The scanning probe microscope: an essential tool for nanotechnologies

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Outline

- A brief history of Scanning Probe Microscopy (SPM)
- **Scanning Tunneling Microscopy (STM)**
- Tunneling: overview of theories
- STM examples
- Atom manipulation by STM
- Scanning Tunneling Spectroscopy (STS)
- **Atomic Force Microscopy (AFM)**
- AFM examples
- …other SPM techniques?

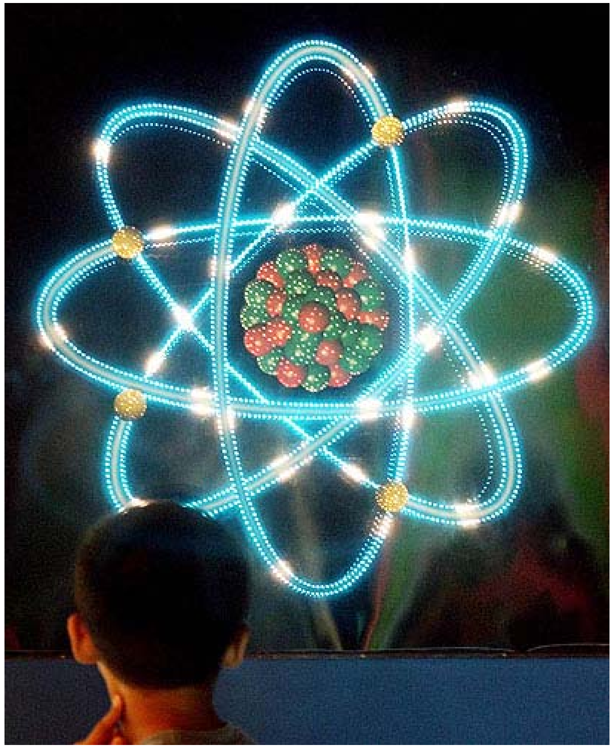
Seeing atoms

ATOM

ατομος «atomos» →

"that cannot be divided"

is it possible to "SEE" atoms?



Today:

- **direct space techniques: Transmission Electron Microscopy (TEM), Scanning Probe Microscopies (STM, AFM)**

- **indirect techniques: e.g. XRD**

A brief history of SPM

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1951: FIELD ION MICROSCOPE (E. Muller), used to image the arrangement of atoms at the surface of a sharp metal tip

1959: FEYNMAN'S visonary talk "There's plenty of room at the bottom"

"We have friends in other fields---in biology, for instance. ……They say `What *you* should do in order for *us* to make more rapid progress is to **make the electron microscope 100 times better**."

…

It is very easy to answer many of these fundamental biological questions; **you just *look at the thing*** !"

…

"But I am not afraid to consider the final question as to whether, ultimately---in the great future---we can arrange the atoms the way we want; the very *atoms*, all the way down! **What would happen if we could arrange the atoms one by one the way we want them ?**"

R. Feynman, There's plenty of room at the bottom, APS, December 1959

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 external adjustable vacuum gap. The observation of vacuum tunneling is establi: dependence of the tunneling resistance on the width of the gap. The expe simultaneous investigation and treatment of the tunnel electrode surfac

PACS numbers: 73.40.Gk

1981: first STM results in laboratory

1982: measurement of tunneling current between a surface and a tip

G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel , APL 140, 178 (1982)

$$R\,(s)\alpha\ \exp(A\phi^{1/2}s),$$

exponential dependence on distance

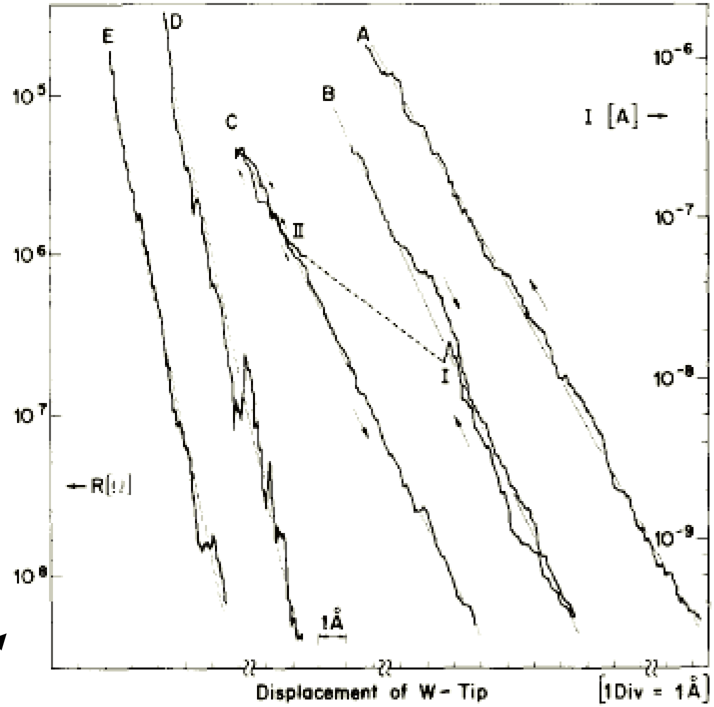

FIG. 2. Tunnel resistance and current vs displacement of Pt plate for different surface conditions as described in the text. The displacement origin is arbitrary for each curve (except for curves B and C with the same origin). The sweep rate was approximately 1 Å/s. Work functions $\phi = 0.6$ eV and 0.7 eV are derived from curves A, B, and C, respectively. The instability which occurred while scanning B and resulted in a jump from point I to II is attributed to the release of thermal stress in the unit. After this, the tunnel unit remained stable within 0.2 Å as shown by curve C. After repeated cleaning and in slightly better vacuum, the steepness of curves D and E resulted in $\phi = 3.2$ eV.

Surface Studies by Scanning Tunneling Microscopy

G. Binning, H. Rohrer, Ch. Gerber, and E. Weibel
IBM Zurich Research Laboratory, 8803 Rüschlikon-ZH, Switzerland
(Received 30 April 1982)

Surface microscopy using vacuum tunneling is demonstrated for the first time. Topographic pictures of surfaces on an *atomic scale* have been obtained. Examples of resolved monoatomic steps and surface reconstructions are shown for (110) surfaces of $CaIrSn_4$ and Au.

PACS numbers: 68.20.+t, 73.40.Gk

1982: Invention of the scanning tunneling microscope at IBM Zurich Laboratory
G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel, PRL 49, 57 (1982)

1986: Nobel prize to Binnig and Rohrer
see Nobel prize lecture G. Binnig, H. Rohrer, Rev. Mod. Phys. 59, 615 (1987)

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7 × 7 Reconstruction on Si(111) Resolved in Real Space

G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel
IBM Zurich Research Laboratory, 8803 Rüschlikon-ZH, Switzerland

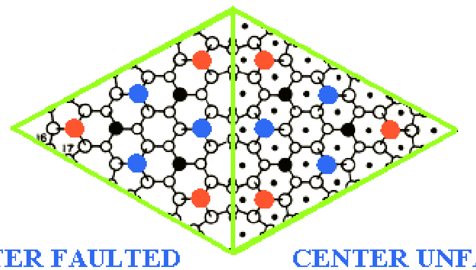
(Received 17 November 1982)

The 7×7 reconstruction on Si(111) was observed in real space by scanning tunneling microscopy. The experiment strongly favors a modified adatom model with 12 adatoms per unit cell and an inhomogeneously relaxed underlying top layer.

PACS numbers: 68.20.+t, 73.40.Gk

1983: first atomic resolution image of Si(111)7x7 surface

G Binnig, H. Rohrer, Ch. Gerber, E. Weibel, PRL 50, 120 (1983)



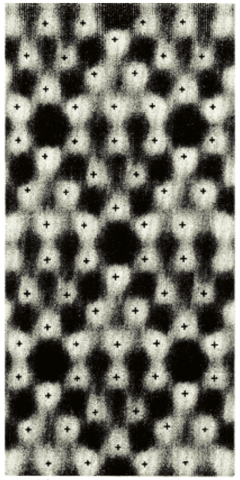


FIG. 2. Top view of the relief shown in Fig. 1 (the hill at the right is not included) clearly exhibiting th sixfold rotational symmetry of the maxima around t rhombohedron corners. Brightness is a measure of the altitude, but is not to scale. The crosses indica adatom positions of the modified adatom model (see Fig. 3) or "milk-stool" positions (Ref. 5).

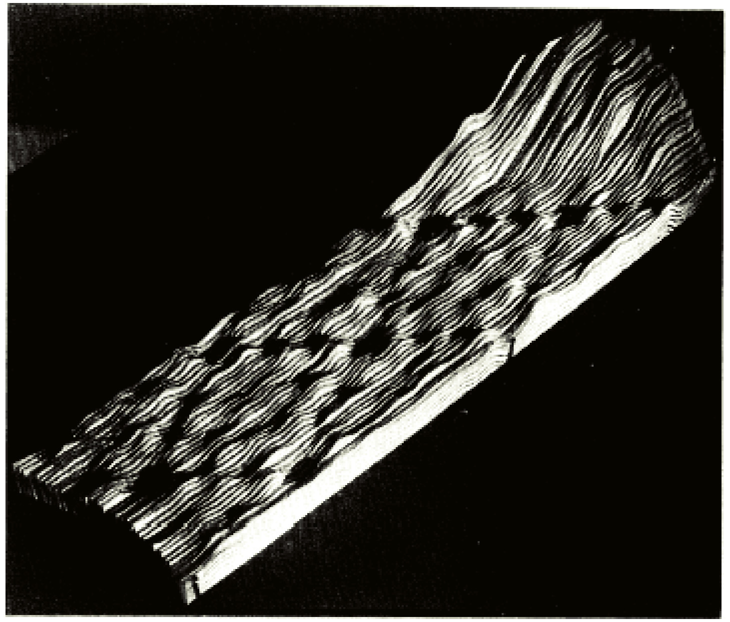


FIG. 1. Relief of two complete 7×7 unit cells, with nine minima and twelve maxima each, taken at 300 °C. Heights are enhanced by 55%; the hill at the right grows to a maximal height of 15 Å. The [$\bar{2}$11] direction points from right to left, along the long diagonal.

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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 N. As one application for this concept, we introduce a new type of microscope c: gating surfaces of insulators on an atomic scale. The atomic force microscope is the principles of the scanning tunneling microscope and the stylus profilometer. probe that does not damage the surface. Our preliminary results *in air* demonstrat tion of 30 Å and a vertical resolution less than 1 Å.

PACS numbers: 68.35.Gy

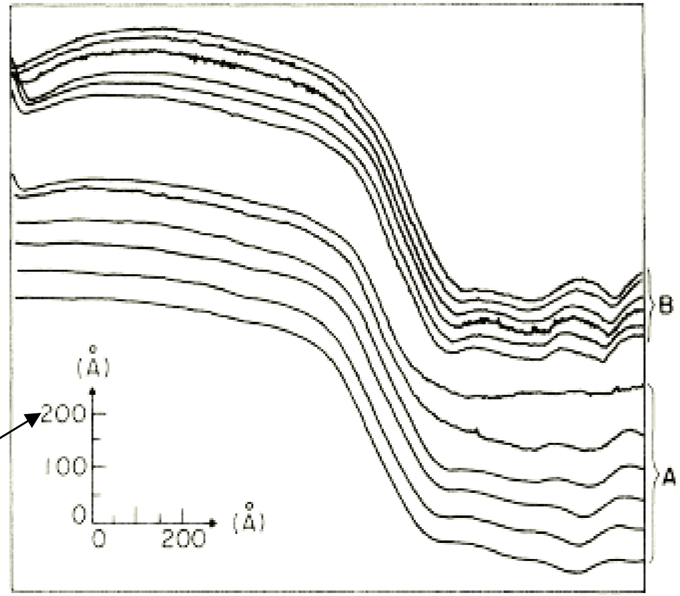


FIG. 4. The AFM traces for another area of the ceramic sample. The curves grouped under *A* were recorded with additional low-pass filtering. For this set the stabilizing force, f_0, was reduced by thermal drifts as we moved from the lowest to the highest traces of set *A*. The force f_0 is near 10^{-8} N for the highest curve. We note that the structure vanishes on the traces when the sample-to-tip force is reduced below this level. The force f_0 was reset to a higher value near 5×10^{-8} N for the traces marked *B*.

1986: Invention of Atomic Force Microscopy AFM

G. Binnig, C.F. Quate, Ch. Gerber, PRL 56, 930 (1986)

Ceramic (non-conducting) surface

2006: ~ 500 papers with STM in the title; ~ 1000 papers with AFM in the title

What is Scanning Probe Microscopy (SPM) ?

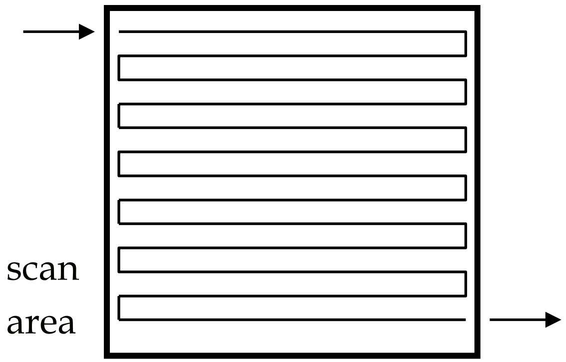
A family of microscopy forms where **a sharp probe is scanned across a surface** and some tip/sample interactions are monitored

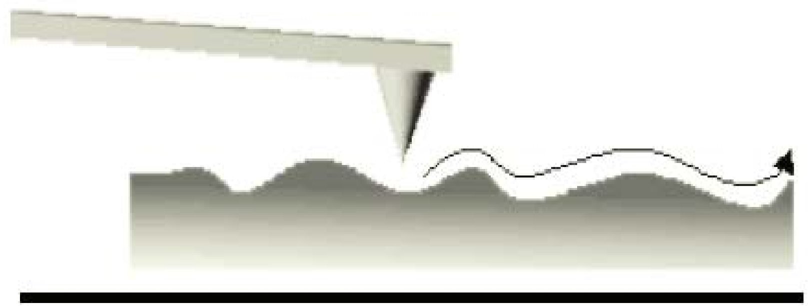
Using the interaction as feedback signal → surface morphology (or other properties, e.g. electronic) can be recovered

-**Scanning Tunneling Microscopy (STM)** (Binnig and Rohrer, 1982): **tunneling current through a vacuum gap between tip and surface**

- **Atomic Force Microscopy (AFM)** (Binnig-Quate-Gerber, 1986): **tip-surface interaction forces**

- Other SPM: **SNOM** (Scanning Near Field Optical Microscopy), **MFM** (Magnetic Force Microscopy), etc.





STM Scanning Tunneling Microscopy

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Realization of Feynman's dream?

STM can:

-"see" atoms
- measure surface electronic properties with atomic resolution
- manipulate atoms

- **Conductive nanometric tip (W, Pt-Ir, …) and surface**

- **Tunneling current (i.e. current through a vacuum gap) depends exponentially on the tip-surface distance:**

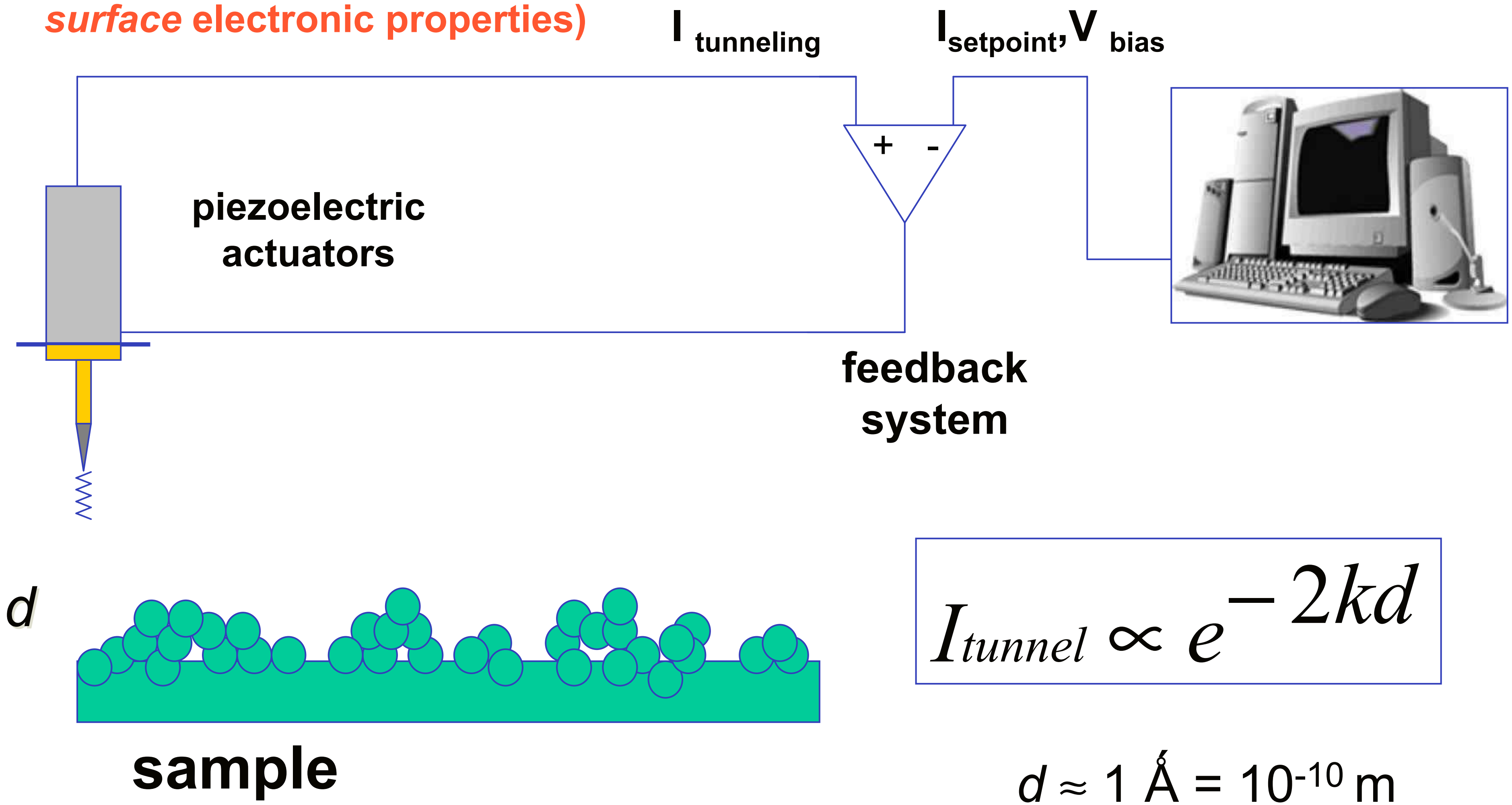
$$I_{tunnel} \propto e^{-2kd}$$

typical $k \approx 10^{10}$ m^{-1} => a change in d of 1 Å results in a change of the current of a factor of about 10 !!

→ current can be used as feedback signal to keep a constant distance from the surface
→ tip follows surface morphology

STM principle

- measurements in UHV (no contaminations, sensitivity to *surface* electronic properties)

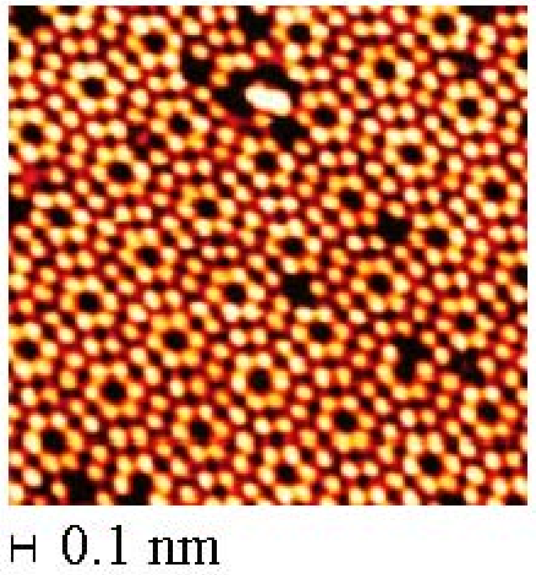


$$I_{tunnel} \propto e^{-2kd}$$

$d \approx 1$ Å $= 10^{-10}$ m

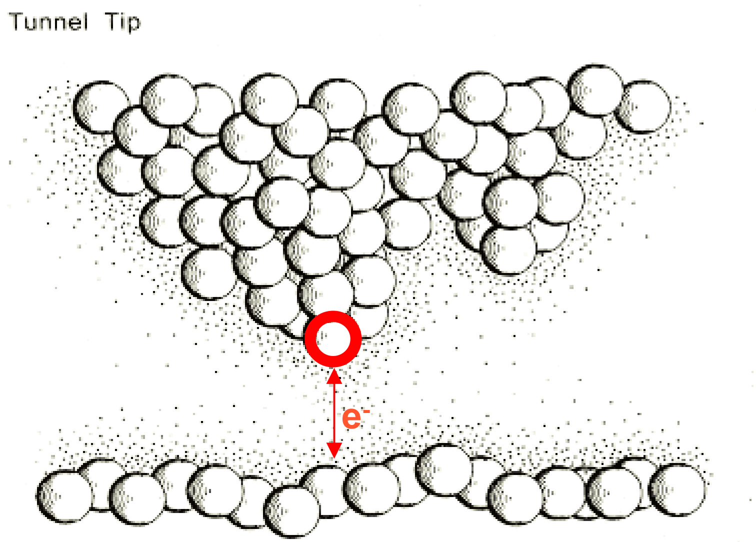
Surface investigation with high resolution
→ on flat, ordered surfaces: atomic resolution !

Si(111)7x7 reconstructed surface



- Lateral resolution ~ 1 Å
if surface is rough: resolution limited by tip curvature radius (~ nm)

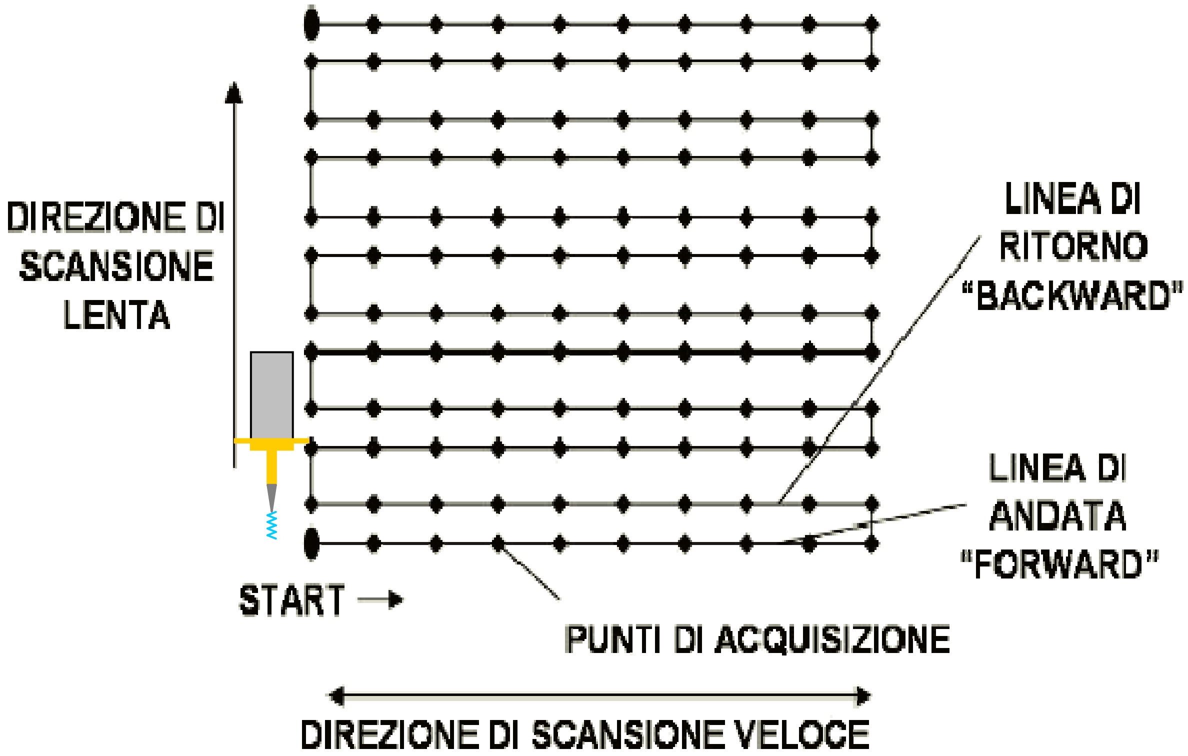
- Vertical resolution ~ 0.1 Å



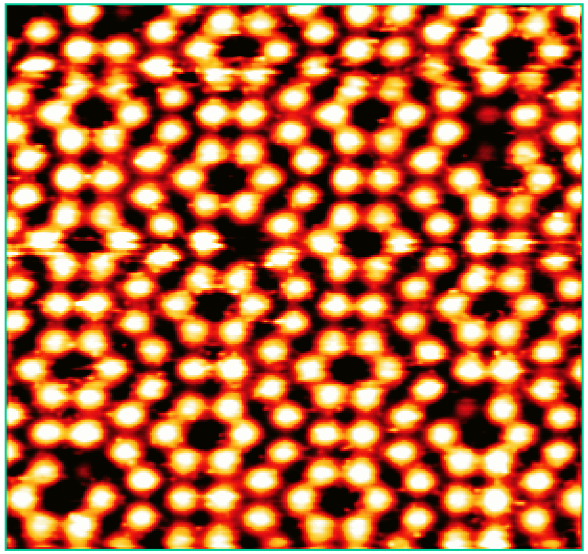
$$I_{tunnel} \propto e^{-2kd}$$

only the atom which is closest to the surface significantly contributes to tunneling current → atomic resolution

STM image acquisition



Si(111)7x7



10 nm

Usually:

bias: 0.1 V-few V

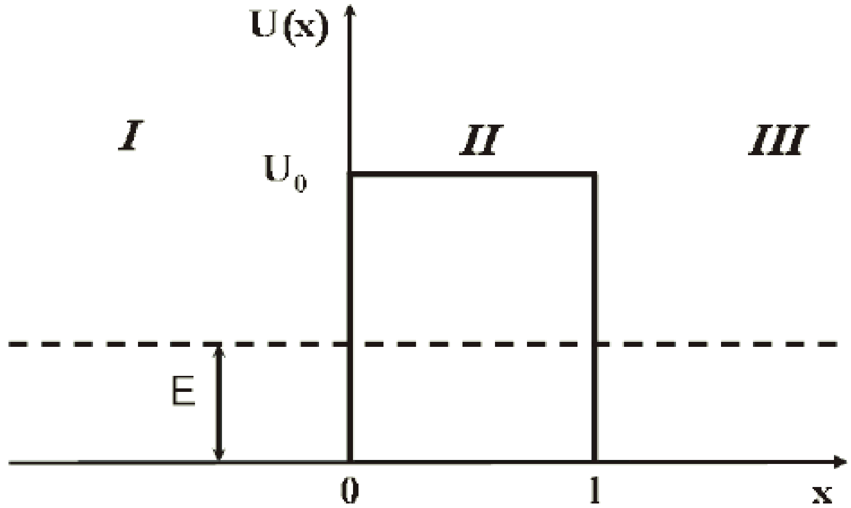
tunneling current: pA- nA

Quantum theory of tunneling

Schrodinger equation for a 1D energetic barrier:

if E < U_0 the barrier is classically impenetrable

$$\hat{H}\psi(x) = E\psi(x)$$



$$\begin{cases} \dfrac{d^2\psi(x)}{dx^2} + \dfrac{2m}{\hbar^2}E\psi(x) = 0 & x < 0 \vee x > l, \\ \dfrac{d^2\psi(x)}{dx^2} + \dfrac{2m}{\hbar^2}(E - U_0)\psi(x) = 0 & 0 < x < l. \end{cases}$$

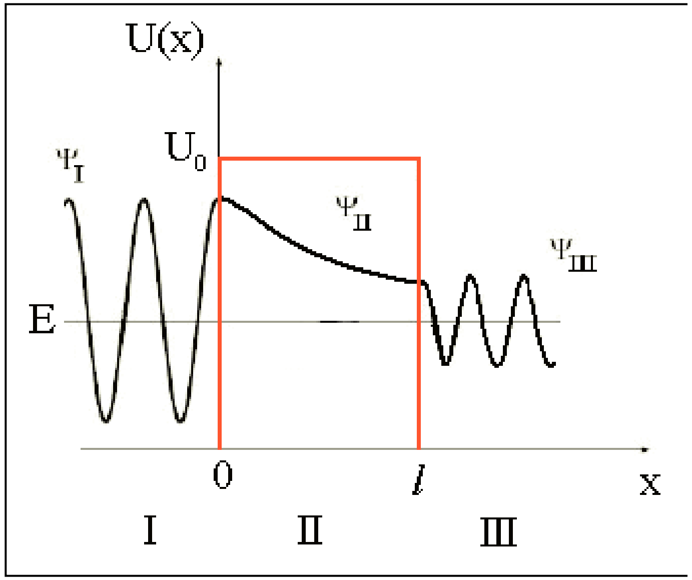
$$\begin{cases} \psi_I(x) = A\exp(ik_0x) + B\exp(-ik_0x) & x < 0 \\ \psi_{III}(x) = C\exp(ik_0x) & x > l \end{cases} \quad \text{con} \quad k_0 = \frac{\sqrt{2mE}}{\hbar}.$$

$$\psi_{II}(x) = \alpha\exp(kx) + \beta\exp(-kx) \qquad 0 \le x \le l \ \text{con} \quad k = \sqrt{\left(\frac{2m}{\hbar^2}\right)(U_0 - E)}.$$

Density of probability current

transmitted $j_t = \frac{-i\hbar}{2m}\left[\psi_3^* \frac{d\psi_3}{dz} - \psi_3 \frac{d\psi_3^*}{dz}\right] = \frac{\hbar k}{m}|C|^2$

incident $j_{inc} = \frac{-i\hbar}{2m}\left[\psi_1^* \frac{d\psi_1}{dz} - \psi_1 \frac{d\psi_1^*}{dz}\right] = \frac{\hbar k}{m}|A|^2$



Transmission probability

$$T = \frac{j_t}{j_{inc}} = \frac{|C|^2}{|A|^2}$$

Hp: $\exp(-2kl) << 1$ **wide and high barrier**

$$T = \frac{16k^2k_0^2}{(k^2+k_0^2)}\exp(-2kl) = \frac{16E(U_0-E)}{U_0^2}\exp(-2kl)$$

$$k = \sqrt{\left(\frac{2m}{\hbar^2}\right)(U_0-E)}.$$

Wavefunction in vacuum (i.e. inside the barrier)

if $\exp(-2kl) << 1$

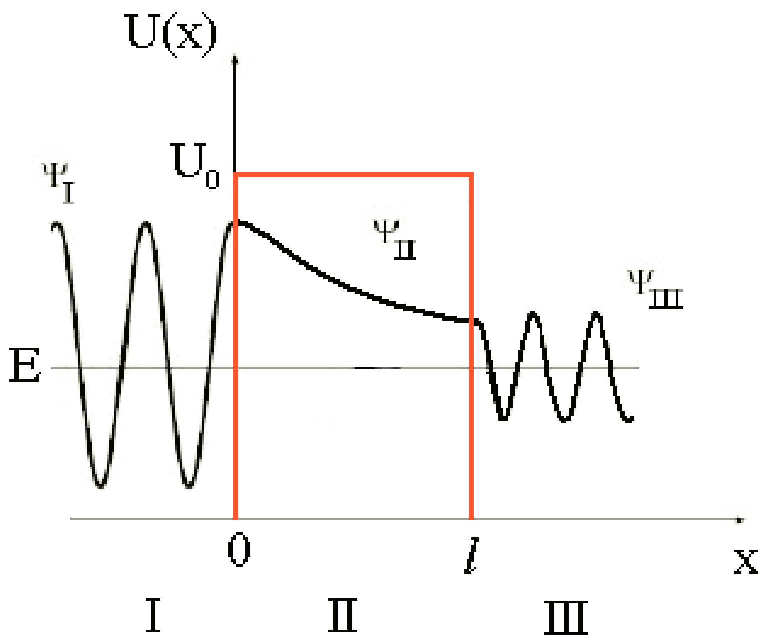
$$\psi(z) = \psi(z=0)\ e^{-kz}$$

$$k^2 = \frac{2m}{\hbar^2}(U_0 - E)$$

$$|\psi(z)|^2 = |\psi(0)|^2\ e^{-2kz}$$

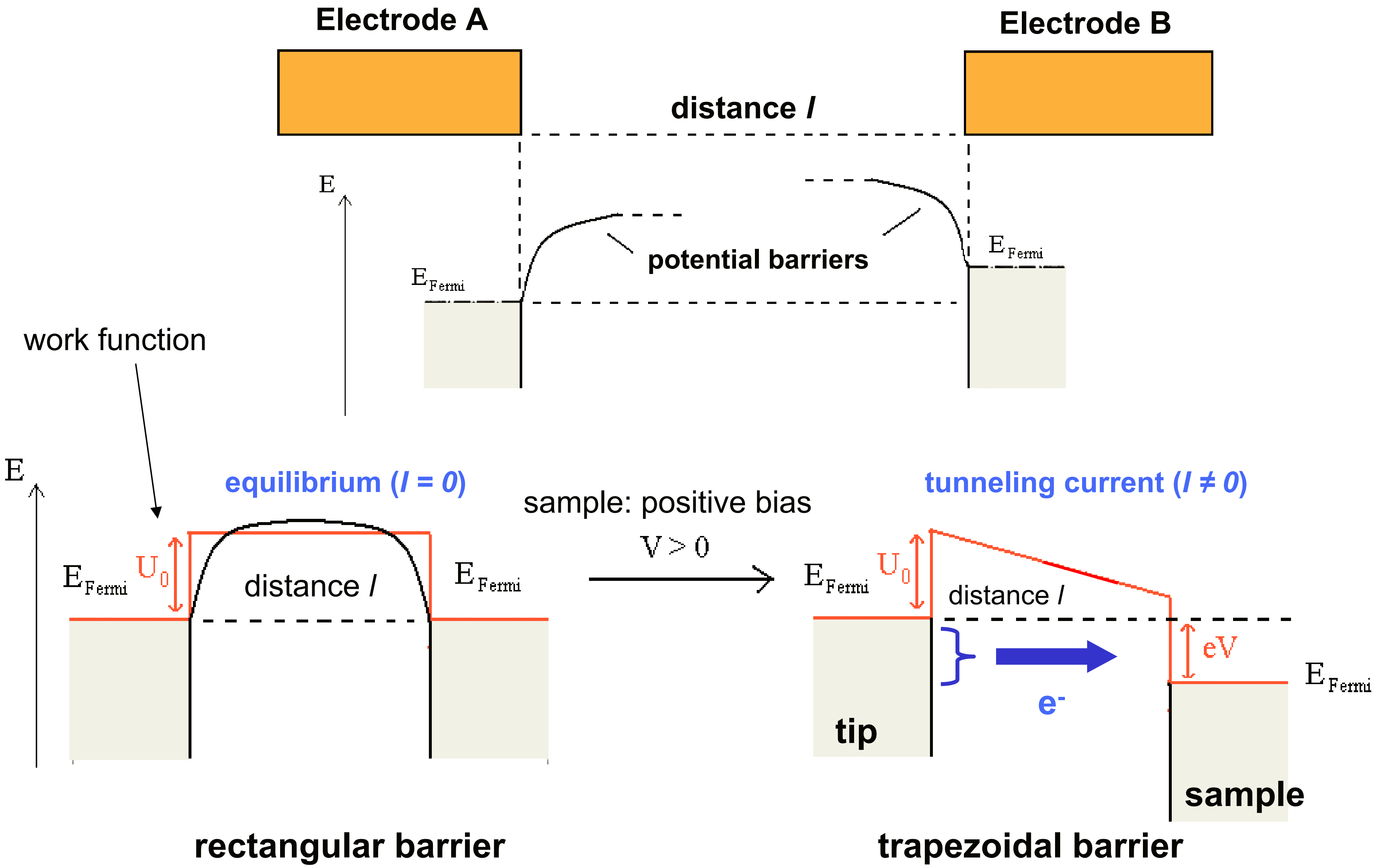
when $z = l$

$$|\psi(z=d)|^2 = |\psi(0)|^2\ e^{-2kd}$$ **exponential decay**



Current carried by 1 electron from left to right: $I \propto |\psi(0)|^2 e^{-2kl}$

Scanning Tunneling Microscope



Summing tunneling current over all sample states between 0 (E_{Fermi}) and eV:

energy conservation

$$I(l) \propto \sum_{n,m} \int_0^{eV} |\psi_n(0)|^2 \exp(-2kl)\delta(E - E_n^I)\delta(E - E_m^{III} - eV)dE.$$

sample local electron density of states (LDOS)

$$\rho_I(x, E) = \sum_n |\psi_n(x)|^2 \delta(E - E_n^I)$$

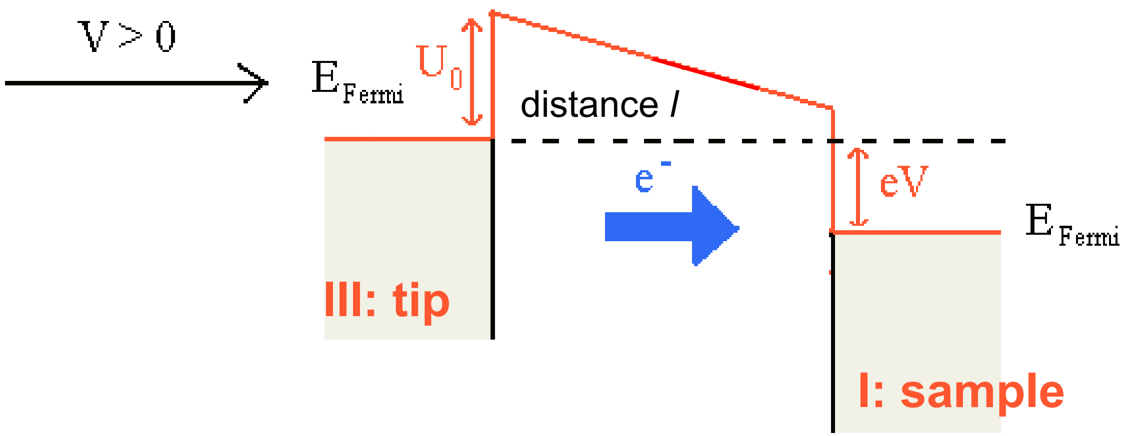
tip electron density of states

$$\rho_{III}(E) = \sum_m \delta(E - E_m^{III}),$$

$$\boxed{I(l) \propto \int_0^{eV} \rho_I(0, E)\rho_{III}(E - eV)\exp(-2kl)dE.}$$

Positive bias to the sample: electrons tunneling from tip to sample
→ probing of UNOCCUPIED sample electron states

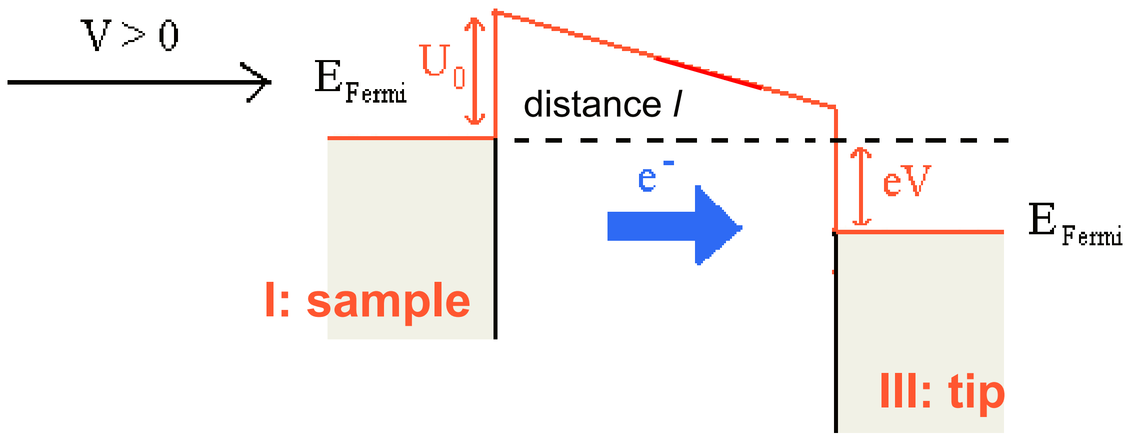
sample



$$I(l) \propto \int_0^{eV} \rho_I(0,E)\rho_{III}(E-eV)\exp(-2kl)dE.$$

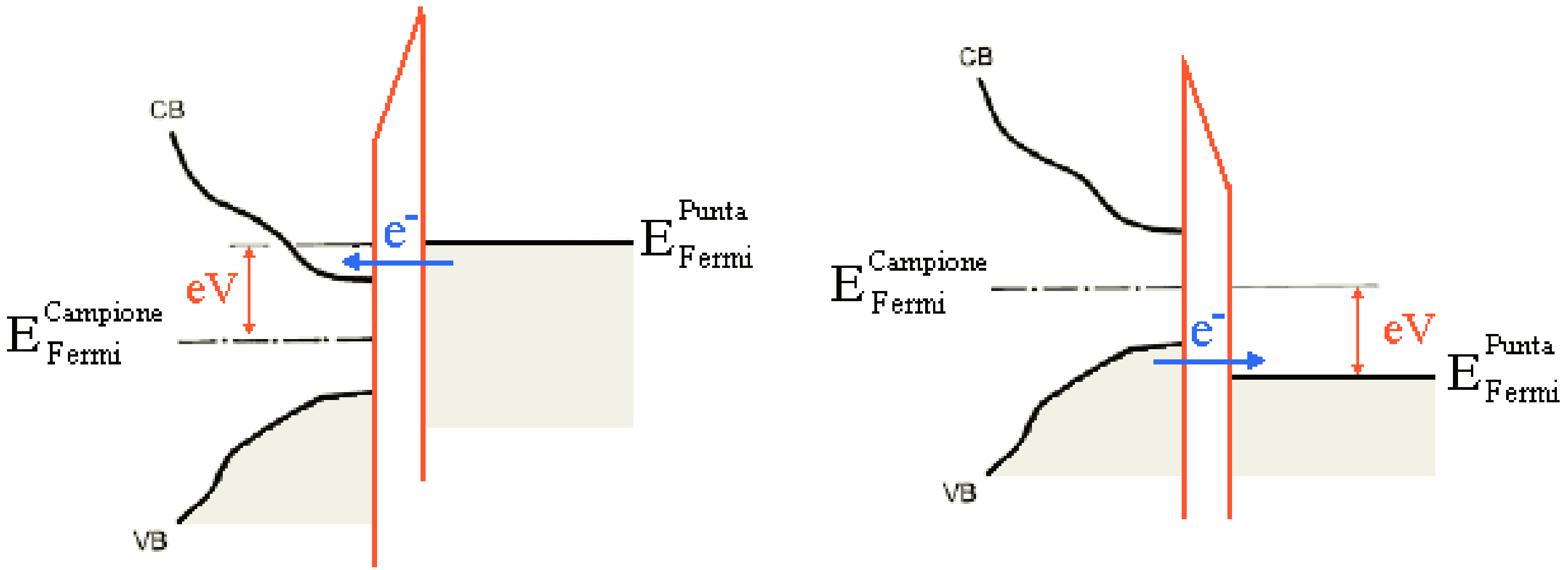
Positive bias to the tip: electrons tunneling from sample to tip
→ probing of OCCUPIED sample electron states

tip: positive bias



$$I(l) \propto \int_0^{-eV} \rho_I(0,E)\rho_{III}(E+eV)\exp(-2kl)dE.$$

e.g. semiconductor sample



sample **tip** **sample** **tip**

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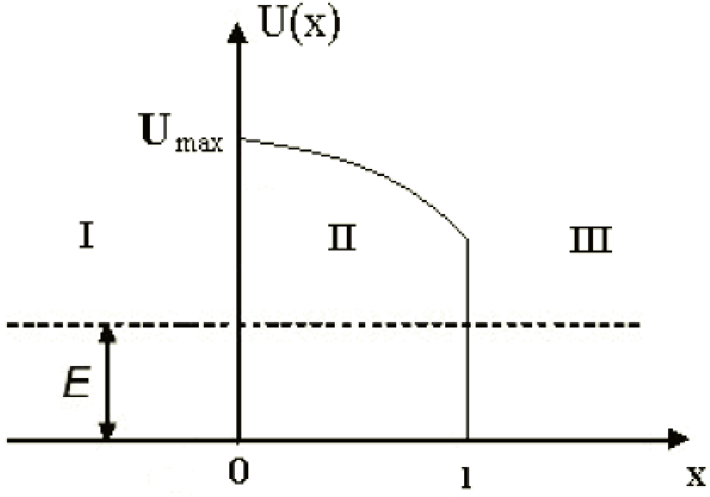
Arbitrary barrier shape (e.g. trapezoidal):
WKB approximation for the transmission coefficient
(like e.g. in alpha decay)



$$T_{WKB} = \frac{16\exp(-2\gamma)}{\left(\frac{b}{a} + \frac{ab}{k_0^2} + \frac{k_0^2}{ab} + \frac{a}{b}\right)} \propto \exp\left[-\frac{2}{\hbar}\int_0^l \sqrt{2m(U(x)-E)}dx\right].$$

$$I(l) \propto \int_0^{eV} \rho_I(0,E) T_{WKB} \rho_{III}(E-eV) dE.$$

Transfer Hamilatonian Theory

Whole system seen as a "left" system (sample) + "right" system (tip) + perturbation related to the close proximity of the two

$$\hat{H} = \hat{H}_R + \hat{H}_L + \hat{H}_T$$

$$I = \frac{4\pi e}{\hbar} \int_{-\infty}^{+\infty} \sum_{\mu,\nu} |M_{s\nu,t\mu}|^2 \left[f(\varepsilon - eV) - f(\varepsilon)\right] \rho_t(\varepsilon - eV, \mu)\rho_s(\varepsilon, \nu) d\varepsilon$$

density of states

transfer matrix element

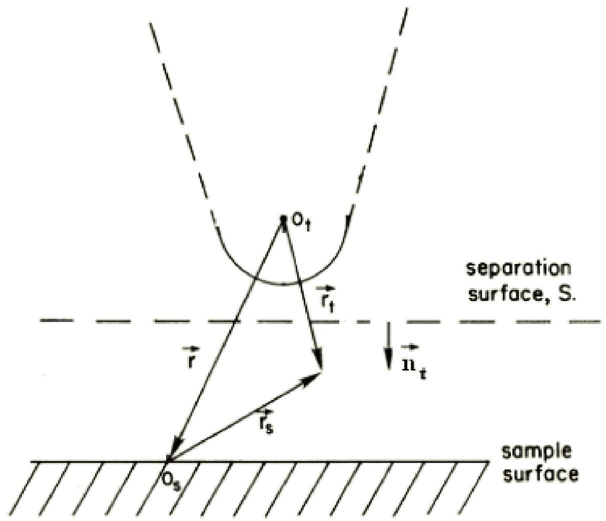
J.R. Oppenheimer, Phys. Rev. 31, 66 (1928) atom ionization under an external electric field
J. Bardeen, Phys. Rev. Lett. 6, 57 (1961)
J. Tersoff and D.R. Hamann, Phys. Rev. Lett. 50, 1998 (1983); J. Tersoff and D.R. Hamann, Phys. Rev. B 31, 805 (1985)

matrix element

$$M_{\nu,\mu} = -\frac{\hbar^2}{2m}\int_S [\psi^*_{s,\nu}(\vec{r}_s)\nabla\psi_{t,\mu}(\vec{r}_t) - \psi_{t,\mu}(\vec{r}_t)\nabla\psi^*_{s,\nu}(\vec{r}_t)]d\vec{S}$$

$$M_{s\nu,t\mu} = -\frac{\hbar^2}{2m}\int_S \left[\psi^*_{s\nu}(\mathbf{r_t}-\mathbf{r})\frac{\partial}{\partial n_t}\psi_{t\mu}(\mathbf{r_t}) - \psi_{t\mu}(\mathbf{r_t})\frac{\partial}{\partial n_t}\psi^*_{s\nu}(\mathbf{r_t}-\mathbf{r})\right] dS$$

calculated on a separation surface between tip and sample



Tersoff-Hamann model

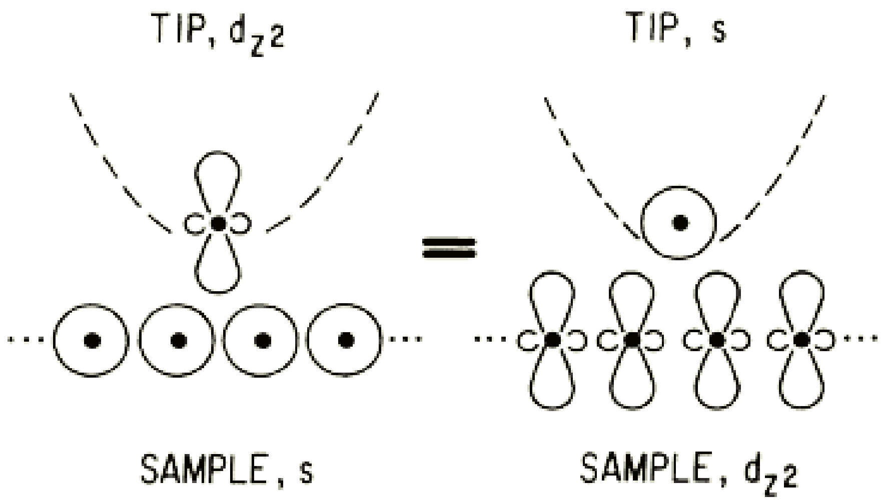
Ψ_{tip} with spherical symmetry (s wave)
→ $M_{\nu,\mu}$ can be explicitly evaluated

sample DOS at the Fermi energy

$$I = \frac{32\pi^3}{\hbar} e^2 V \phi^2 \rho_t(-\vec{R}, E_f) R_0^2 k^{-4} \exp(2kR_0) \rho_s(-\vec{R}, E) \propto \rho_s(-\vec{R}, E_f),$$

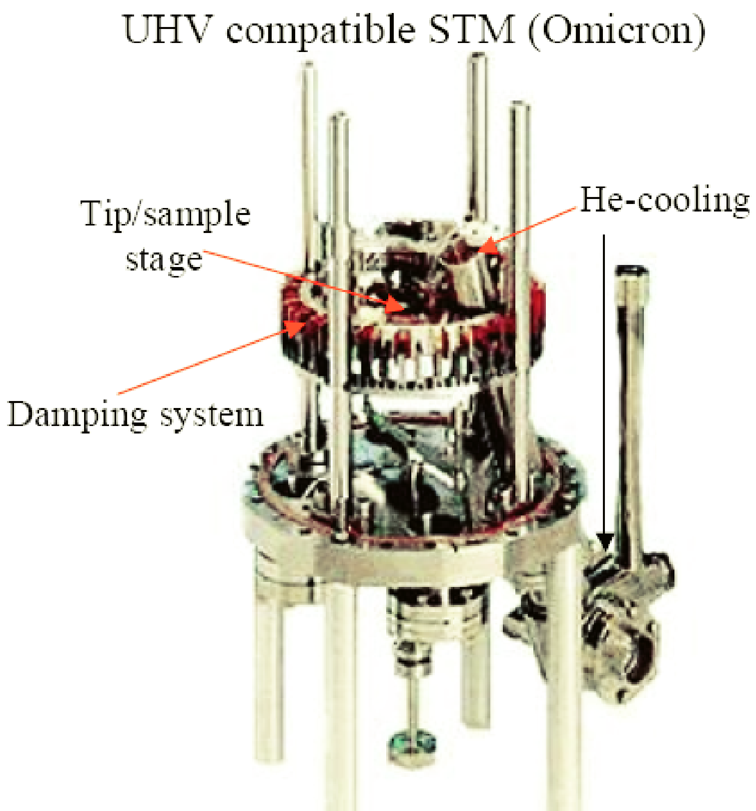
Hp: zero (small) applied bias

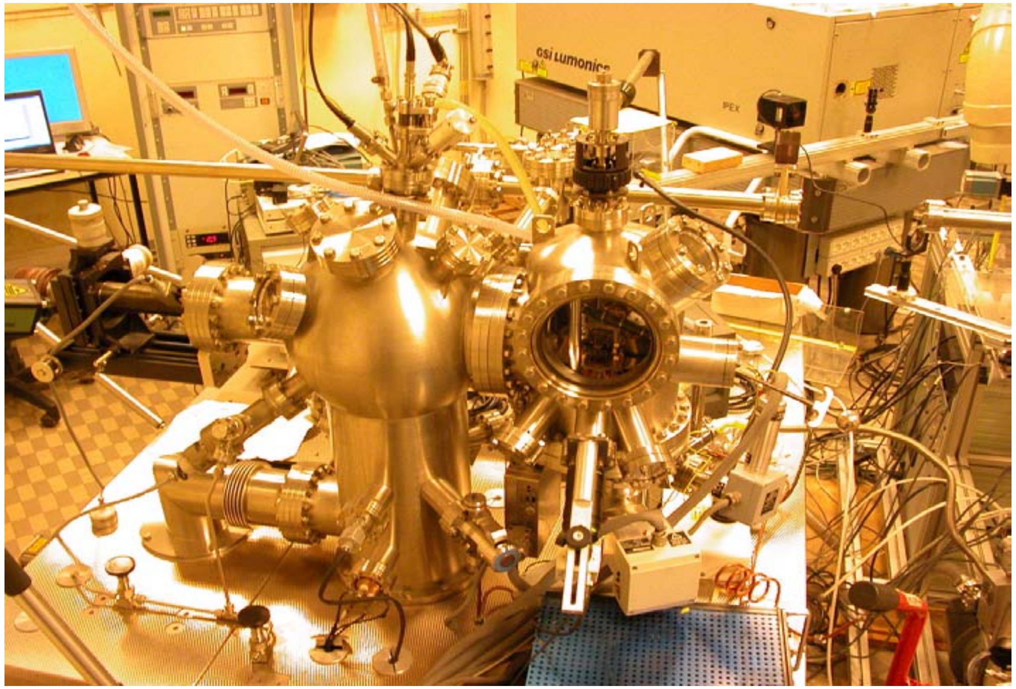
Chen showed that atomic resolution is due to *d* states (e.g. W tips)



C.J.Chen, *Phys.Rev.Lett.* 65, 448(1990)

Scanning Tunneling Microscope





UHV chamber (no contaminations, atomic resolution!)

STM imaging modes

constant current (feedback ON)

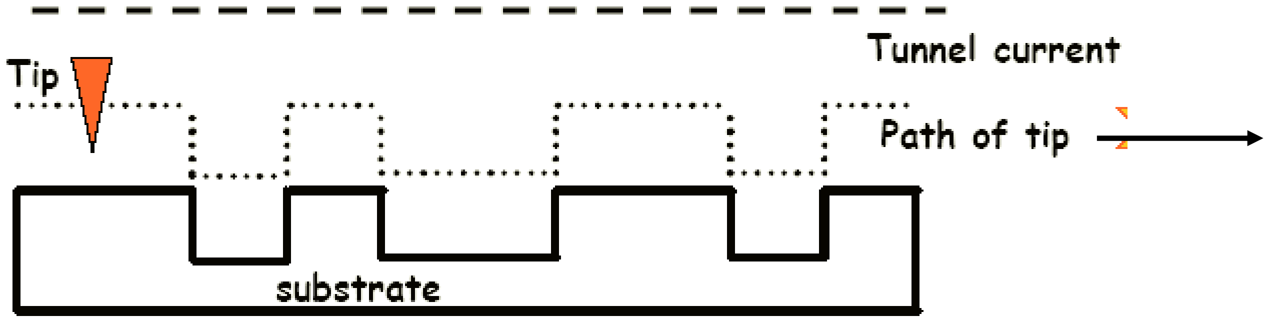


image (tip height)

constant height (feedback OFF – high speed)

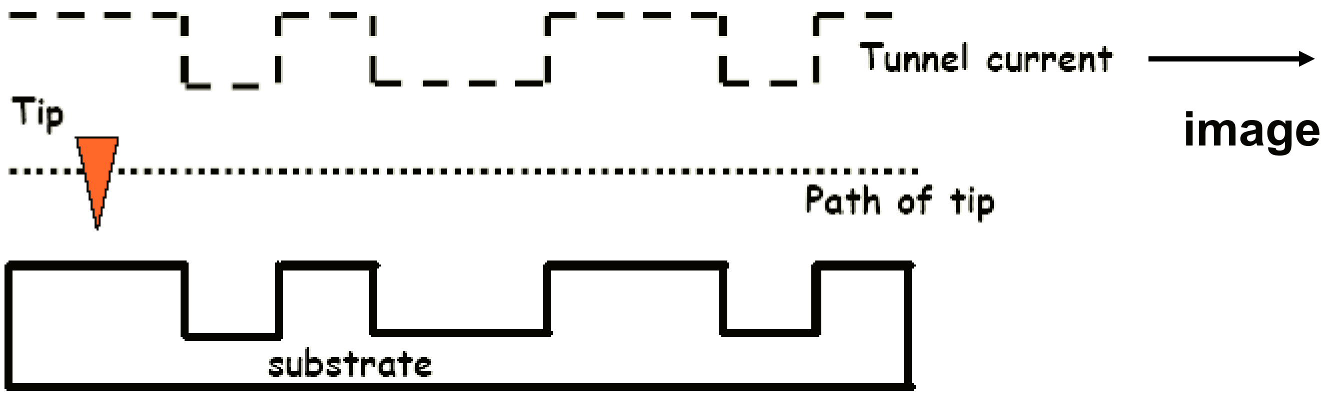
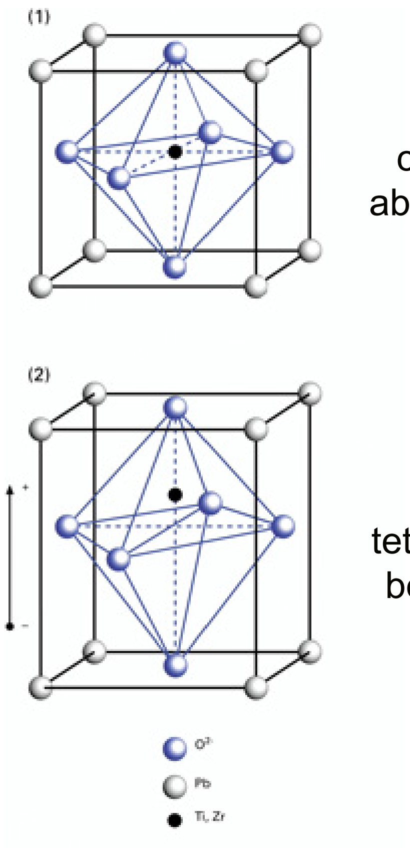


image (measured current)

How can we control the stage/tip movement with sub-nm resolution?

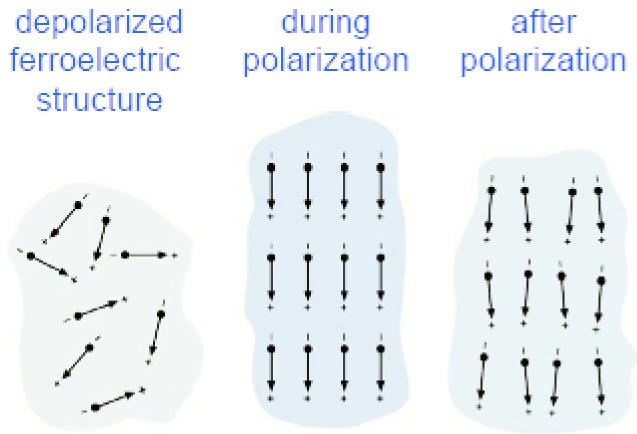
Piezoelectric actuators



cubic, above T_C

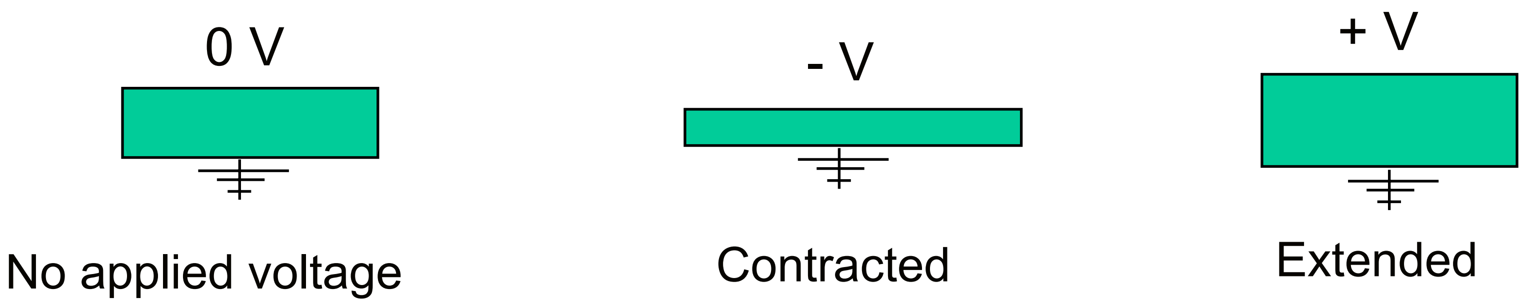
tetragonal, below T_C

e.g. barium titanate, lead zirconate titanate (PZT)

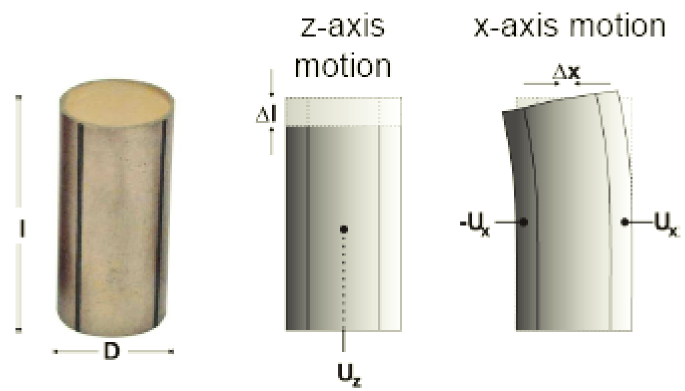


Piezoelectric scanners

SPM scanners are made from a piezoelectric material that expands and contracts proportionally to an applied voltage



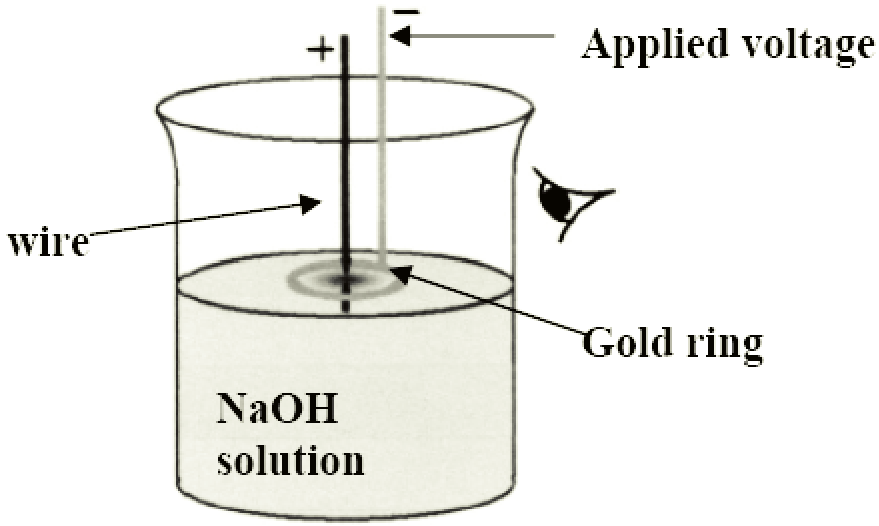
- **in some versions, the piezo tube moves the sample relative to the tip; in other models, the sample is stationary while the scanner moves the tip**



Typical STM tips

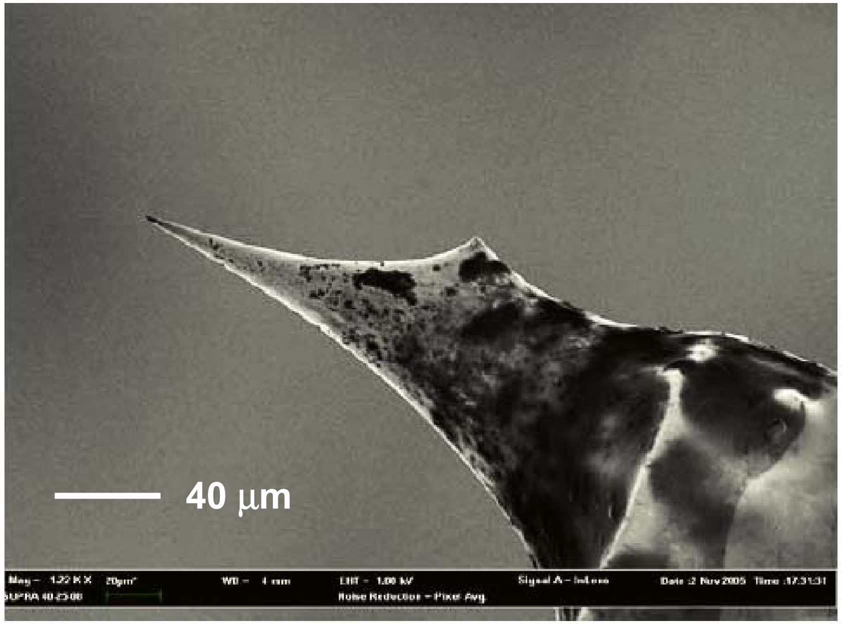
Pt-Ir (cut with scissors!)

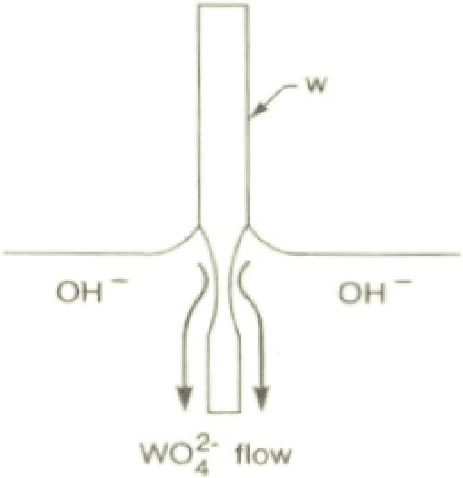
W: electrochemical etching

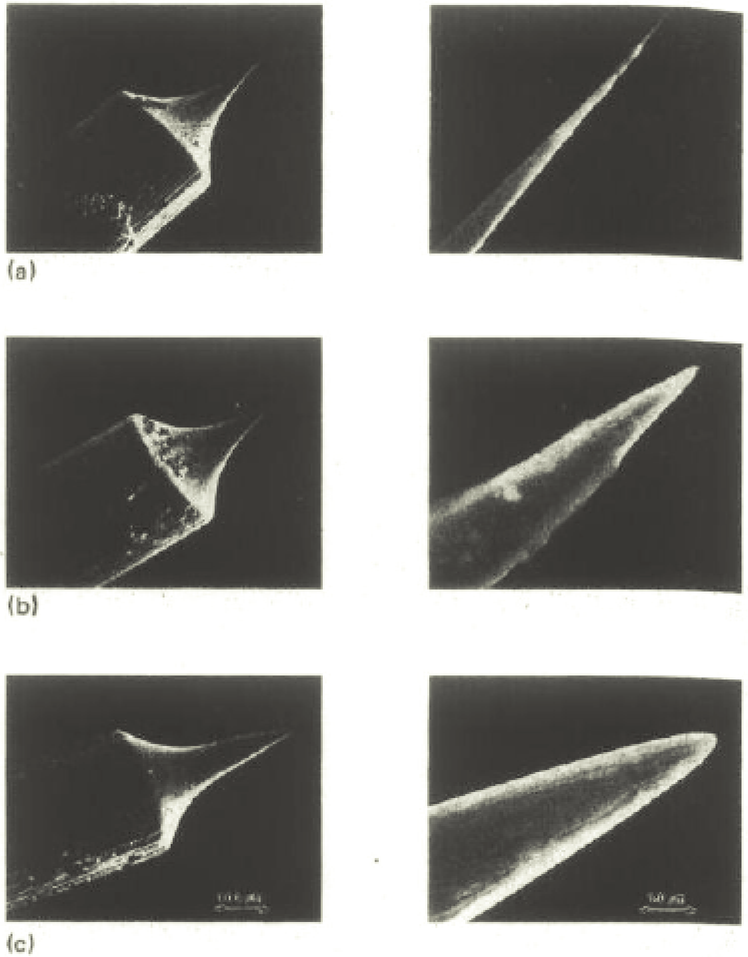


or **KOH** solution

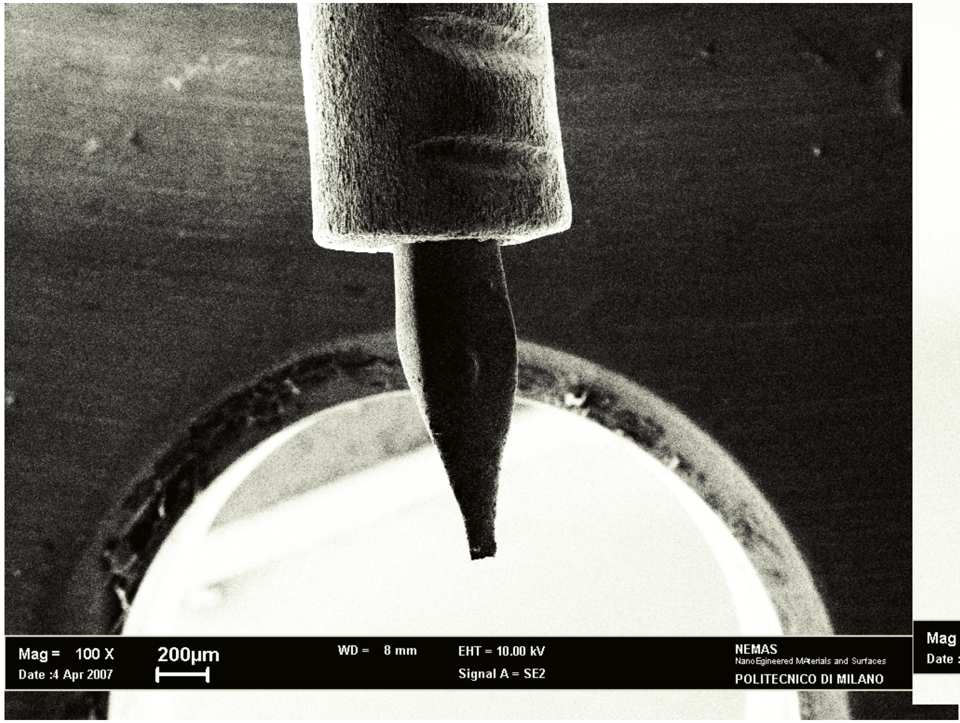
W tips

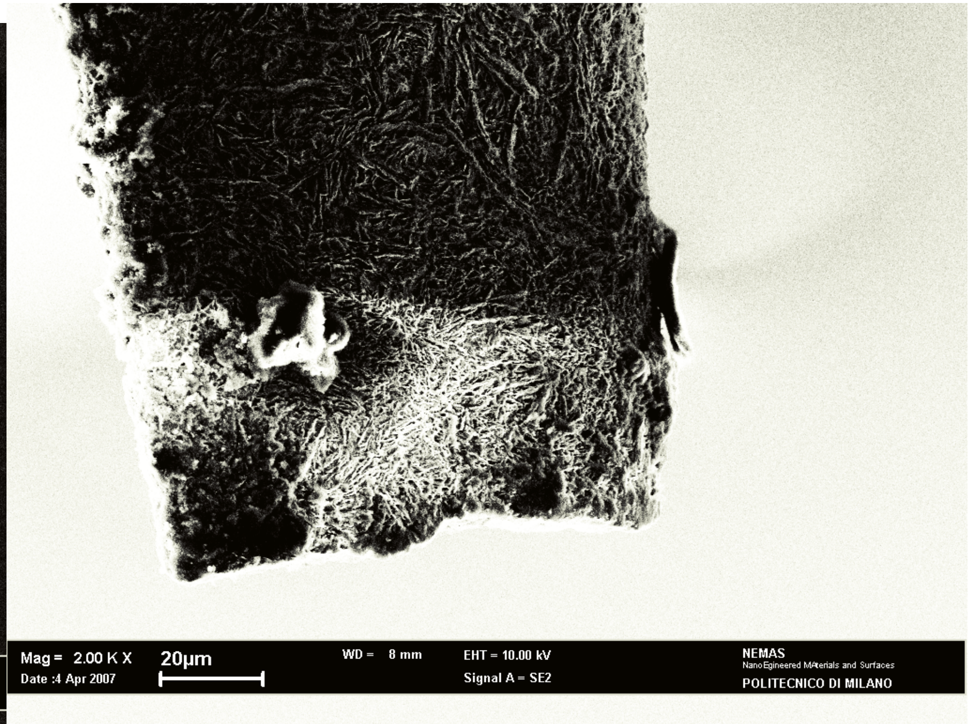




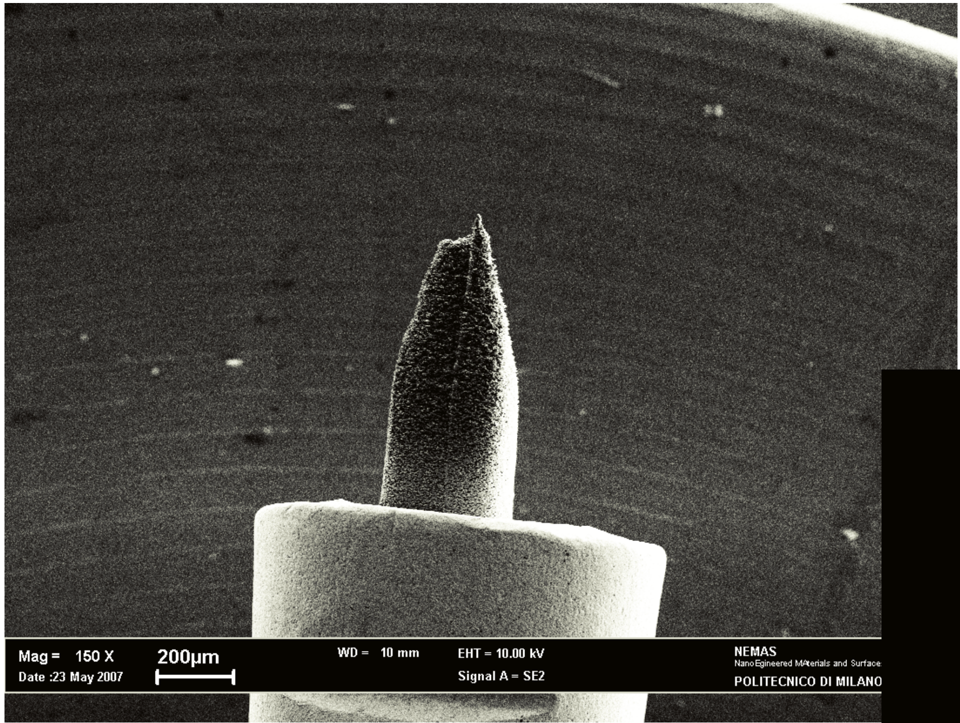


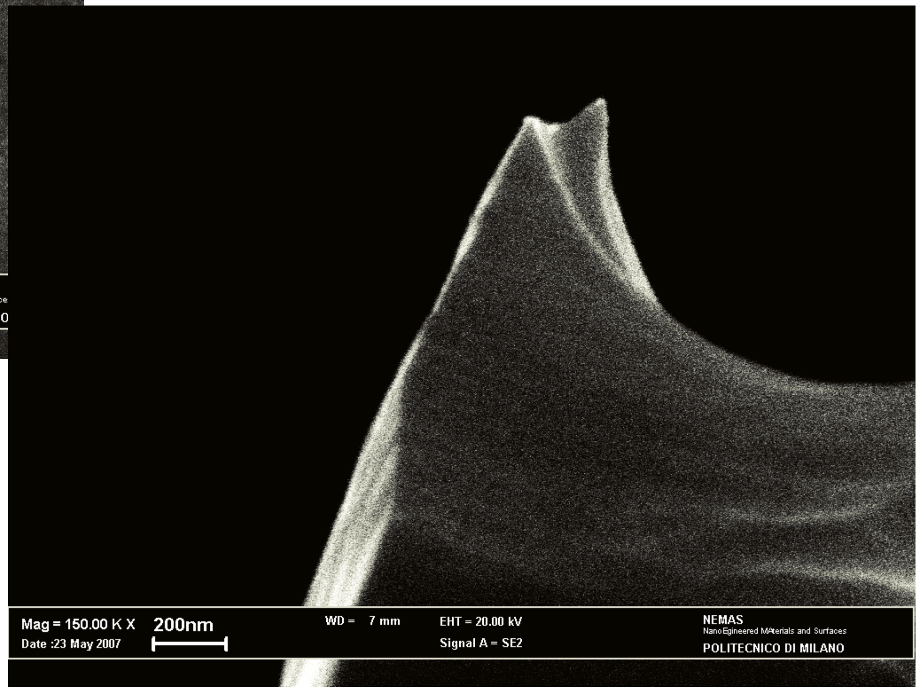
Cr tip (KOH etching)



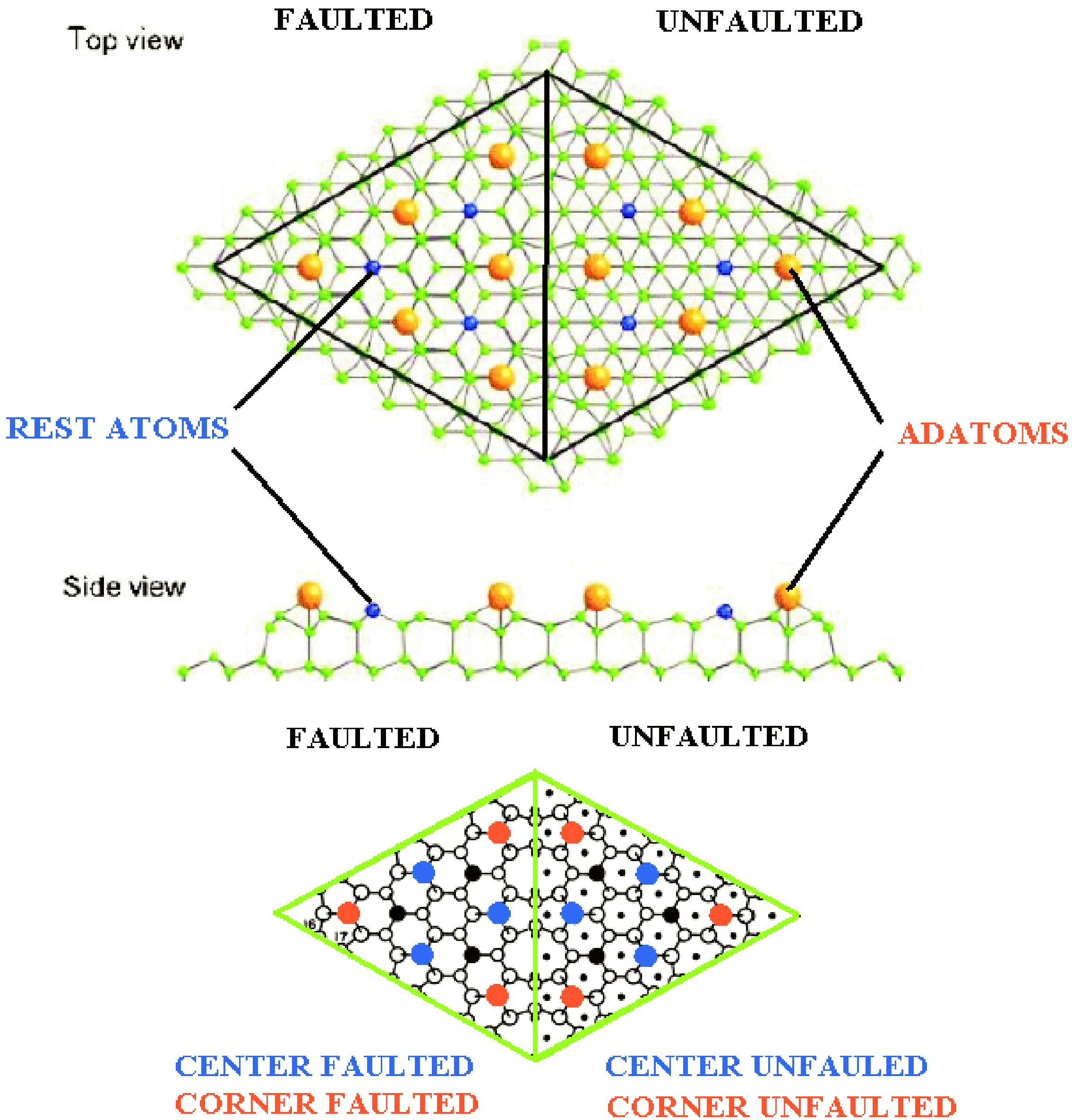


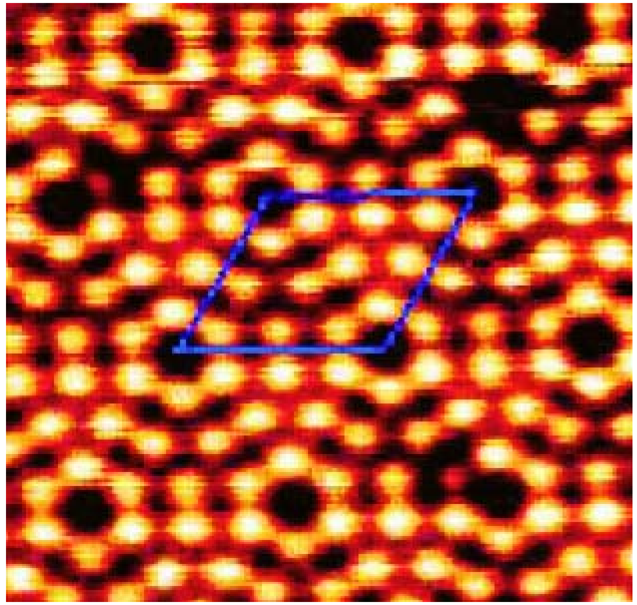
Cr tips (NaOH etching)



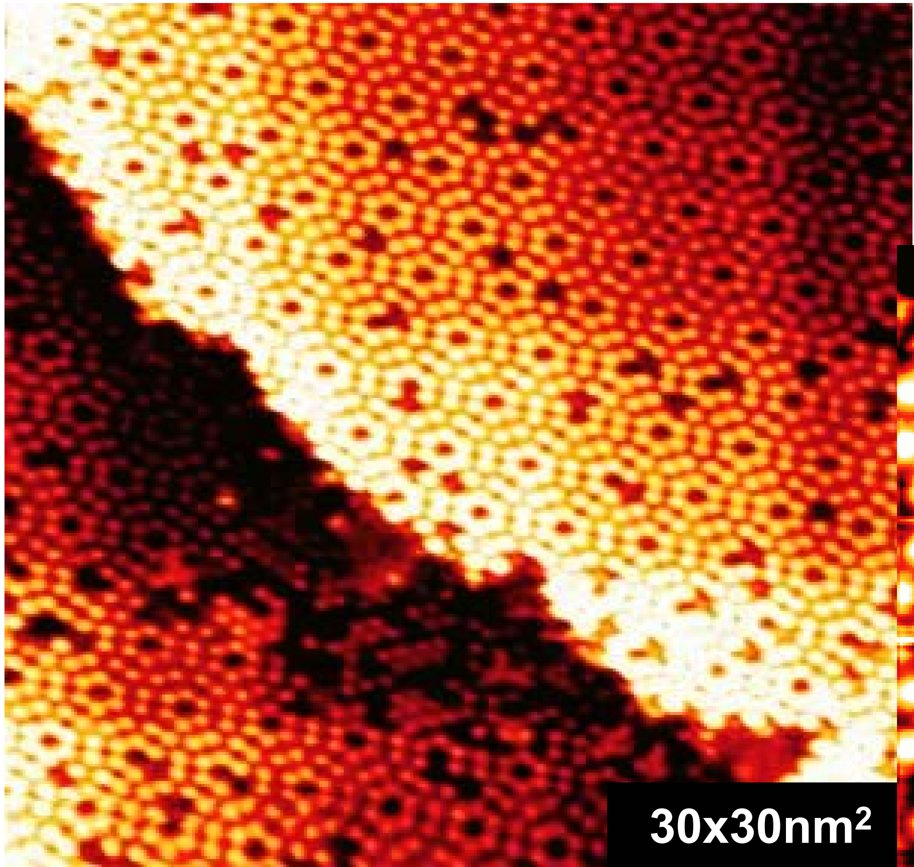


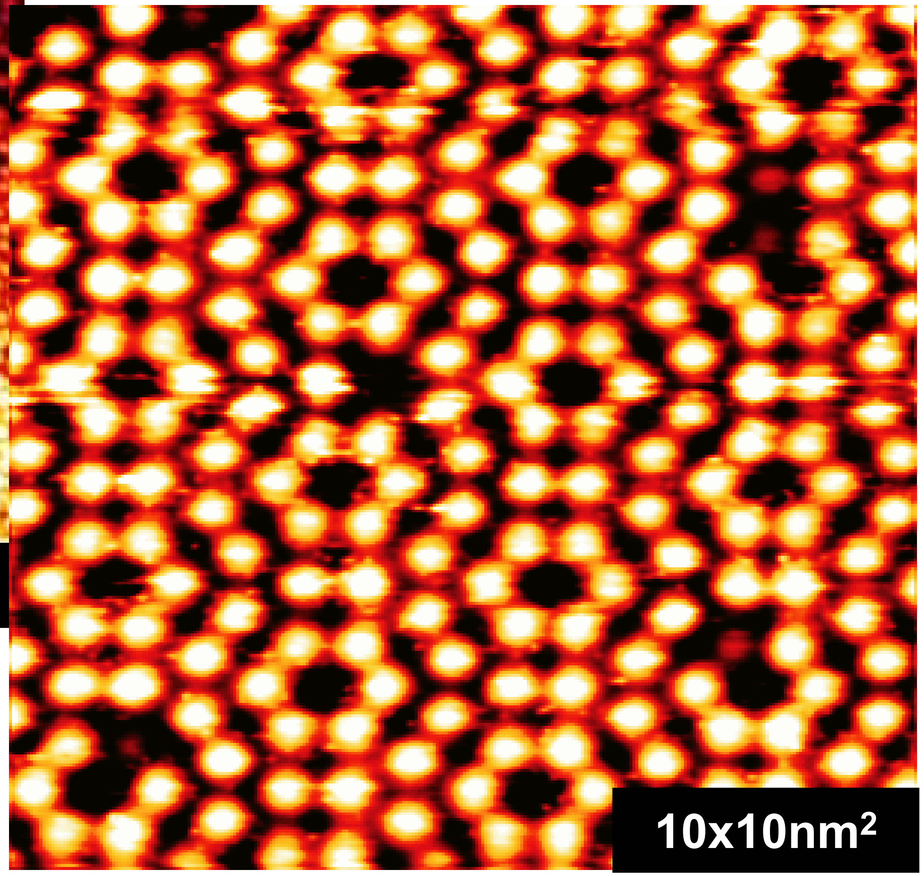
STM EXAMPLES: Si(111)(7x7)





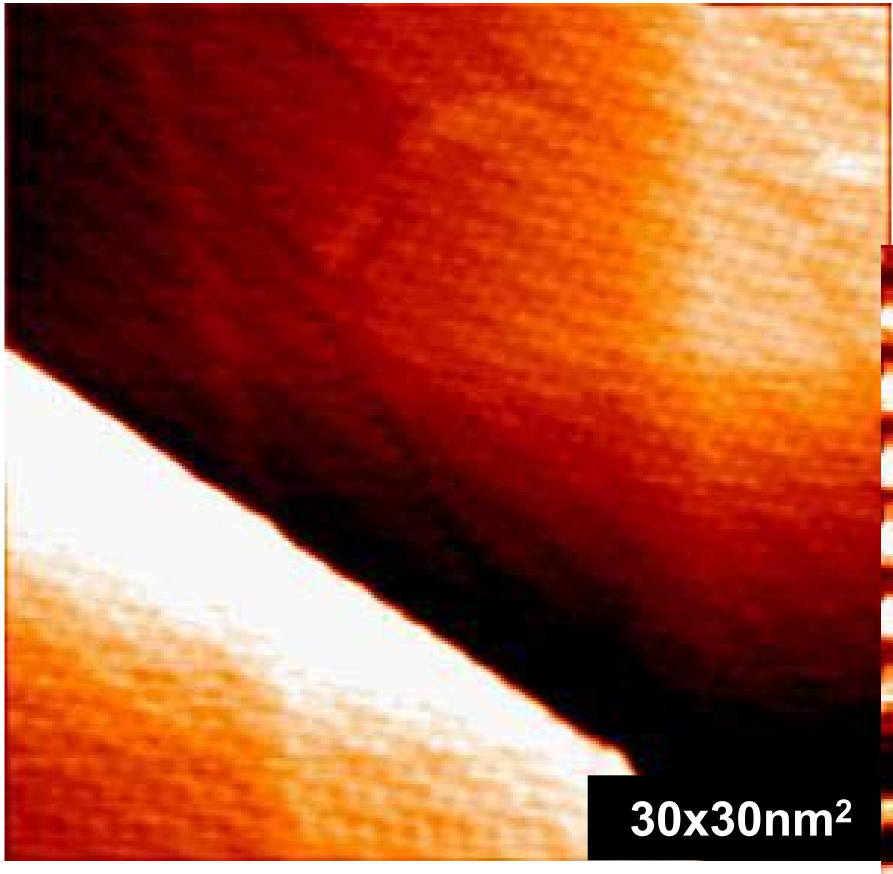
STM atomic resolution

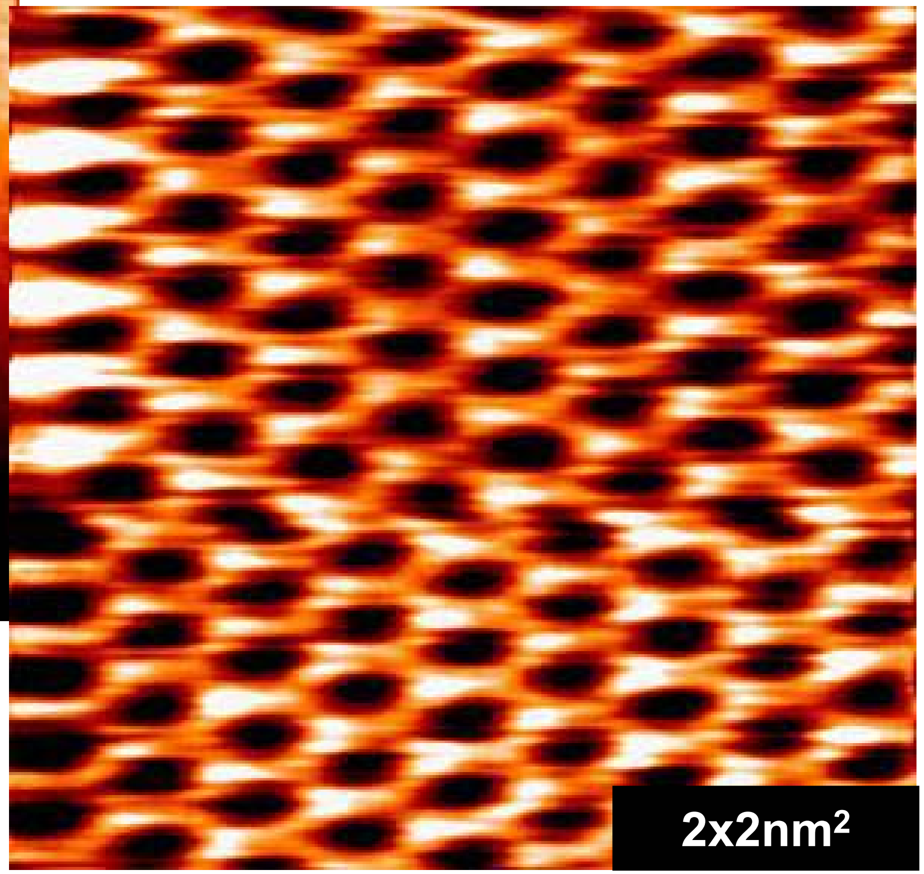




Si(111)7x7

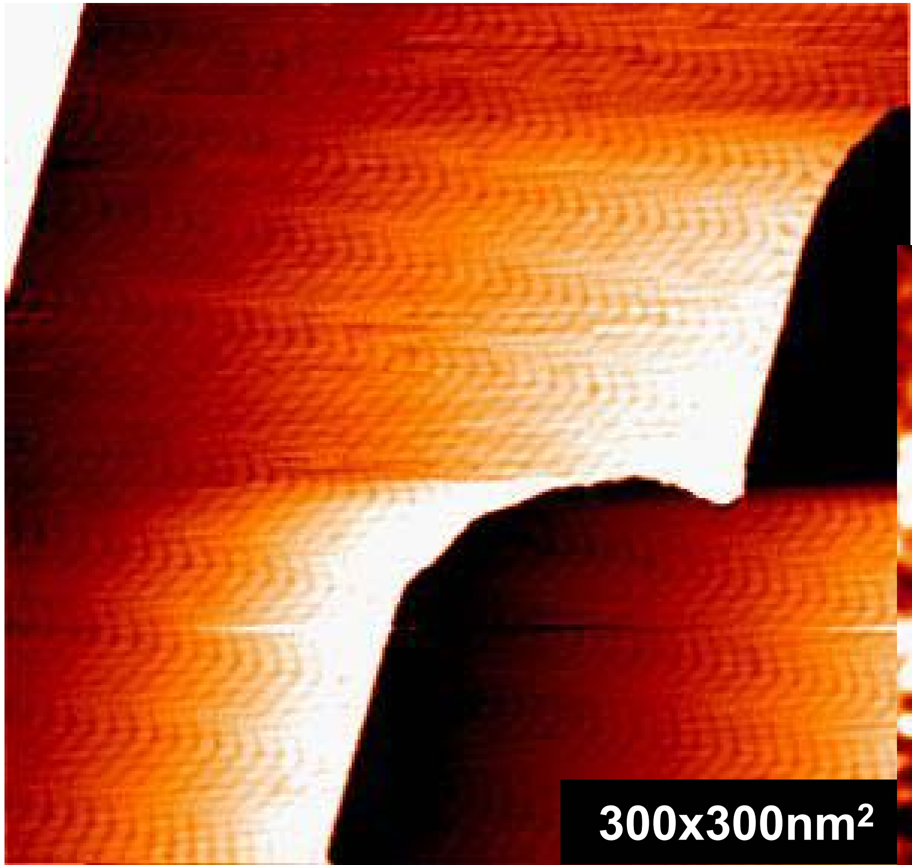
STM atomic resolution



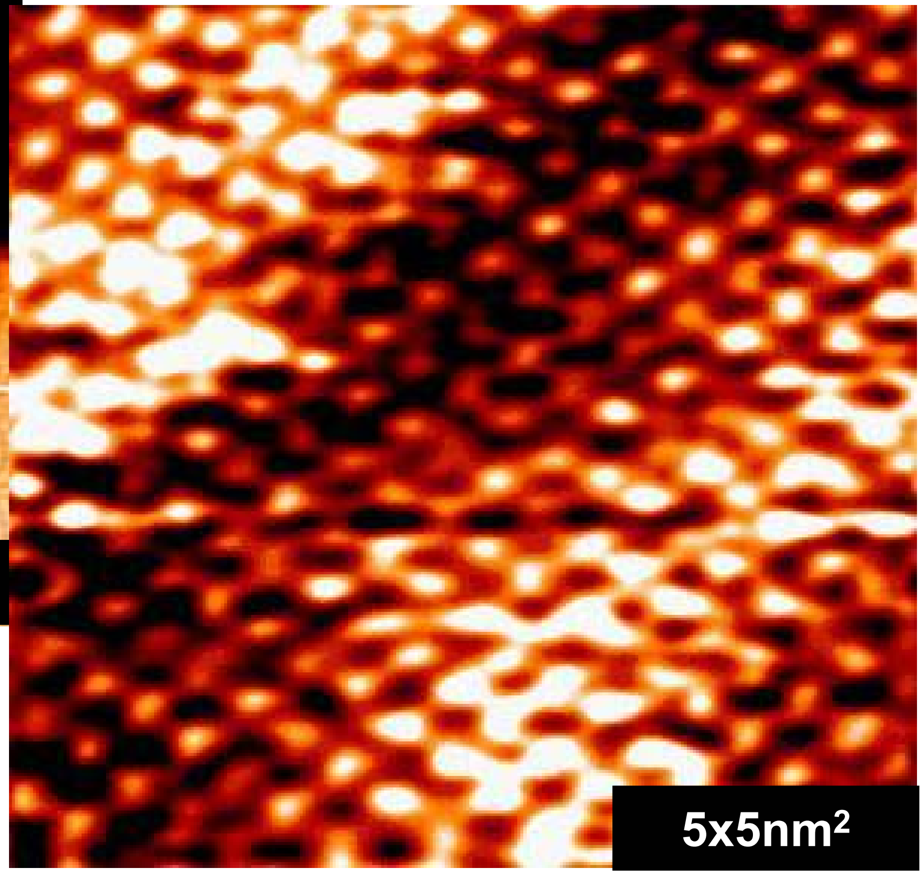


HOPG

STM atomic resolution



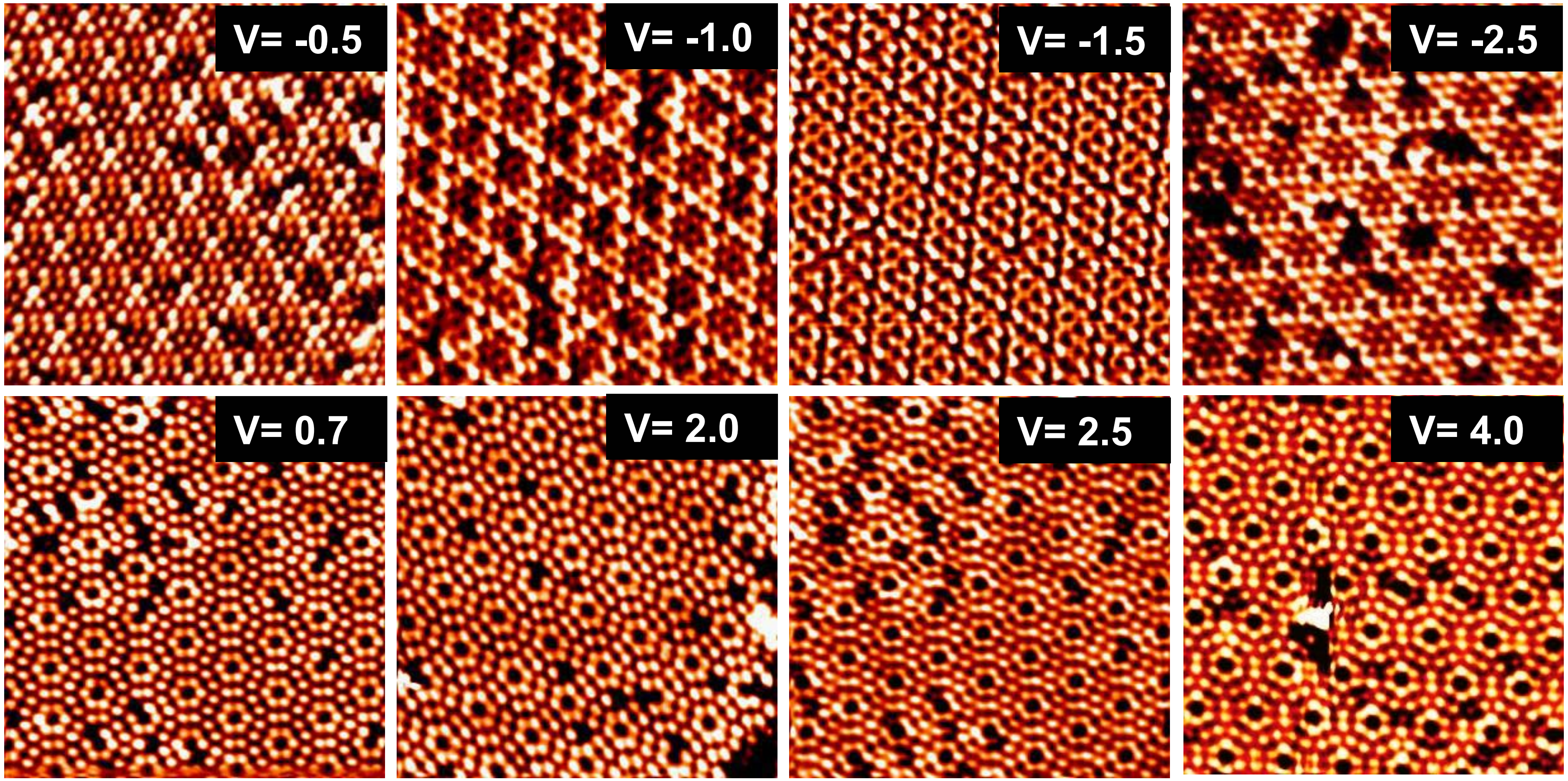
Au(111)



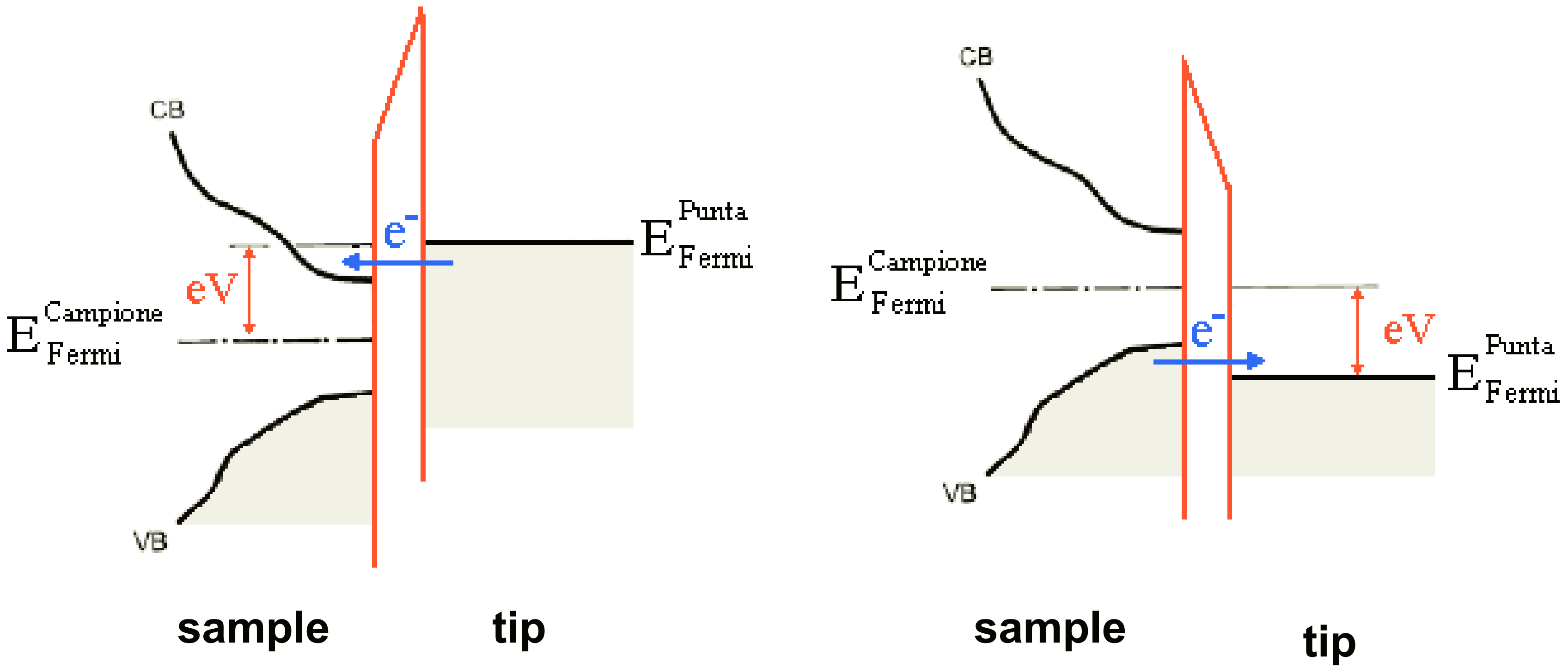
STM and electronic properties

Does STM really measure surface topography?

Si(111)7x7 constant current images at different bias



Scanning Tunneling Spectroscopy (STS)



tunneling current is related to sample and tip density of states, and to tip-sample bias

Scanning Tunneling Spectroscopy (STS)

$$I(V) = \int_{E_f}^{E_f+eV} \rho_t(E-eV)T(E,V,l)\rho_s(E)dE,$$

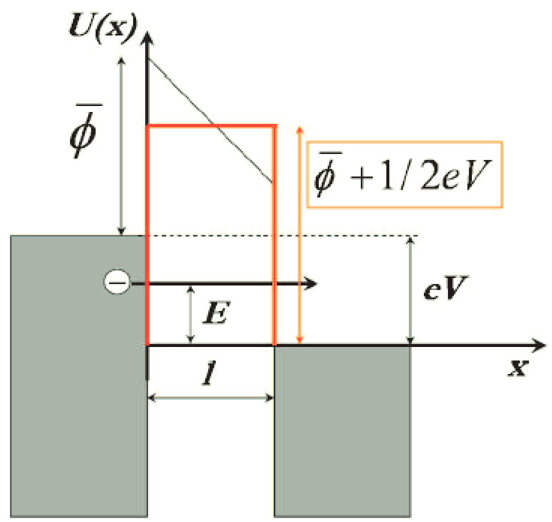
$$T(E,U(x),l) \simeq \exp\left(-2\frac{\sqrt{2m}}{\hbar}\int_0^l \sqrt{U(x)-E}dx\right)$$ **WKB**

rectangular barrier approximation:

$$T(E,V,l) =\simeq \exp\left\{-2l\left[\frac{2m}{\eta^2}\left(\bar{\phi}+\frac{eV}{2}-(E-E_{//})\right)\right]^{\frac{1}{2}}\right\}$$

considering only states with $k_{//} = 0$:

$$T(E,V,l) \simeq \exp\left\{-2l\left[\frac{2m}{\eta^2}\left(\bar{\phi}+\frac{eV}{2}-E\right)\right]\right\}$$



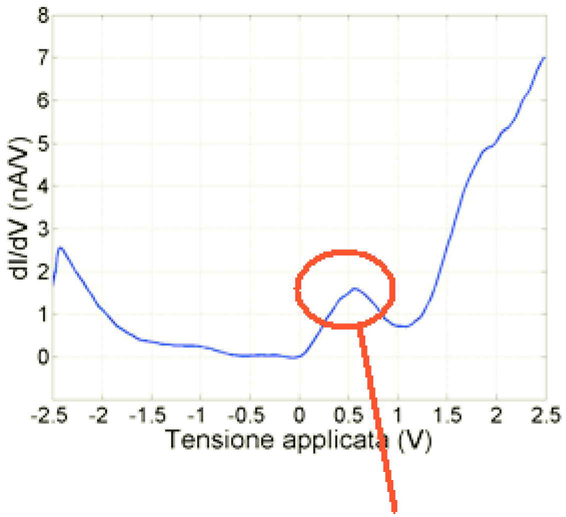
STS: interpretation in terms of sample LDOS

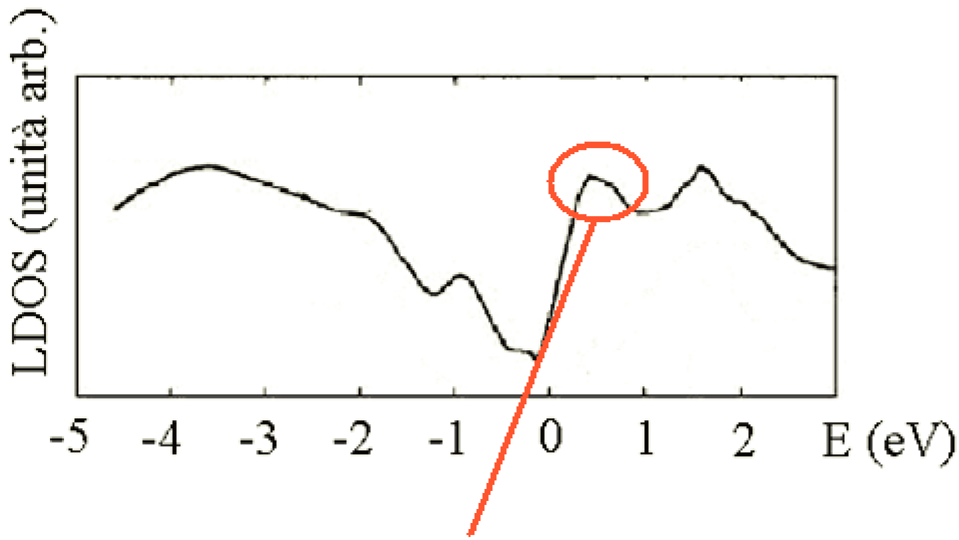
$$\frac{dI(V)}{d(eV)} \propto \rho_t(0)\rho_s(eV)T(eV,V,l) + \int_0^{eV} \frac{\rho_s(E)d(\rho_t(E-eV)T(E,V,l))}{d(eV)}dE$$

LDOS at energy eV

current derivative: 2 terms, the first is related to the sample LDOS at eV, weighted by the transmission factor, the second has a smaller weight….

current derivative





peak in the dI/dV curve at V ⟷ **energy level at eV in the LDOS**

POLITECNICO DI MILANO

dI/dV needs normalization to extract LDOS (i.e. to eliminate exponential behavior of T)

Two proposed methods (neglecting the 2nd term)**:**

Normalize by T (calculated, e.g. WKB)

$$\frac{\frac{dI(V)}{d(eV)}}{T(eV,V,l)} \approx \rho_t(0)\rho_s(eV)$$

Normalize by I/V (experimental curve)

$$\frac{\frac{dI(V)}{d(eV)}}{\frac{I(V)}{V}} \approx \frac{\rho_t(0)\rho_s(eV)T(eV,V,l)}{\frac{1}{V}\int_0^{eV} T(E,V,l)\rho_t(E-eV)\rho_s(E)dE}$$

dI/dV measurement

POLITECNICO DI MILANO

1) Measure I(V), then differentiate

2) Lock-in amplifier

small AC bias (e.g. 100 mV) superimposed to DC bias

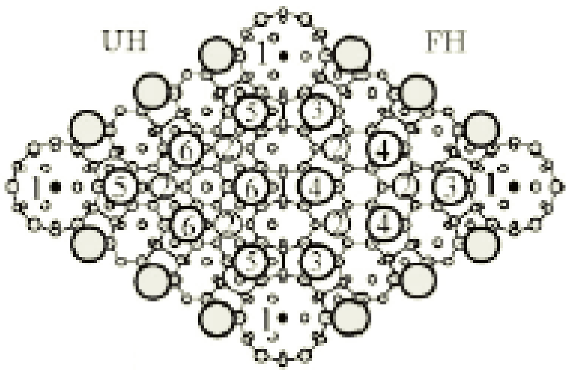
$$V_{tip}(t) = \overline{V} + \Delta\widetilde{V}\sin(\omega t)$$

$$I_{tunn}(t) = \overline{I} + \Delta\widetilde{I}\sin(\omega t + \phi)$$

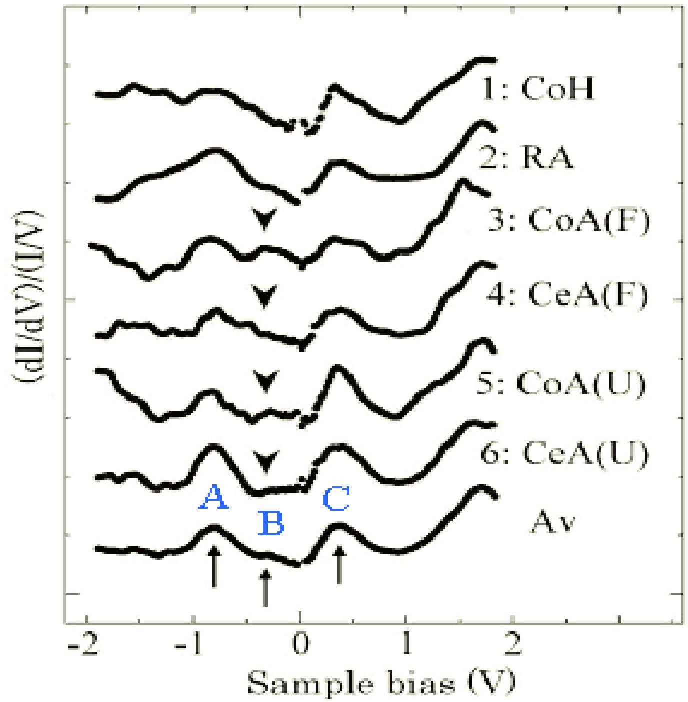
$$\left.\frac{dI(V)}{dV}\right|_{V=\overline{V}} \cong \frac{\Delta\widetilde{I}}{\Delta\widetilde{V}}$$

1) fix setpoint I and V (i.e. determine tip-sample distance)
2) swith feedback off (open loop) → fix distance
3) perform dI/dV lock-in measurement
4) proper normalization to be compared with LDOS

Si(111)(7x7): LDOS spectroscopy

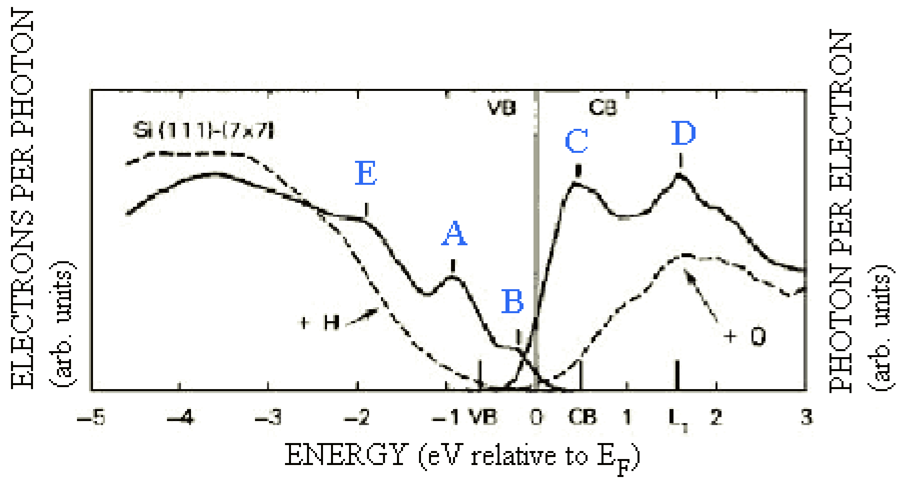


STS



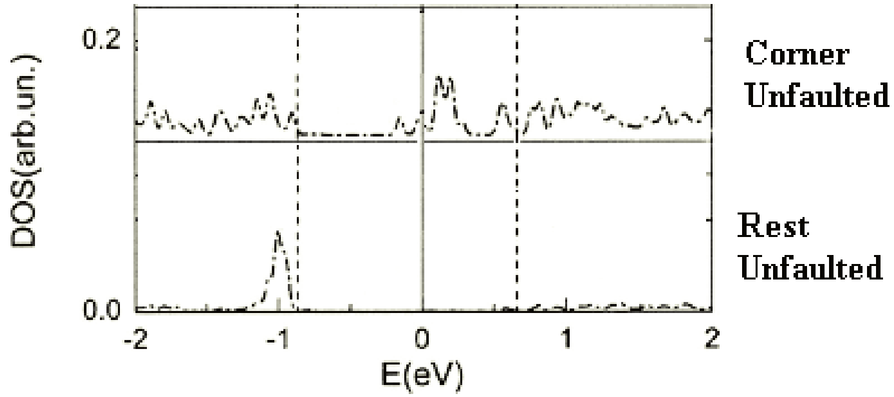
R. Negishi, Surf. Sc. **507,** 582 (2002)

Photoemission (UPS e IPS)



T. Fauster, J. Vac. Sci. technol. A **1, 2**

numerical simulations



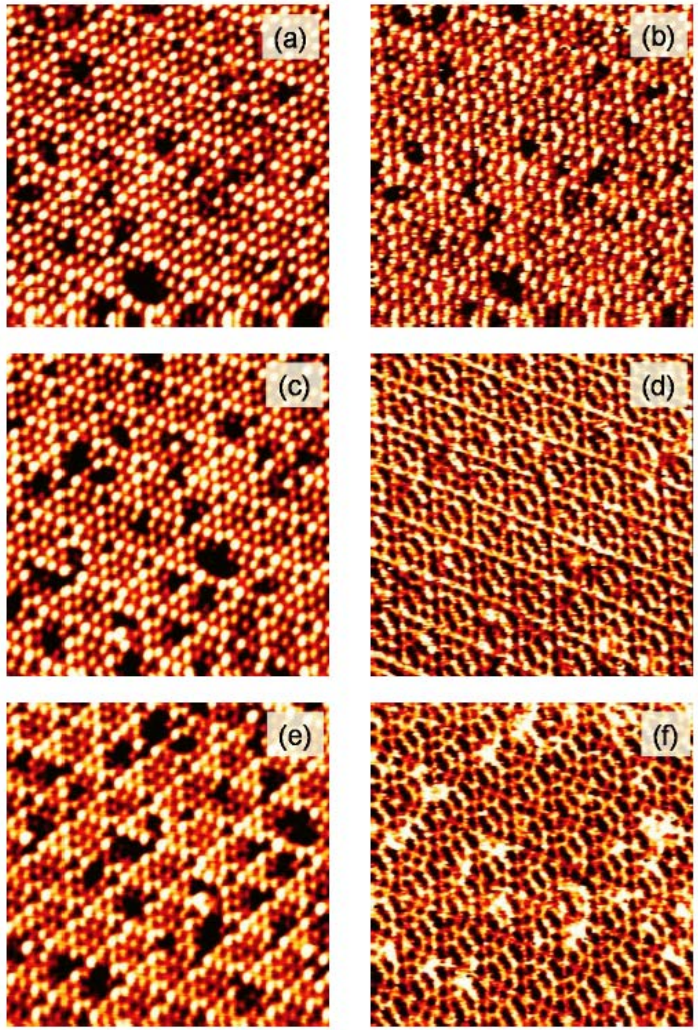
M. Hupalo, Phys. Rev. B **67**, 115333 (2003)

Conductivity maps:

Scanning and imaging of dI/dV at fixed V

(imaging of surfaces of constant DOS at the energy eV)

constant I maps | **dI/dV maps**



V = -1.5V

V = -2V

V = -2.5V

20nmx20nm

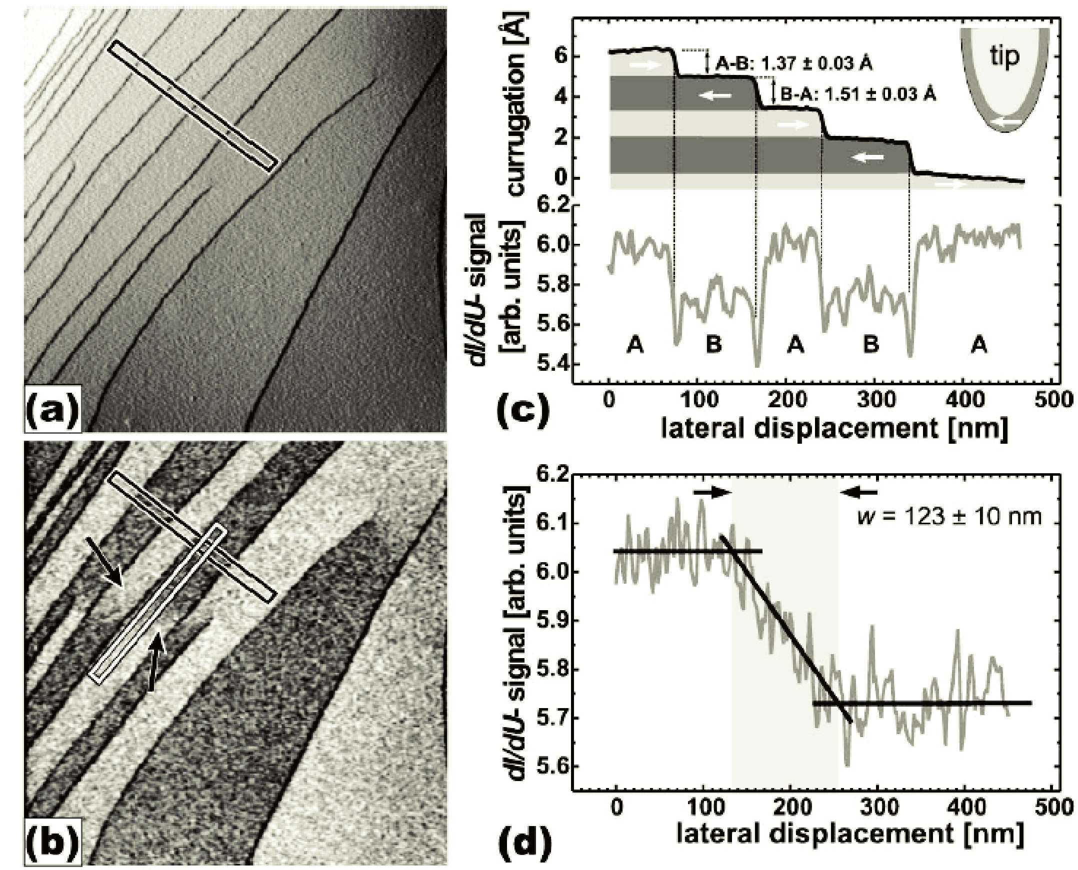
Figura 2.11: *Confronto fra mappe di topografia STM e di conduttività STS 20x20nm, I=1.13nA. (a-b)$V_{tip-sample} = -1.5V$. (c-d)$V_{tip-sample} = -2V$. (e-f)$V_{tip-sample} = -2.5V$.*

SP-STM: Spin Polarized STM

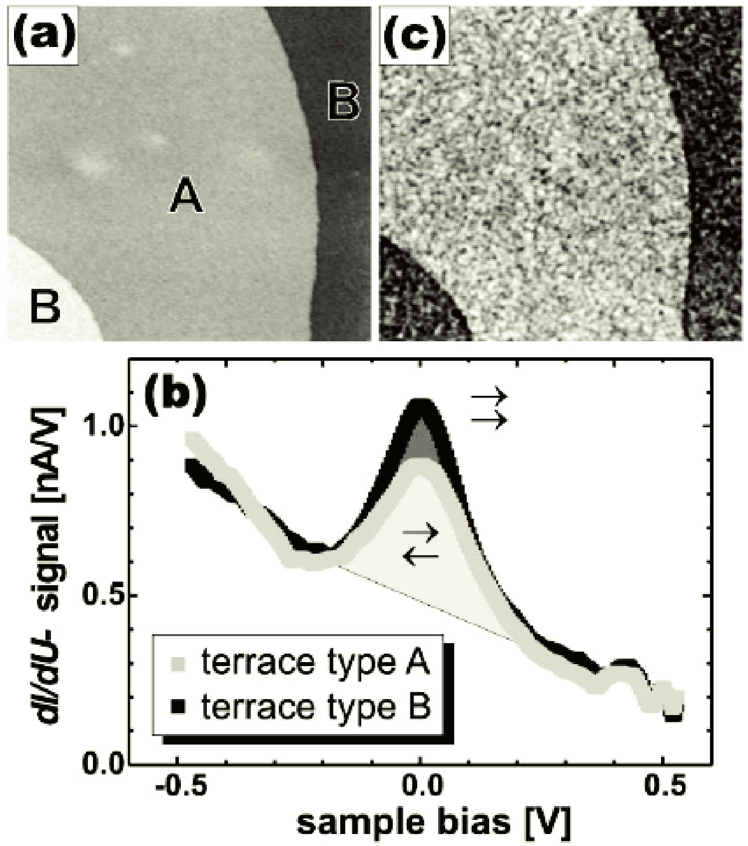
POLITECNICO DI MILANO

Use of ferromagnetic or antiferromagnetic tips (Fe, Cr, …): tunneling current depends on relative spin orientation

Cr terraces



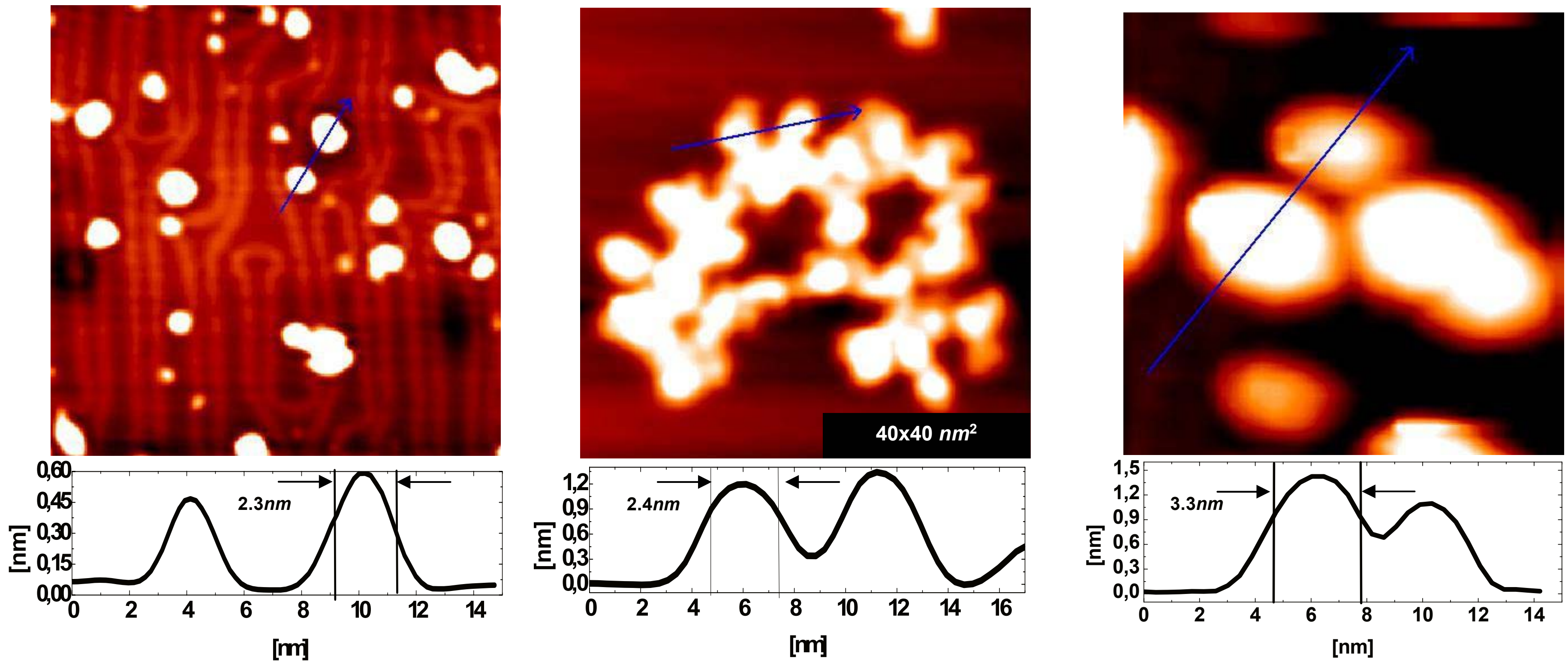
) Large scale constant-current STM image (1 μm × 1 μm) of the Cr (001) surface showing many terraces



M. Kleiber et al. PRL 85, 4606 (2000)

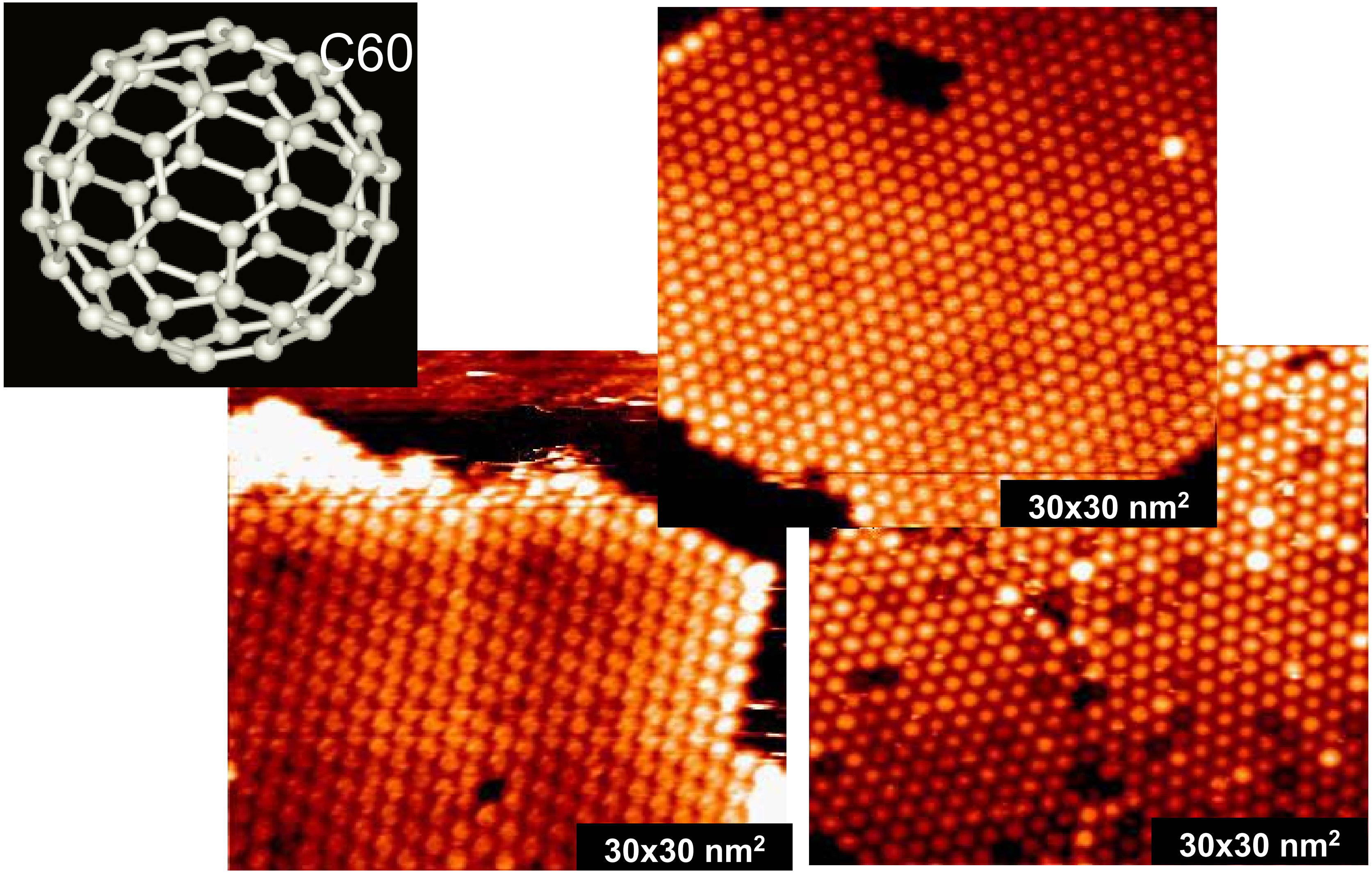
STM and clusters

D. Cattaneo et al. Surf. Sci 2007

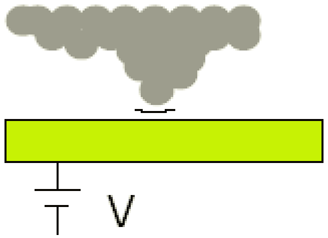


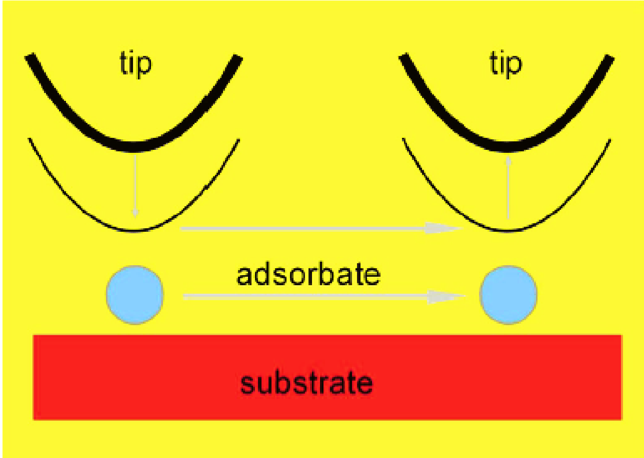
W cluster deposition, diffusion and aggregation

STM and molecules: C_{60} fullerenes on Au(111)



Manipulation by SPM



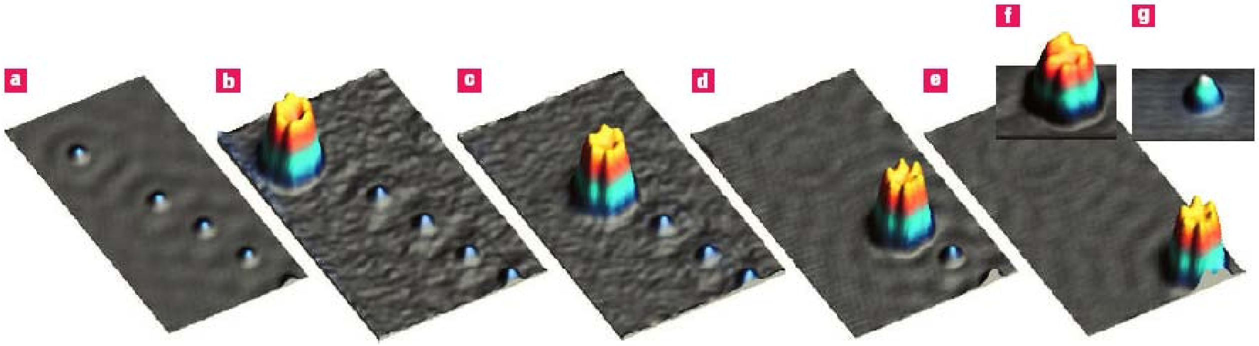


Van der Waals or chemical forces between tip and adsorbate

constant current or constant height modes

chemical forces

Taken by F. Moresco tutorial “STM-based atom/molecule manipulation and dI/dV spectroscopy”



hexa-*tert*-butylhexaphenyphenyl

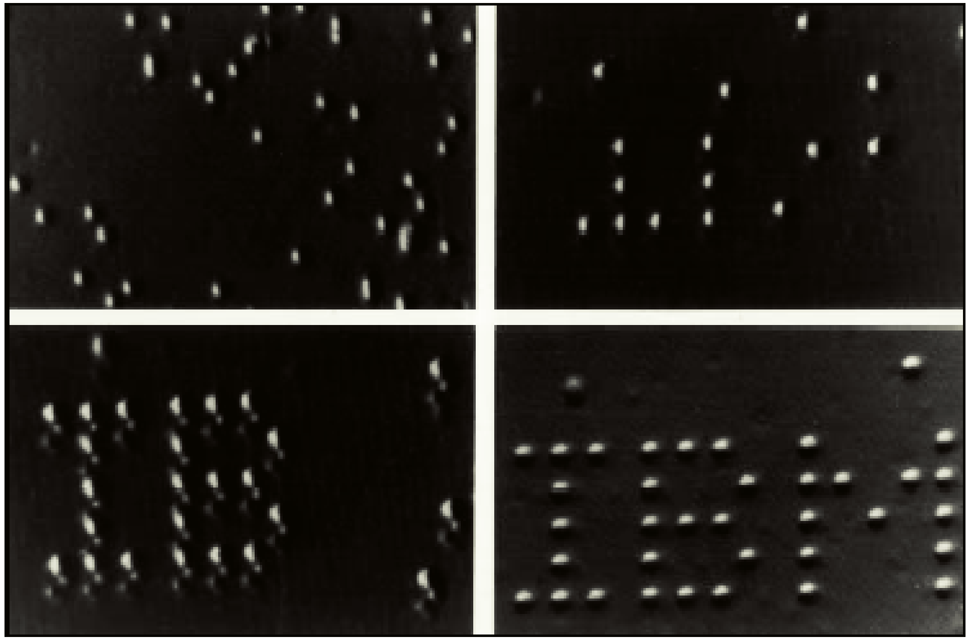
Figure 2 Trapping, moving and releasing adatoms. A series of pseudo-three-dimensional images of a single HB-HPB molecule. By manipulating the molecule to the adsorption positions of the adatoms, in **a–e**, four single Cu atoms are absorbed by the molecule, one at a time. All images are recorded with identical bias, $U = 0.1$ V, but with different currents: **a** and **d–g**, with a current of $I = 0.1$ nA, whereas the tunnelling current had to be reduced to $I = 5$ pA in **b** and **c**, owing to the low diffusion barrier of the molecule with one or two absorbed atoms. **f**, An HB-HPB molecule with five Cu atoms. After picking up the molecule with the tip, a Cu_5 cluster is left on the surface (**g**). The $n = 5$ cluster is identified by comparison with clusters directly assembled by atom-by-atom STM manipulation (see Supplementary Information).

L. Gross et al., Nature Mater. 4, 892 (2005)

Atomic manipulation

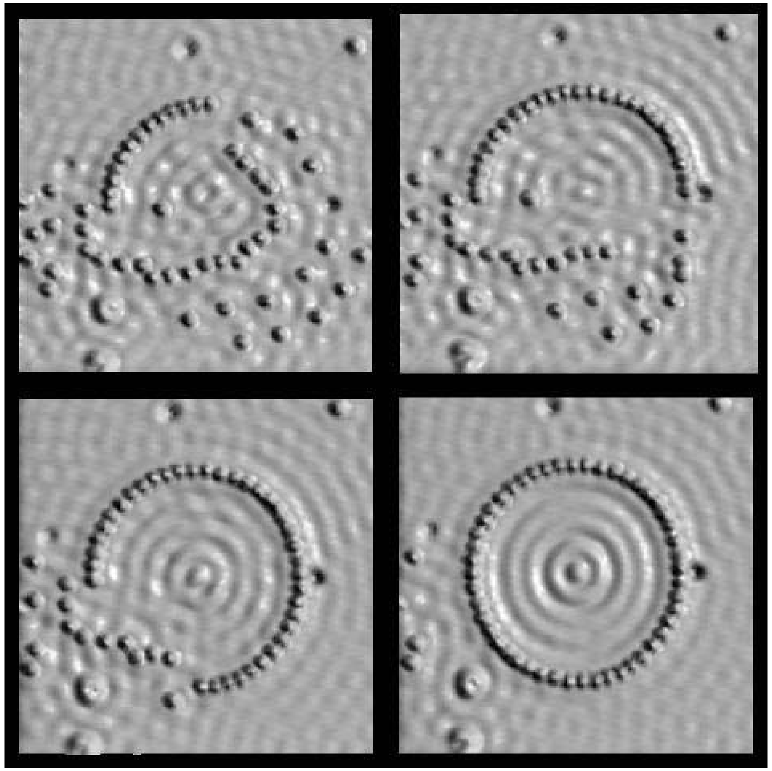
positioning single atoms with STM

electron standing waves



Smallest Writing. This famous set of images, now about 10 years old, helped prove to the world that people indeed can move atoms. The series shows how 35 atoms were moved to form a famous logo.

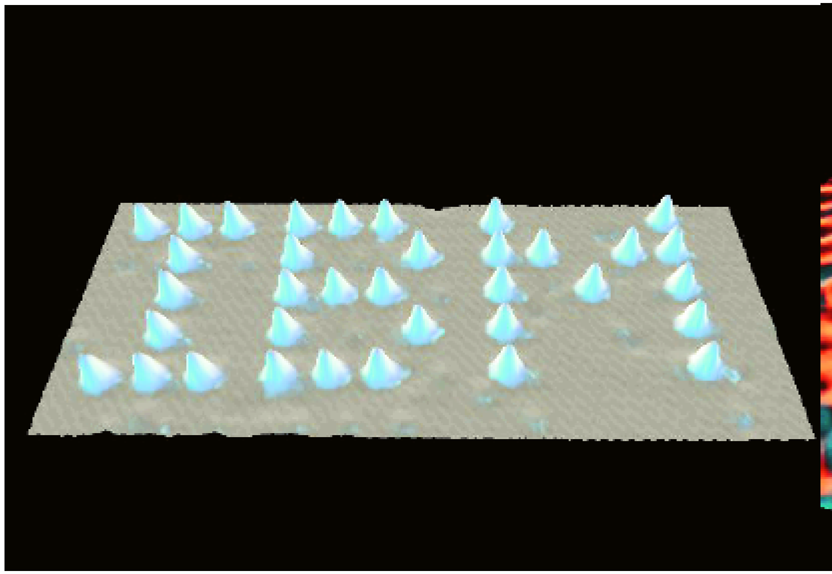
Xe on Ni(100)



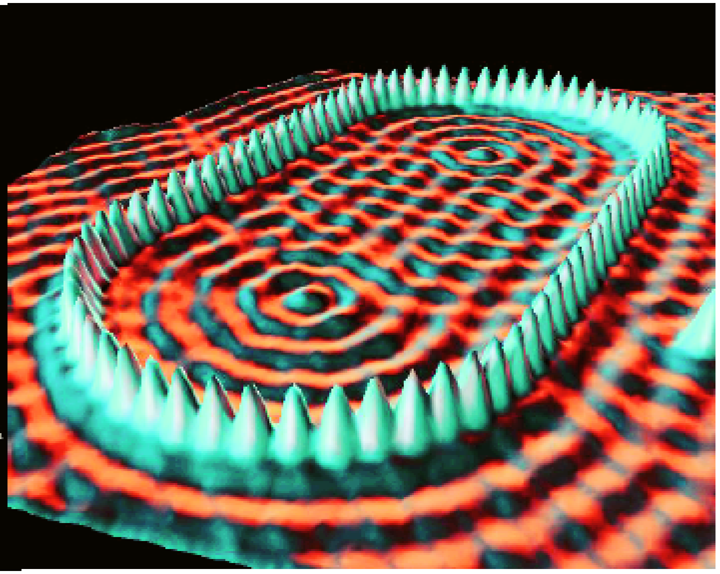
Fe on Cu(111)

Manipulation by SPM

Quantum corral

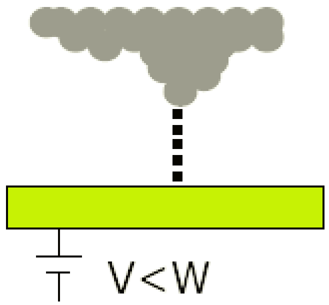


- D.M. Eigler, E.K. Schweizer. Positioning single atoms with a scanning tunneling microscope. Nature 344, 524-526 (1990).
- Xenon on Nickel (110)



- M.F. Crommie, C.P. Lutz, D.M. Eigler, E.J. Heller. Waves on a metal surface and quantum corrals. Surface Review and Letters 2 (1), 127-137 (1995).
- Iron on Copper (111)

Manipulation by SPM



tunneling electrons

single-molecule dissociation with tunneling electrons

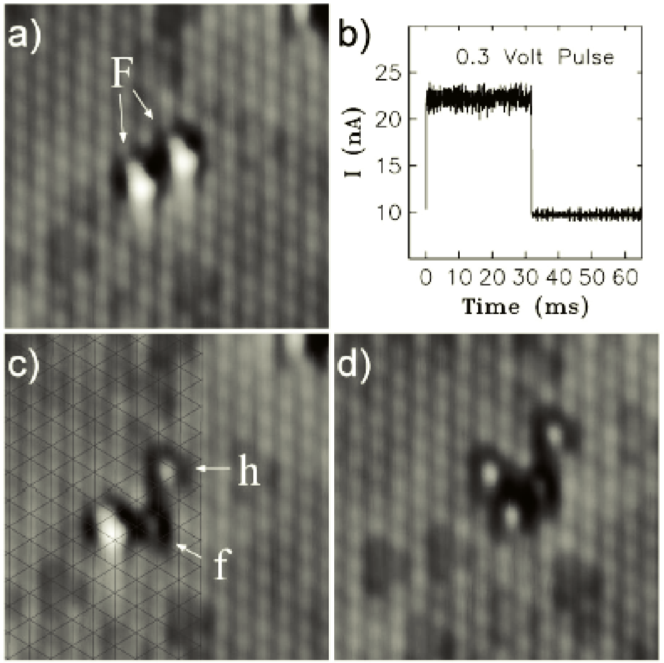
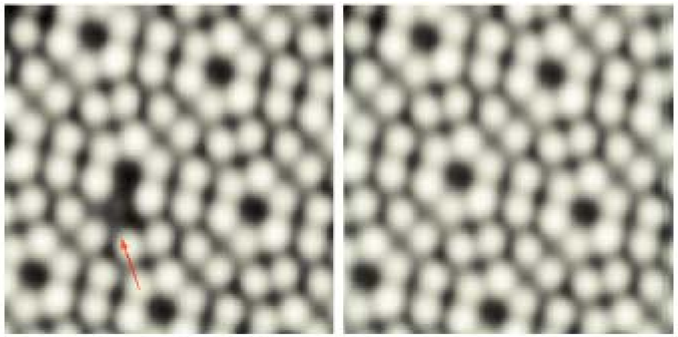


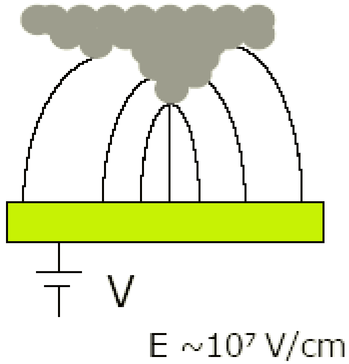
FIG. 2. (a) STM image of two adjacent pear shaped O_2 molecules on fcc sites. (b) Current during a 0.3 V pulse over the molecule on the right showing the moment of dissociation (step at t ~ 30 ms). (c) After pulse image with a grid fit to the platinum lattice showing one oxygen atom on an fcc and one on an hcp site along with the unperturbed neighboring molecule on an fcc site. (d) STM image taken after a second pulse with the tip centered over the molecule showing two additional oxygen atoms on hcp sites. Raw data images scanned at 25 mV sample bias and 5 nA tunneling current.

B.C. Stipe, M.A. Rezaei, W. Ho, S. Gao, M. Persson, B.I. Lundqvist, Phys. Rev. Lett. 78, 4410 (1997)

Manipulation by SPM

Field induced desorption of NO from Si(111)7x7





high electric field

local desorption observed by scanning at 1.5 V

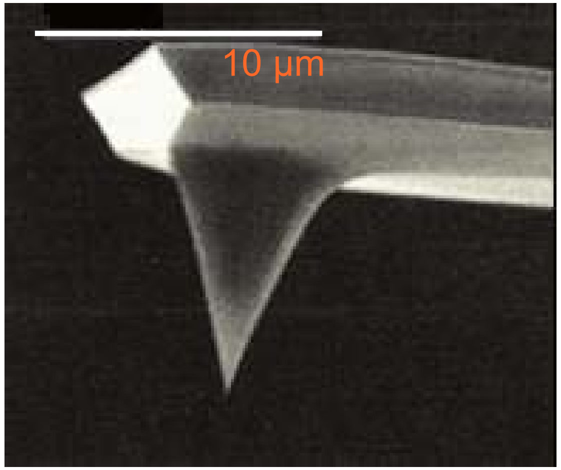
M.A. Rezaei, B.C. Stipe, W. Ho, J. Chem. Phys. 110, 4891 (1999)

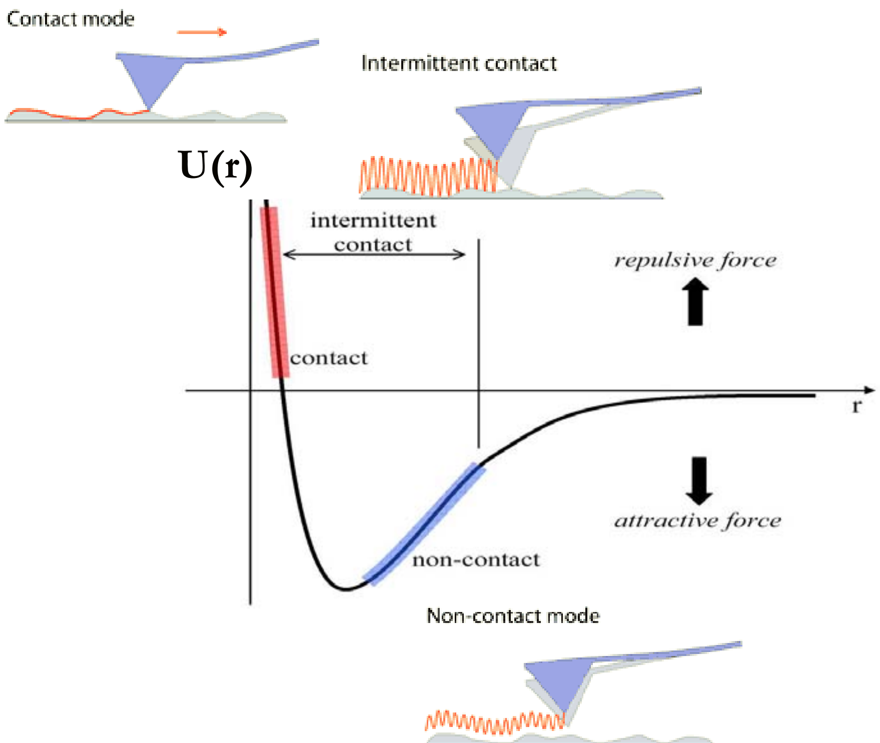
Atomic Force Microscopy

POLITECNICO DI MILANO

- **tip mounted on a cantilever**
- **feedback signal is the cantilever deflection, related to tip-surface atomic distance**

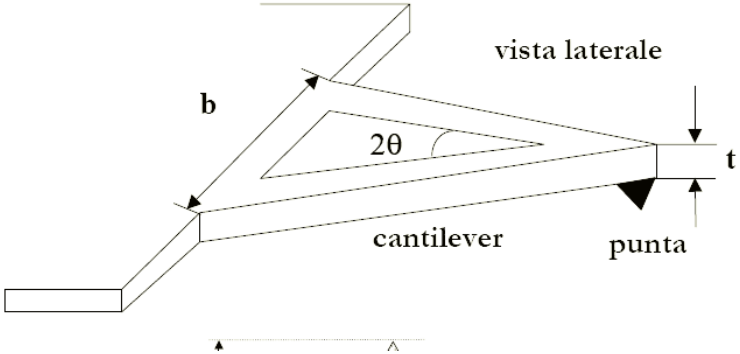
→ imaging of the surface topography

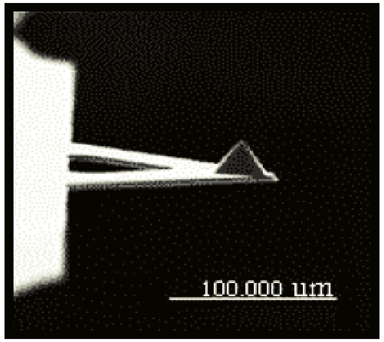


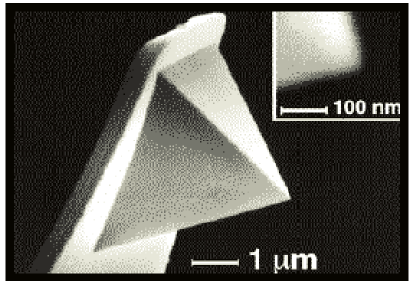


Probe material: Si, SiC, diamond, even C nanotubes!

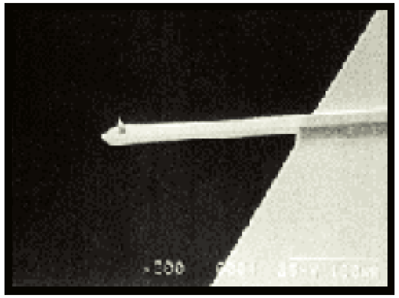
tip mounted on a cantilever

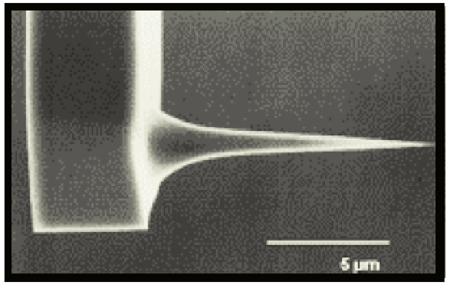


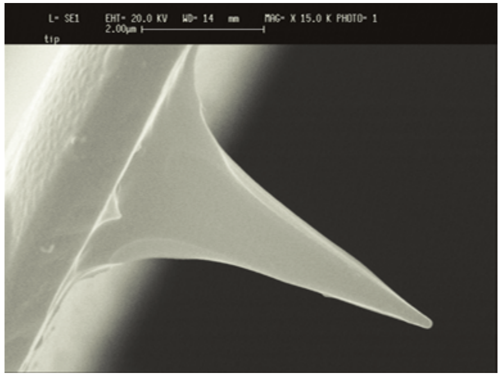


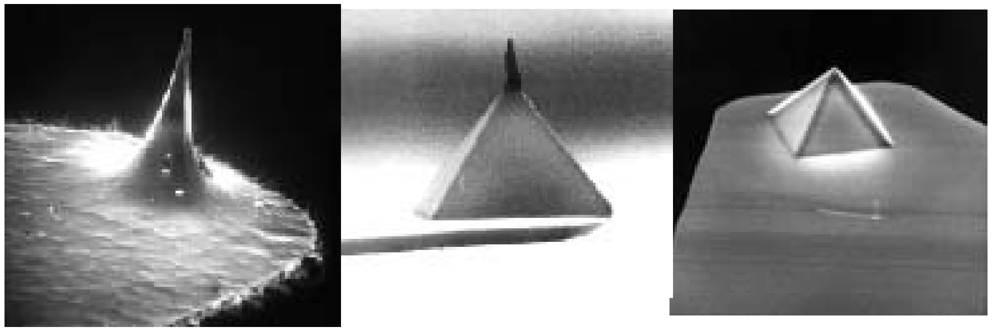


AFM can achieve a resolution of 10 pm, and unlike electron microscopes, can image samples in air and under liquids









AFM beam deflection detection

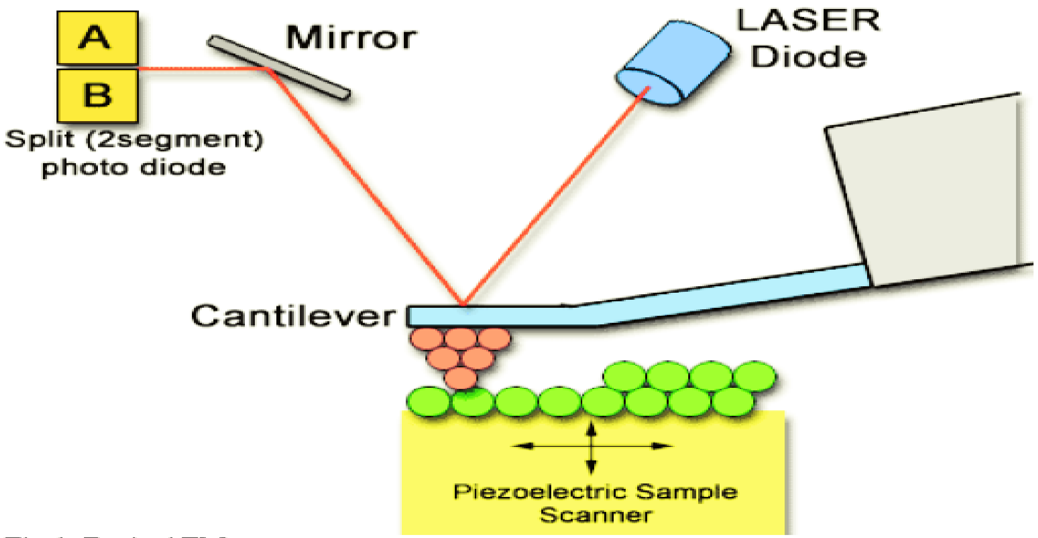


Fig.1. Basic AFM concept.

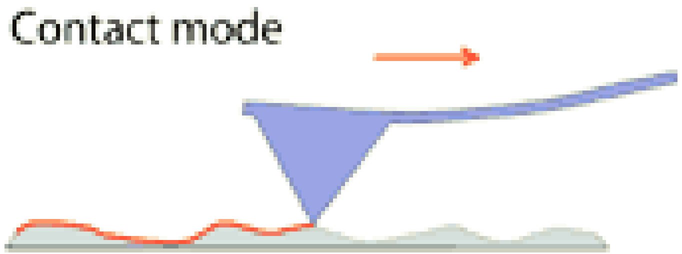
• laser light from a solid state diode is reflected off the back of the cantilever and collected by a position sensitive detector (PSD, 2 closely spaced photodiodes)

• angular displacement of the cantilever results in one photodiode collecting more light than the other → the resulting output signal is proportional to the deflection of the cantilever

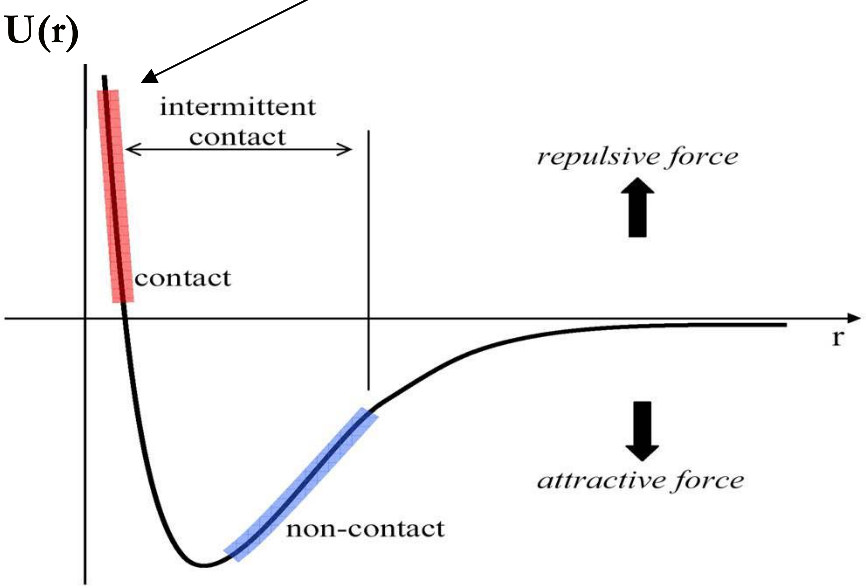
• detects cantilever deflection < 1 Å

AFM imaging modes: Contact Mode

- **tip is scanned across the sample while a feedback loop maintains a constant cantilever deflection (i.e. force)**
- **the tip contacts the surface through the adsorbed fluid layer**
- **forces range from nano to micro N in ambient conditions and even lower (0.1 nN or less) in liquids**

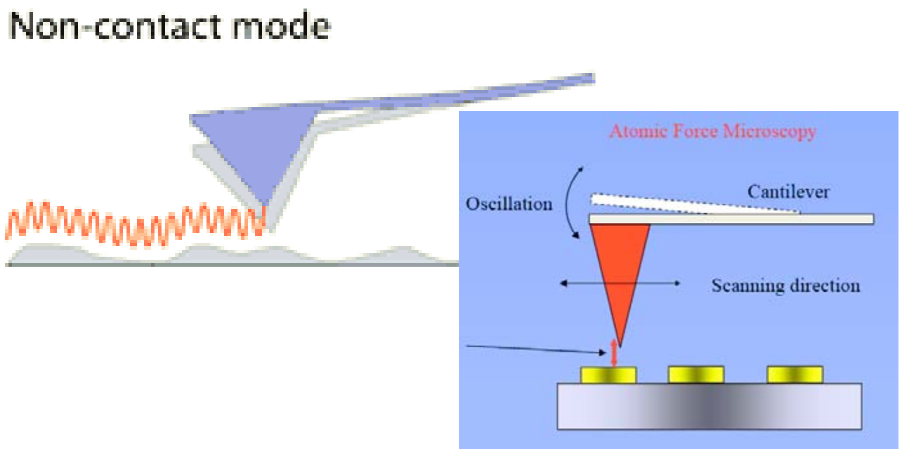


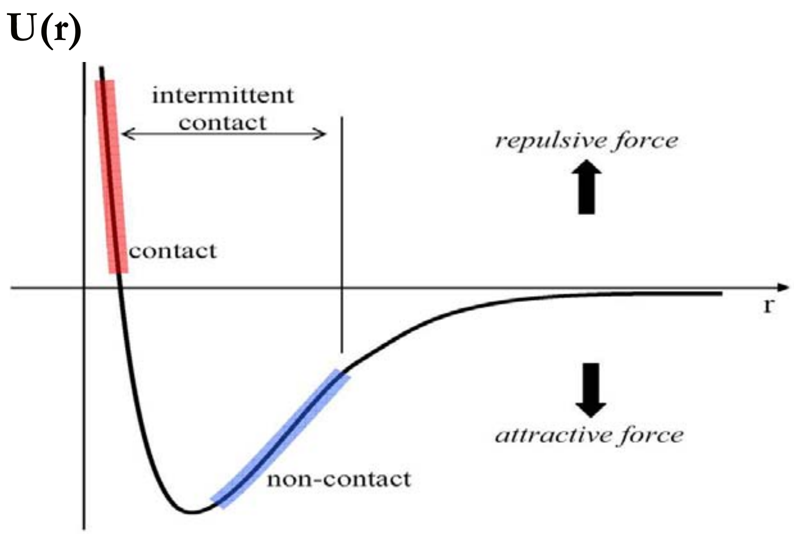
repulsion due to wavefunction overlapping



AFM imaging modes: Non-Contact Mode

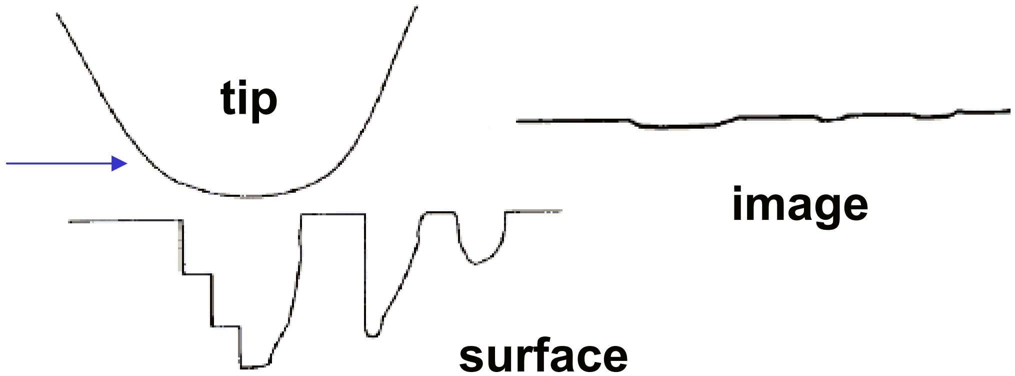
- cantilever is oscillated slightly above its resonant frequency (oscillations < 10 nm)
- tip does not touch the sample, instead, it oscillates above the adsorbed fluid layer
- the resonant frequency of the cantilever is decreased by the van der Waals forces which extend from 1-10 nm above the adsorbed fluid layer, this in turn changes the amplitude of oscillation
- a constant oscillation amplitude is maintained (feedback signal) → constant tip-surface distance (sometimes, constant frequency is the feedback signal, e.g. AFM in vacuum)



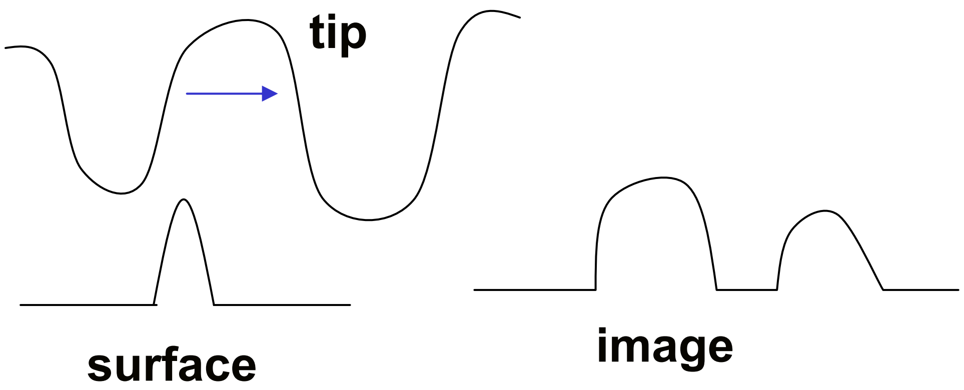


Tip shape effects

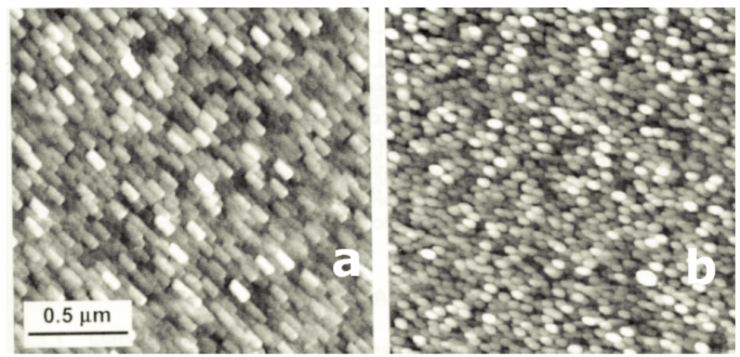
Lateral resolution is limited by tip radius of curvature (usually some nm or tens nm)



Artifacts can be introduced by the tip shape



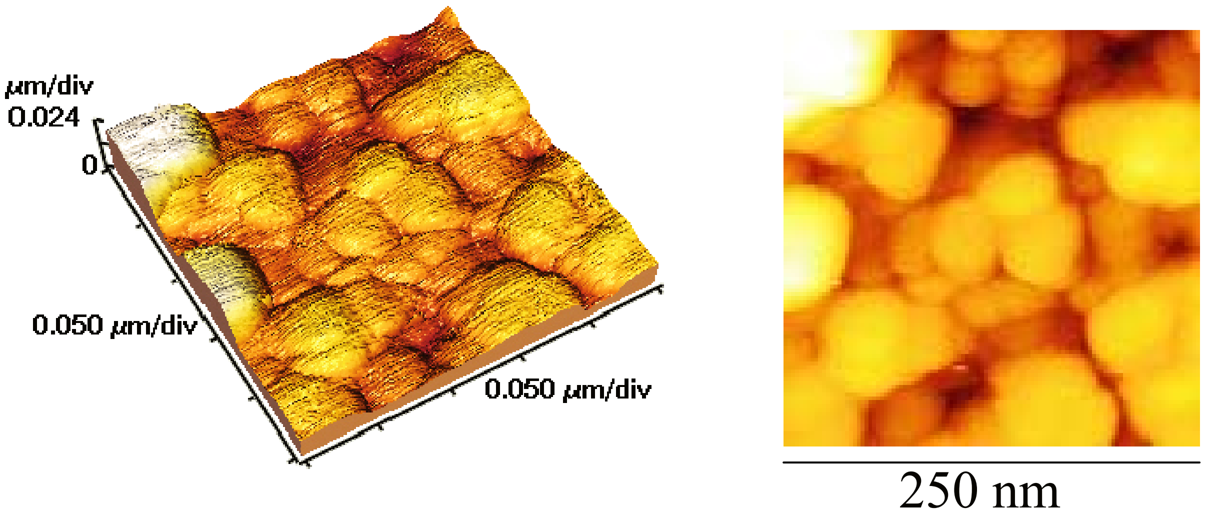
2 different tips

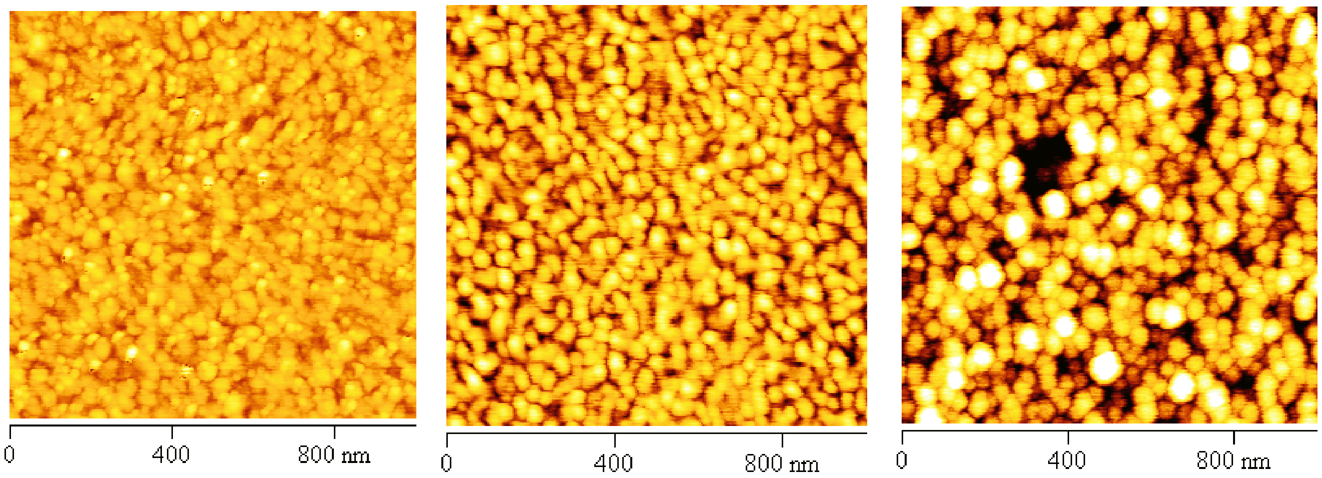


AFM EXAMPLES

cluster-assembled carbon films

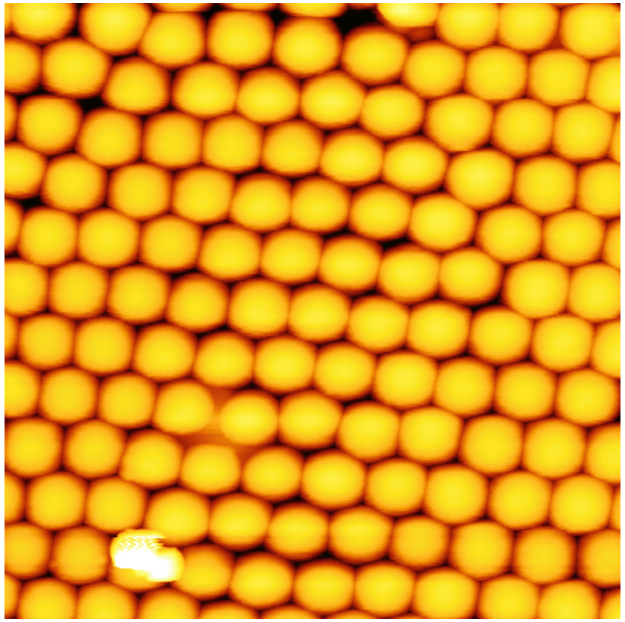
- non-contact AFM





TiO_2 thin films

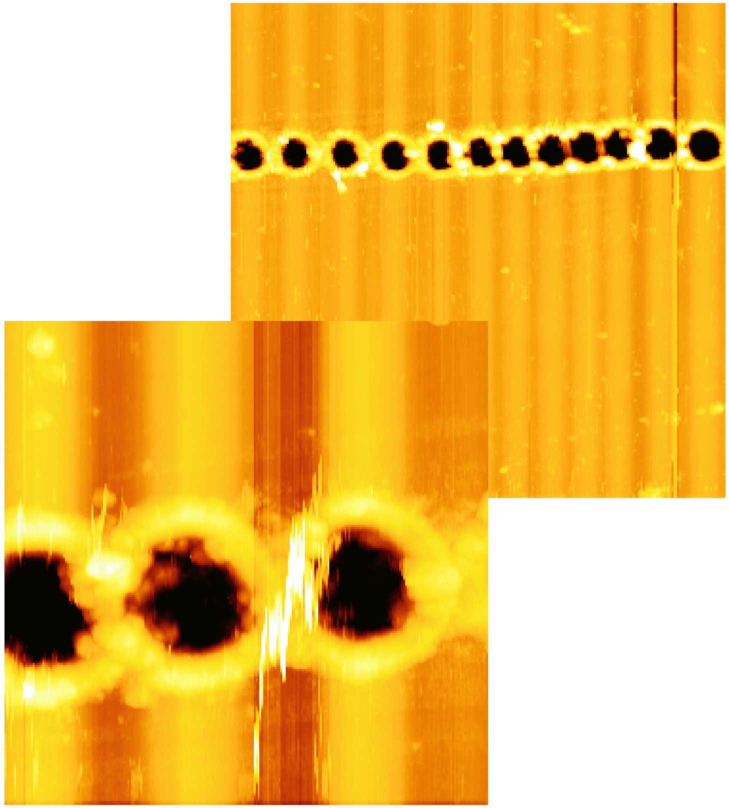
polystyrene self-assembled nanoparticles



3 micron

- **contact AFM**

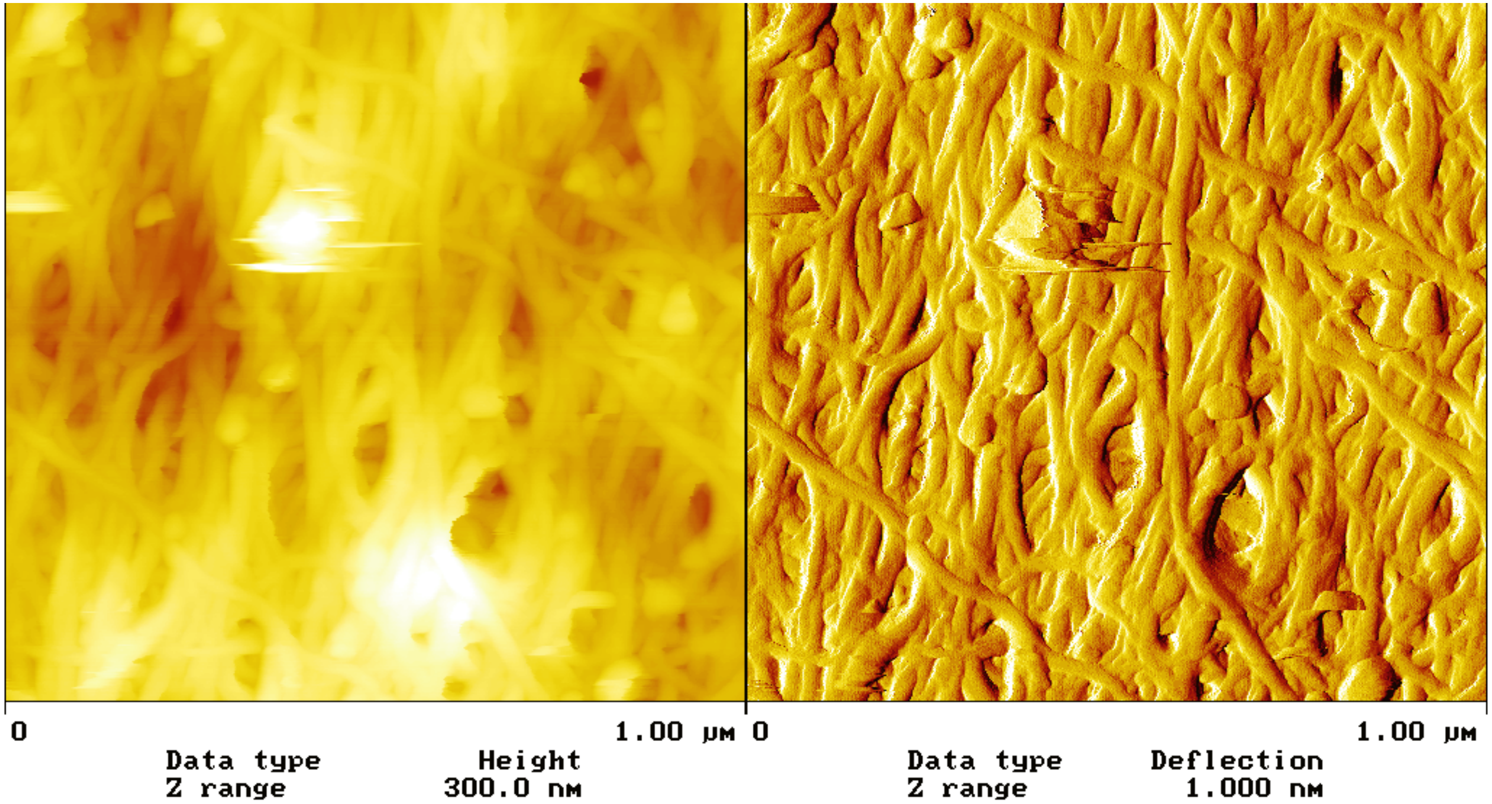
20 micron



5 micron

ultrashort laser pulses on glass

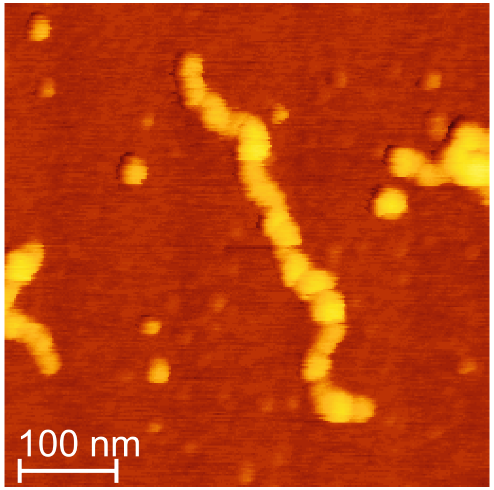
SWNT bundles



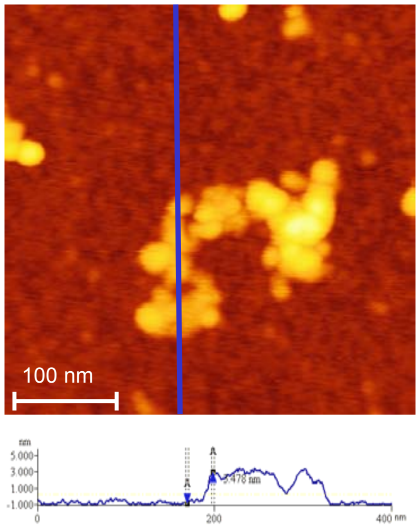
AFM of biomolecules (e.g. proteins, DNA)

aggregation of Ataxin-3 (responsible for neurodegenerative disease SCA-3)

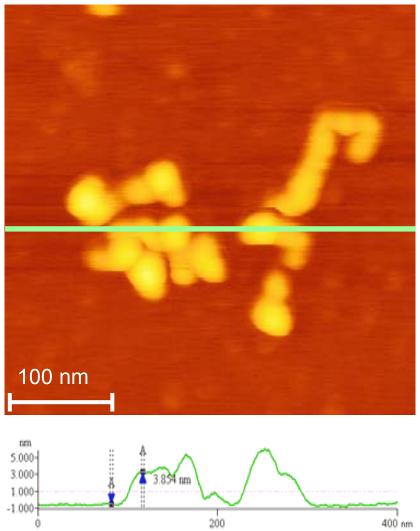
observation on mica (inert, flat substrate)



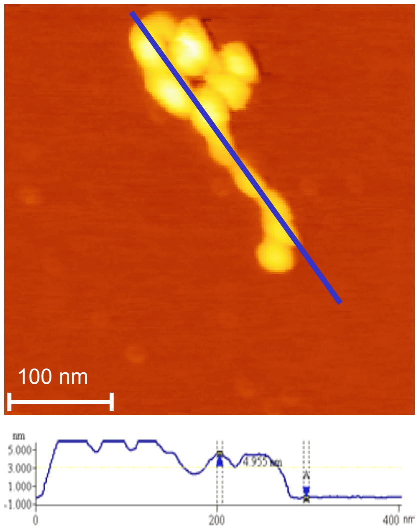
182



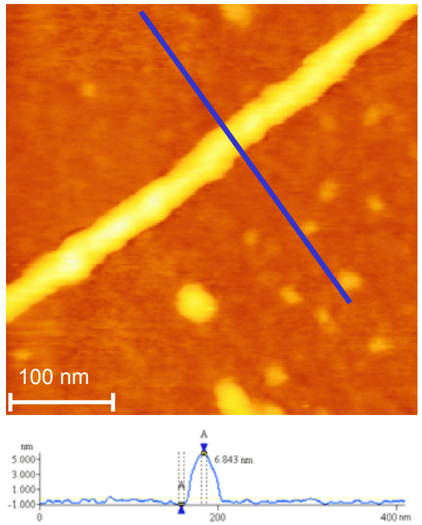
291



Q6



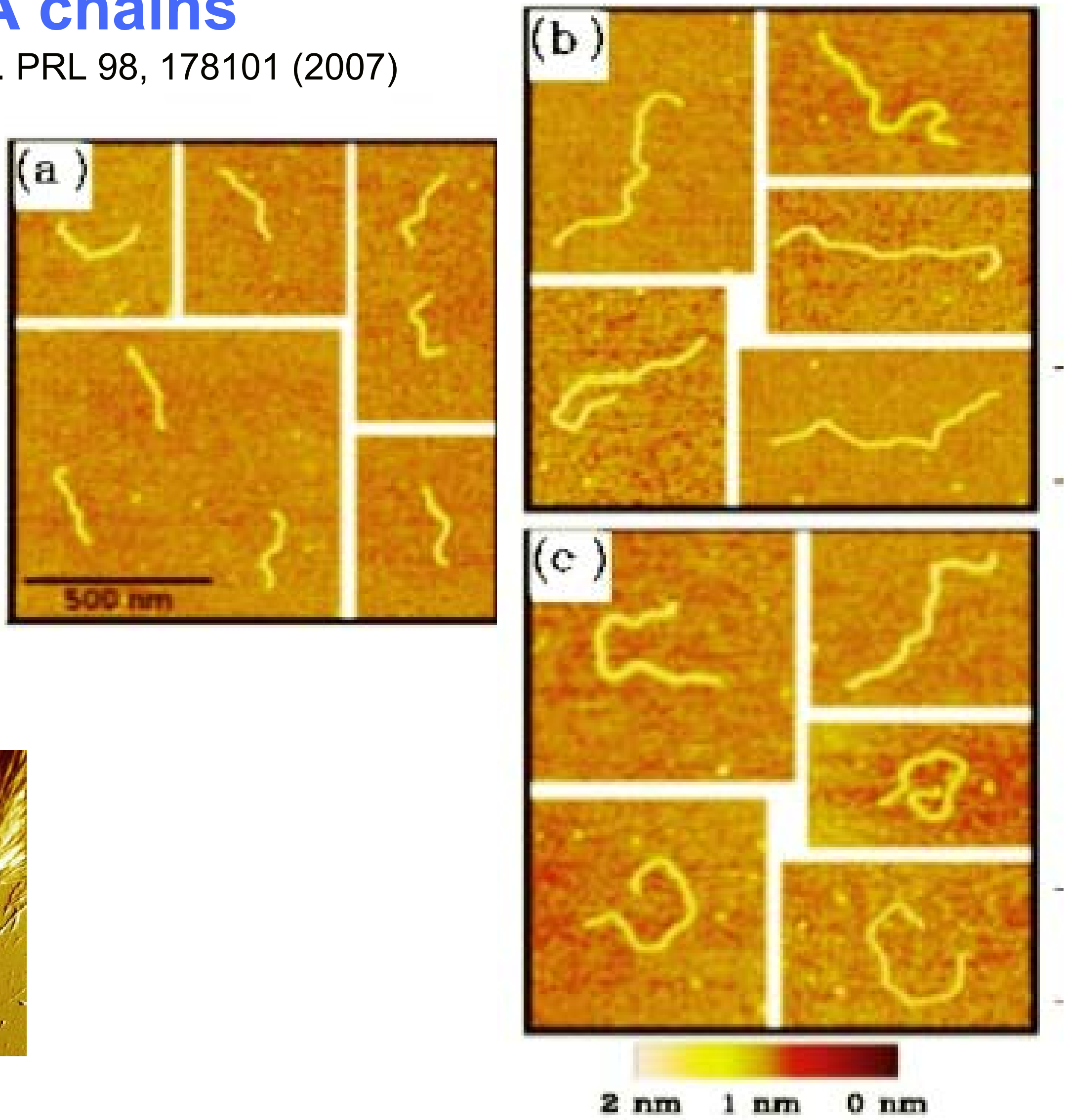
Q36



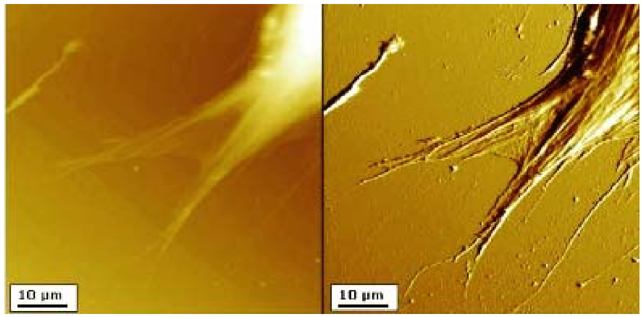
unpublished material

DNA chains

J. Moukhtar et al. PRL 98, 178101 (2007)



cell imaging

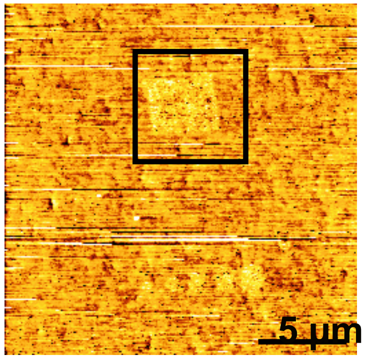


Alessandrini A., Meas. Scie. Technol. 2005

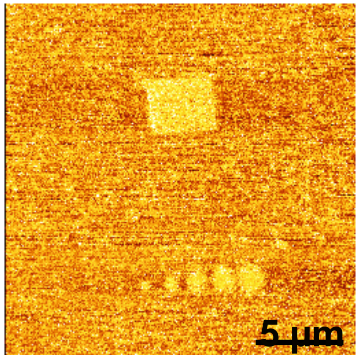
DPN, Dip Pen Nanolitography

AFM tip functionalized with organic molecules (“ink”) to “write” on a surface (usually gold)

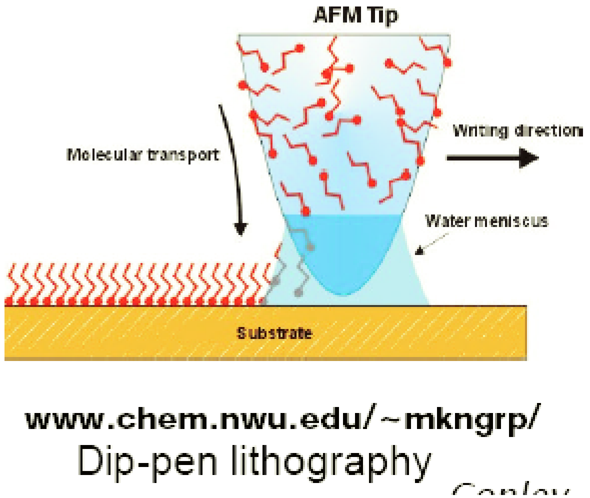
Topography



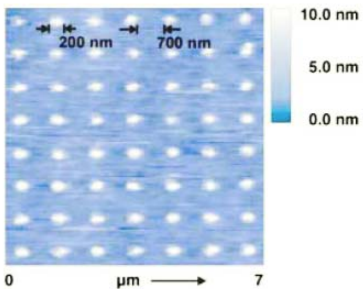
Lateral Force



mercaptan



Dip Pen Nanolithography of DNA and Protein Micro and Nanoarrays

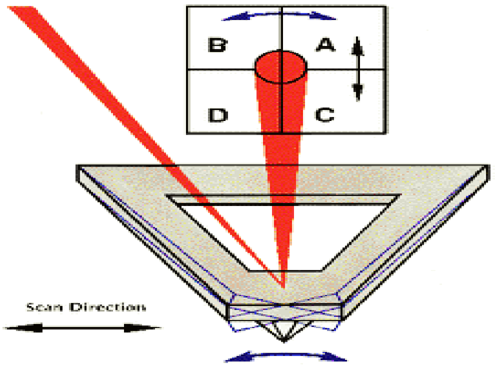


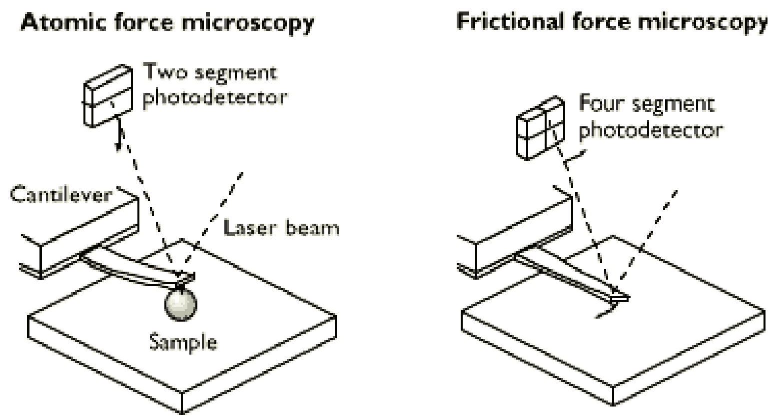
K.B. Lee et al., Science 295, 1702 (2002), proteins

Other SPM modes

Lateral Force Microscopy

While topographic imaging uses the up-and-down deflection of the cantilever, friction imaging uses torsional deflection



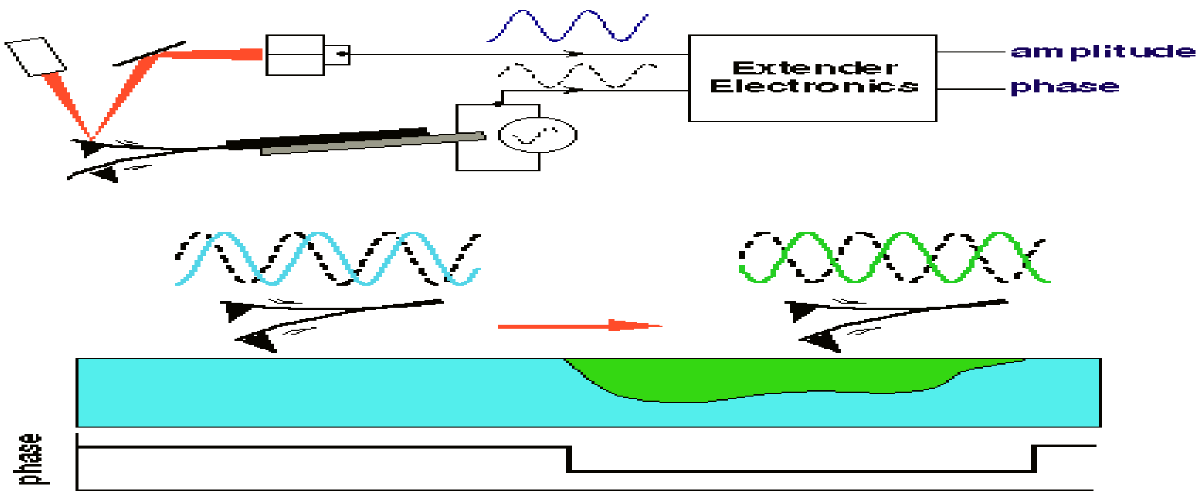


- **the degree of torsion of the cantilever is used as a relative measure of surface friction caused by the lateral force exerted on the probe.**
- **e.g. identify transitions between different components in a polymer blend, in composites or other mixtures**

Other SPM modes

Phase Imaging

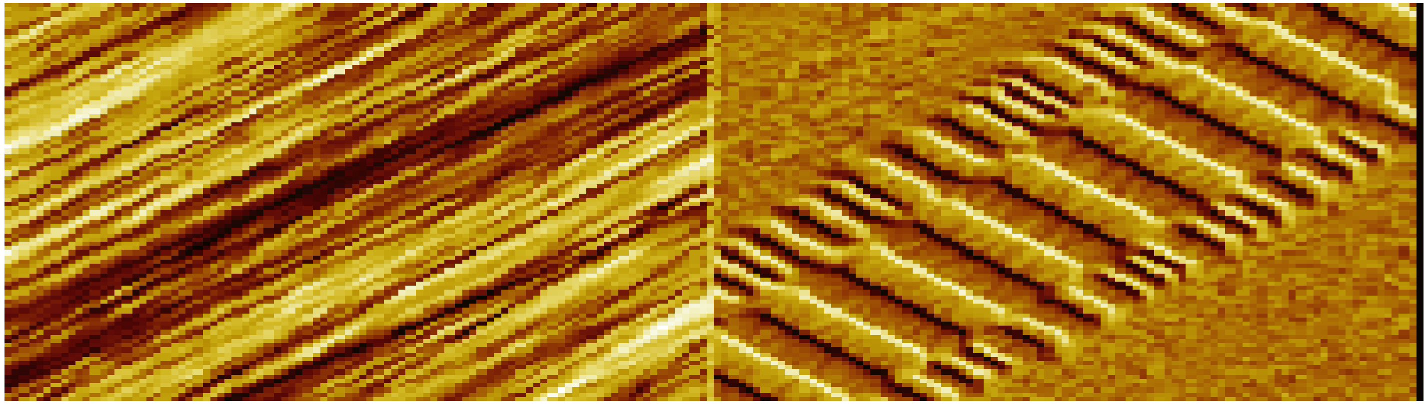
Oscillate the cantilever at its resonant frequency. The amplitude is used as a feedback signal. The phase lag is dependent on several things, including composition, adhesion, friction and viscoelastic properties



- Identify two-phase structure of polymer blends
- Identify surface contaminants that are not seen in height images
- Less damaging to soft samples than lateral force microscopy

Other SPM modes

MFM: Magnetic Force Microscopy



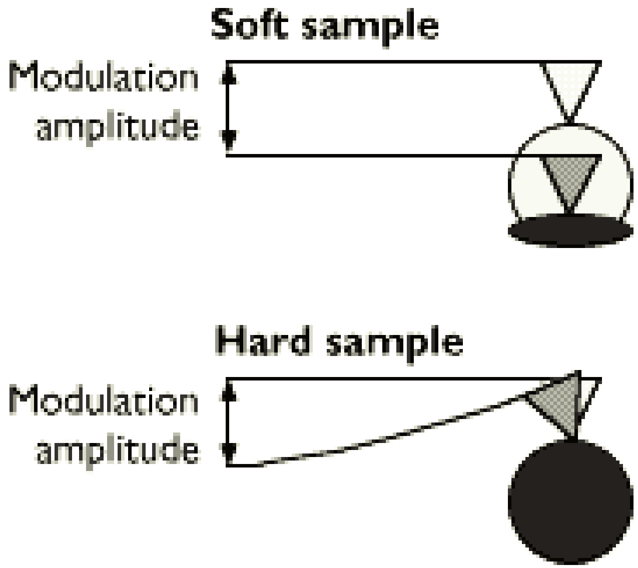
Overwritten tracks on a textured hard disk, 25 micron scan

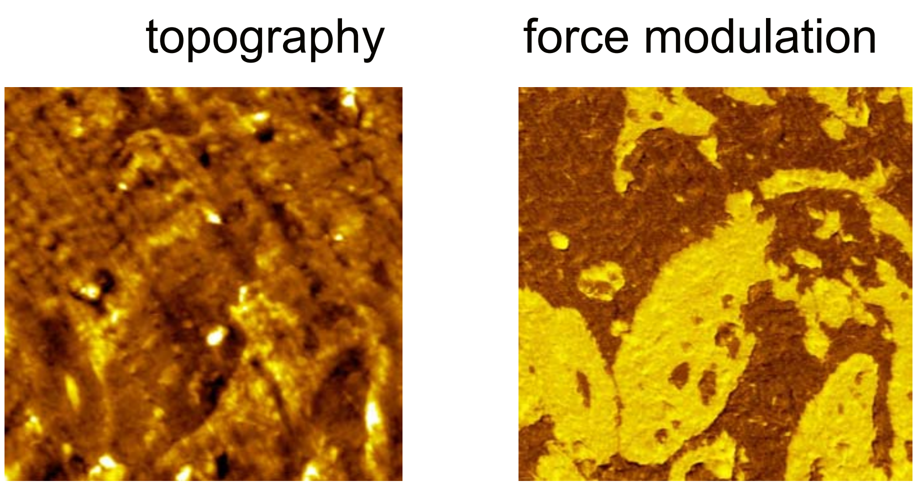
- MFM tips are coated with a **ferromagnetic material**.
- The cantilever is oscillated, **gradients in the magnetic forces on the tip shift the resonant frequency of the cantilever** →magnetic force image

Other SPM modes

Force Modulation Imaging

- **Oscillate the cantilever vertically at a rate that is significantly faster than the scan rate**
- **The amplitude of the oscillations changes in response to the sample stiffness**





polymer

Mechanical properties: nanoindenting and scratching

- a **diamond** tip is mounted on a metal cantilever and scanned
- **indenting mode** presses the tip into the sample
- **scratch mode** drags the tip across the sample at a specific rate and with a specified force

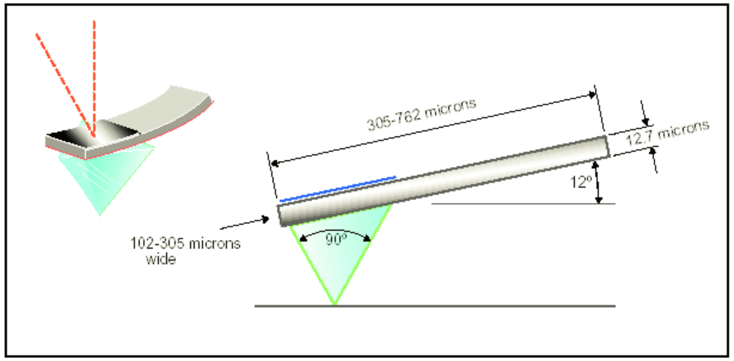
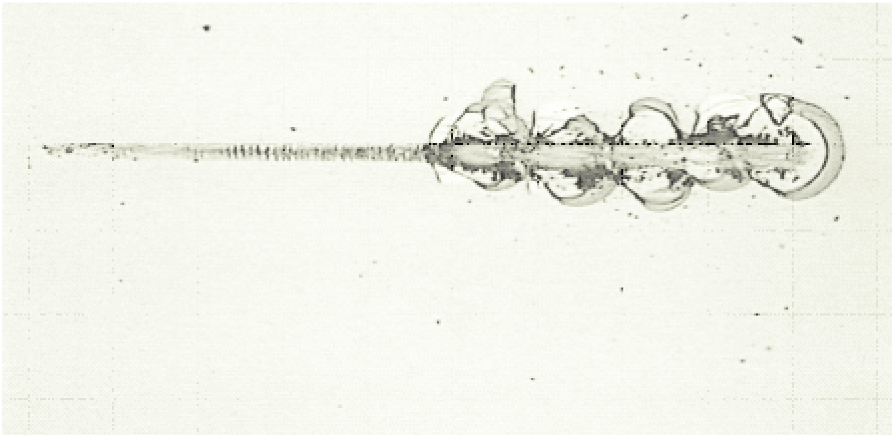
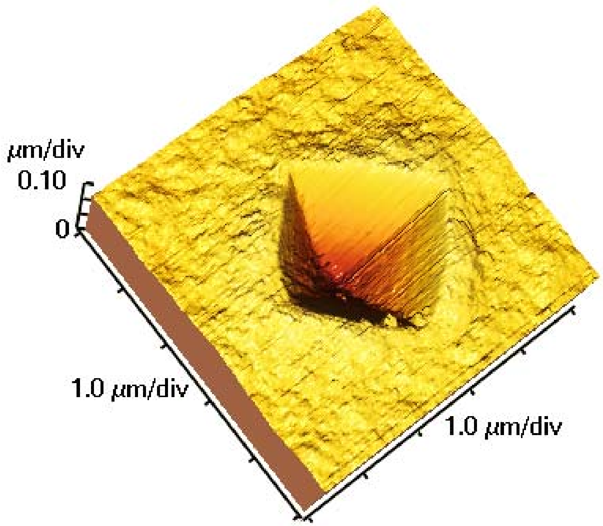


Figure 1: Typical indentation cantilever with dimensions.





Some articles and books:

- G. Binnig, H. Rohrer, Rev. Mod. Phys. 59, 615 (1987) Nobel Prize lecture
- R. Wiesendanger, *Scanning Probe Microscopy and Spectroscopy – Methods and Applications*, Cambridge University Press 1994
- *Scanning Tunneling Microscopy*, Edited by J.A. Stroscio and W.J. Kaiser, Academic Press 1993
- *Scanning Probe Microscopy and Spectroscopy – Theory, Techniques and Applications*, Edited by D. Bonnel, Wiley 2001
- C. Bai, *Scanning Tunneling Microscopy and Its Applications*, Springer 2000
- C.B. Duke, *Tunneling in solids*, Academic Press 1969

"Tunneling is an art, not a science".

G.Binnig. Nobel prize lecture, November 1986