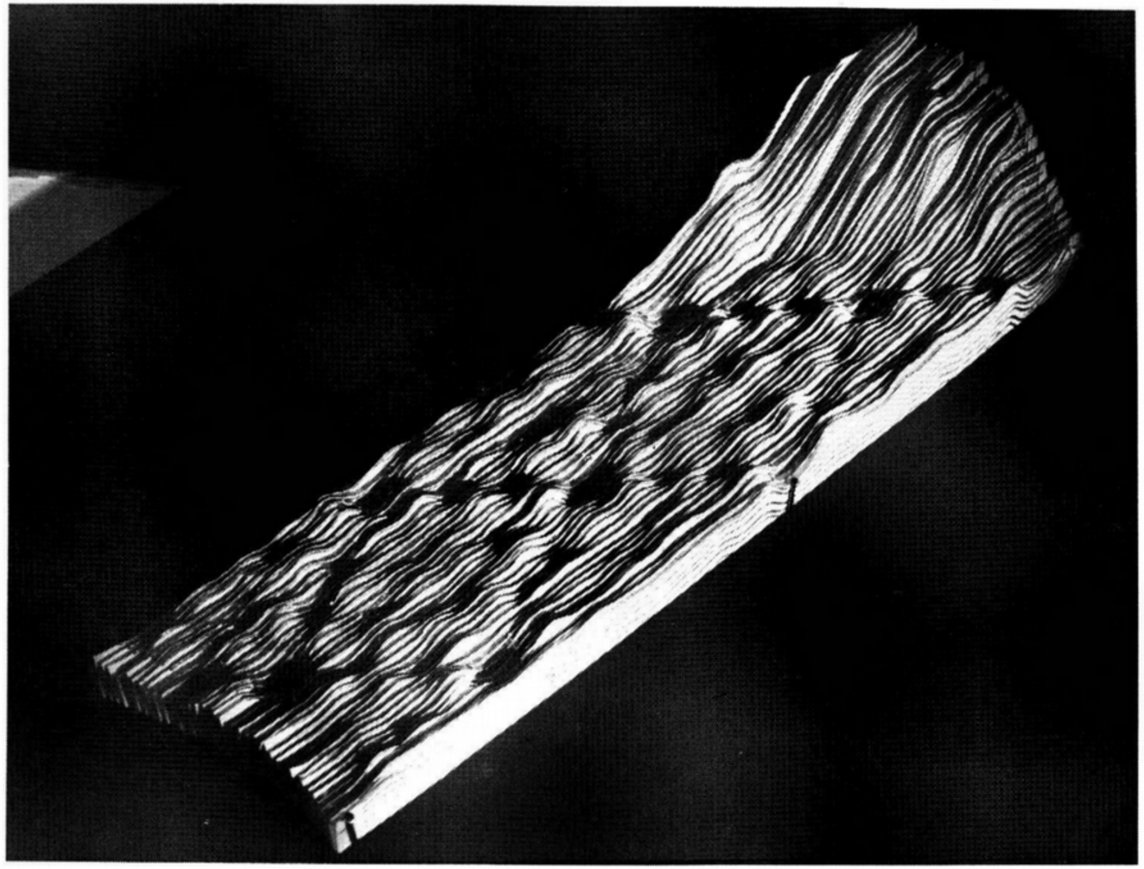
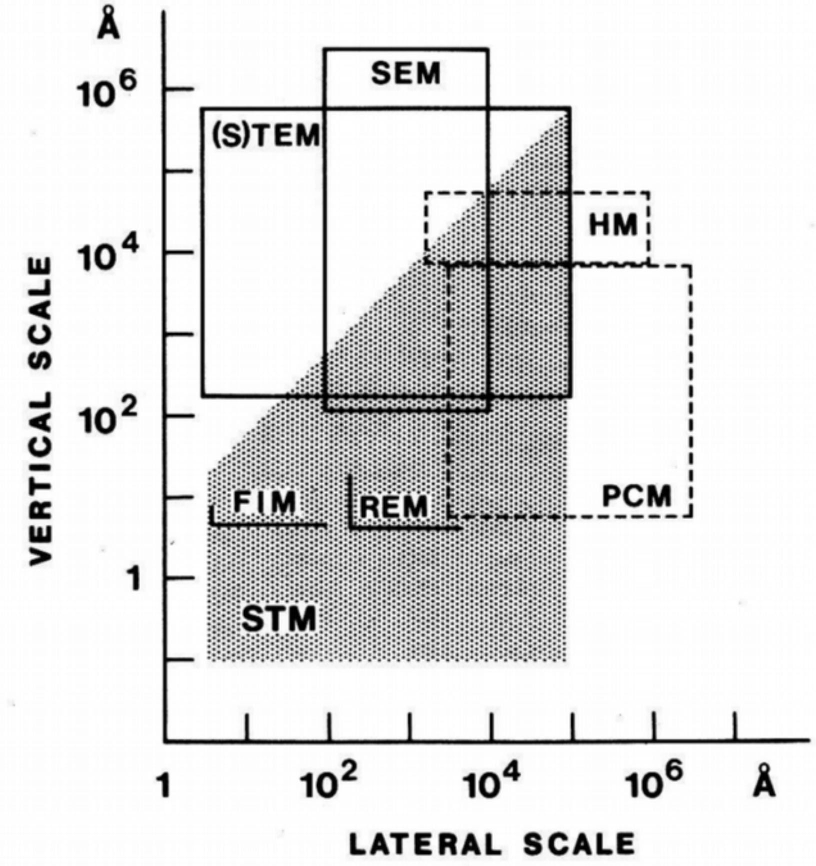


Figure 5
STM graph in relief form of the 7×7 reconstruction on Si(111), showing two complete rhombohedral unit cells. Deep minima (−2.1 Å) at the corners, minima (−0.9 Å) along the edges and 12 maxima (+0.7 Å) in the cell inside. © 1983 The American Physical Society.

Introduction to scanning probe microscopy

STM method extended material characterization into a new size range



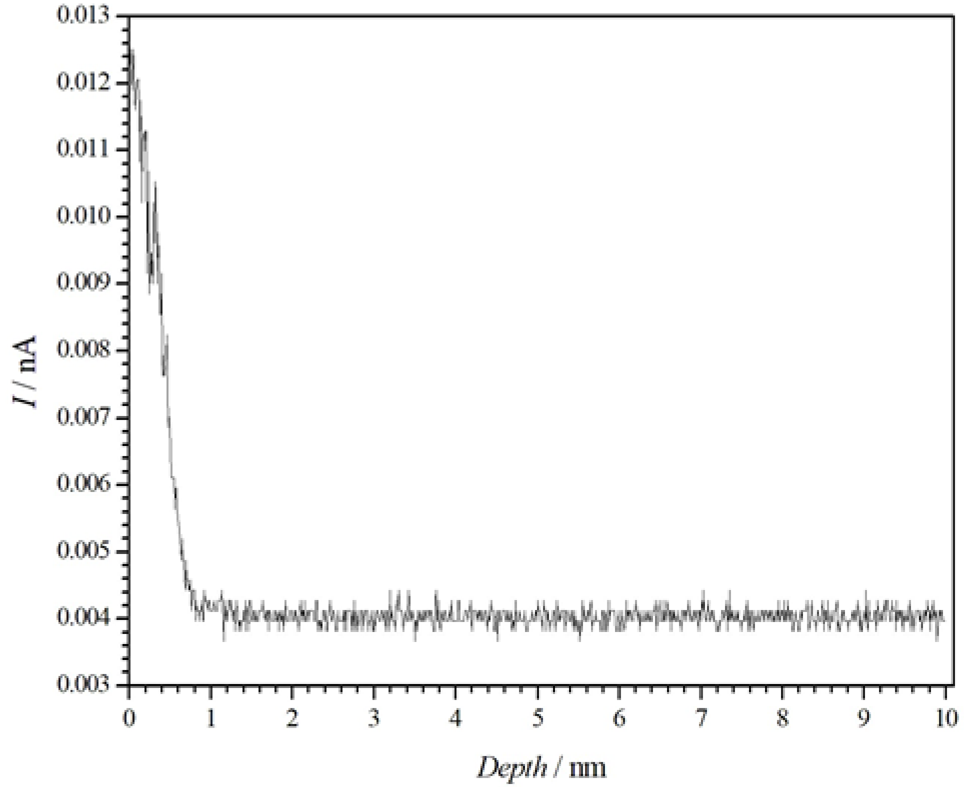
Several scanning probe microscopy variants were developed:

- Atomic force microscopy (AFM)
- Electric force microscopy (EFM)
- Magnetic force microscopy (MFM)
- Near-field scanning optical microscopy (NSOM)
- Tip enhanced Raman spectroscopy (TERS)

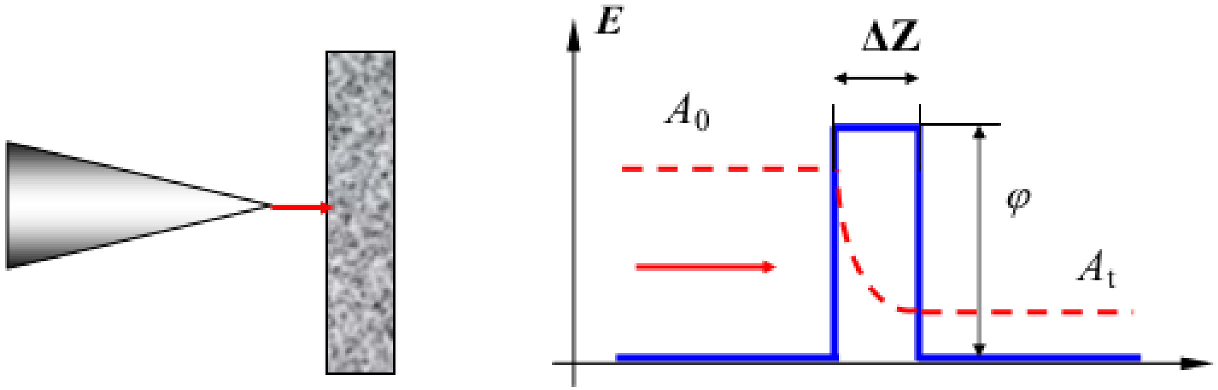
…

In 1986, they received the Nobel Prize in physics for their achievement.

Scanning tunneling microscopy



Tunneling current vs. surface distance



Tunneling of electrons between a conductive sample and the conductive tip through an insulator air gap.

Scanning tunneling microscopy

STM modes by setting the feedback loop

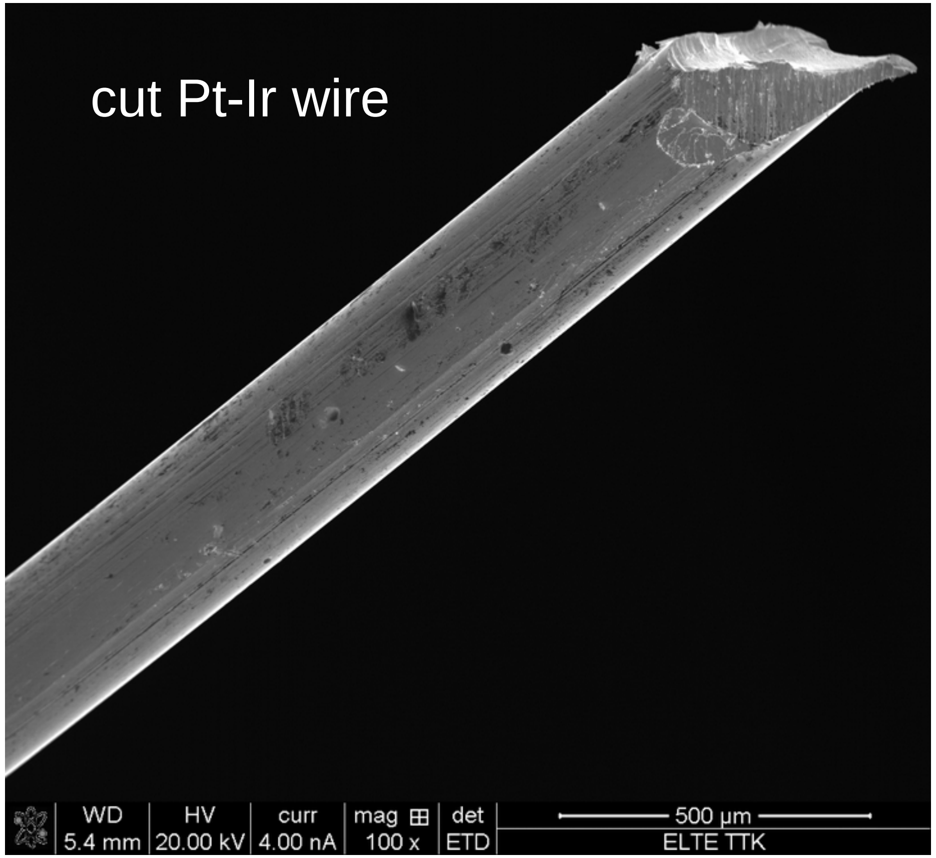
Constant height mode:
STM image from the spatial distribution of the tunneling current

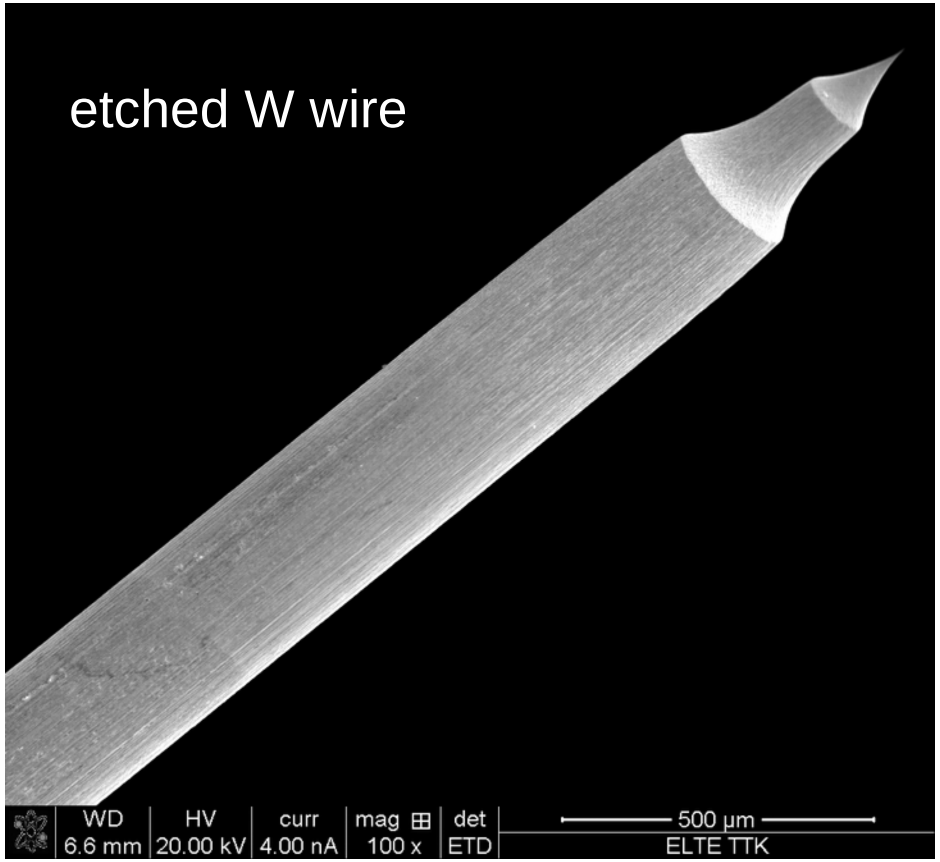
Constant current mode:
Feedback loop adjusts the tip distance above the surface for constant tunneling current

STM method requires conductive sample
Other method is required for non-conductive samples: Atomic Force Microscopy

Scanning tunneling microscopy

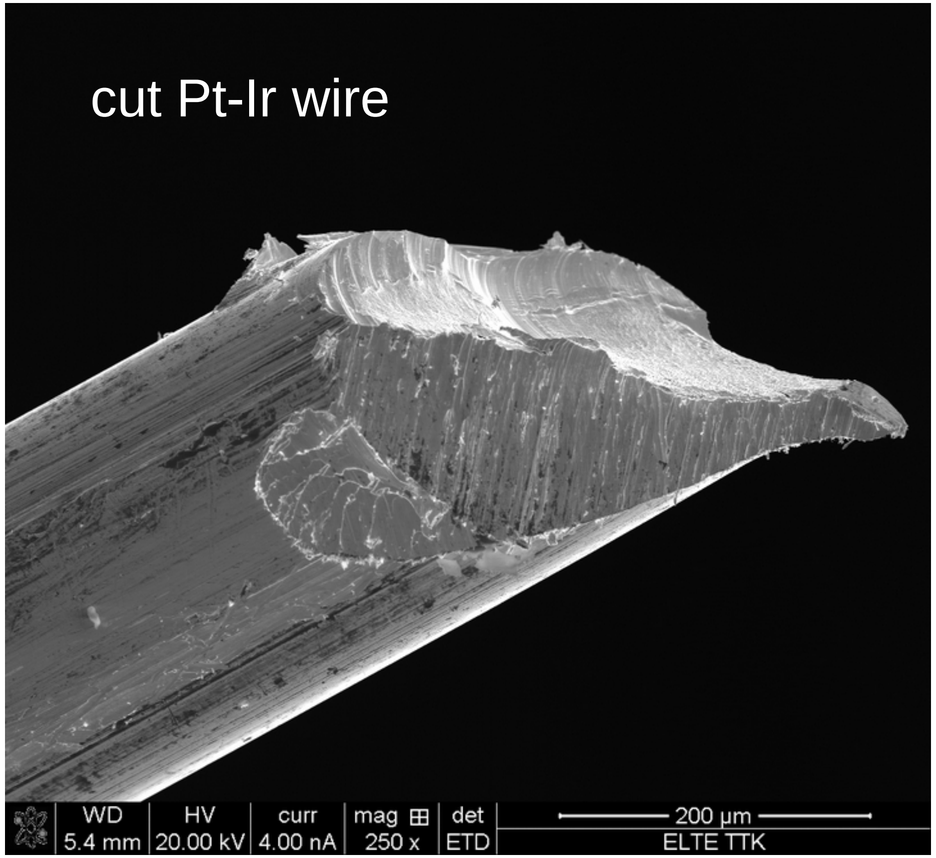
STM tips

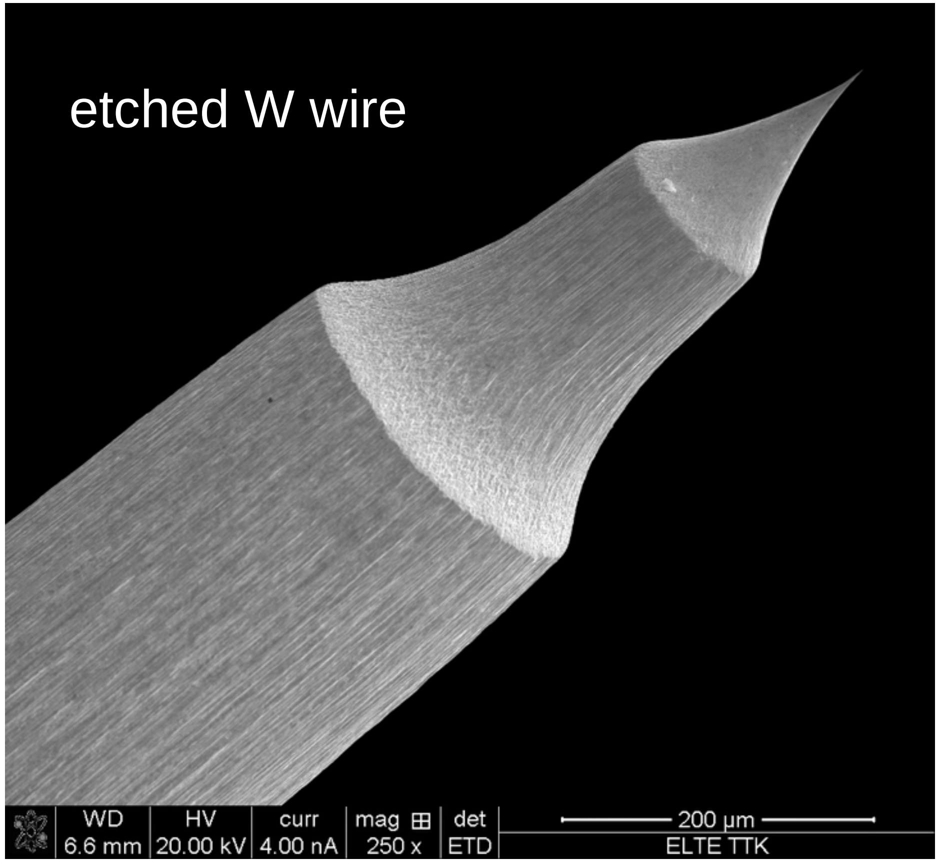




Scanning tunneling microscopy

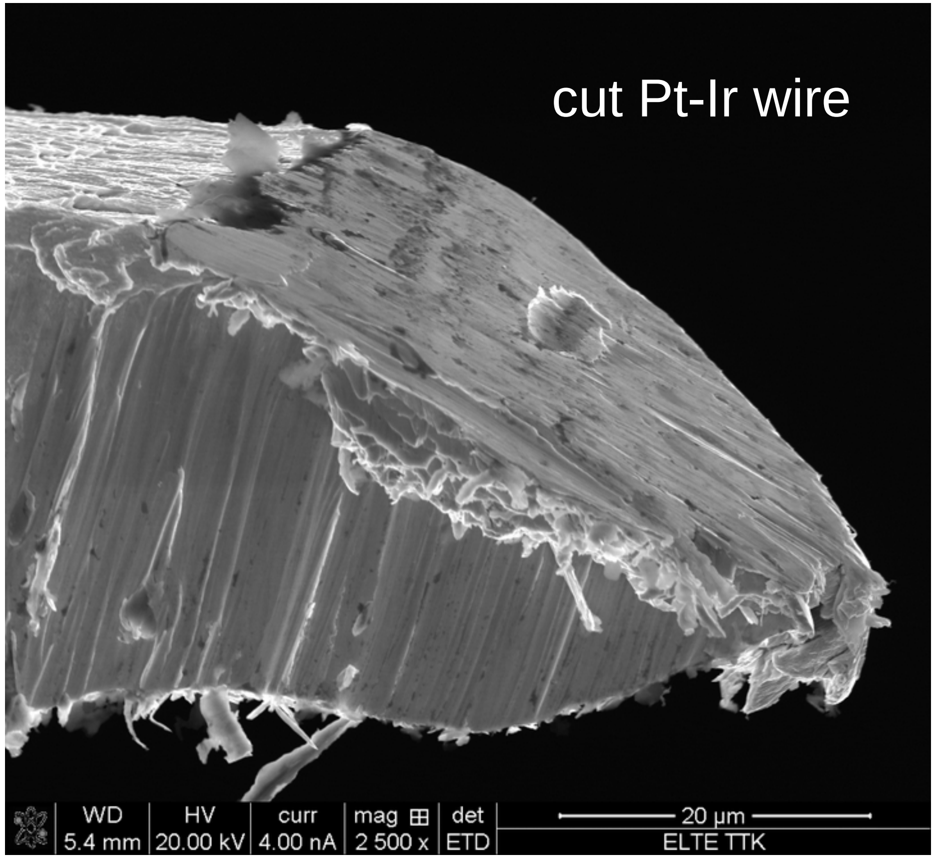
STM tips:



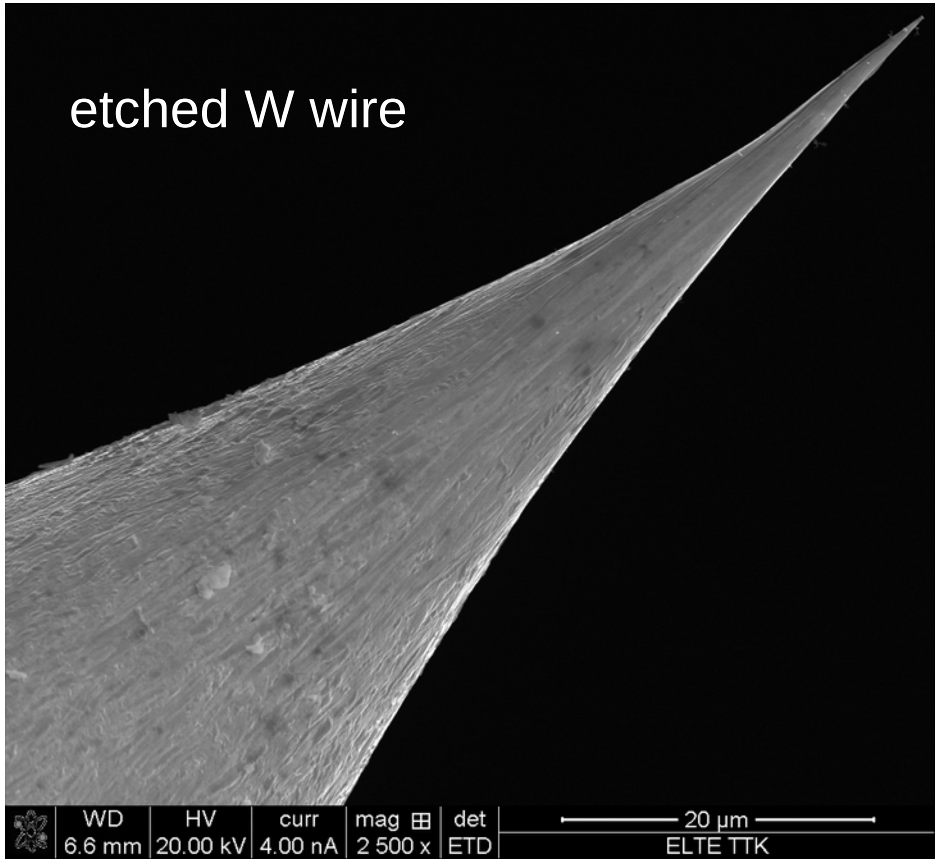


Scanning tunneling microscopy

STM tips:



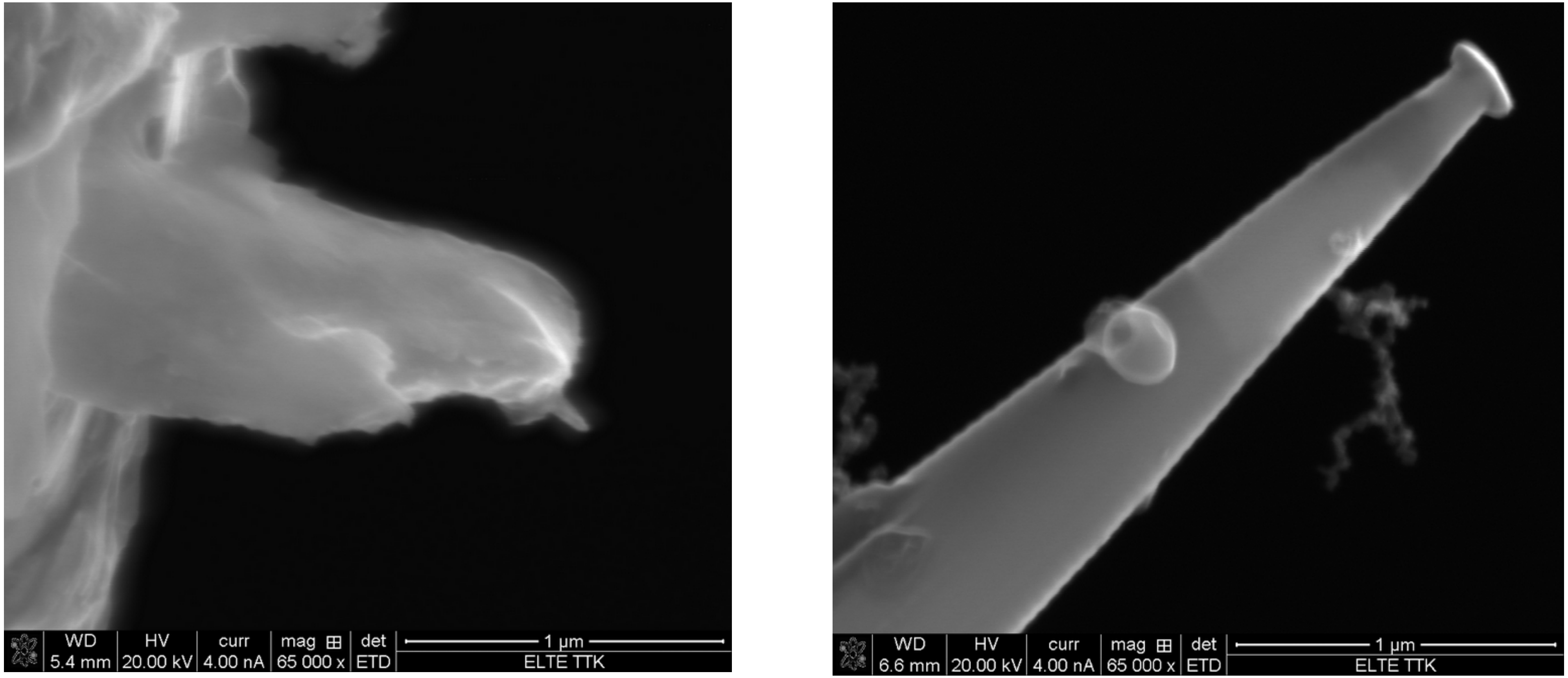
cut Pt-Ir wire



etched W wire

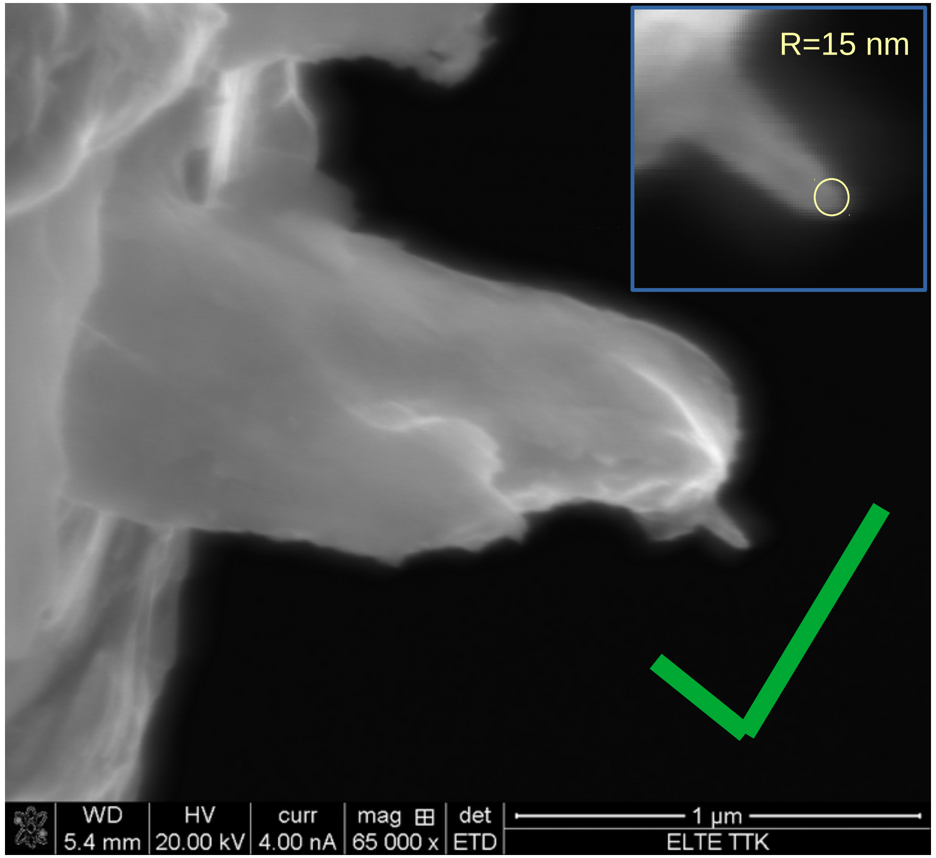
Scanning tunneling microscopy

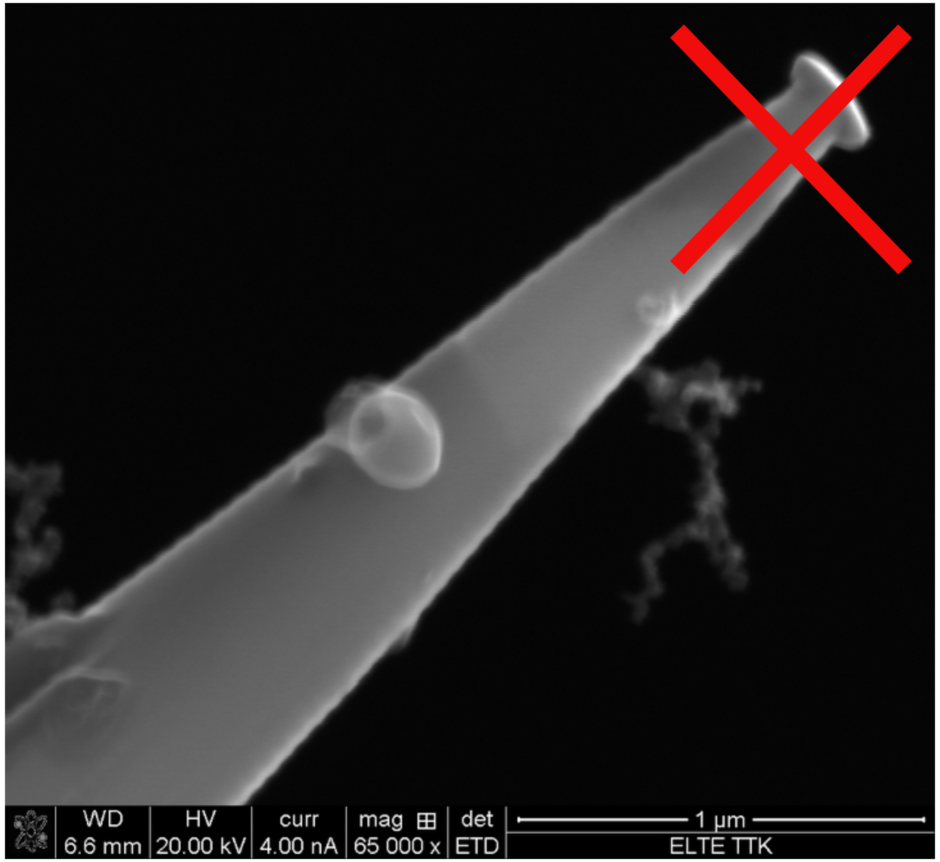
STM tips:



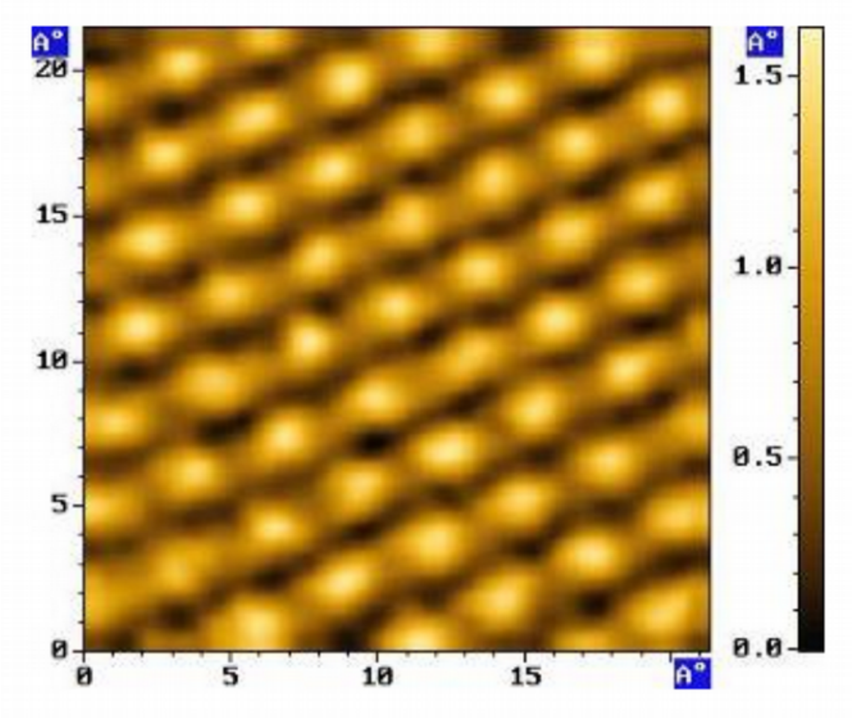
Scanning tunneling microscopy

STM tips:

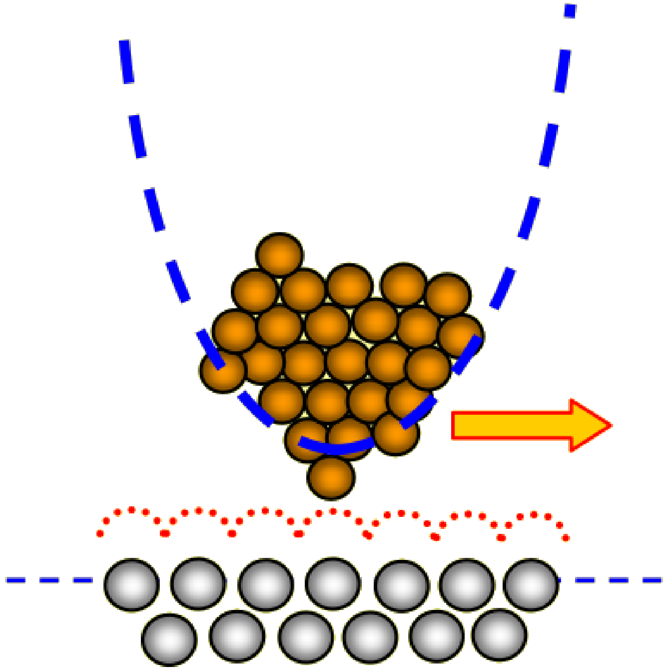




Scanning tunneling microscopy

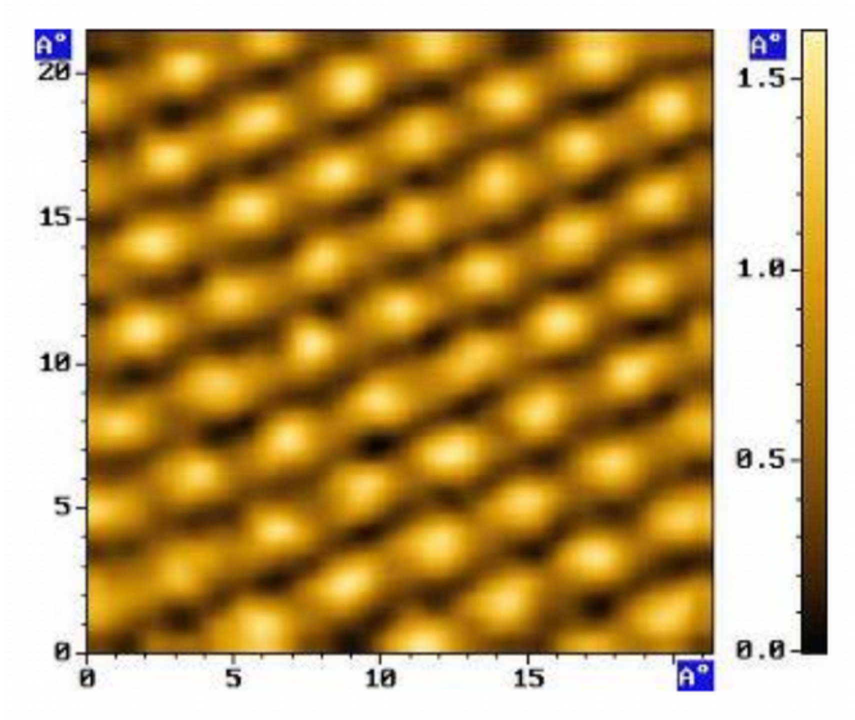


Surface of HOPG sample



Tunneling of electron between a conductive sample and the conductive tip through an insulator air gap.

Scanning tunneling microscopy



Surface of HOPG sample

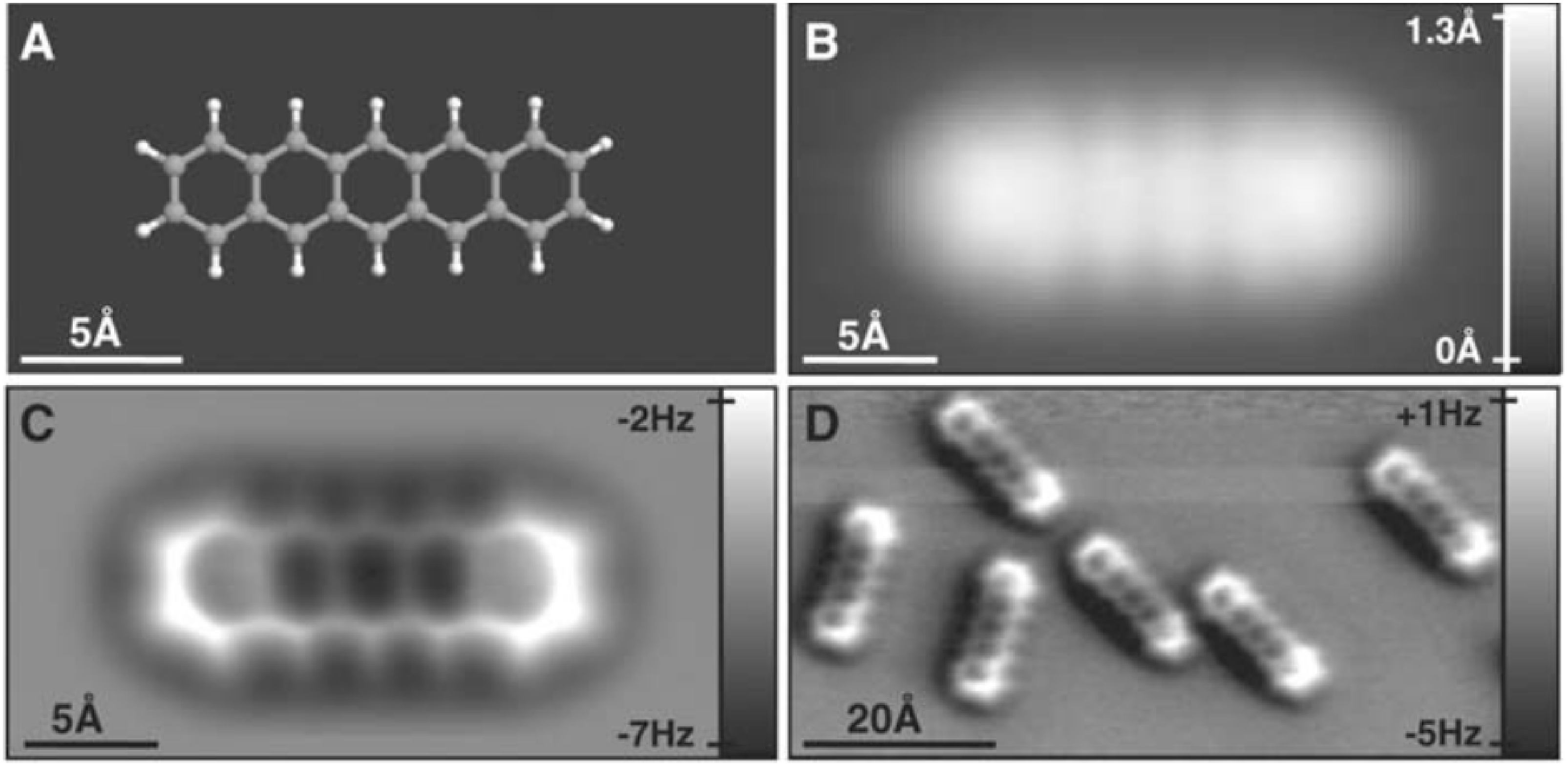
Tunneling current (*I*) can flow when electron waves in the two conductive elements overlap

When bias voltage (V_{bias}) is applied, a proportional tunneling current flows between the tip and the surface

$$I \propto V_{bias}\,\rho_s\left(E_F\right)\exp\left[-4\pi\frac{\sqrt{2m\left(\phi-E\right)}\,z}{h}\right]$$

Scanning tunneling microscopy

Image of a single pentacene molecule



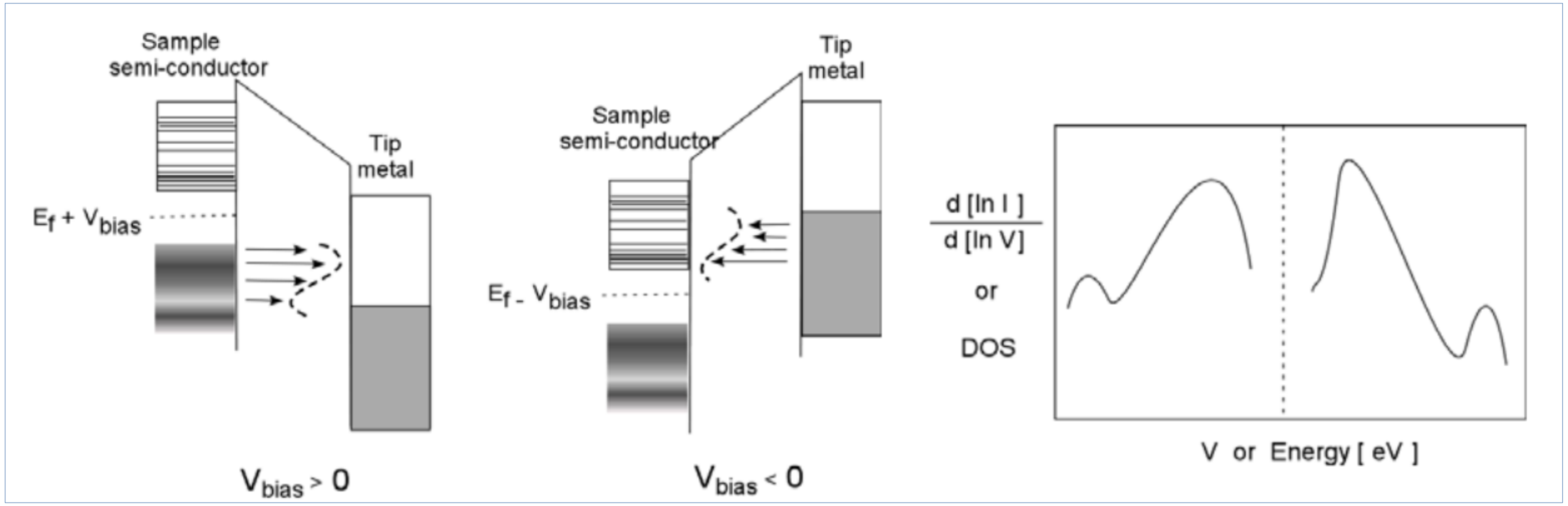
A: model B: STM image with constant current C-D: non-contact AFM with constant height and special tip with an CO molecule [Science 25, 1110 – 14 (2009)]

Scanning tunneling microscopy

Tunneling spectroscopy

electron density of states (DOS) change only slightly near Fermi energy (E_f) for metals and semi-metals

DOS is strongly energy dependent due to the bands structure for semiconductors



Electrons near the Fermi level participate in tunneling, therefore energy dependence of DOS can be measured from dI/dV_{bias} by varying V_{bias} at a constant tip-sample distance

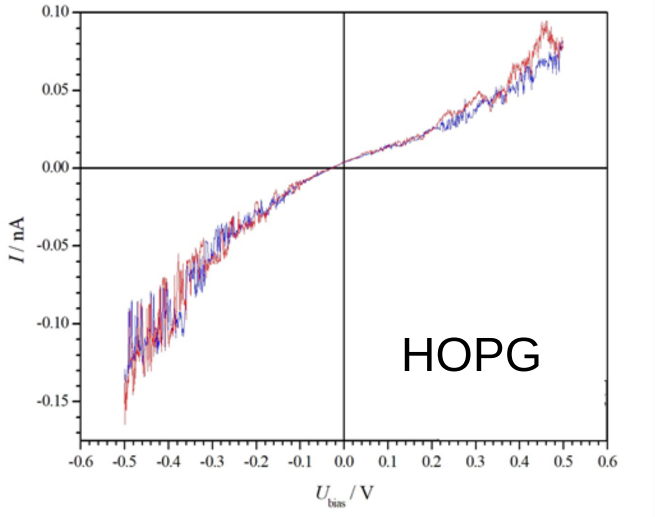
Scanning tunneling microscopy

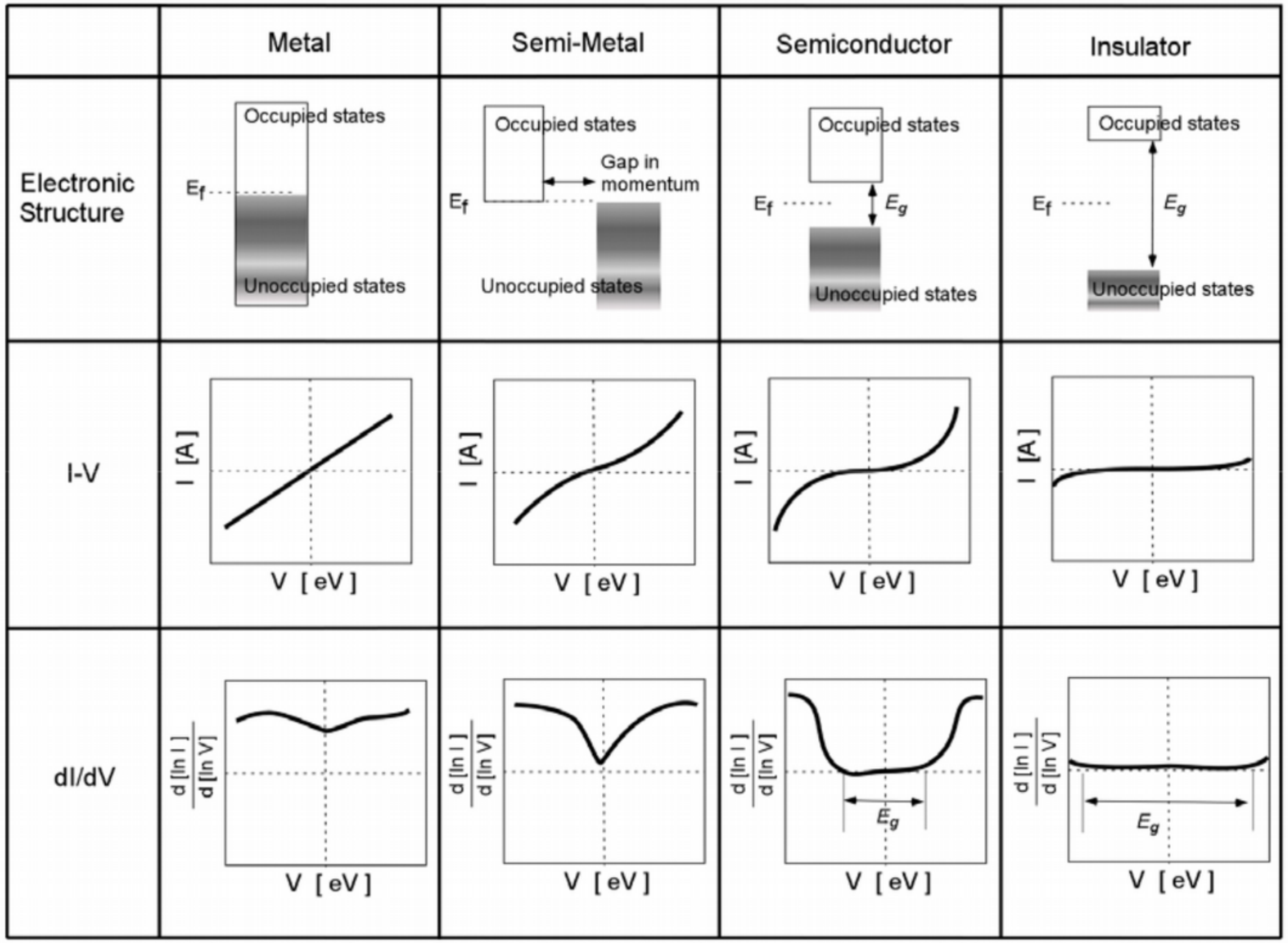
Tunneling spectroscopy

Metals: smooth change in DOS, no gap between valence and conduction bands

Semi-metals: local decrease in DOS at the Fermi level

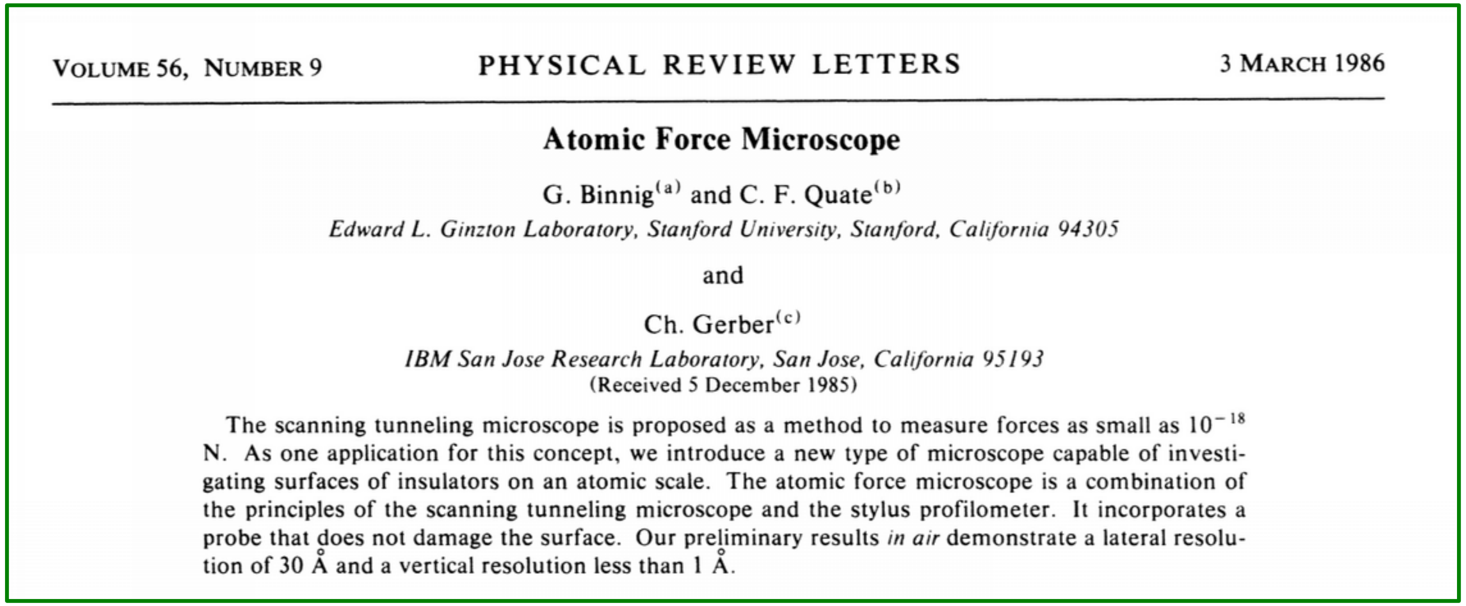
Semiconductors and insulators: conductance is zero near the Fermi level band gap, $E_g = |+V_{bias}| + |-V_{bias}|$





Atomic force microscopy

Atomic force microscopy (AFM) was invented in 1986 by
Gerd Binnig, Calvin F. Quate and Christopher Herber



VOLUME 56, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1986

Atomic Force Microscope

G. Binnig(a) and C. F. Quate(b)
Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305

and

Ch. Gerber(c)
IBM San Jose Research Laboratory, San Jose, California 95193

(Received 5 December 1985)

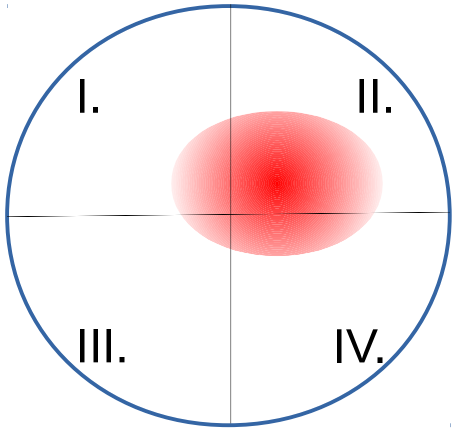
The scanning tunneling microscope is proposed as a method to measure forces as small as 10^{-18} N. As one application for this concept, we introduce a new type of microscope capable of investigating surfaces of insulators on an atomic scale. The atomic force microscope is a combination of the principles of the scanning tunneling microscope and the stylus profilometer. It incorporates a probe that does not damage the surface. Our preliminary results *in air* demonstrate a lateral resolution of 30 Å and a vertical resolution less than 1 Å.

Basic idea: measurement of the force between the sample and the probe.
The probe is an elastic cantilever with a sharp tip.

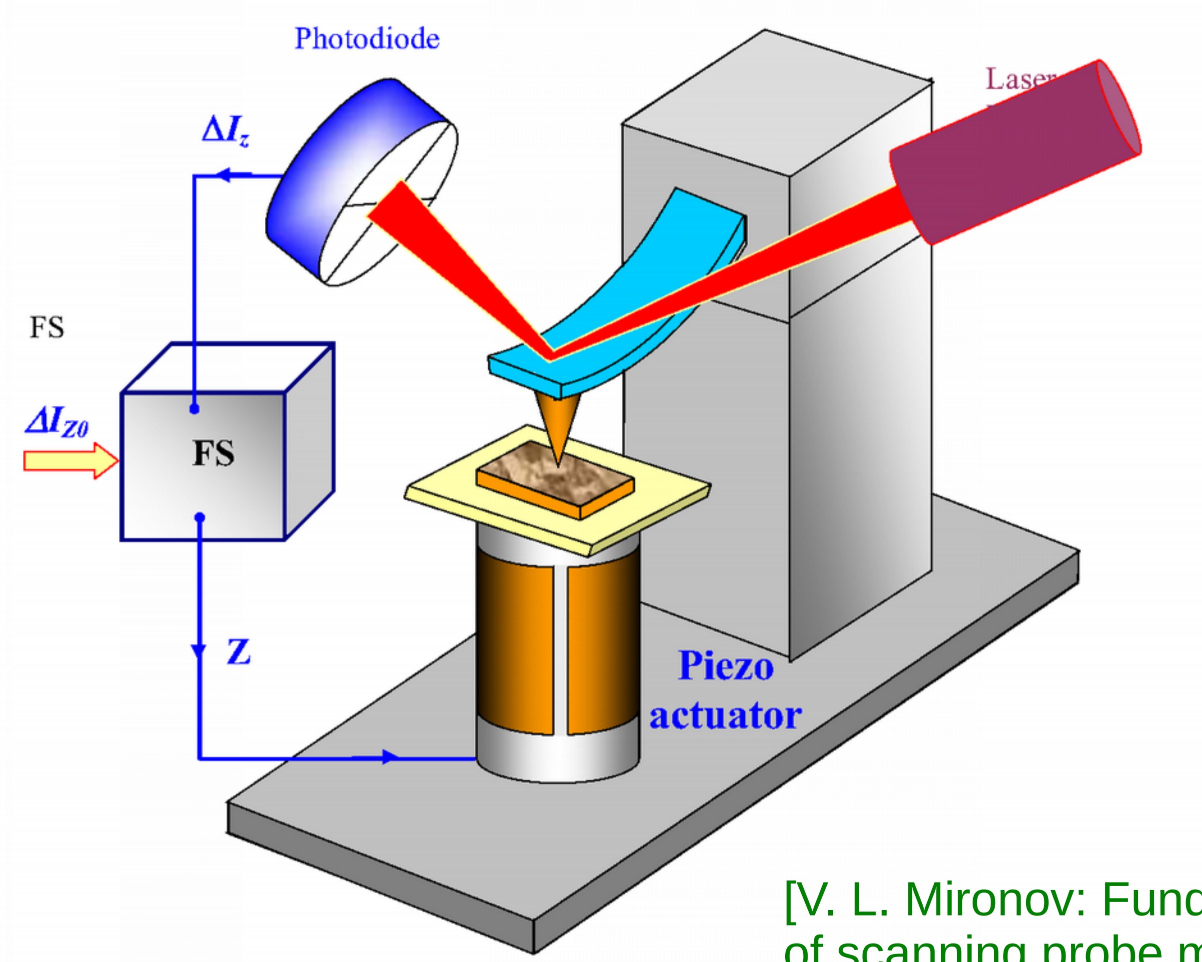
Atomic force microscopy

Elastic cantilever with a sharp tip

Force/displacement measured by a laser and a four-sectioned photodiode



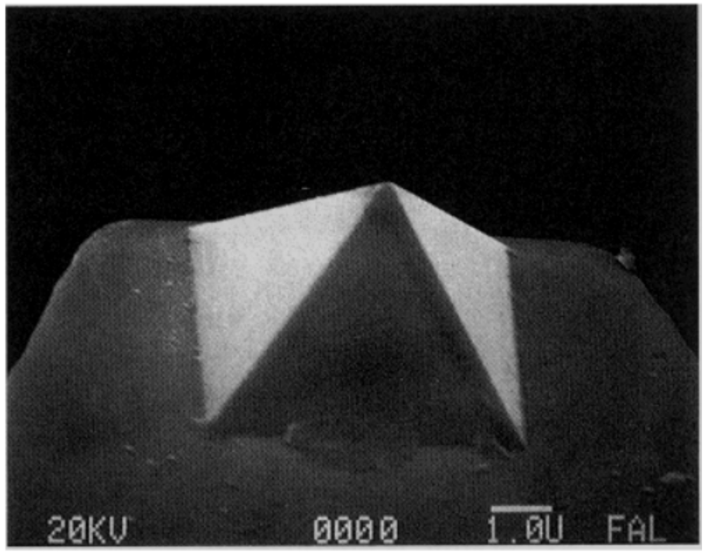
by the ratios of the current in the diode’s sections



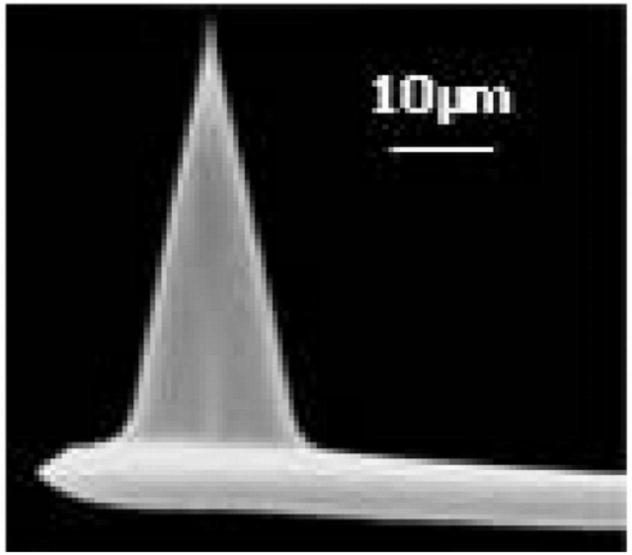
[V. L. Mironov: Fundamentals of scanning probe microscopy]

Atomic force microscopy

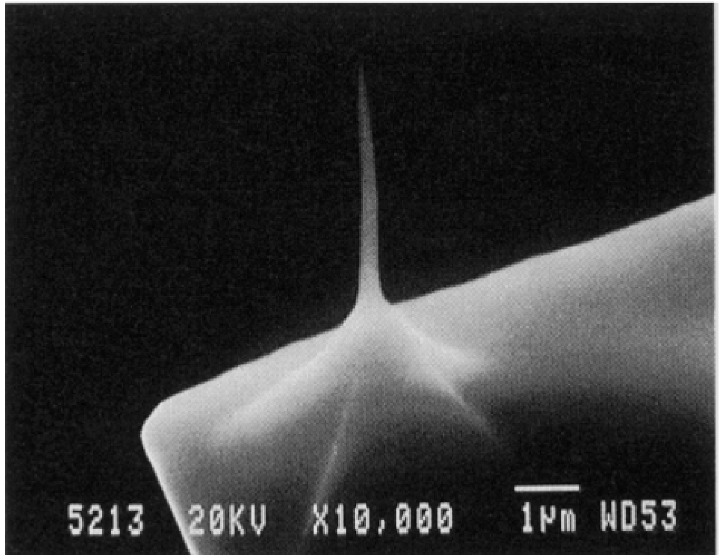
AFM tips for various problems



common tips are typically Si_3N_4 pyramids
size: 5 µm
tip radius: 20-50 nm



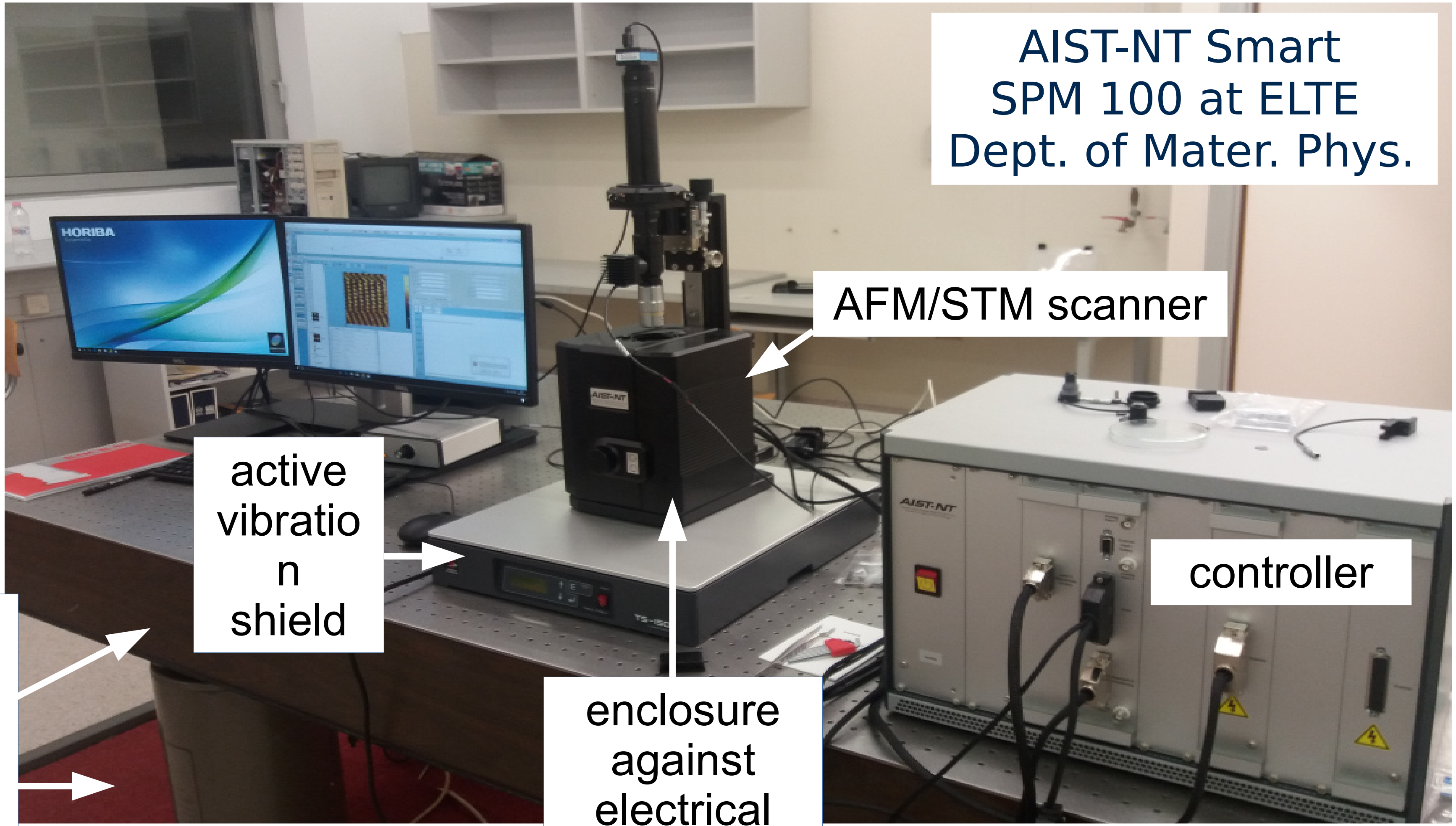
conical tips
base radius: 3-6 µm
height: 10-30 µm
tip radius: 10-20 nm.



whisker type tips have high aspect ratio
height: 1.5-2 µm
tip radius: 10 nm.

Atomic force microscopy

Vibration shield



AIST-NT Smart
SPM 100 at ELTE
Dept. of Mater. Phys.

AFM/STM scanner

controller

active
vibratio
n
shield

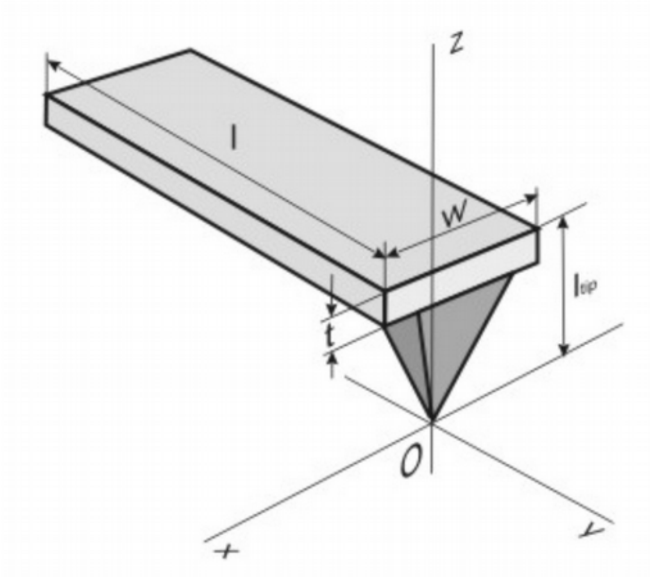
enclosure
against
electrical
and sound
waves

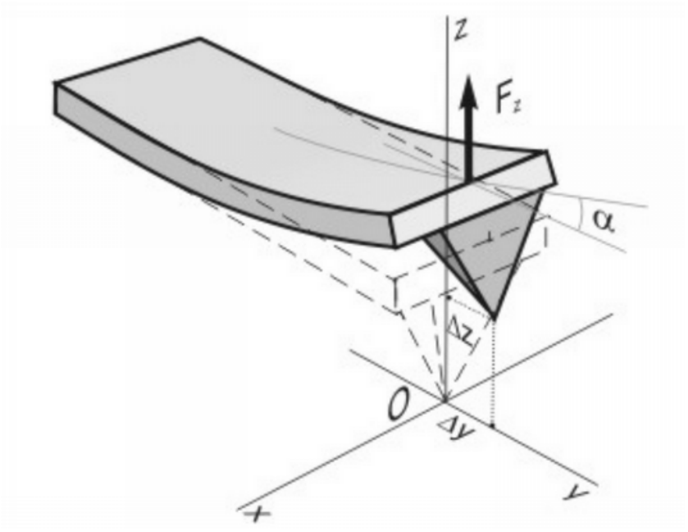
passive vibration shield:

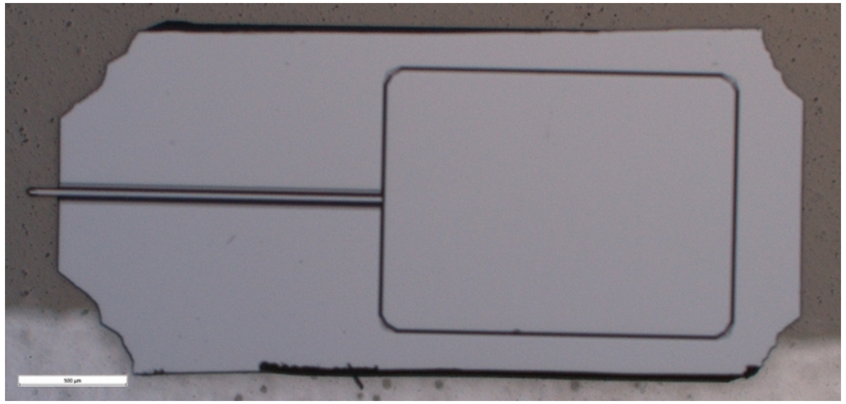
vibration free, high mass
desk on elastic or air
stand
vibration free basement

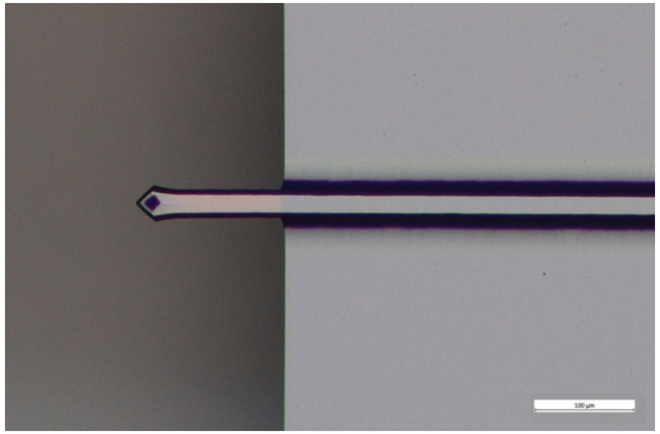
Atomic force microscopy

AFM cantilever: elastic slab









[V. L. Mironov: Fundamentals of scanning probe microscopy]

Contact force is in the range of 0.1-100 nN

Atomic force microscopy

Elastic behavior of the cantilever:

Quasi-static cantilever → **Contact mode**
constant force or constant height
(Direct mechanical interaction between the tip and the surface. Fracture of the tip and damage of the samples surface may occur.)

Oscillating cantilever → **Oscillatory modes**
non-contact mode,
tapping mode (semi-contact mode)

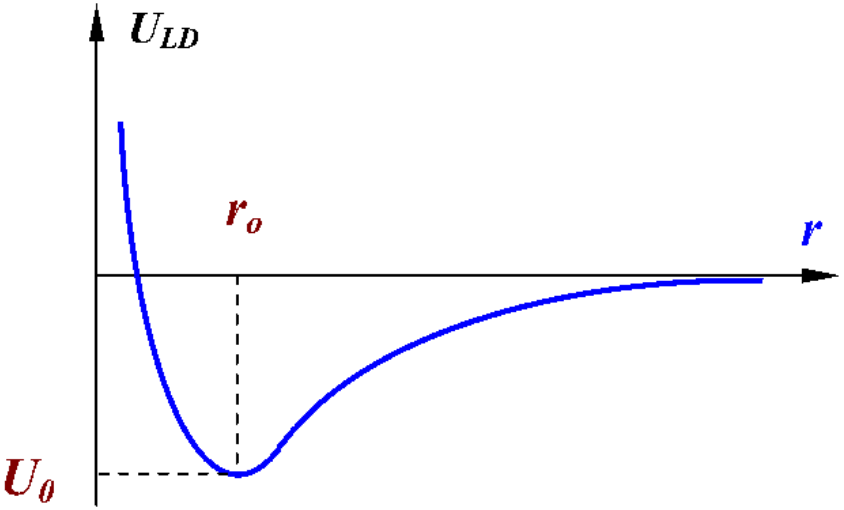
$$\omega_0 = \frac{1.029t}{l^2}\sqrt{\frac{E}{\rho}}$$

vertical vibration
of the cantilever

amplitude and phase variation is measured

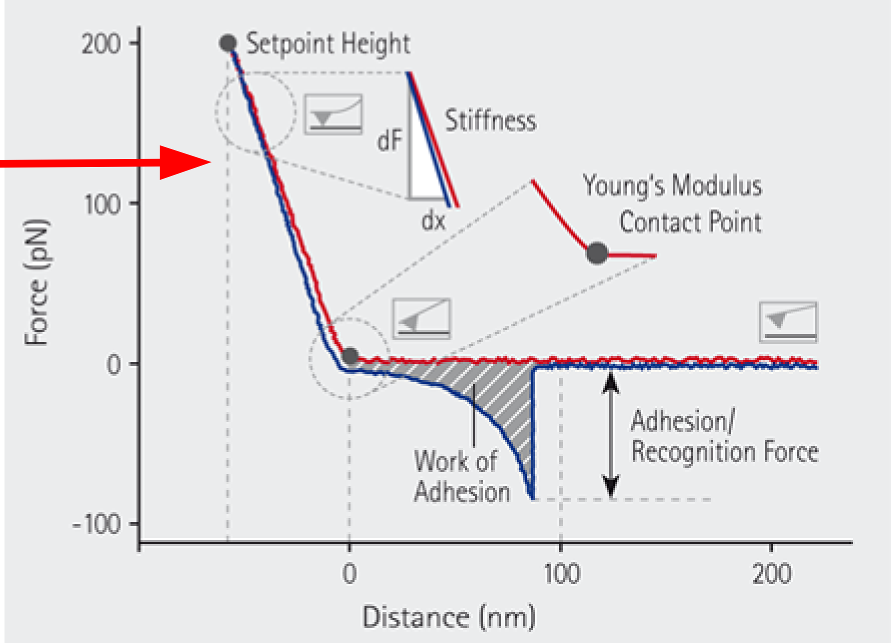
Atomic force microscopy

Sample tip interaction: AFM tip is attracted by the sample at large distances and repelled at small distances.



force curve and info on adhesion can be measured

lateral force components also exist for rough surfaces



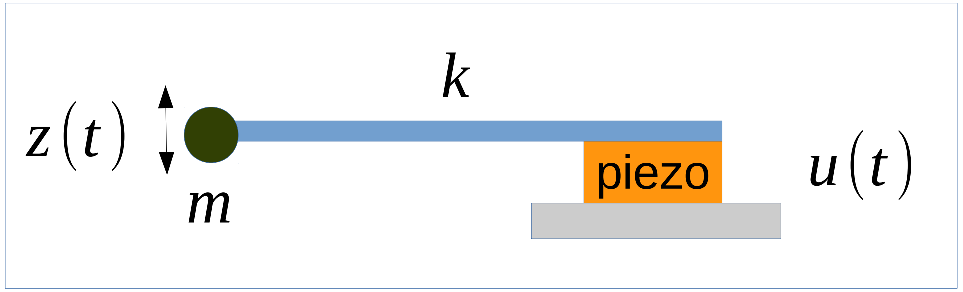
Images: either topographic or related to local sample properties

Atomic force microscopy

Oscillatory AFM techniques

Cantilever periodically vibrated by a piezo stage

$$m\ddot{z}+\gamma\dot{z}+\left(k-F'(z)\right)\cdot z=k\,u_0\cos(\omega t)$$



Non-contact mode:
oscillation with small amplitude (~1 nm)
linear approximation is valid

$$\longrightarrow\quad \ddot{z}+\frac{\omega_0}{Q}\dot{z}+\left(\omega_0^2-\frac{F'}{m}\right)\cdot z=\omega_0^2u_0\cos(\omega t)$$

Resonance curve shifts because of the F’ force gradient

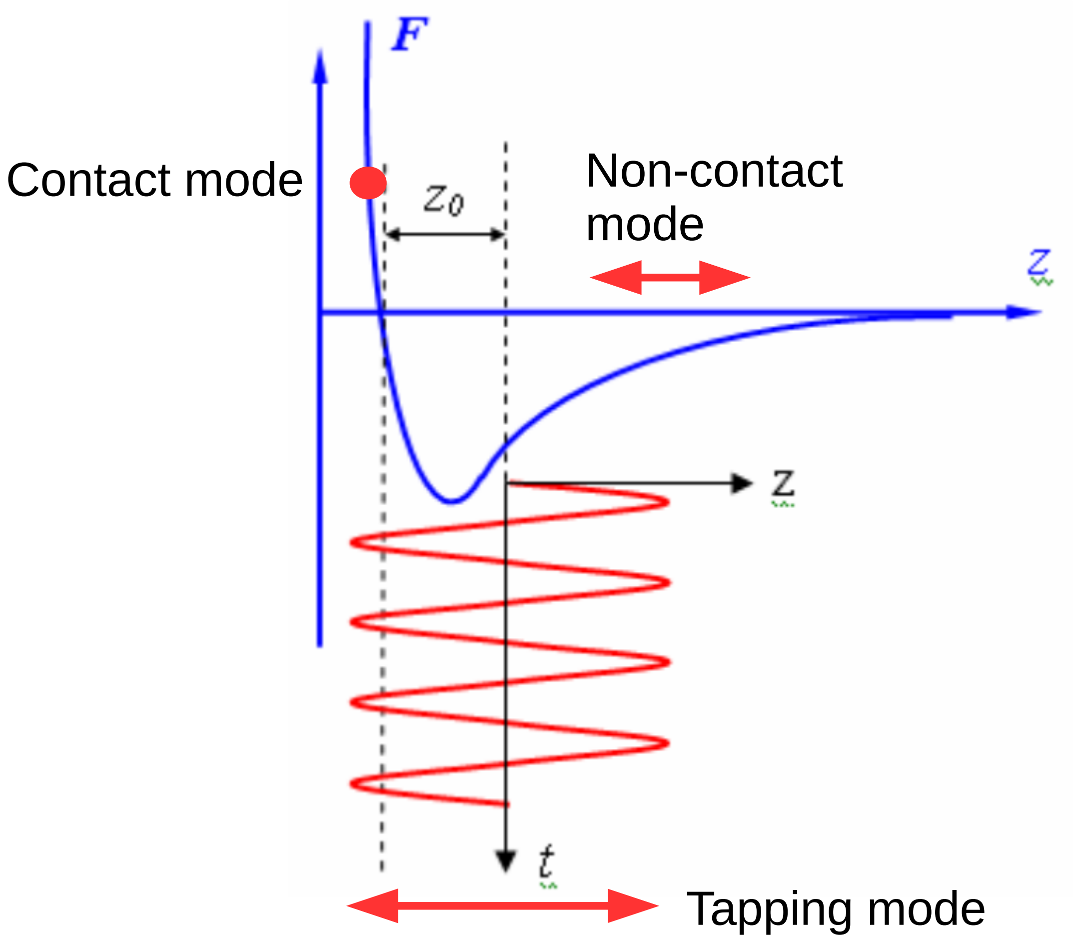
$$A(\omega)=\frac{u_0\,\omega_0^2}{\sqrt{(\omega_0^2-\omega^2-F'/m)^2+\omega^2\,\omega_0^2/Q^2}}$$

amplitude shift

$$\phi(\omega)=\arctan\left(\frac{k}{QF'}\right)\approx\frac{\pi}{2}-\frac{QF'}{k}$$

phase shift

Atomic force microscopy



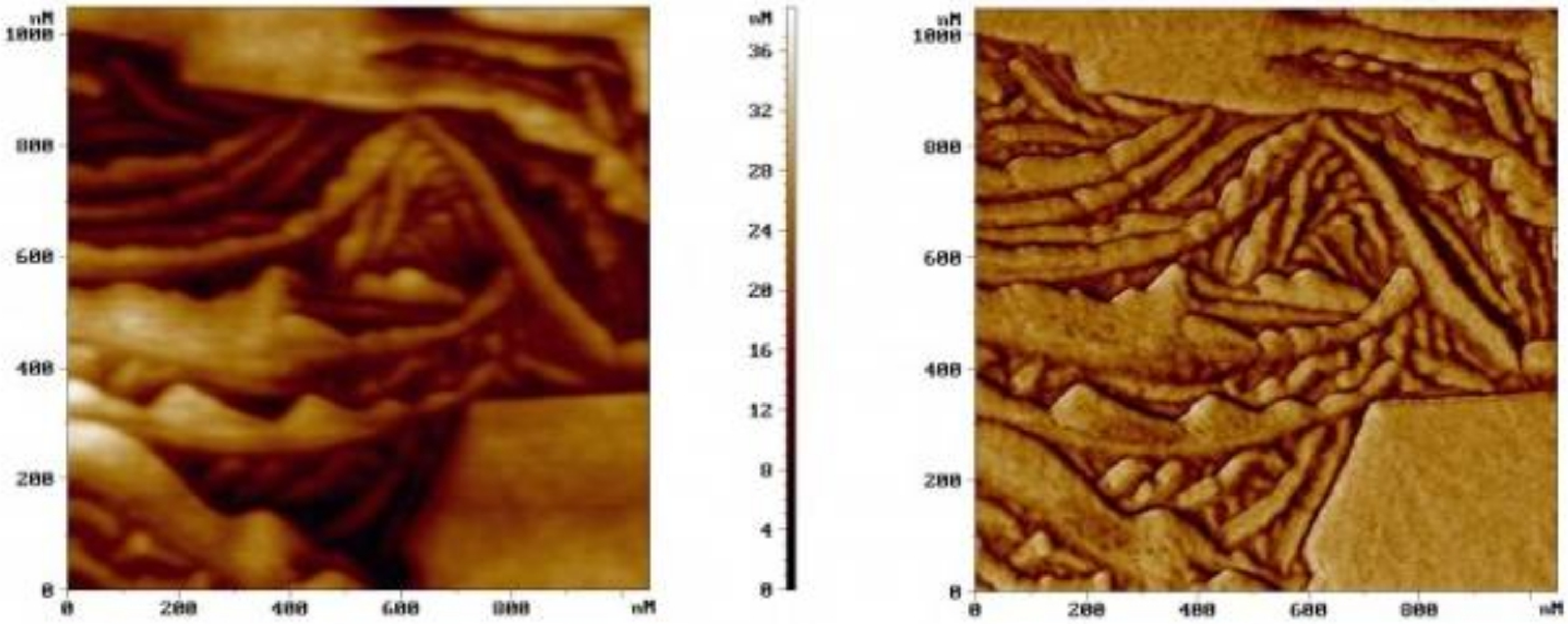
Tapping mode:
oscillation with larger amplitude (~20 nm)

No simple analytical description, but this mode is used most widely for general surface characterization

More sensitive to surface features than non-contact mode, but less destructive than contact mode

Atomic force microscopy

AFM image of polythene sample in tapping mode



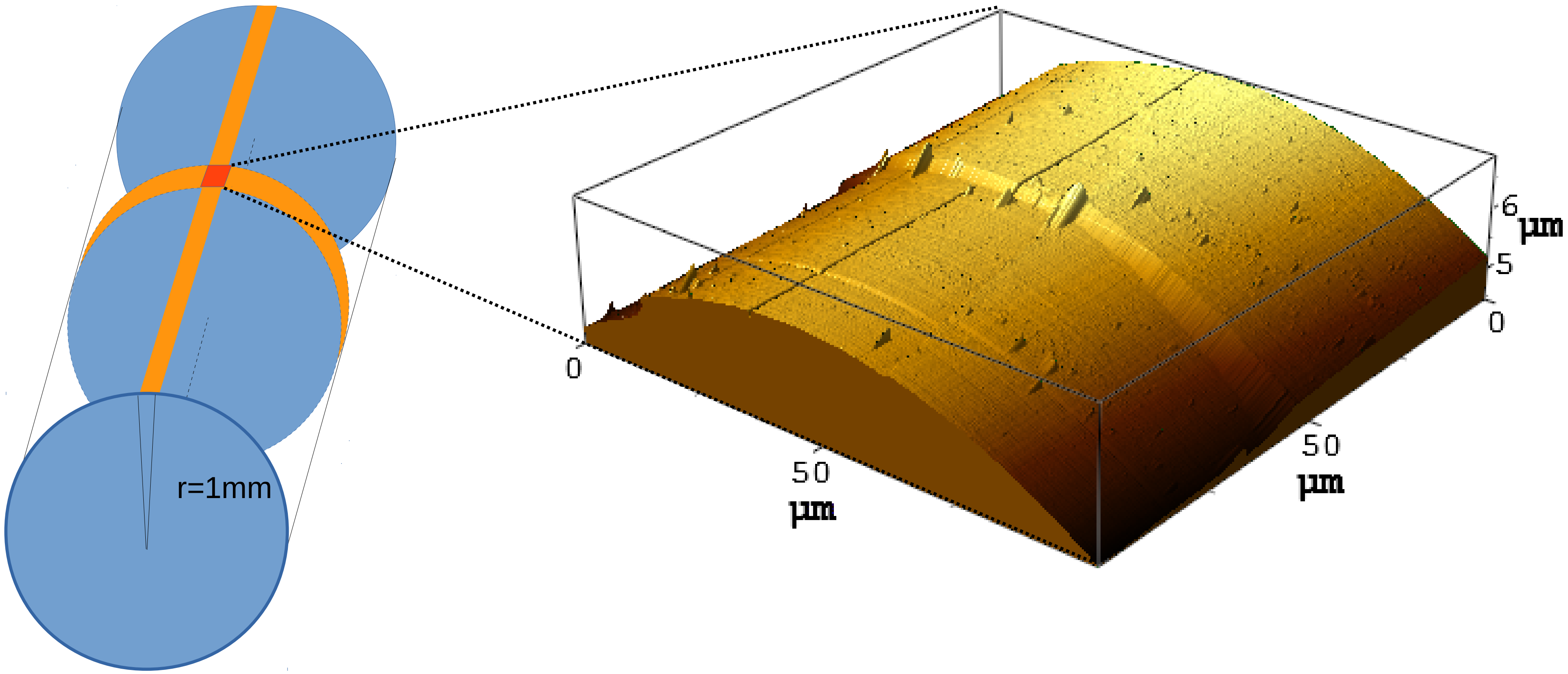
surface topography (from amplitude)

phase contrast

[V. L. Mironov]

Atomic force microscopy

Scanning range: AFM image of a deformed Vit1b BMG cylinder in tapping mode

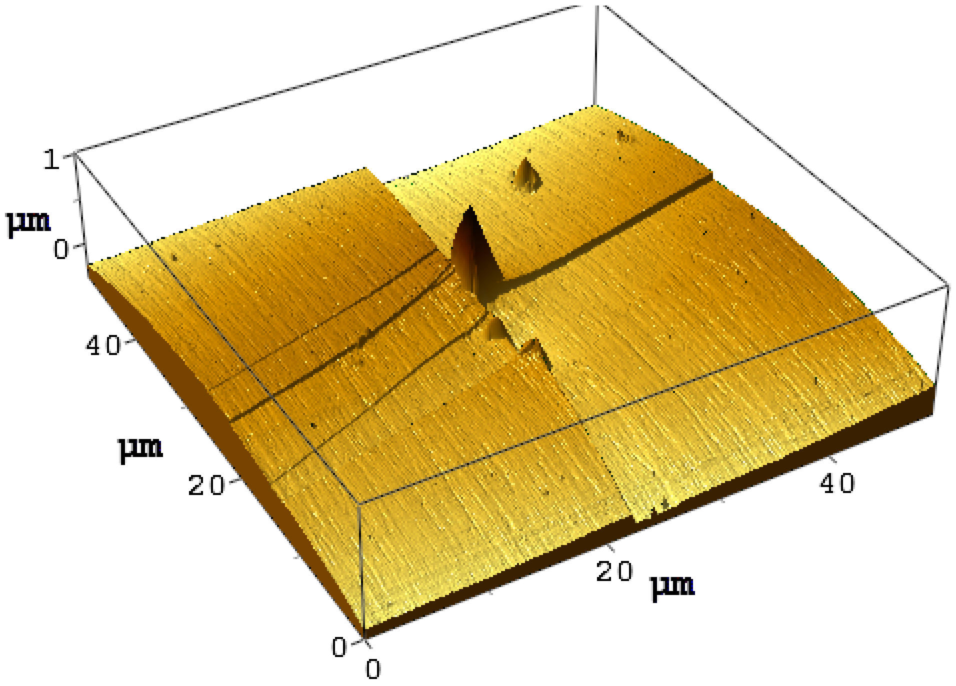


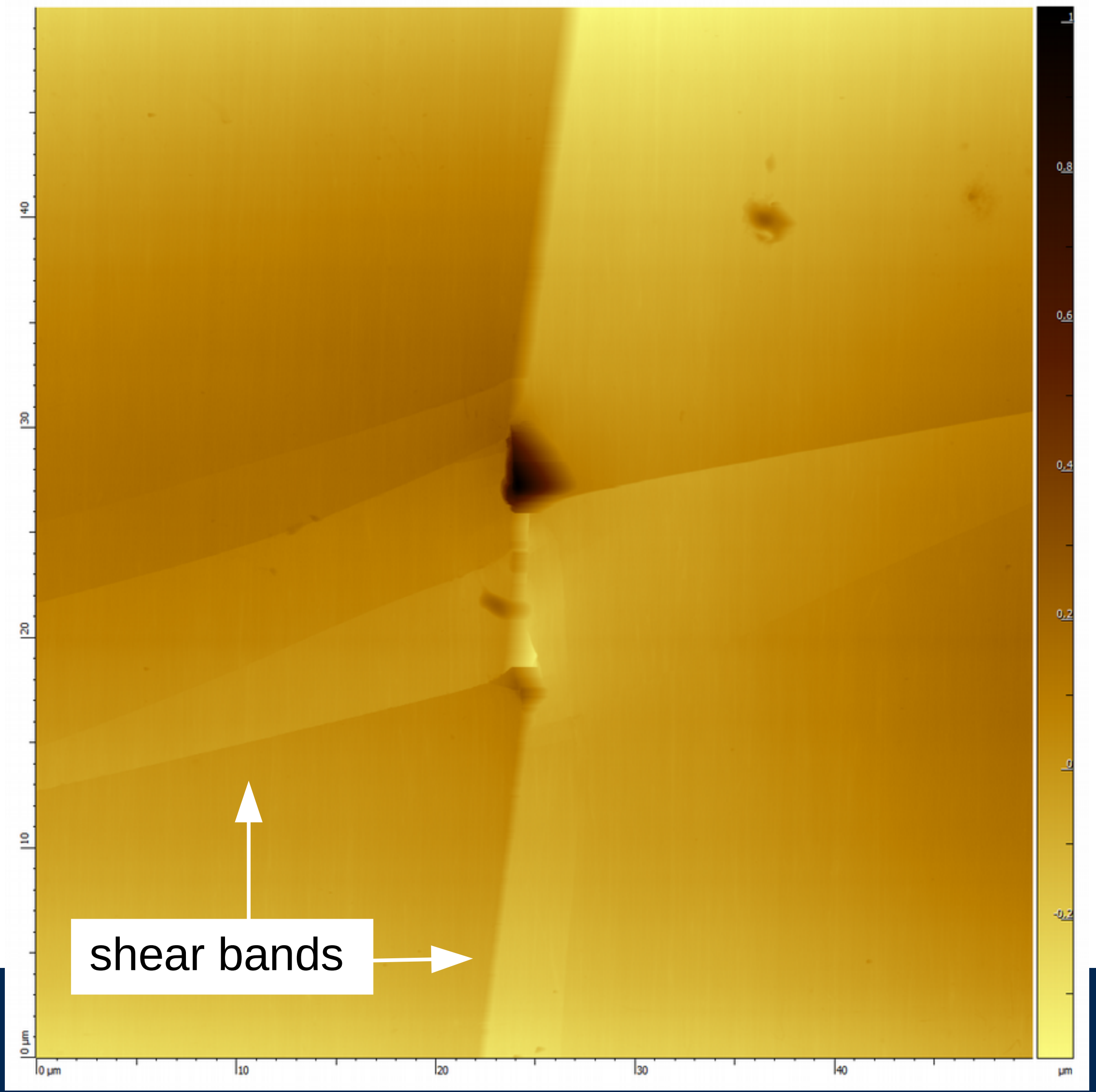
<u>piezo stage</u>
X: 100 µm
y: 100 µm
z: 10 µm

<u>motorized stage</u>
x: 5000±1
y: 5000±1
z: 15000±1
(in µm)

Atomic force microscopy

AFM image of shear bands in tapping mode





Atomic force microscopy

Single pass techniques:

- Scanning tunneling microscopy (STM)
- Atomic force microscopy (AFM)
  - contact mode + force curve measurement
  - semi-contact mode (tapping mode)
  - non-contact mode
- Lateral force microscopy (LFM)

Double pass techniques:

- 1st pass: height profile in AFM mode

- 2nd pass: scan with constant distance above the surface, where direct interaction (van der Waals forces) between the tip and the sample can be separated from other (electric or magnetic) forces

Electric Force Microscopy (EFM)

Double pass techniques using an AFM tip with conductive coating

- electric tip-sample interaction is used to collect information
- potential between the tip and the sample varies periodically
- sample is a thin layer of material on a conducting substrate
- synchronous detection of mechanical oscillation at 2ω
- van der Waals forces do not have contribution to the 2ω oscillation

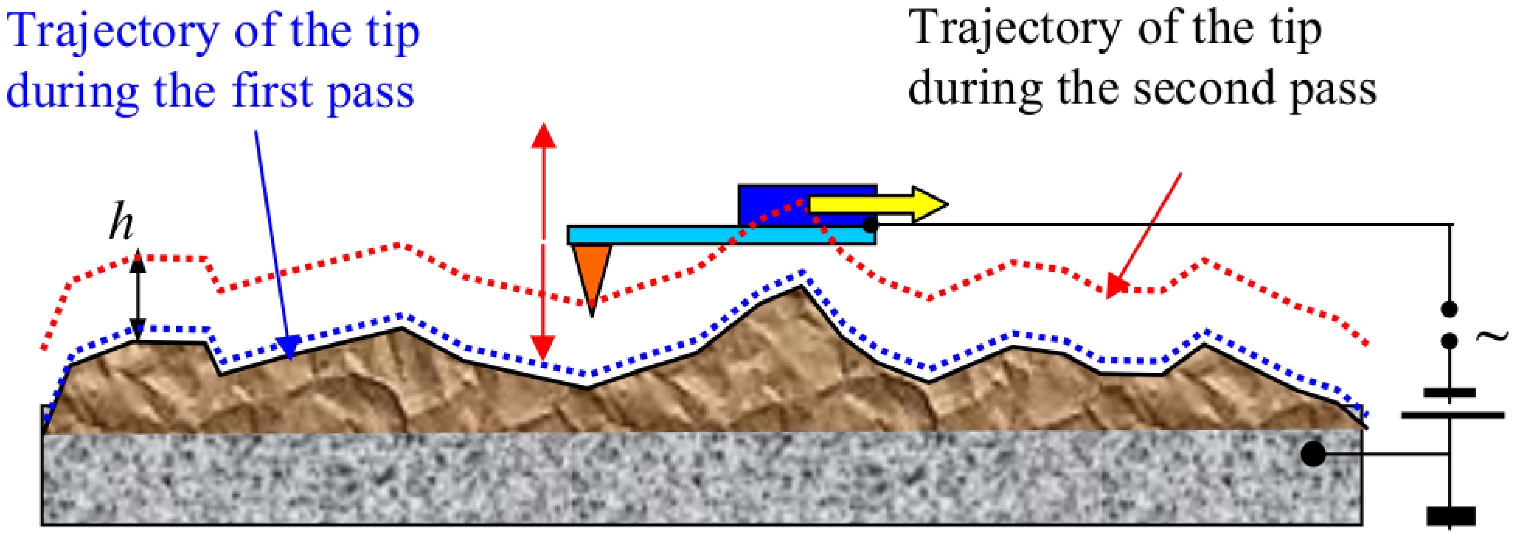
$$U = U_0 + U_1 \cdot \sin(\omega t) - \phi(x, y)$$

$$F = grad(E) \qquad E = C U^2/2$$

$$F_z = \frac{\partial C}{\partial z} \cdot \left(-\frac{1}{2}\left[(U_0 - \phi(x,y))^2 + U_1^2\right] - \left[U_0 - \phi(x,y)\right] \cdot U_1 \sin(\omega t) + \frac{1}{4}\left[U_1^2 \cos(2\omega t)\right] \right)$$

Scanning Capacitance Microscopy (SCM)

Electric Force Microscopy (EFM)



Trajectory of the tip
during the first pass

Trajectory of the tip
during the second pass

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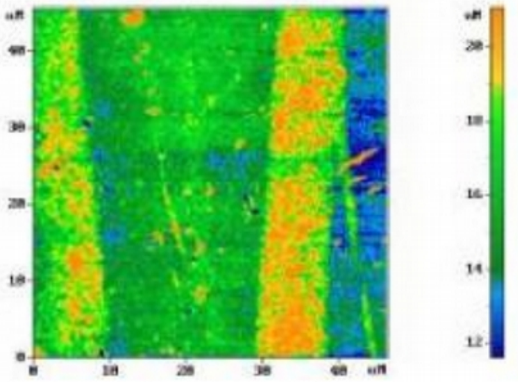
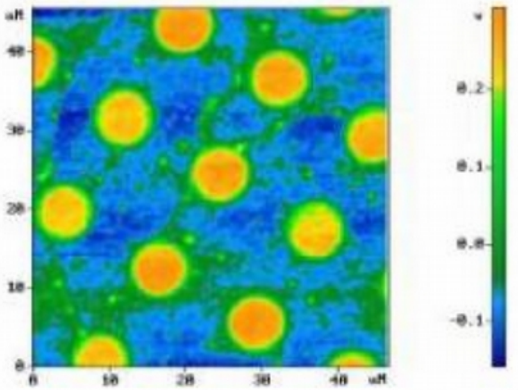
of scanning probe microscopy]



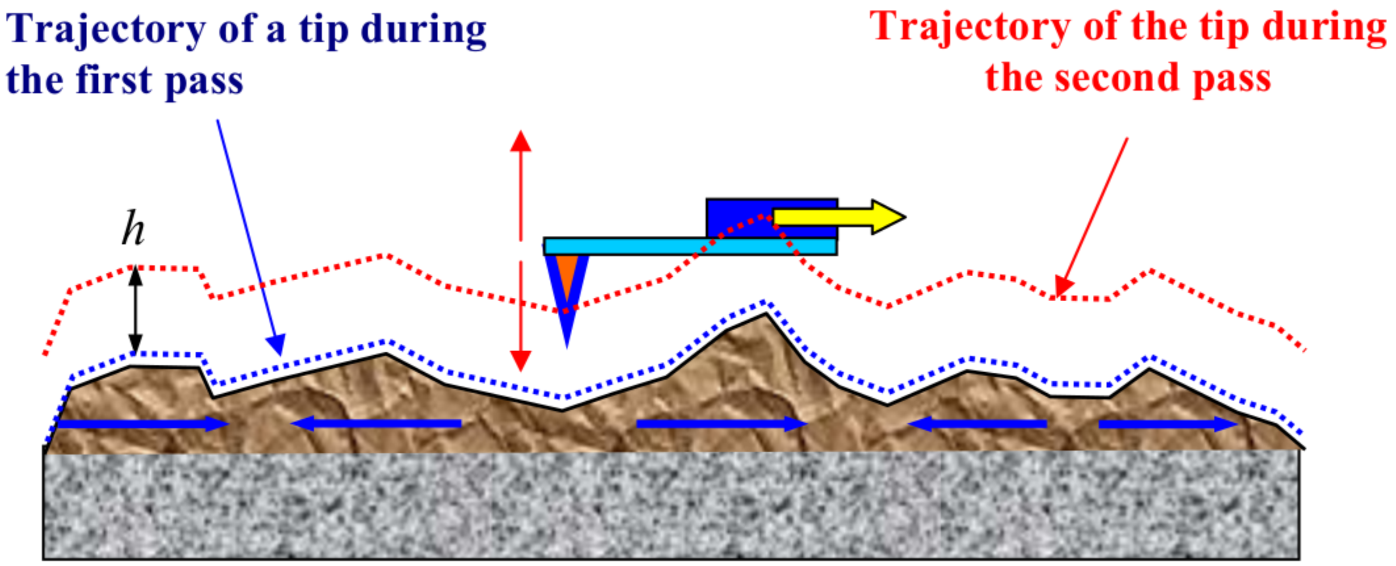
topography



azobenzene
molecules
with strong
dipole moment

Magnetic Force Microscopy (MFM)

Double pass techniques using an AFM tip with magnetic coating
Invented by Y. Martin and H.K.Wickramasinghe in 1987



$$F_z = \int_{V_{layer}} \left(M_x \frac{\partial H_x}{\partial z} + M_y \frac{\partial H_y}{\partial z} + M_z \frac{\partial H_z}{\partial z} \right) dV$$

Static technique
- 1 pass: tapping mode
- 2 pass: h should be large to neglect van der Waals forces comparing to magnetic forces

Oscillatory technique
- 1 pass: tapping mode
- 2 pass: amplitude and phase is modified by the magnetic force gradient of the sample

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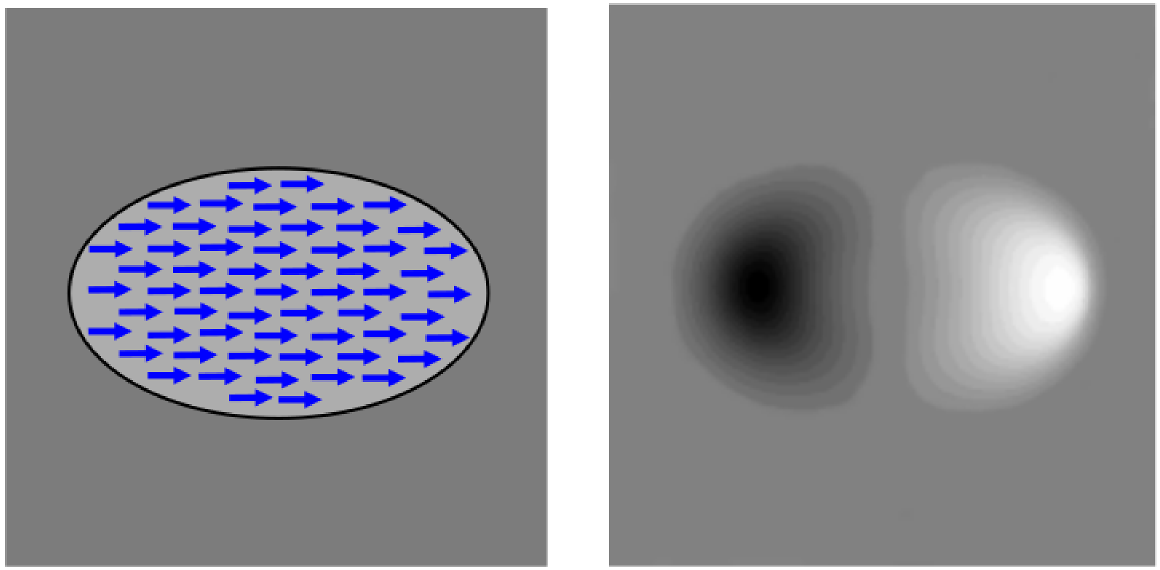
Magnetic Force Microscopy (MFM)

magnetic nanoparticle



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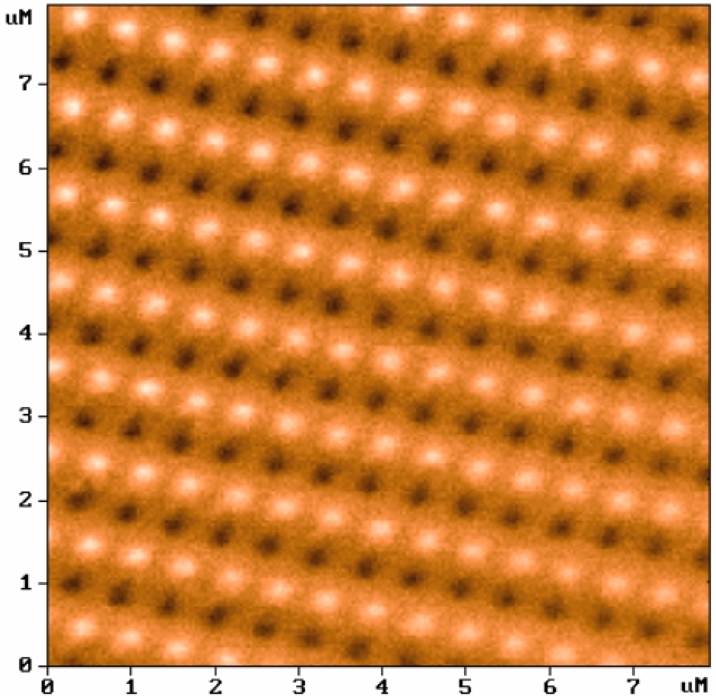

Fe-Cr magnetic nanoparticles

Acknowledgement

Majority of the content of this presentation is from the textbook of V. L. Mironov (see below)

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Thank you for your attention!

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Experimental methods of condensed materials
23 Nov 2021.