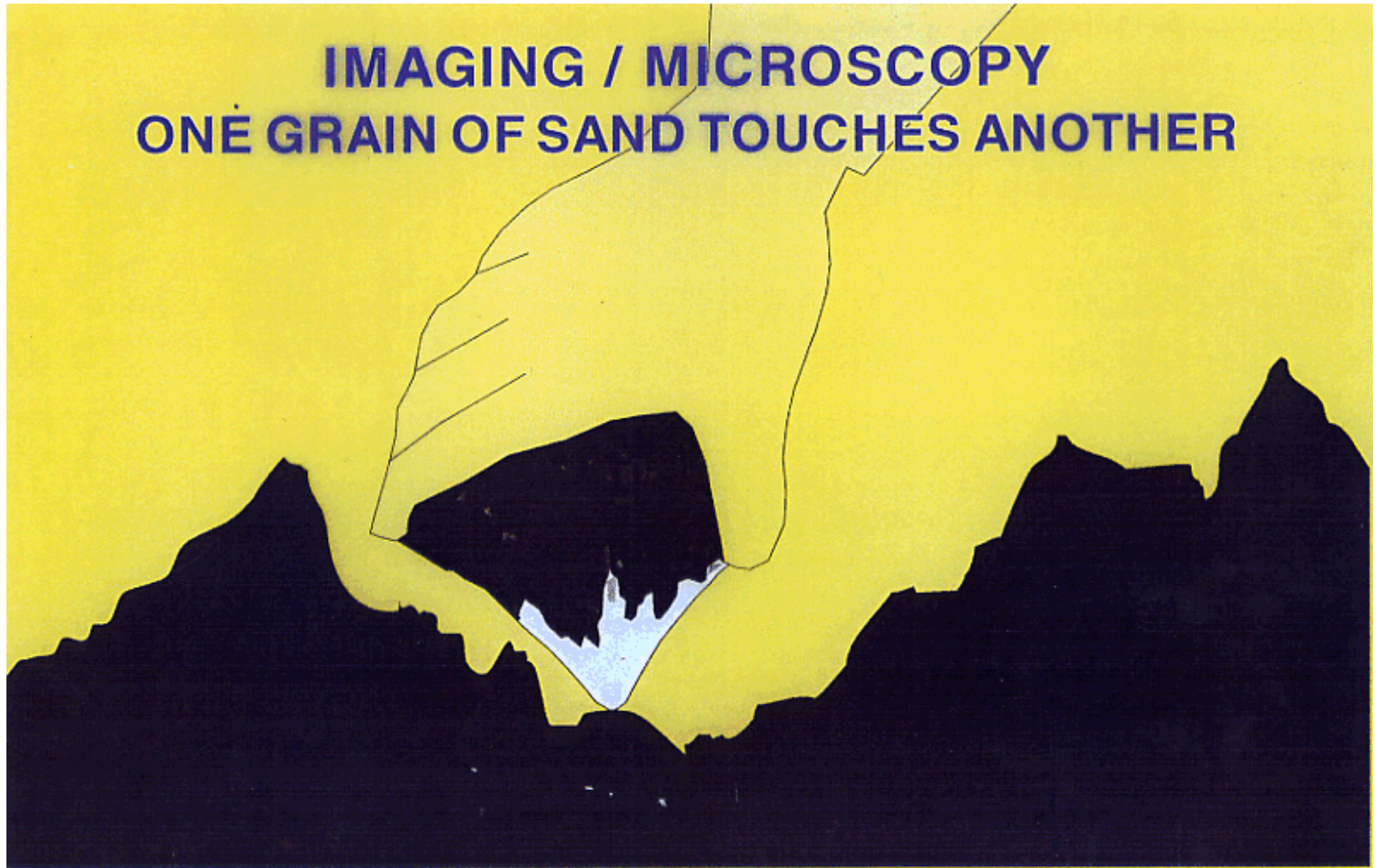


IMAGING / MICROSCOPY

ONE GRAIN OF SAND TOUCHES ANOTHER



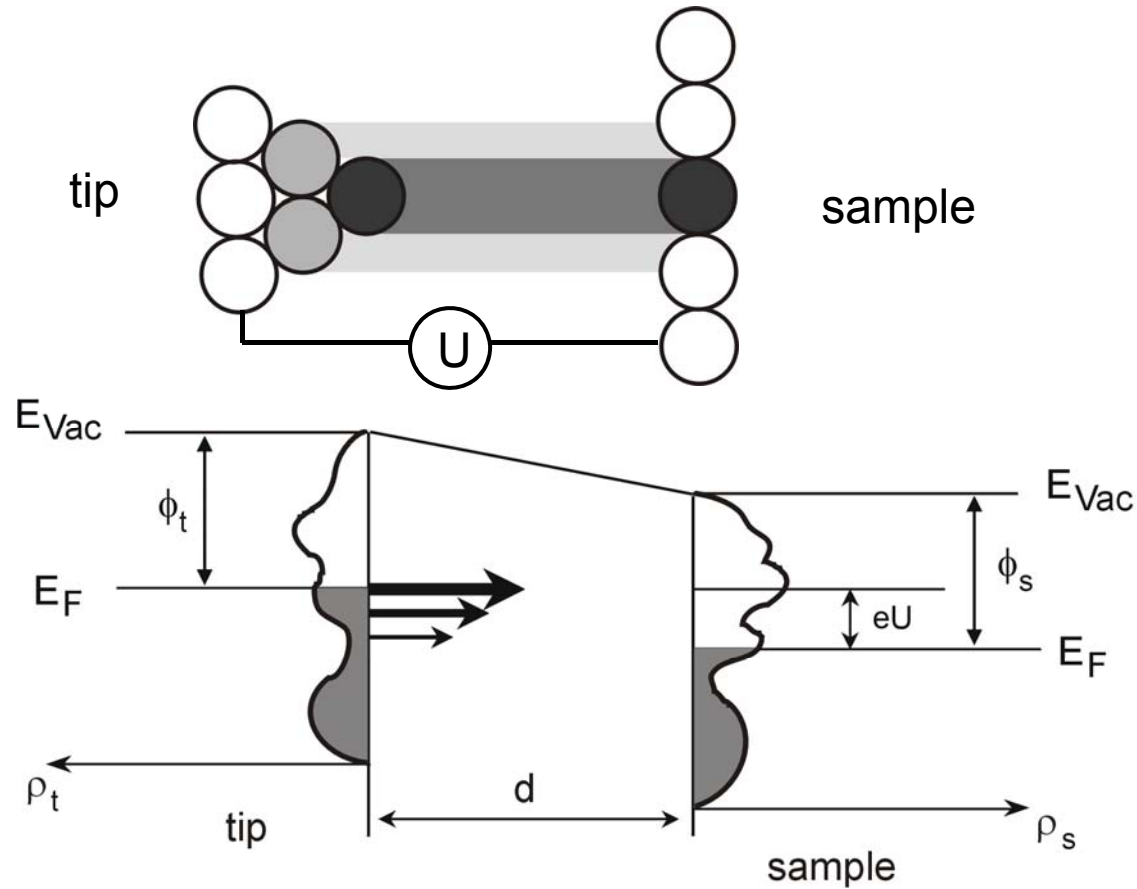
H. Rohrer

IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

Repetition VII

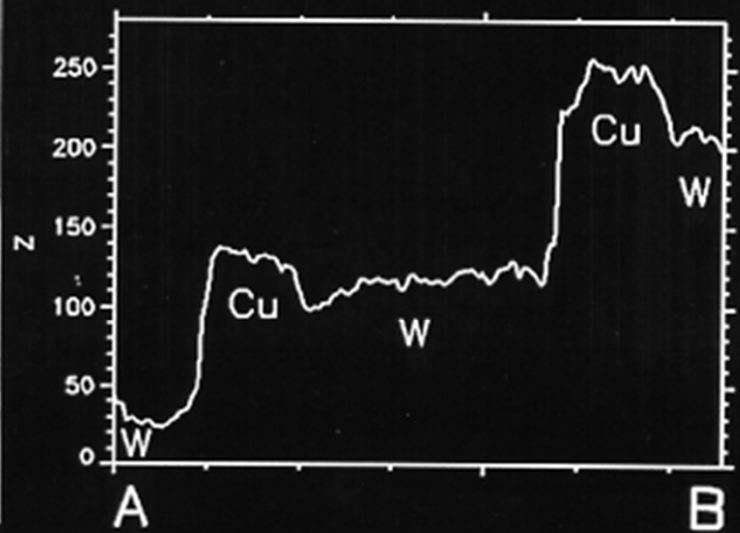
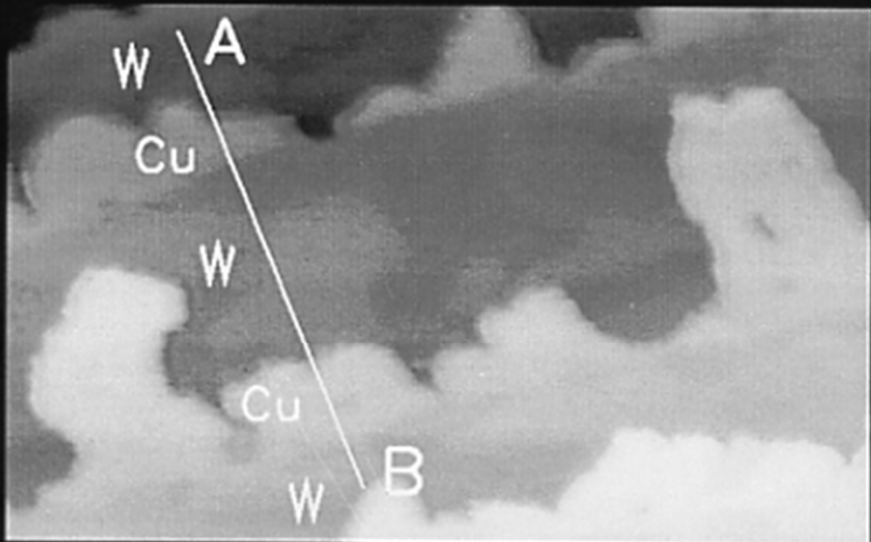
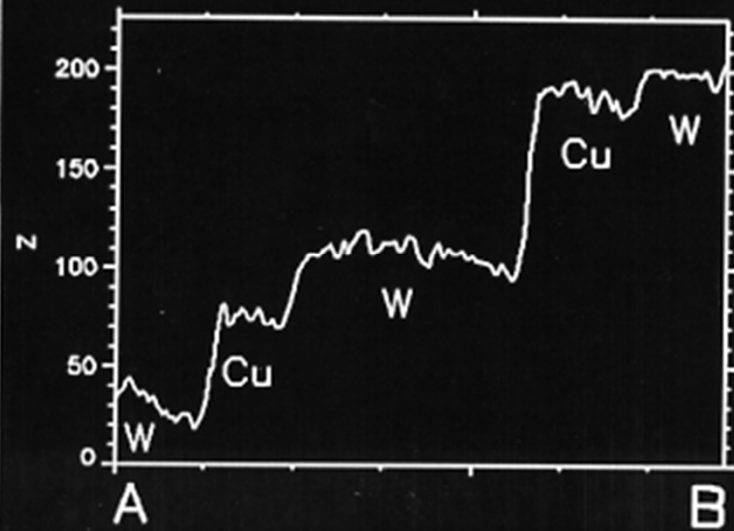
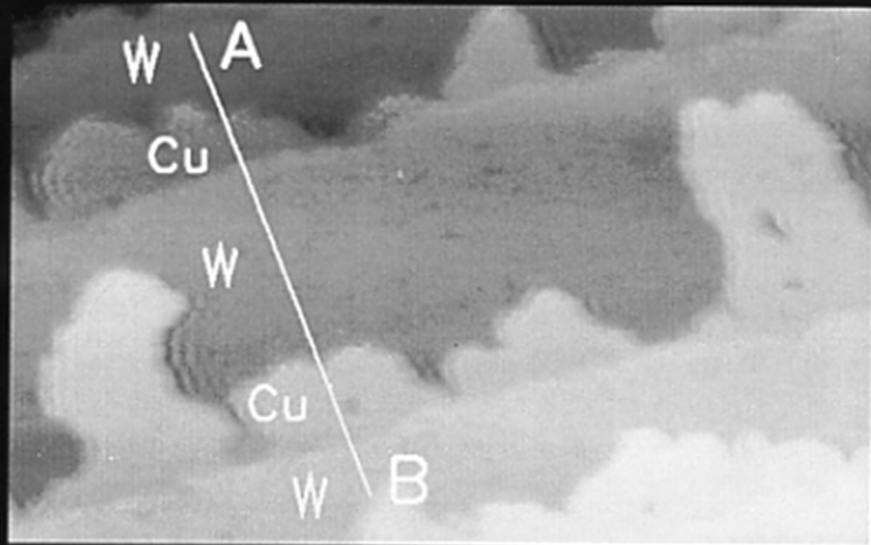
- Scanning Tunneling Microscopy
- Principle, Creep, Non-linearities, Tip Artefacts
tip preparation
- Beyond Microscopy: Imaging, Mapping, Manipulation
- Quantum mechanical Tunneling: Tip and Surface
States: Spectroscopy

Scanning Tunneling Microscopy

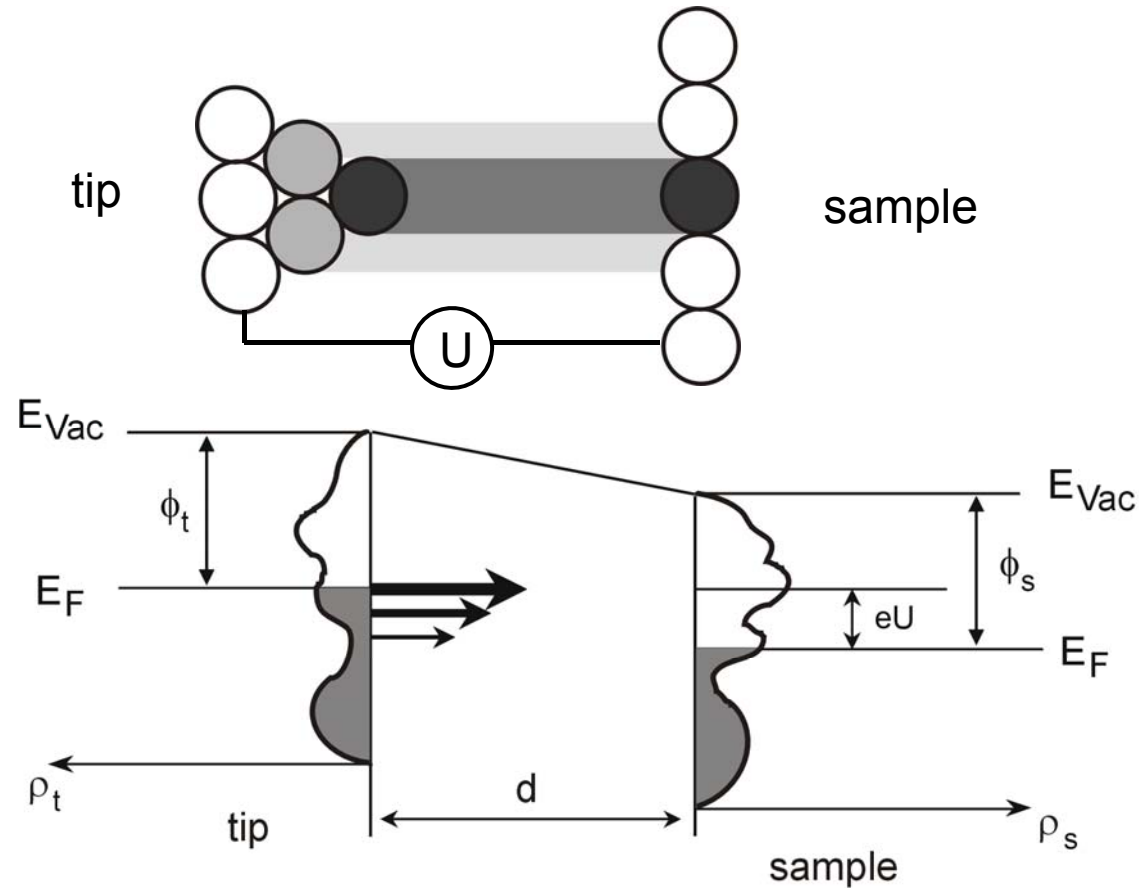


Tunneling current: $I_{tunnel} \sim U \rho_t \rho_{s(x,y)} e^{-const d}$ (Tersoff and Hamann)

=> sensitivity to local electronic structure of the sample



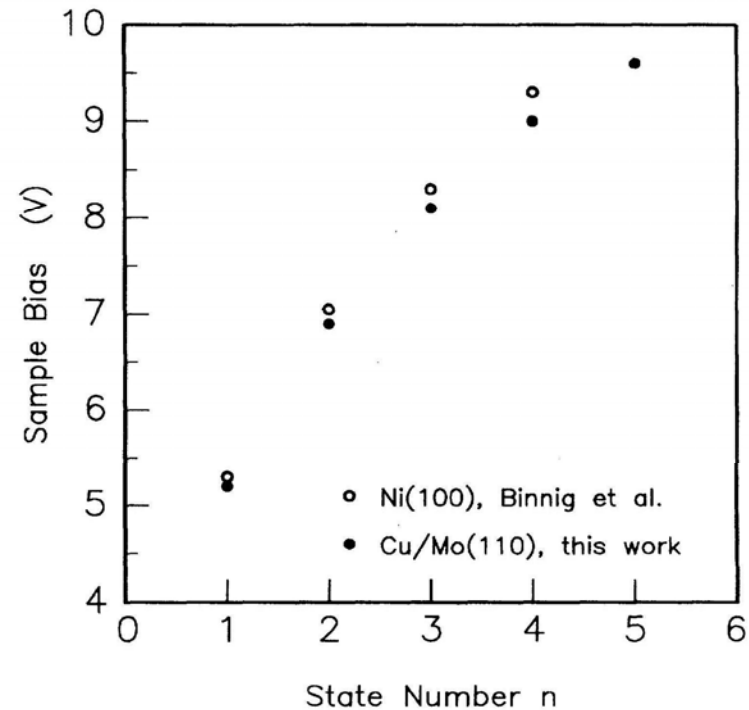
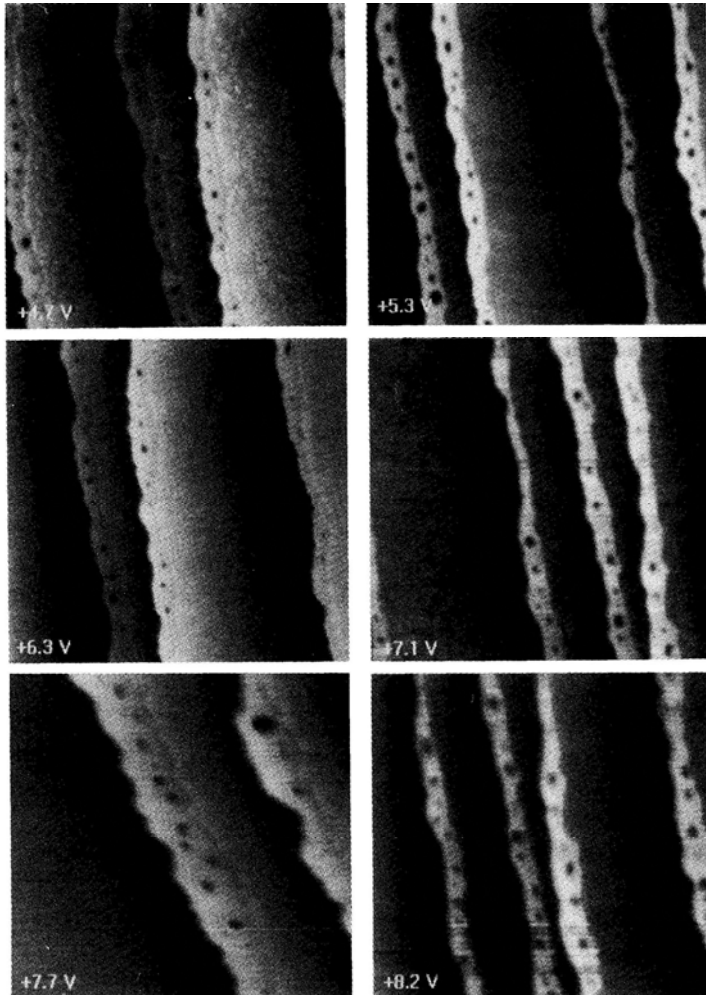
Scanning Tunneling Microscopy



Tunneling current: $I_{\text{tunnel}} \sim U \rho_t \rho_{s(x,y)} e^{-\text{const} d}$ (Tersoff and Hamann)

=> sensitivity to local electronic structure of the sample

Chemical Sensitivity in STM: surface states vs image states



Periodic Contrast Change in U_{gap} : Image Resonant Enhancement !

T. Jung et al. Phys. Rev. Lett. 74, 1641 (1995)

Chemical Sensitivity in STM: surface states vs image states

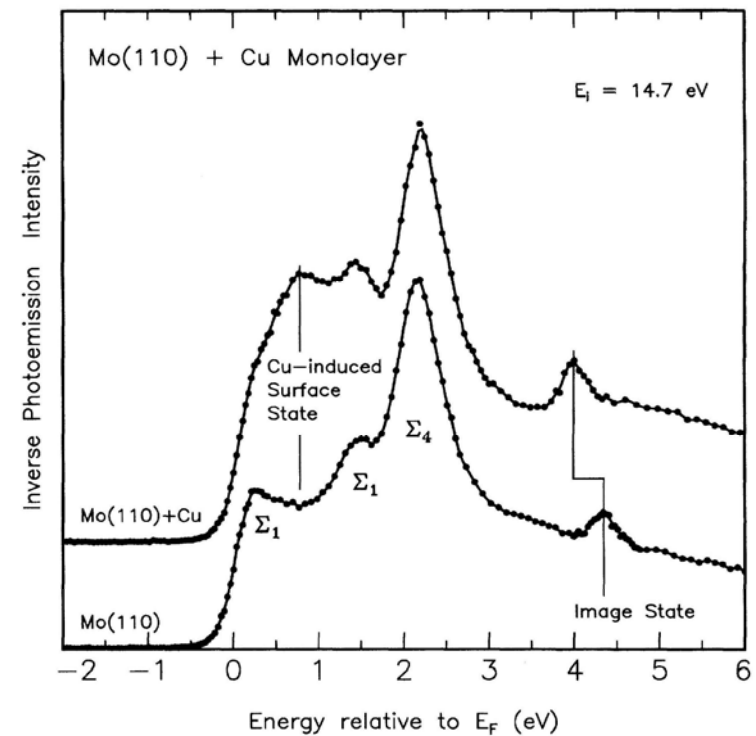
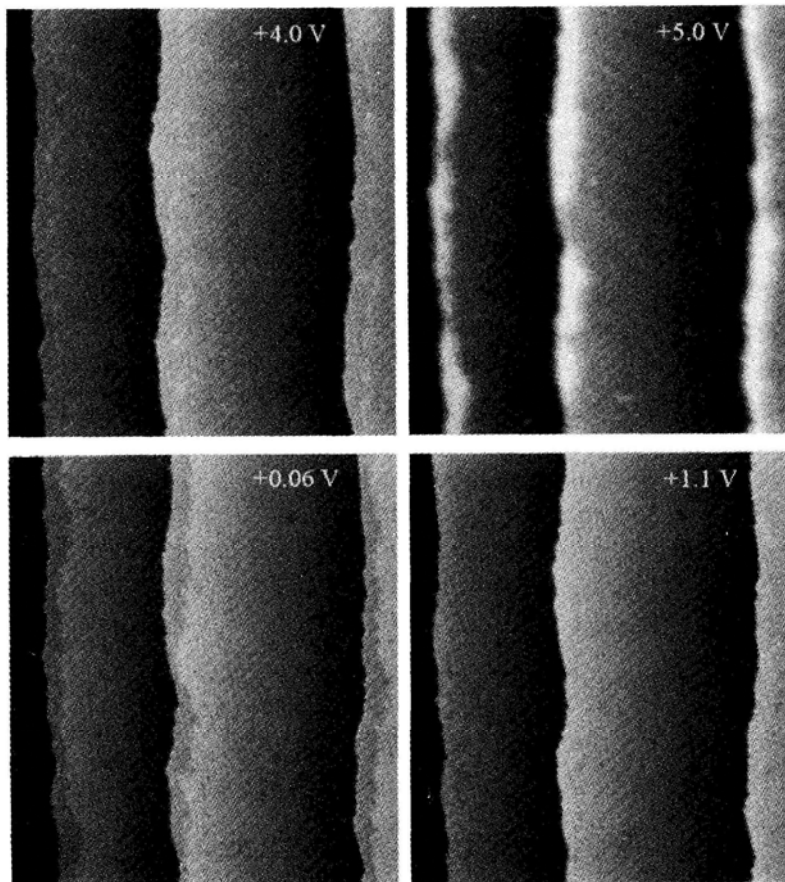
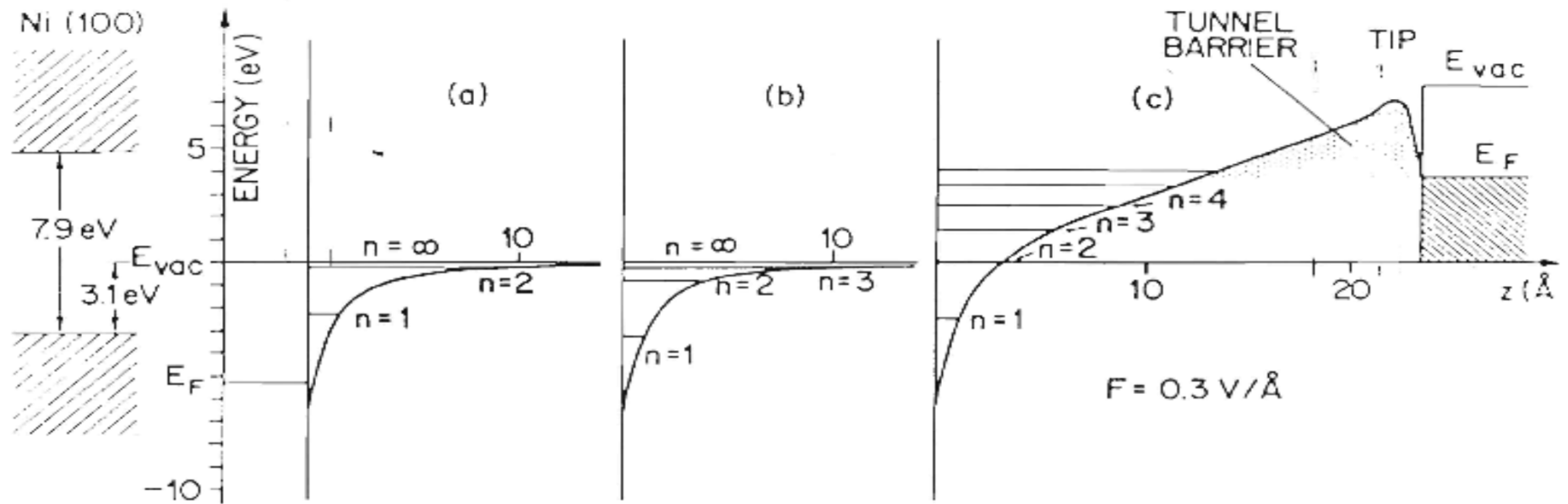


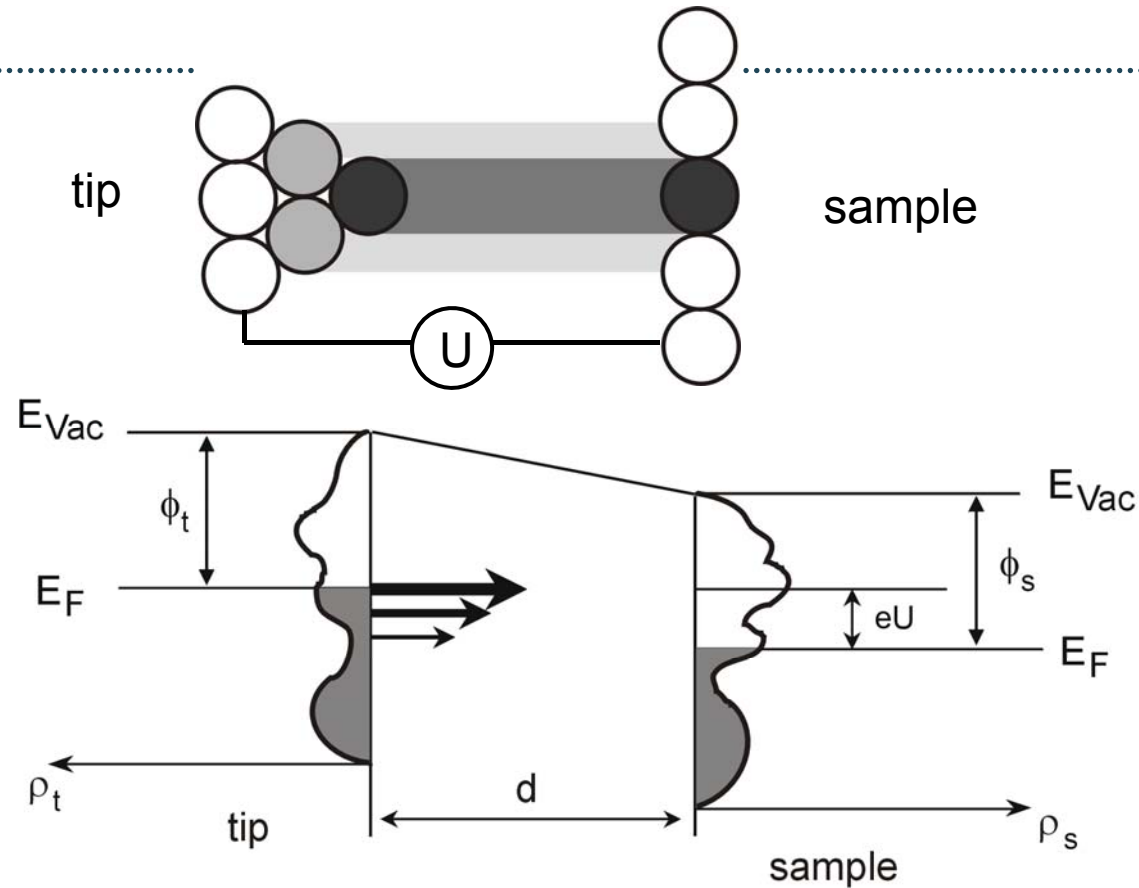
Image State Contrast \gg Surface State Contrast

Bildladungspotential ueber leitender Oberflaeche



- a) idealer Leiter
- b) hohe Stufendichte
- c) Potentialverschiebung im STM

Scanning Tunneling Microscopy

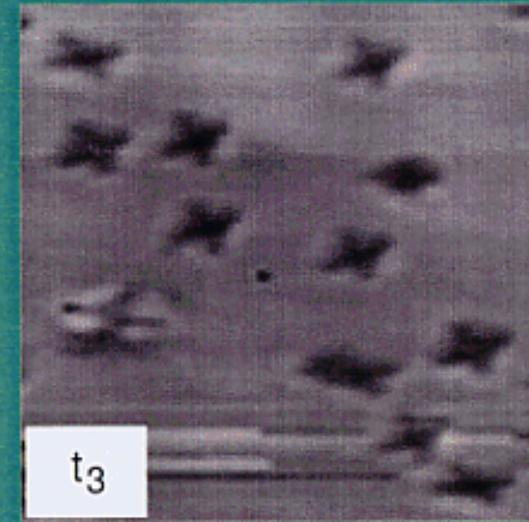
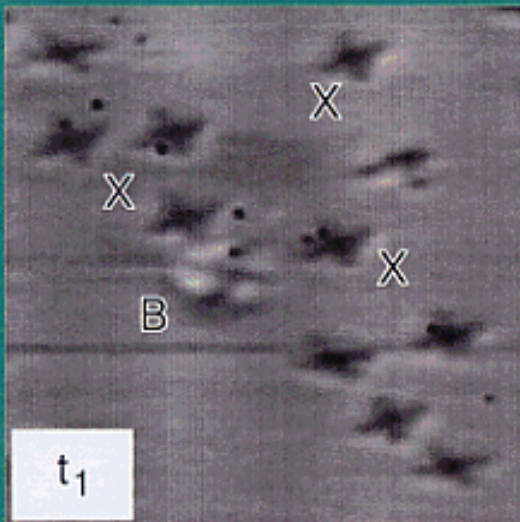


Tunneling current: $I_{tunnel} \sim U \rho_t \rho_{s(x,y)} e^{-const d}$ (Tersoff and Hamann)

=> sensitivity to local electronic structure of the sample

Molecular Motion Constrained to Two Dimensions

co-evaporation of Cu-tetraphenyl porphyrin (pins, X) and
Cu-tetra-di-t-butyl-phenyl porphyrin (balls, B)



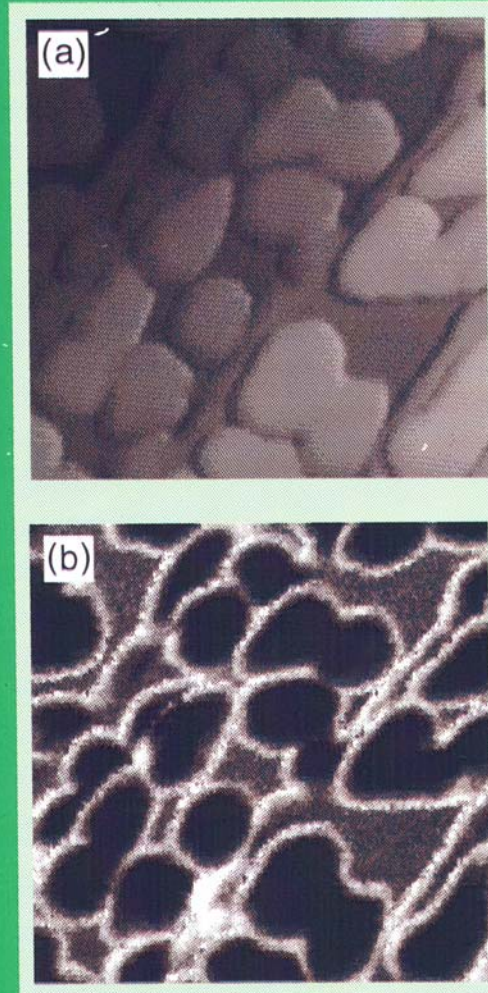
Molecular structure influences: STM - Contrast
DE Adsorption
Mobility



T.A. Jung, R.R. Schlittler and J.K. Gimzewski
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

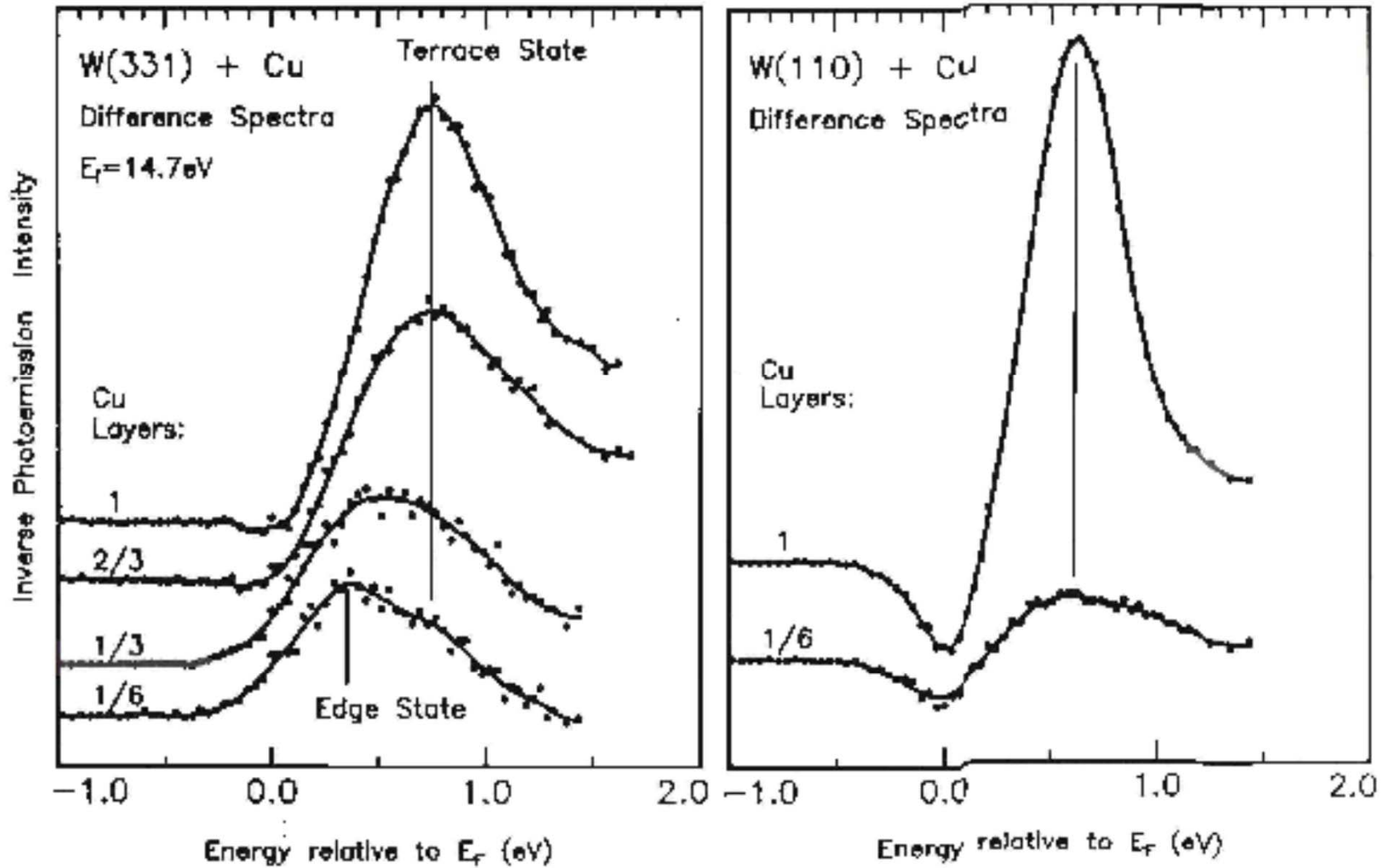
Chemical Information from SPM / Spectroscopy

Spectroscopic Changes at the Edge of Fe Islands on W(110)



- (a) From Bode et al., Phys. Rev. B 54, R 8385 (1996);
(b) From Wiesendanger et al., J. Vac. Sci. Technol. A 14, 1161 (1996).

Stufenzustände und Oberflächenzustände auf W(331)

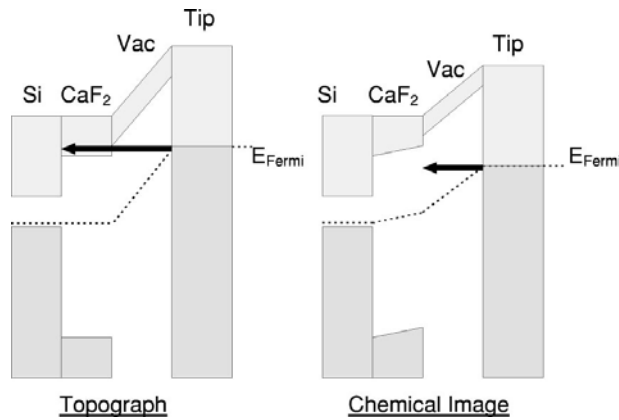


Dimensionaliteit

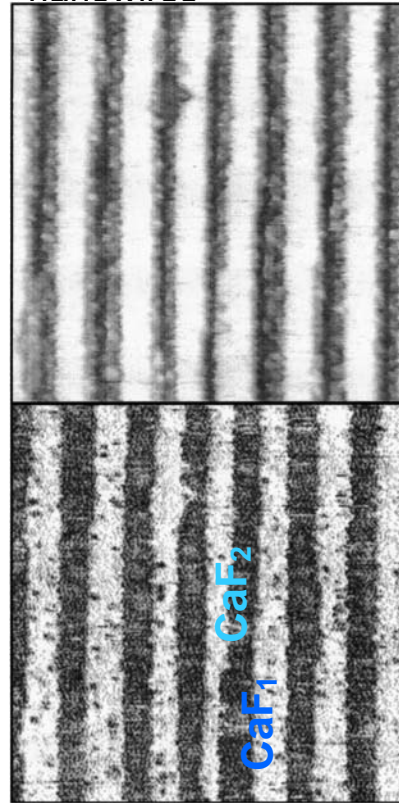
3D(bulk) – 2D (flaech) – 1D (draht) – 0D (punkt)

- Wachstumsverhalten
- Elektronische Zustände
- ... andere kooperative Phänomene

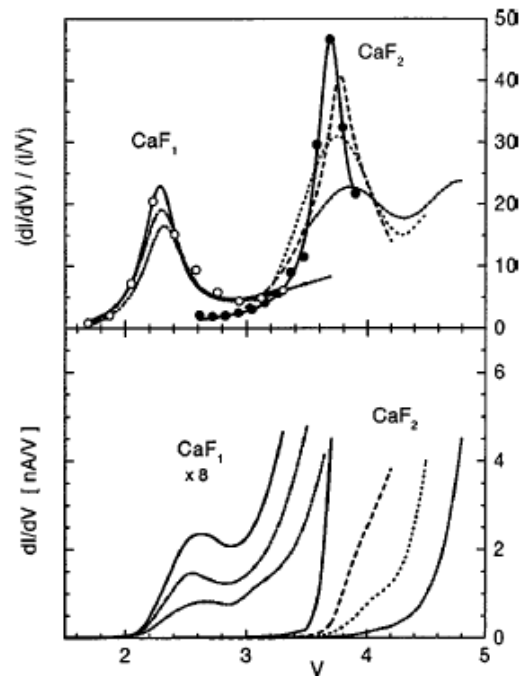
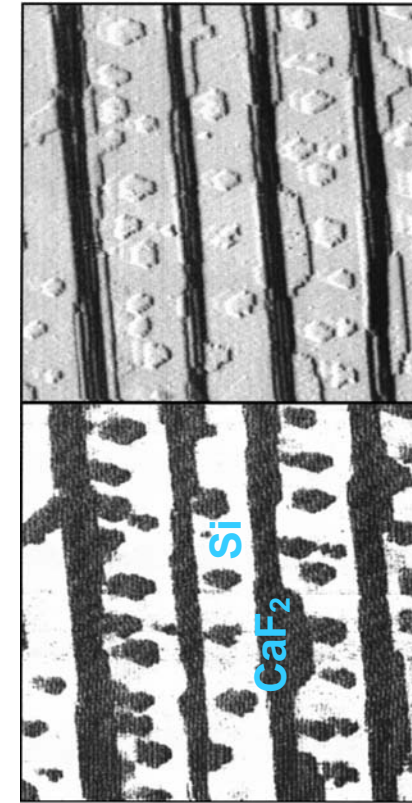
Scientific Background: Chemical Imaging



CaF₁ / CaF₂
nanowires



CaF₂ on Si(111)



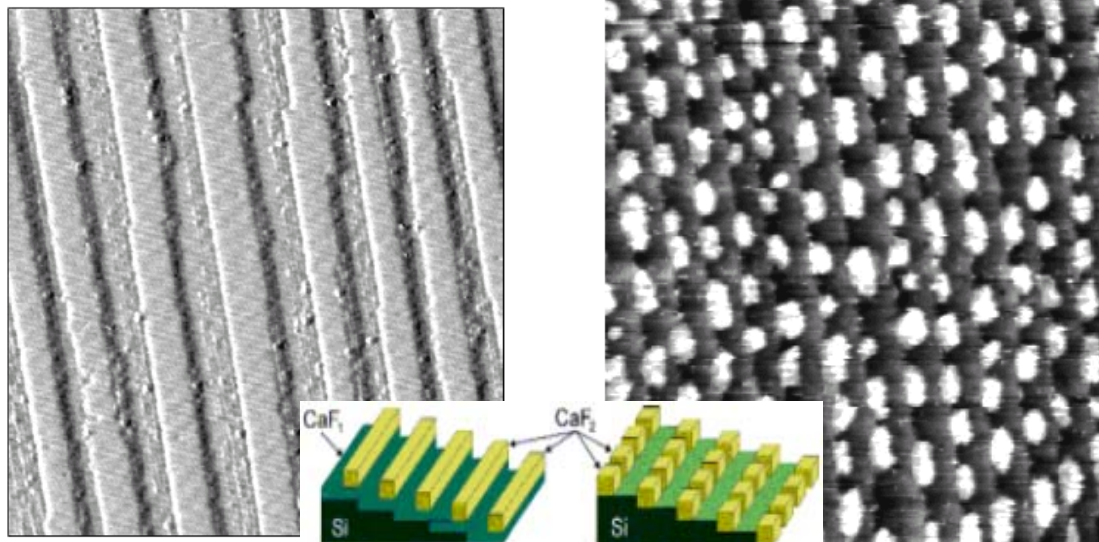
Chemical imaging of insulators by STM

J. Viernow et al., *Phys Rev. B* 59 (1999) 10356

Self- Assembly durch Stufendekoration: TD Gleichgewicht und eingefroren im kinetischen Grenzfall

CaF₂ nanowires' and 'dots' can be produced by combination of:

- step decoration
- submonolayer precision of deposition
- controlled growth kinetics and annealing

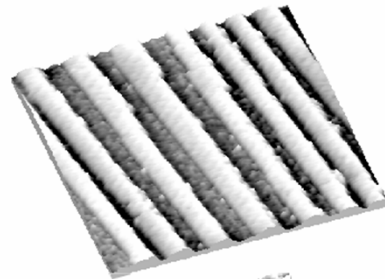


Self organised Growth of CaF₂ on Si(111)

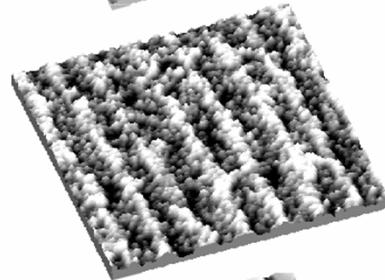
J. Viernow et al., *Appl.Phys.Lett.* **72** (1998) 948

J.-L. Lin et al., *J.Appl.Phys.* **84** (1998) 255

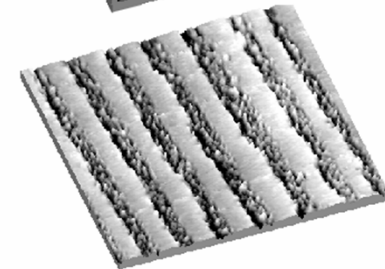
One-dimensional confinement of molecules via selective adsorption



CaF₂ / CaF₁ wires



After deposition of
DPP molecules



After subsequent
annealing

H. Rauscher et al., *Chem. Phys. Lett.* **303** (1999) 363

One-dimensional confinement of molecules via selective adsorption

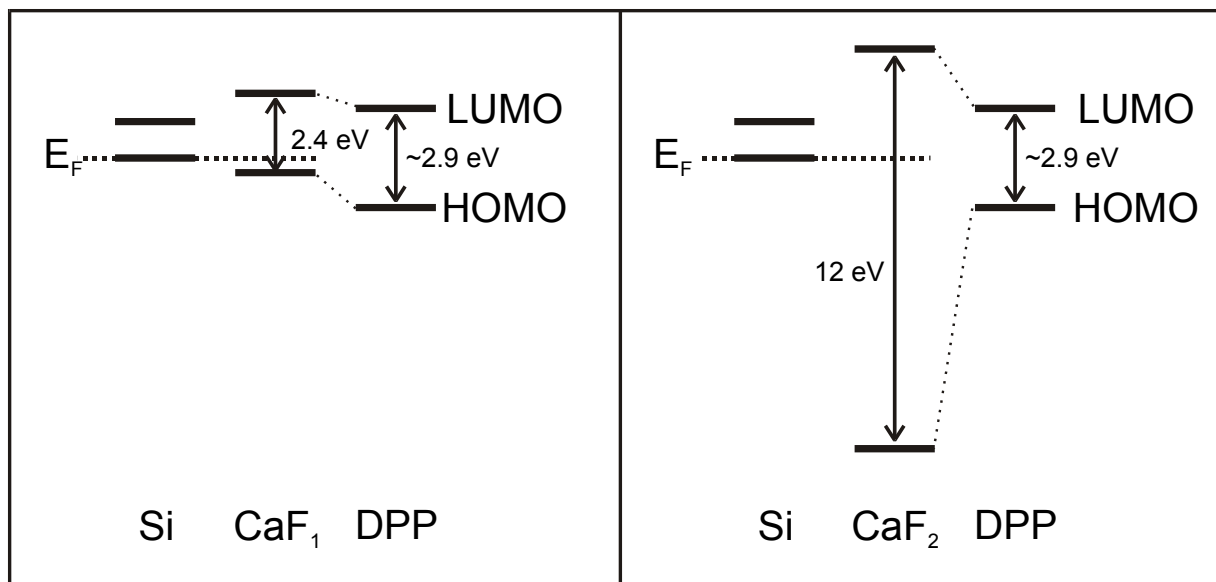


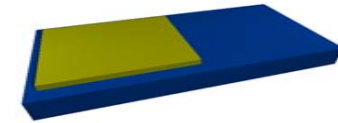
Fig. 4

H. Rauscher et al., *Chem. Phys. Lett.* **303** (1999) 363

.....



Growth of ultrathin insulator layers



NaCl



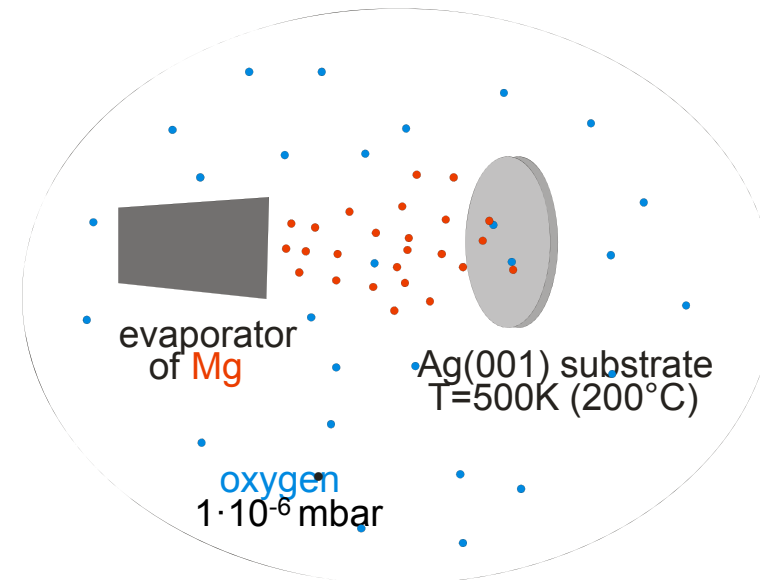
sublimation of NaCl

- Evaporator rate $\sim 1 \text{ \AA} / \text{min}$
- Substrate temperature $\sim 400 \text{ K}$

NaCl dimer formation upon sublimation
Rothberg *et al.* Journal of Chemical Physics
30, 517 (1959)



MgO

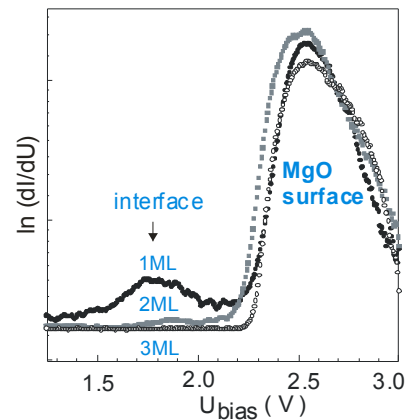
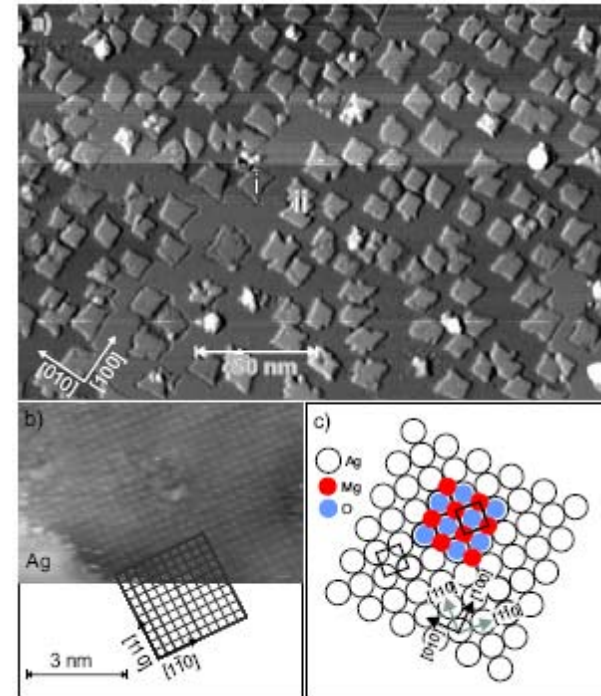
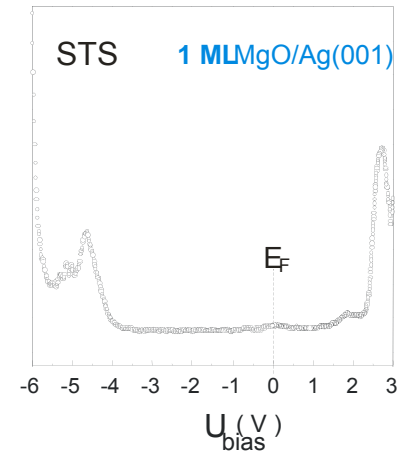
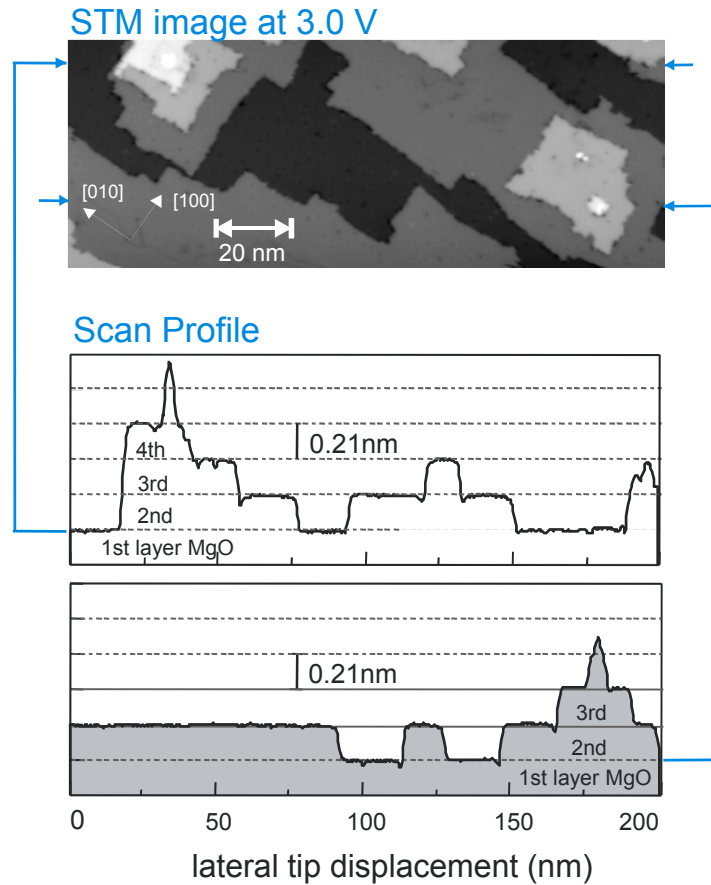


sublimation of Mg in oxygen background

- Evaporator rate $\sim 1 \text{ \AA} / \text{min}$
- Substrate temperature $\sim 500 \text{ K}$
- oxygen $1 \cdot 10^{-6} \text{ mbar}$



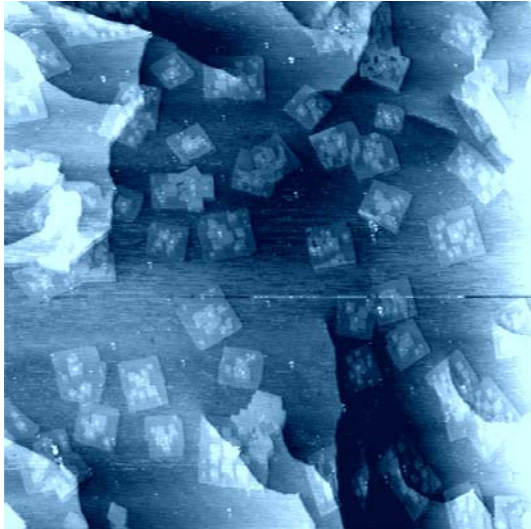
MgO/Ag(001): Insulator at the limit



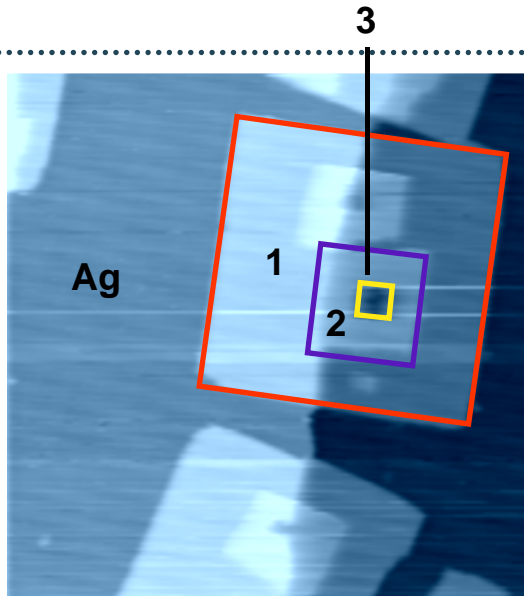
S. Schintke et al., *Insulator at the ultrathin limit: MgO on Ag(001)*, Phys. Rev. Lett. **87**, 276801 (2001)

S. Schintke and W.-D. Schneider, *Insulators at the Ultrathin Limit: Electronic Structure studied by Scanning Tunneling Microscopy and Scanning Tunneling Spectroscopy*, J. Phys.: Condens. Matter **16**, R49-R81 (2004)

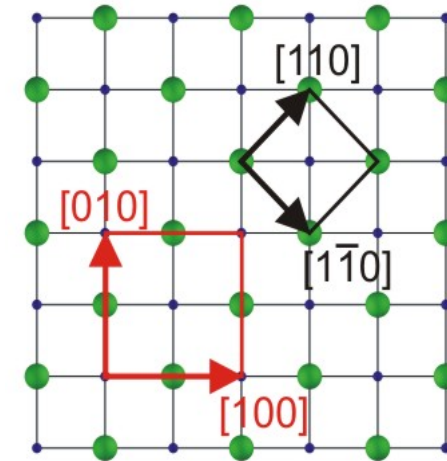
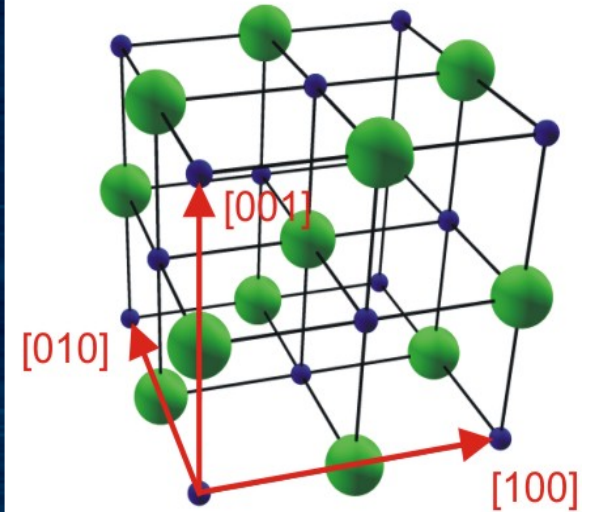
NaCl layers



NaCl on Ag(111)
1.25 μm x 1.25 μm

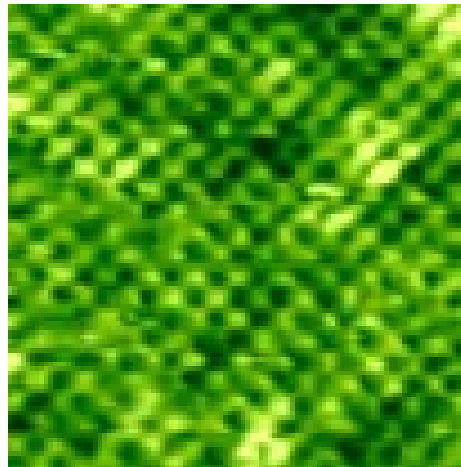


NaCl on Ag(111) 200 nm x 200 nm
U = 4.0 V, I = 15 pA



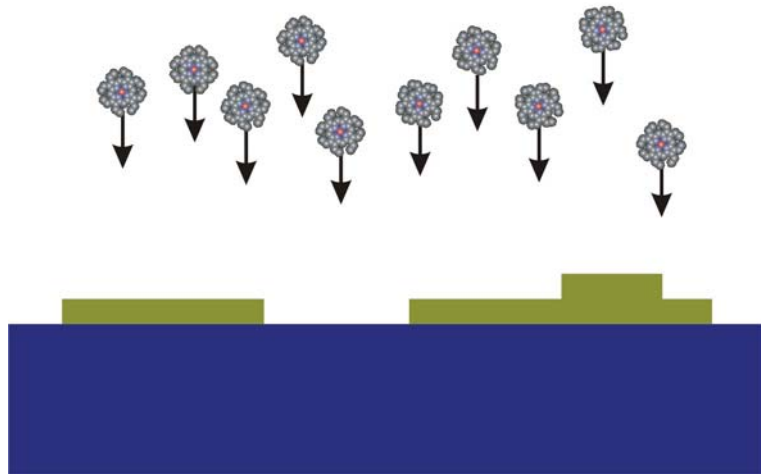
$a_0 = 5.65 \text{ \AA}$

atomic resolution: one
type of the ions is imaged



NaCl on Cu(111)
5 nm x 5 nm
U = -1.5 V, 50 pA

CuOEP on NaCl/Metal



Substrate

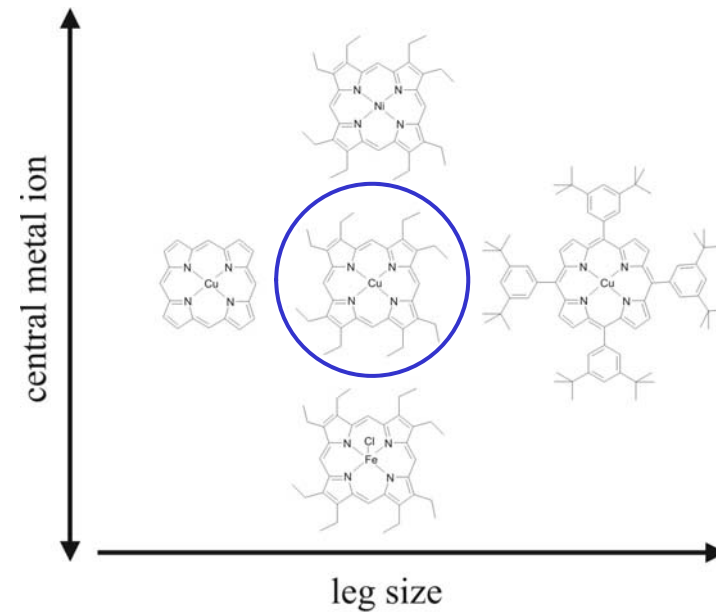
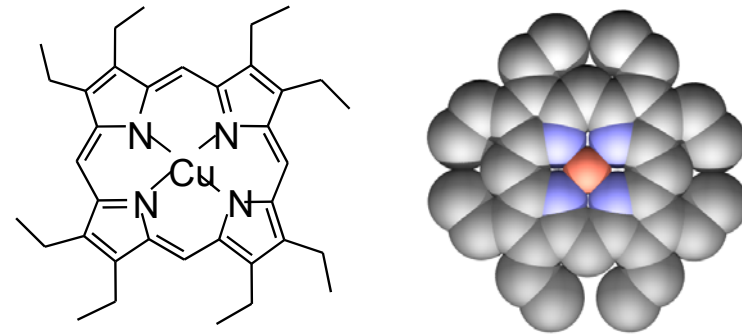
- Metal with 0.3-0.7 ML NaCl
- NaCl structures: 0 to 3 atomic layers thick

Molecule deposition: sublimation

- Evaporation rate $\sim 1\text{-}2 \text{ \AA} / \text{min}$
- Substrate temperature $\sim 300 \text{ K}$



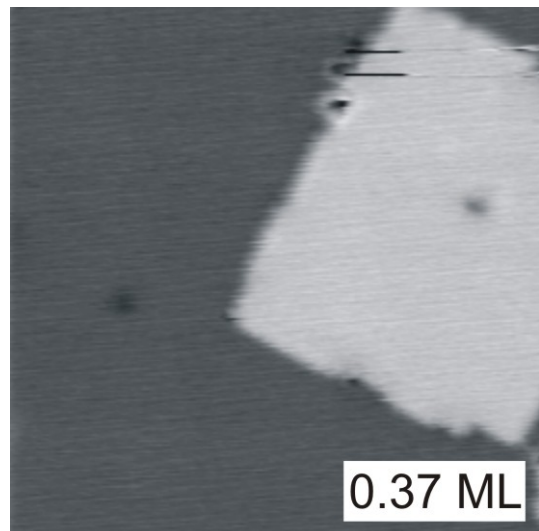
copper(II) octaethyl-porphyrin (CuOEP)



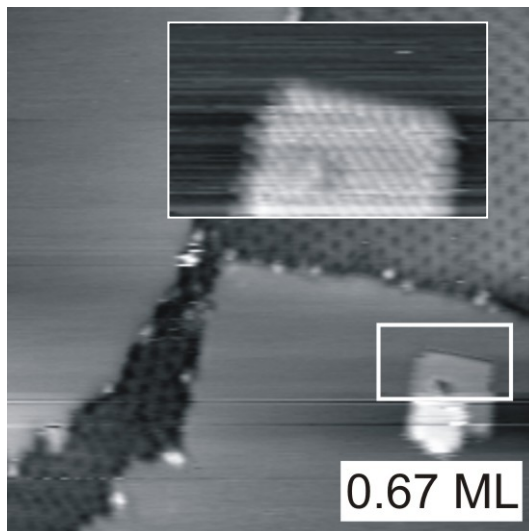
S. Schintke, Seminar @ MIT, April 2006



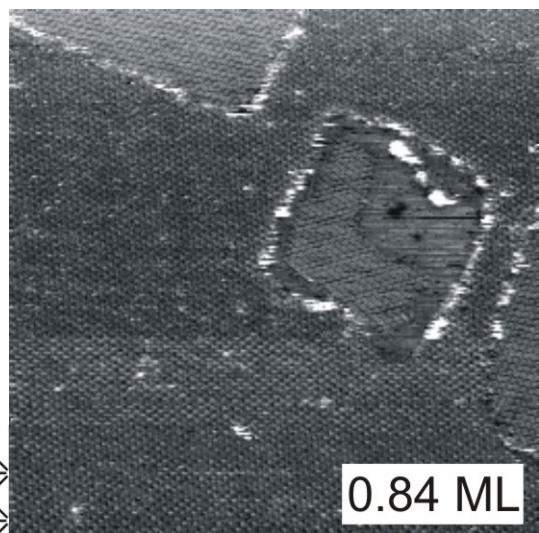
Layer selective adsorption



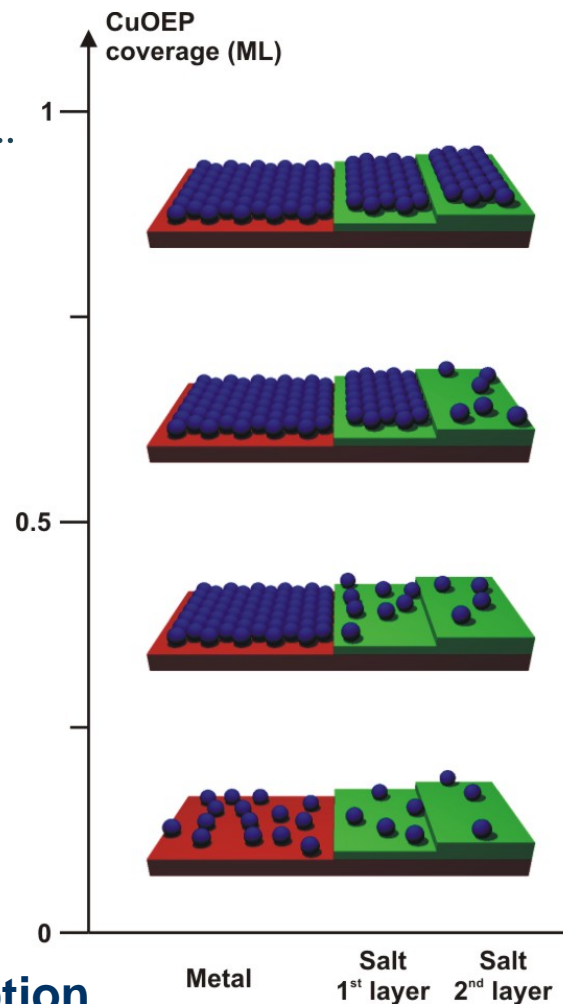
25 × 25 nm, 1.0 V, 24 pA



40 × 40 nm, -2.9 V, 45 pA
inset 10 nm × 6 nm



100 × 100 nm, -1.6 V, 24 pA



⇒ **layer-selective adsorption**

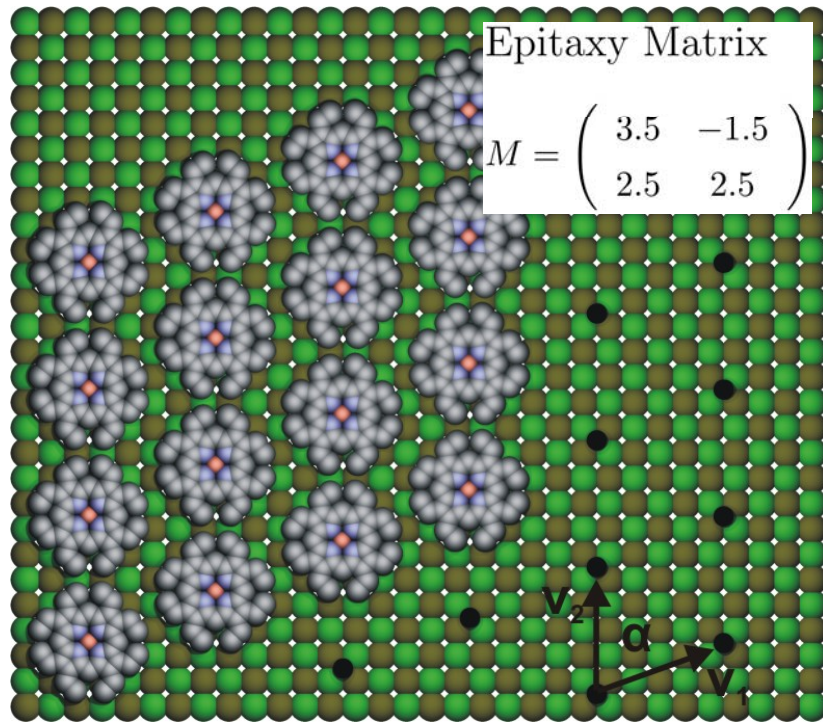
adsorption energy depends on NaCl layer thickness:

$$E_{ads}^{(metal)} > E_{ads}^{(1^{st} \text{ layer NaCl})} > E_{ads}^{(2^{nd} \text{ layer NaCl})}$$

L. Ramoino, M. von Arx, S. Schintke, A. Baratoff, H.-J. Güntherodt, T.A. Jung
Chem. Phys. Lett. **417**, 22 (2006)

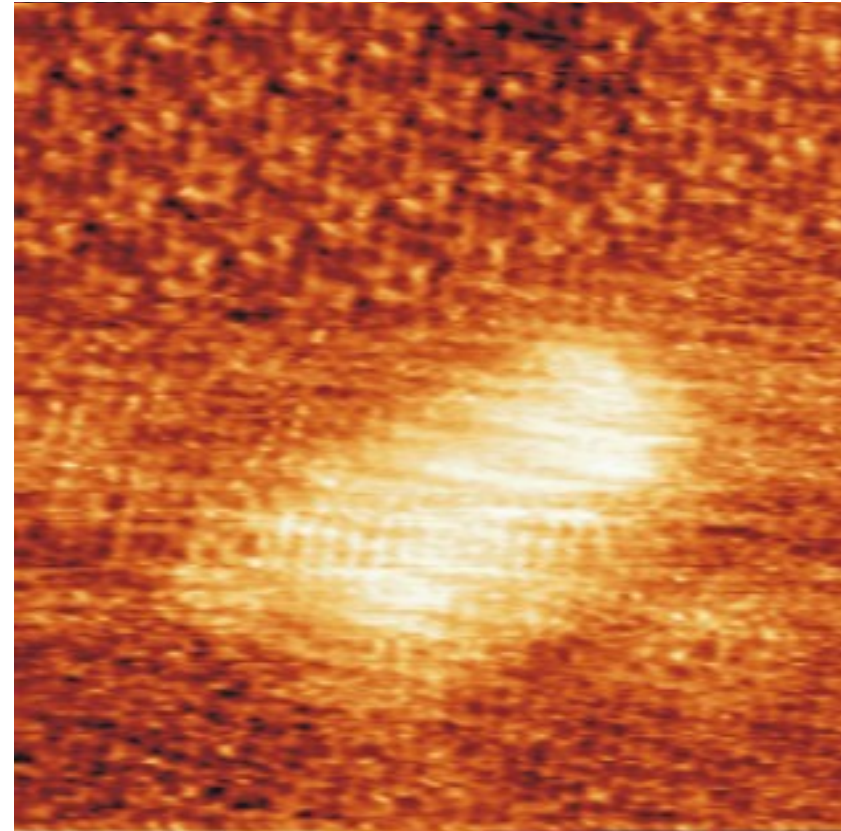
S. Schintke, Seminar @ MIT, April 2006

CuOEP Self-Assembly on Salt



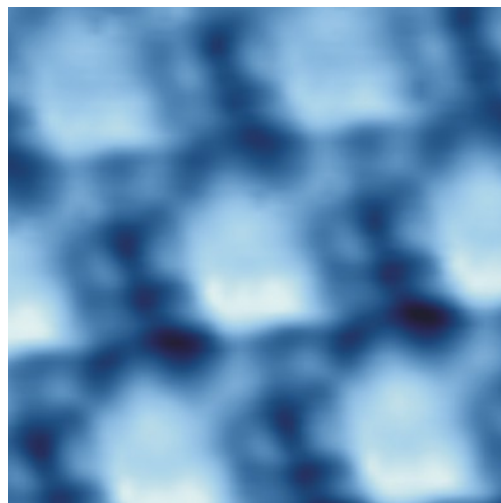
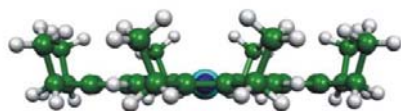
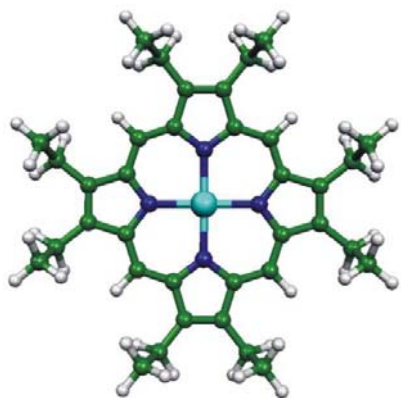
	model	experiment
v_1	14.6 Å	14.3 ± 0.3 Å
v_2	13.5 Å	13.5 ± 0.3 Å
α	68.2°	$69.0 \pm 1^\circ$

CuOEP on NaCl/Ag(111)

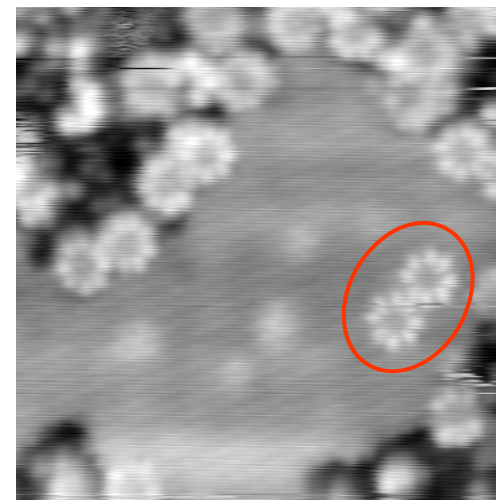


15 × 15 nm, U = -0.25 V, I = 81 pA

CuOEP molecules on metal and NaCl/metal



CuOEP on Cu(111)
(averaged image)
3.0 nm × 3.0 nm, U = -0.55 V, I = 24 pA

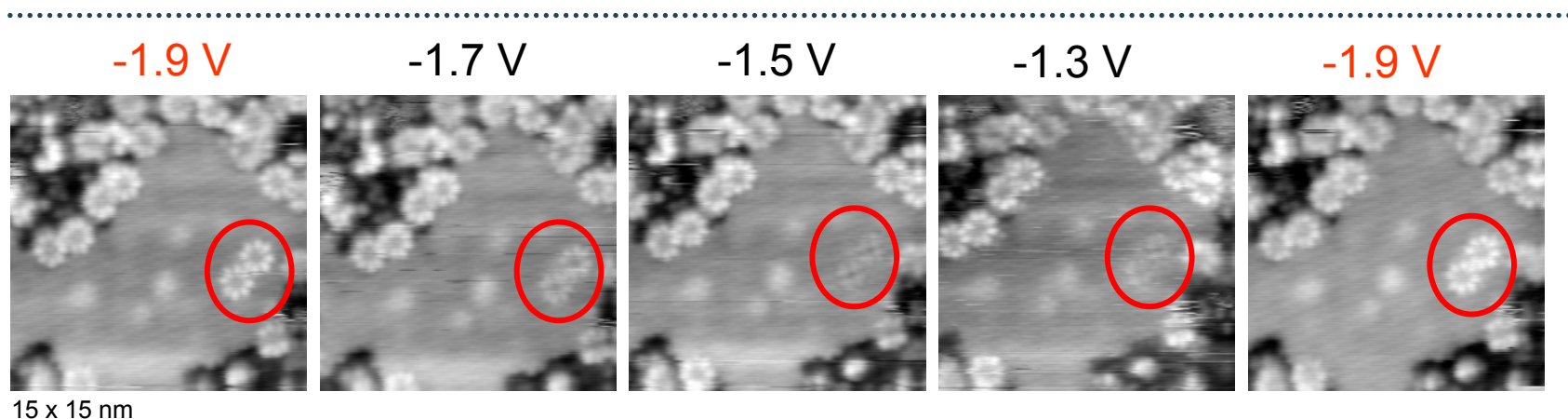


CuOEP on
Pd(111) and on NaCl/Pd(111)
15.0 nm × 15.0 nm, U = -1.9 V

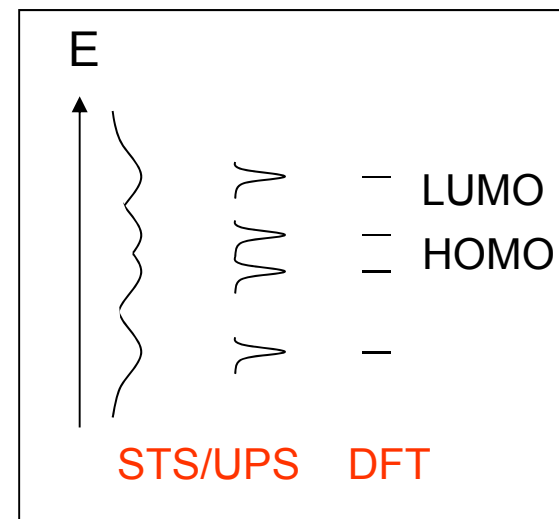
- on Pd(111) no assembly of CuOEP
=> stronger molecule-metal substrate interaction than on Cu(111)
- stable adsorption of individual molecules on NaCl
- **smaller broadening of electronic states on NaCl than on metal**
=> **reduced molecule-substrate interaction !**

Bias dependence: CuOEP on NaCl/Pd(111)

S. Schintke et al. submitted (2007)



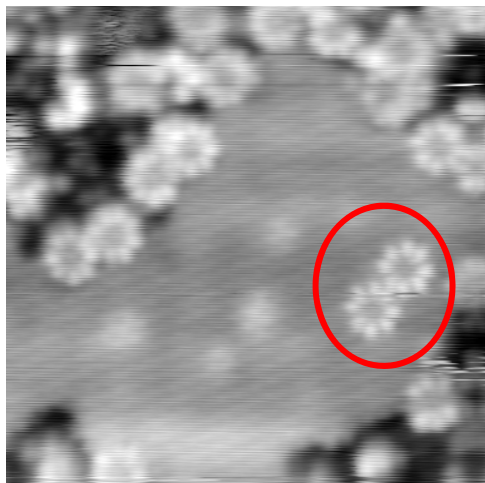
- Small broadening of the HOMO on NaCl
=> confirming decoupling from metal
- CuOEP on Pd(111): eight lobe structure
=> HOMO level broadening



Isolated molecule on ultrathin insulator

CuOEP on NaCl/Pd(111)

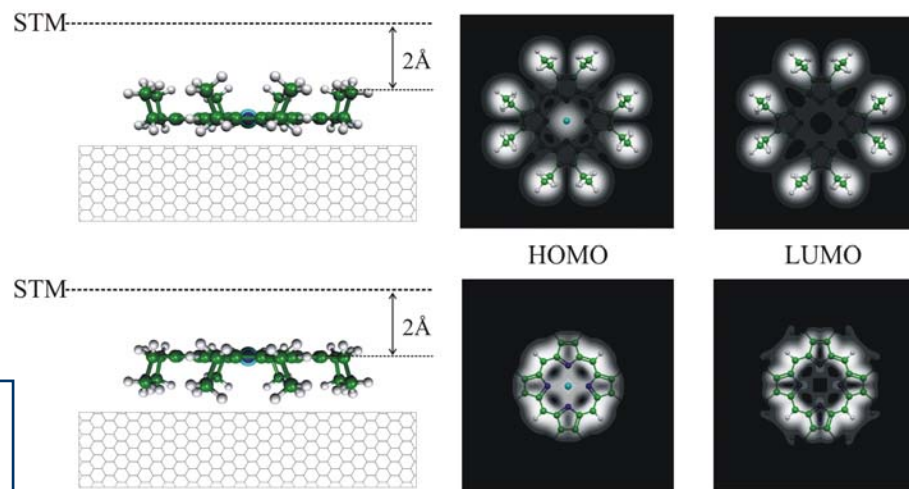
S. Schintke et al. submitted (2007)



-1.9 V
(HOMO)

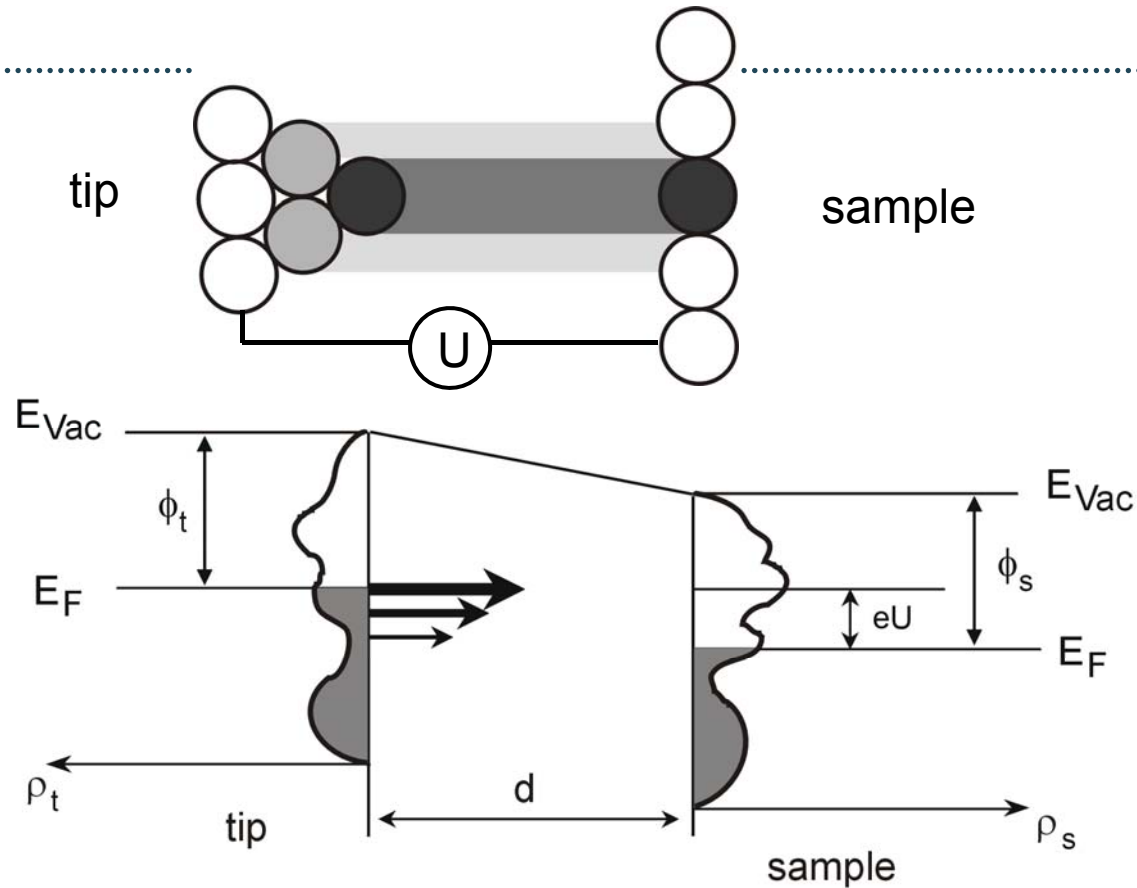
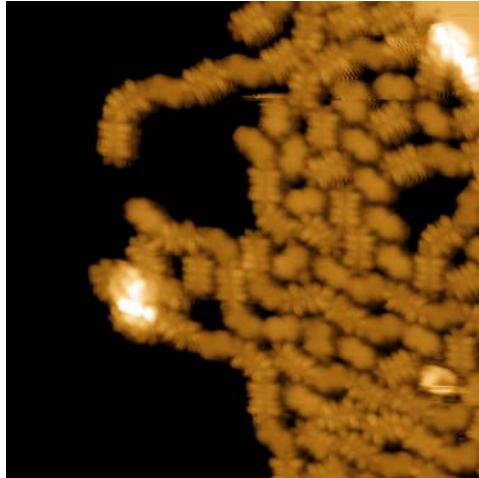
Resonant tunneling via HOMO states
⇒ eight lobe structure

side groups imaged in STM although
HOMO belongs to the porphine ring!



Compare: simulated STM images
⇒ adsorption geometry:
porphine ring towards substrate

Scanning Tunneling Microscopy



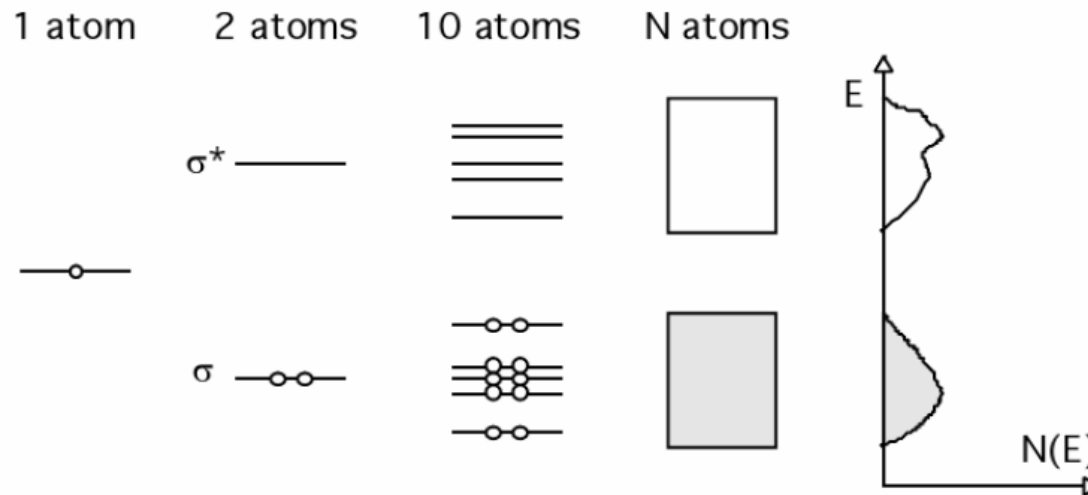
Tunneling current: $I_{tunnel} \sim U \rho_t \rho_{s(x,y)} e^{-const d}$ (Tersoff and Hamann)

=> sensitivity to local electronic structure of the sample

STS (scanning tunneling spectroscopy)



Density of States (DOS)

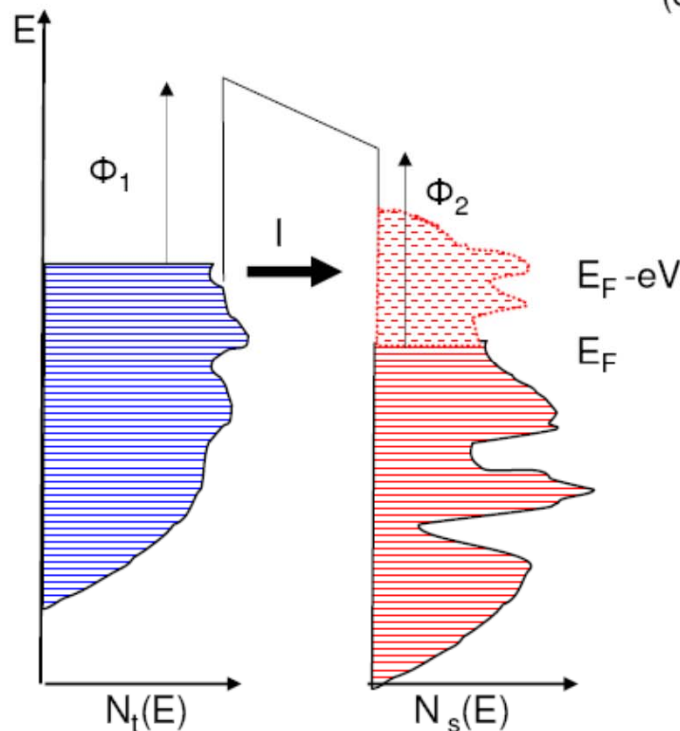


Density of States (DOS), $N(E)$ is the number of energy levels between E and $E+dE$ (states per eV)

States can have s,p,d,f or mixed (hybrid) character
Bands may be separated by band-gaps E_g

Voltage dependence of tunneling current

By changing the voltage, the density of states can be recorded as function of the voltage (e.g., band structure of semiconductors)



$$I \propto \int_0^{eV} N_1(E) N_2(E - eV) T(E, V) dE$$

where N_1 N_2 are the densities of states at the Fermi niveau and $T(E, V)$ the transmission probability.

$$T(E, V) = \exp\left\{-2s\left[\phi - E + \frac{eV}{2}\right]^{1/2}\right\}$$

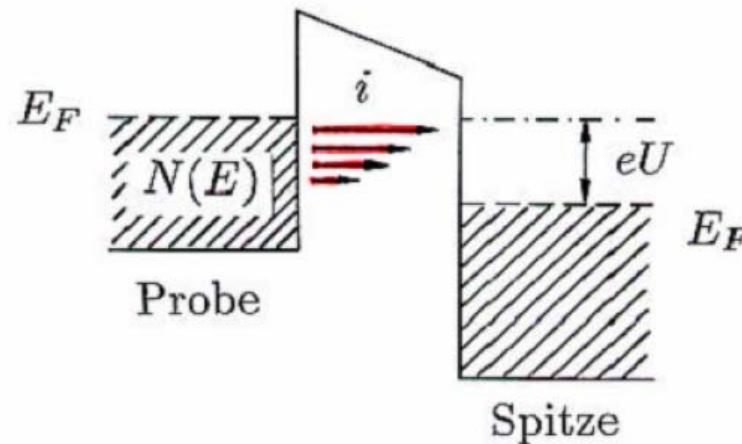
The contribution of the states to the tunneling process decays exponentially with their energetic distance to the Fermi niveau. Core levels do not contribute at all.

Spektroskopie

Spektroskopie

Lokale Messung der I/U -Charakteristik bei $x, y, z = const$ (R.J. Hamers, R.M. Tromp and J.E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986))

Information über lokale elektronische Zustandsdichten $N(E)$ enthalten in



$$I/U$$

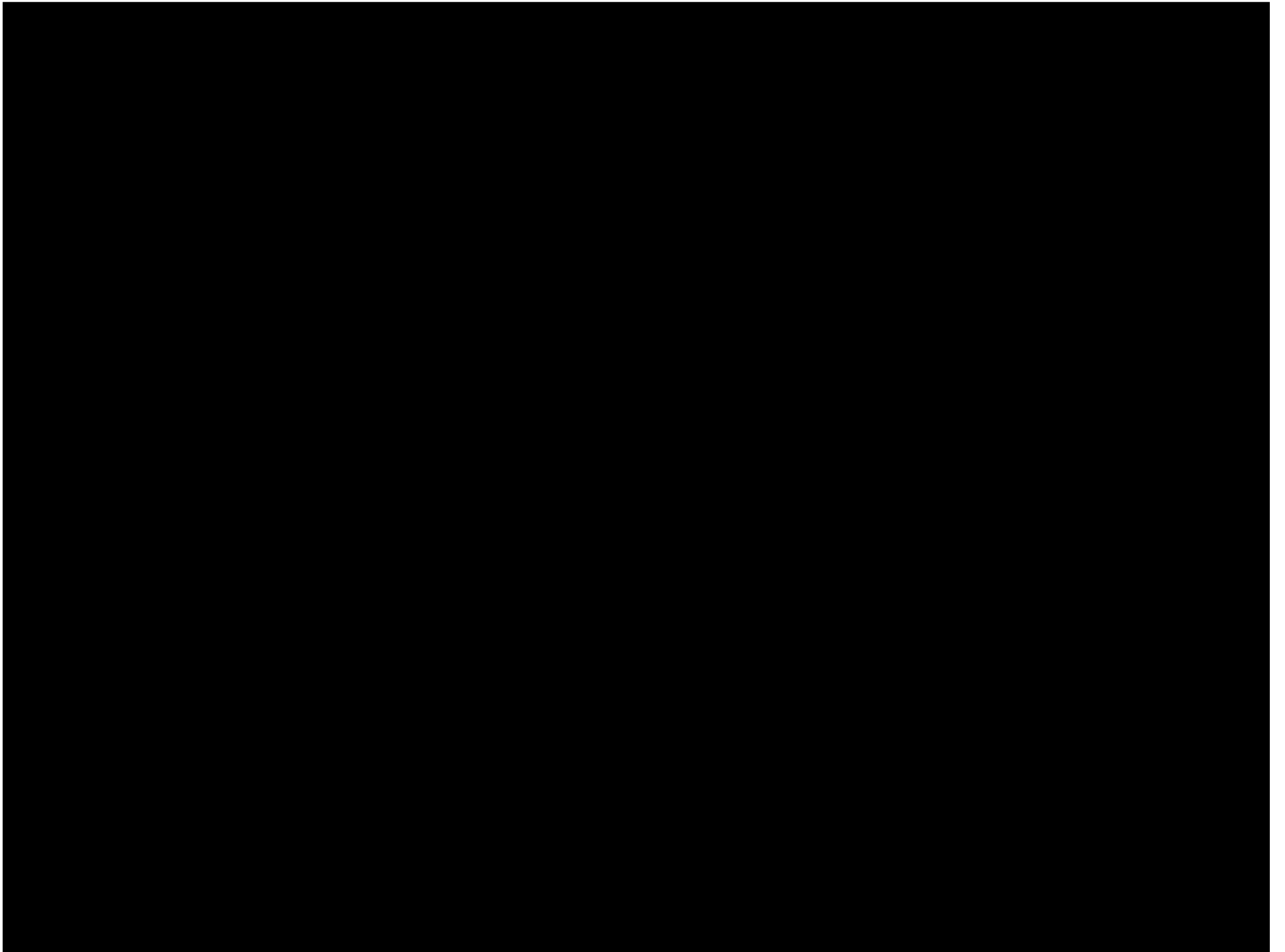
$$dI/dU$$

$$\frac{dI}{dU} / \frac{I}{U} = \frac{d \ln I}{d \ln U}$$

CCT's mit $+U$ und $-U$

Stabilisierungsspannung U_0 und U sind Parameter

Zustandsdichte der Wolframdichte im Bereich der Fermienergie ändert sich wenig, d.h. es wird primär die Zustandsdichte der Probe beobachtet (+; unbesetzte Zustände, -, besetzte Zustände)

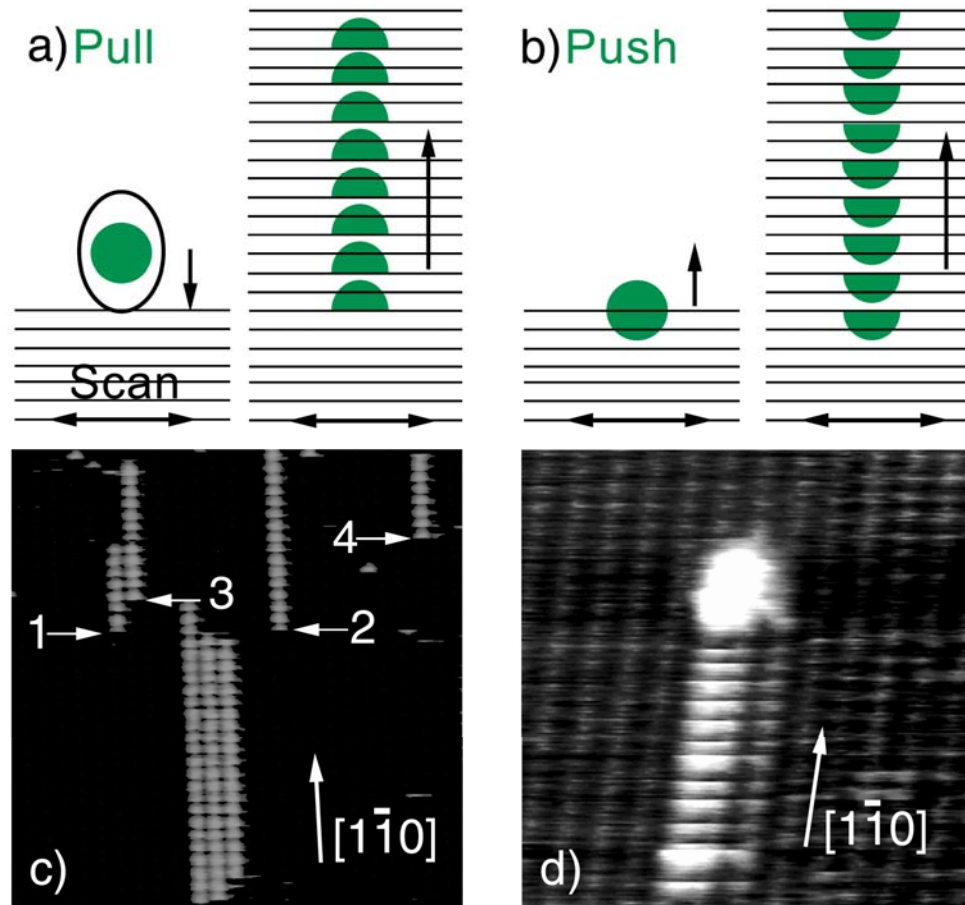


2. STM beyond imaging

- **STM a tool for nanofabrication:**
Adsorbate manipulation

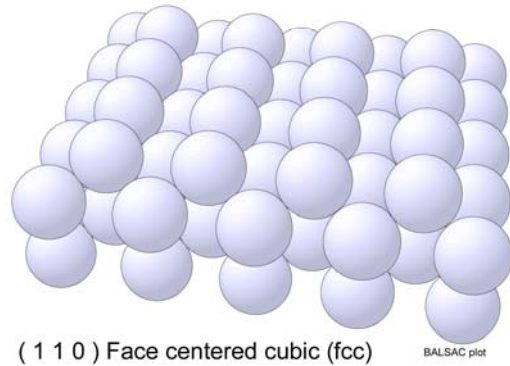
- **STM a local spectroscopy tool:**
Scanning Tunneling Spectroscopy (STS)
Inelastic Tunneling Spectroscopy (IETS)
Local Photonemission spectroscopy

Tip-sample interaction

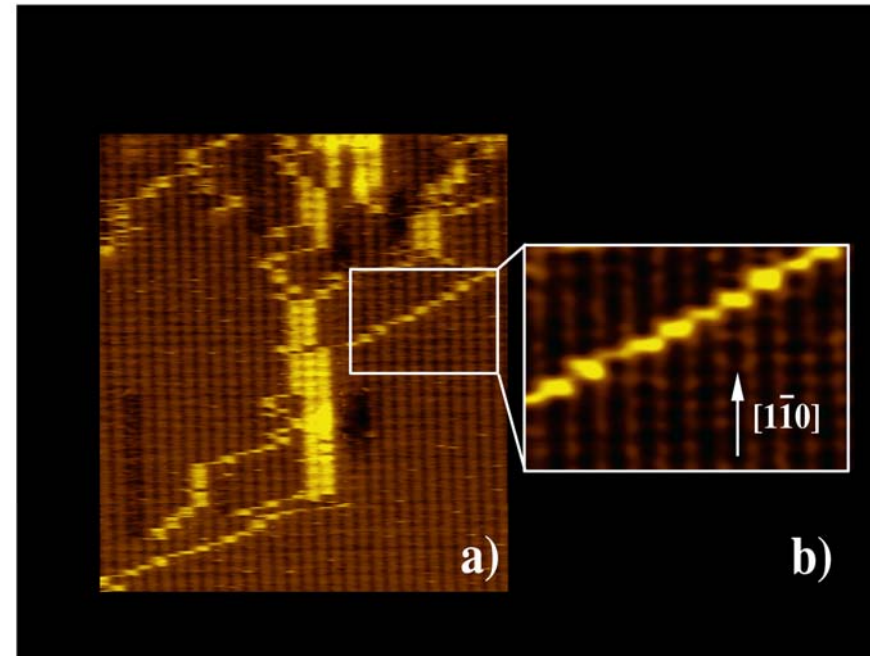
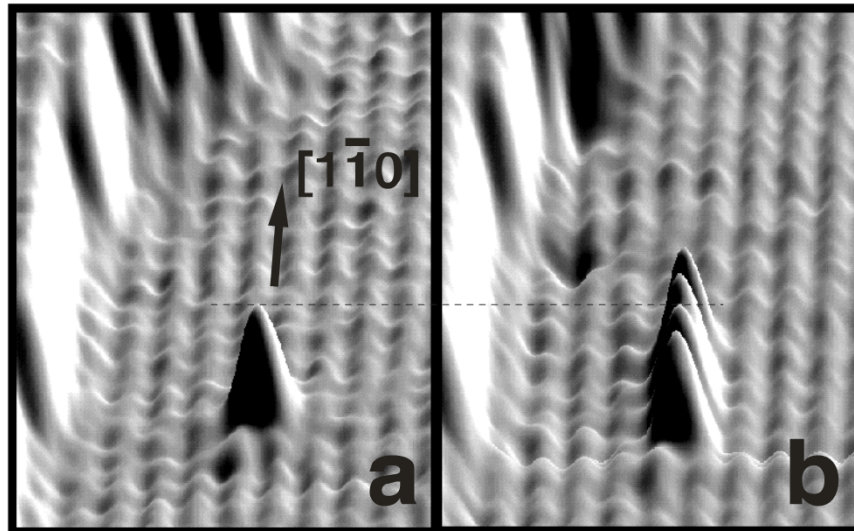


*Low-temperature manipulation of Ag atoms and clusters on a Ag(110) surface, J.T. Li, W.-D.Schneider, and R. Berndt, *Appl. Phys. A*, 66, 575 (1998).*

Tip-sample interaction

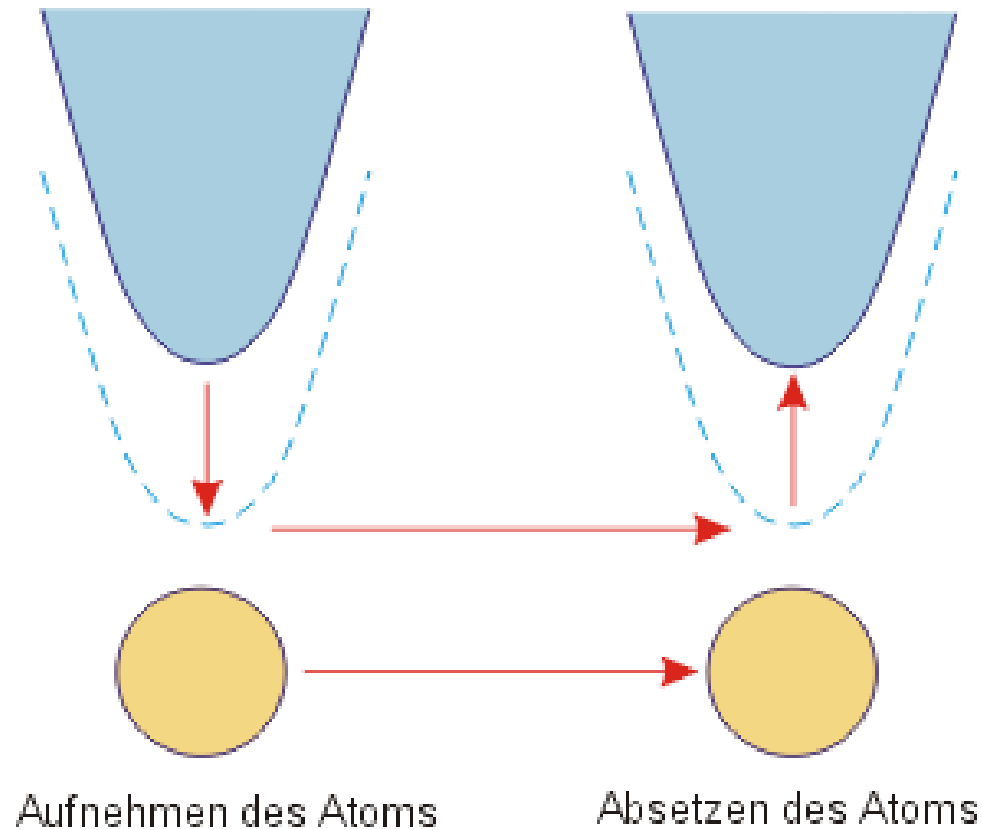


Diagonal Ag adatom motion along [1-11] direction (atom exchange)

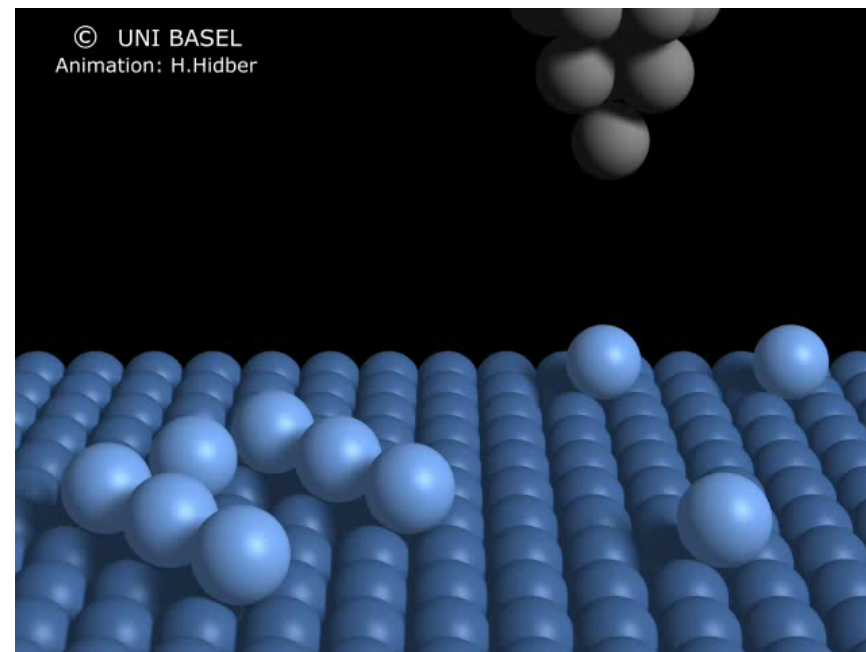
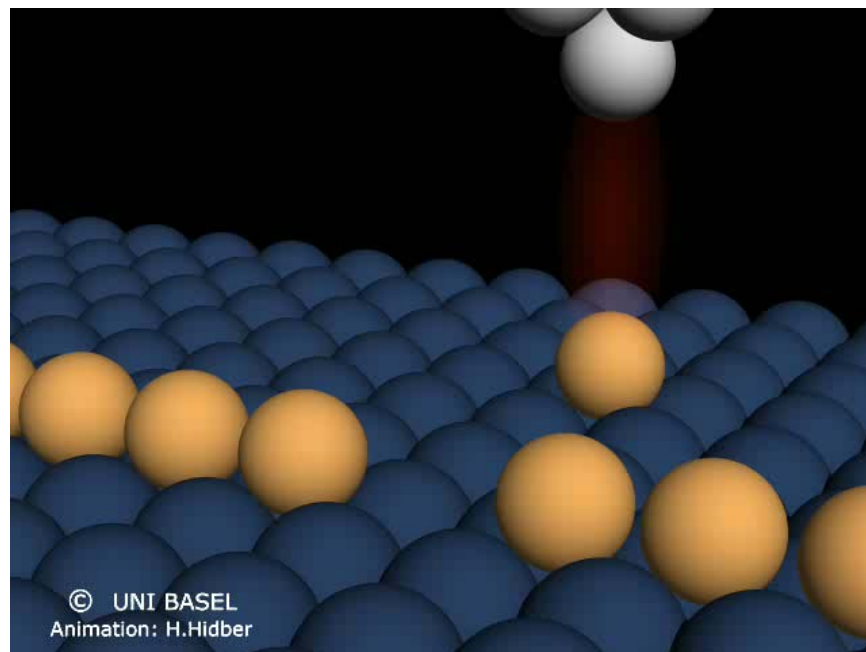


Low-temperature manipulation of Ag atoms and clusters on a Ag(110) surface, J.T. Li, W.-D.Schneider, and R. Berndt, Appl. Phys. A, 66, 575 (1998).

Bewegen eines Atoms



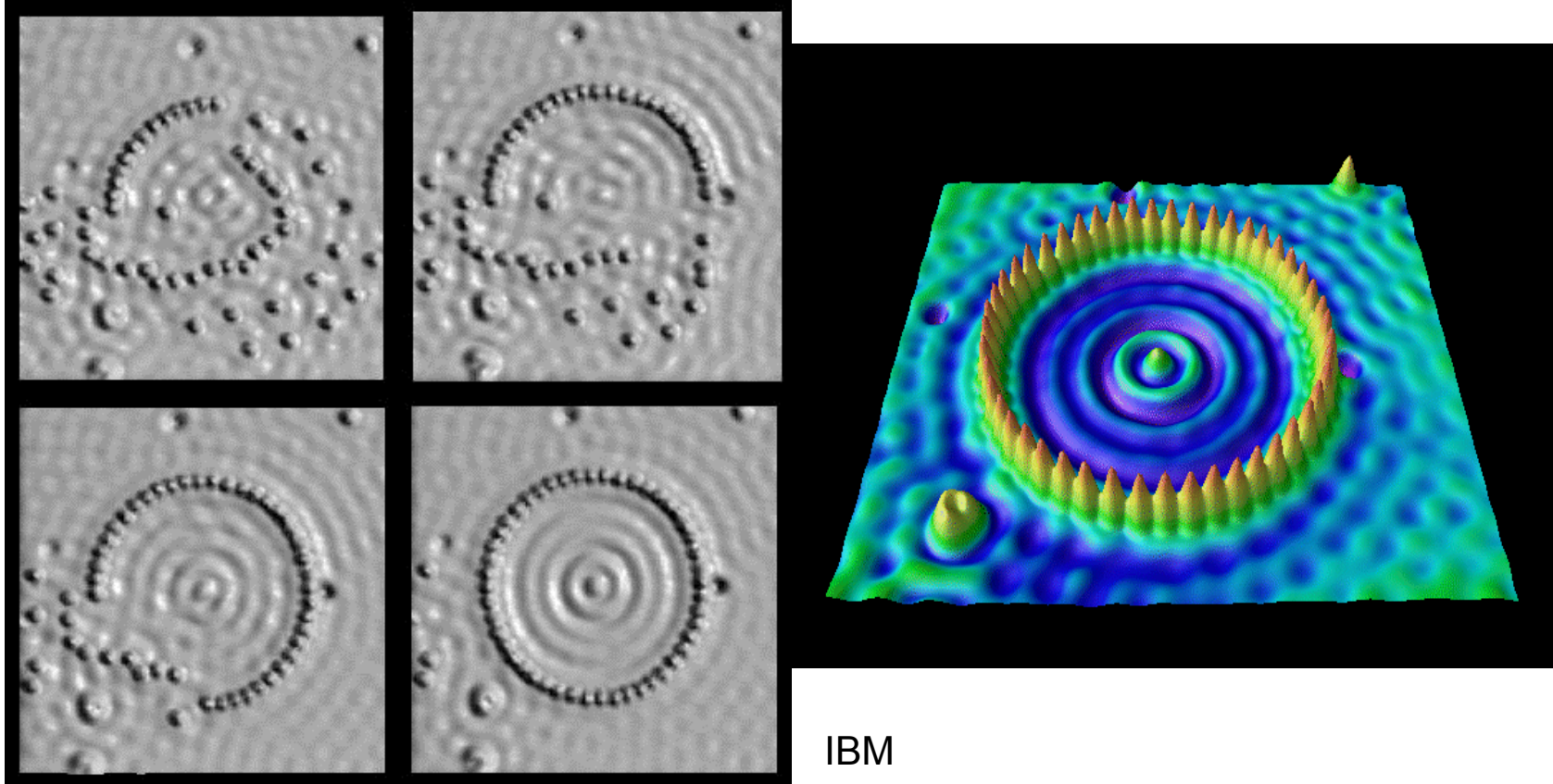
Déplacer des atomes ou molécules



Animations: H. Hidber, Université de Bâle



Quantum Corral



IBM

Oberflächenzustände auf Cu(111)

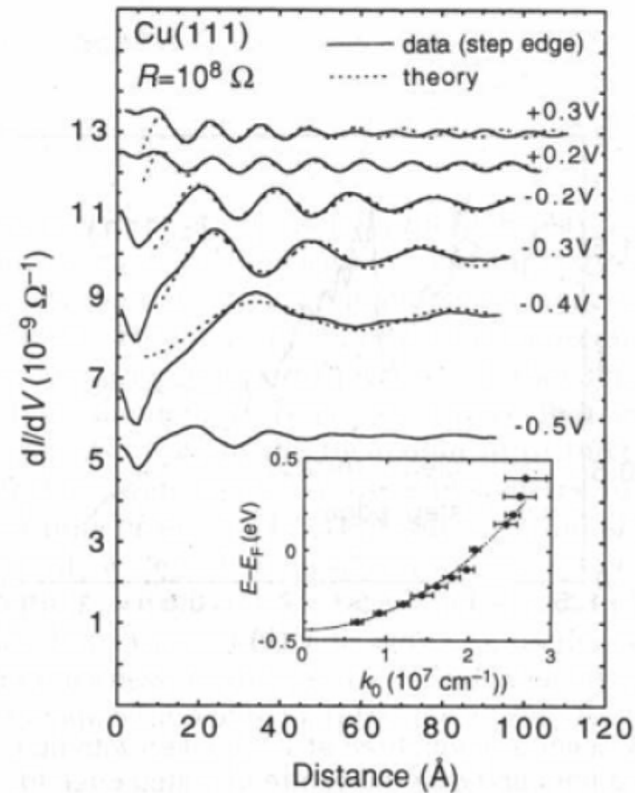


Fig. 2.16. Spatial dependence of dI/dV across a step edge on Cu(111) at 4K. For details see text. From [80].

„Confined electrons“

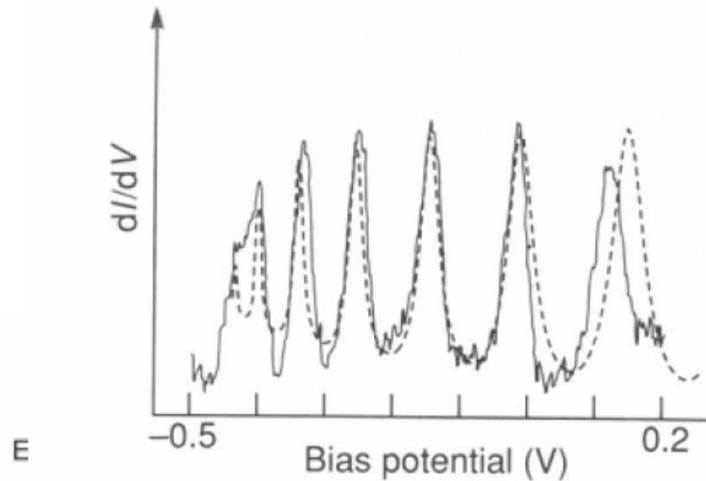
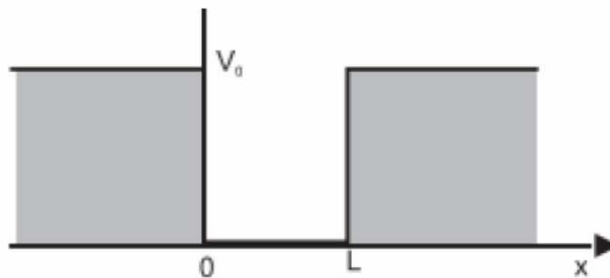


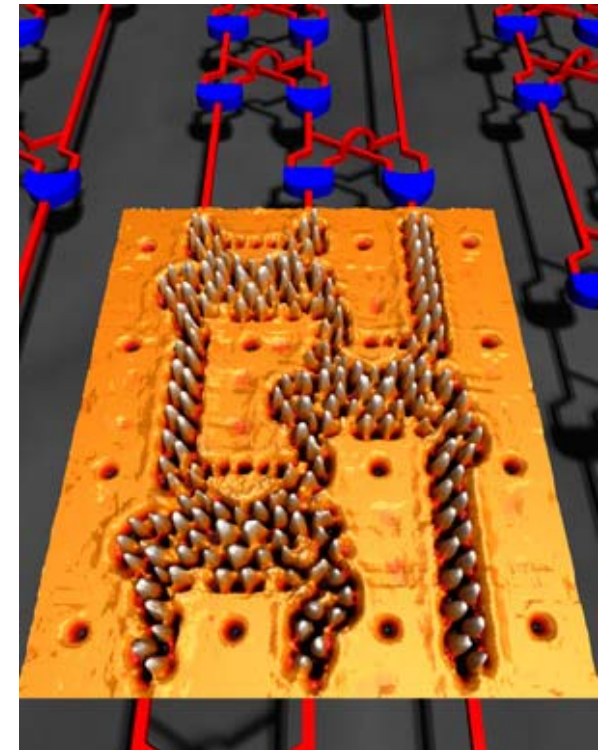
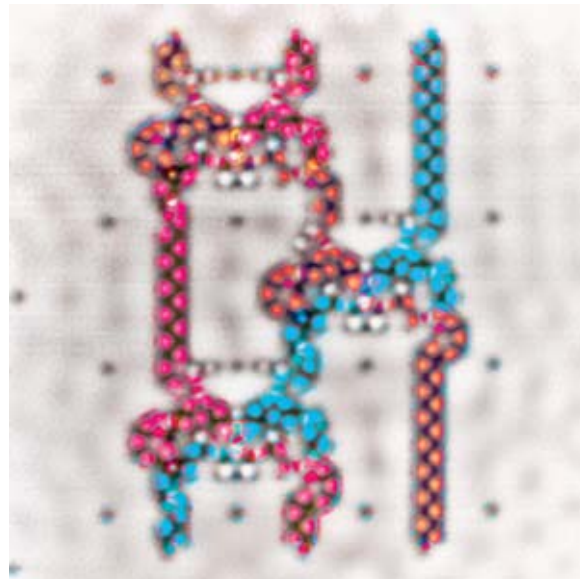
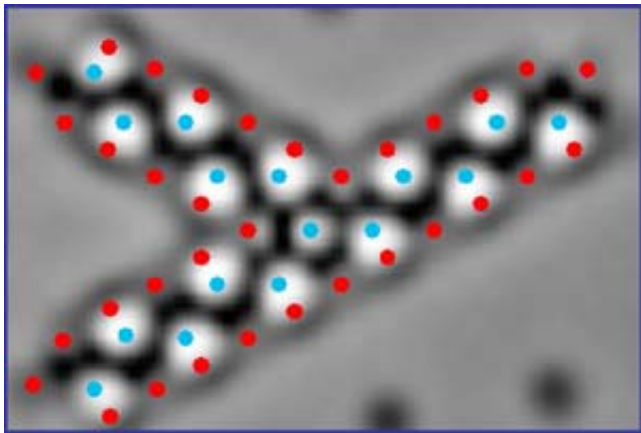
Fig. 2.18. The experimental (solid line) and theoretical (dashed line) voltage dependence of dI/dV , with the top of a STM located at the center of a 88.7 Å diameter, 60-atom circle of Fe atoms on a Cu(111) surface. From [84].



$$E_n = \frac{h^2}{8mL^2} n^2$$

E.Heller, M.Crommie, C.Lutz, D.Eigler: Nature 369, 464 (1994)

Construction of exciting molecular cascades at IBM Almaden



- **3-input sorter cascade with electrical schematic**
- **AND Gate**

T. A. Jung SPM Tutorial

Atomic Scale Memory at a Silicon Surface

R. Bennewitz*, J. N. Crain, A. Kirakosian, J.-L. Lin, J. L. McChesney, D. Y. Petrovykh, and F. J. Himpsel
 Nanotechnology Aug. 2002; 13(4): 499-502

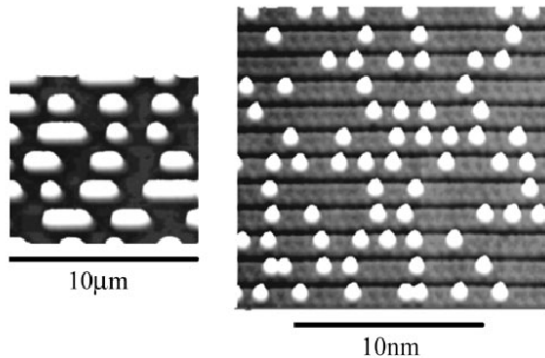


Figure 1. Comparison of the atomic memory on silicon with a CD-ROM [5]. Extra silicon atoms occupy lattice sites on top of tracks that are five atom rows wide (1.7 nm). The scale is reduced from μm to nm, which leads to a 10^6 times higher density.

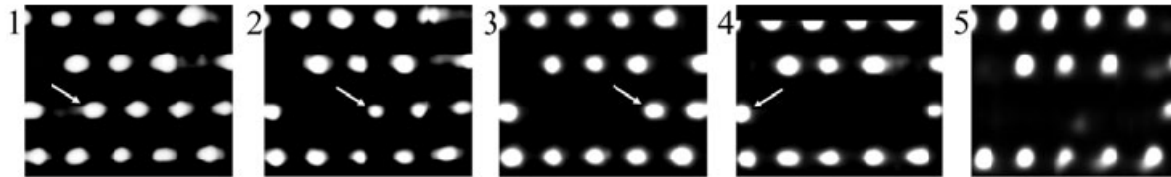


Figure 3. Writing a sequence of four zeros. Silicon atoms are transferred to the STM tip one by one (arrows).

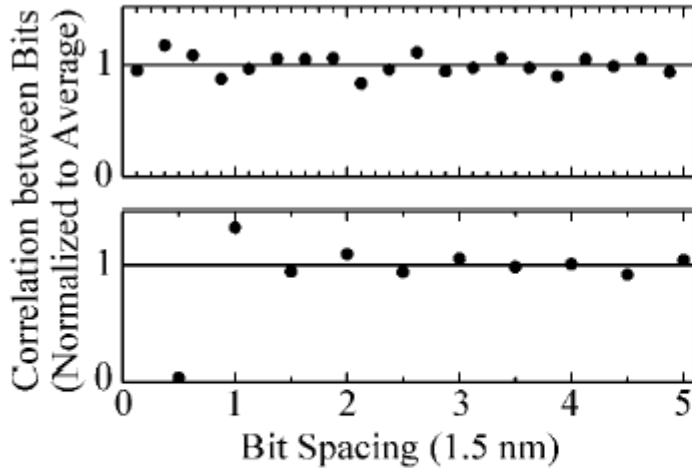


Figure 4. The autocorrelation between neighbouring Si atoms as a test of interactions between adjacent bits. The closest 5×2 site along a track is nearly excluded (bottom), showing that 5×4 atoms form the minimum viable cell. Neighbouring tracks are not correlated (top).

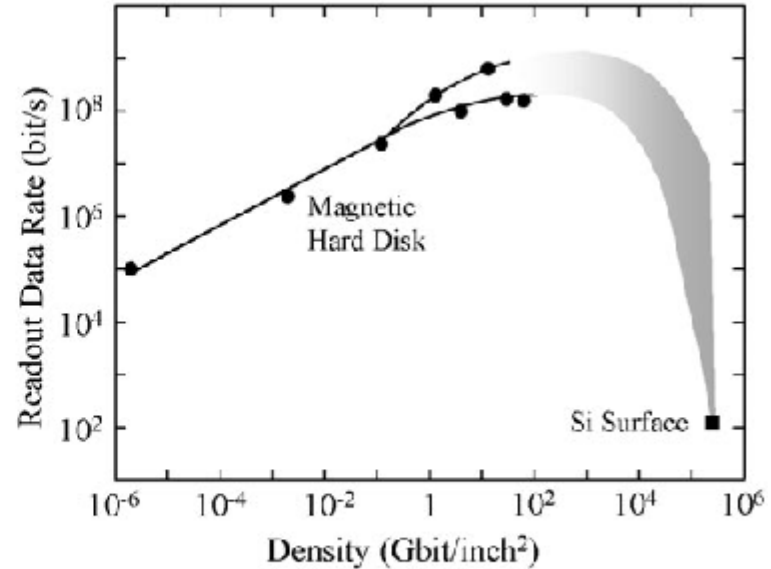
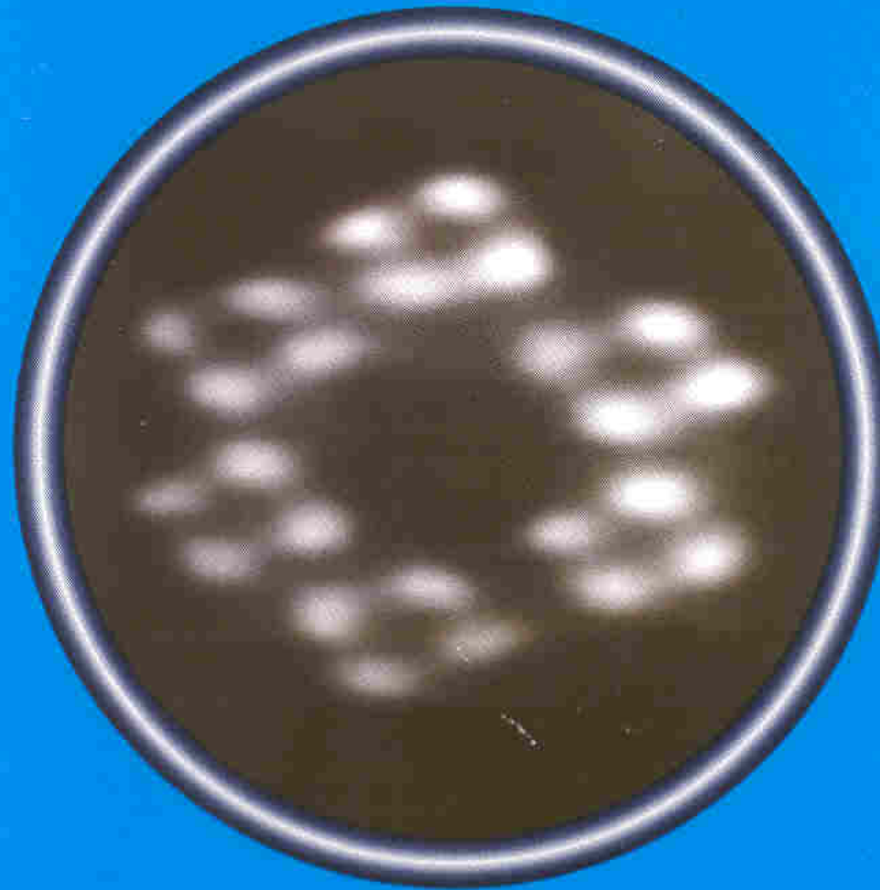


Figure 5. Trade-off between readout speed and storage density at the atomic limit.

Molecular Positioning

T.A. Jung, R.R. Schlittler and J.K. Gimzewski
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland



IBM

Science 271, 181-184 (1996)

Manipulation mit dem STM

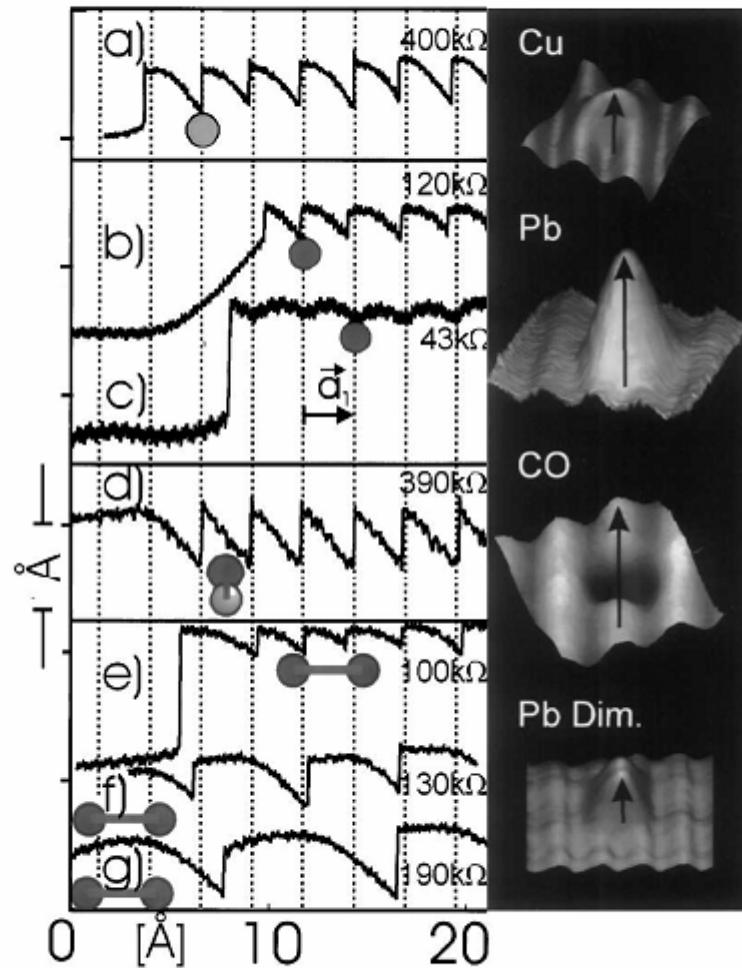
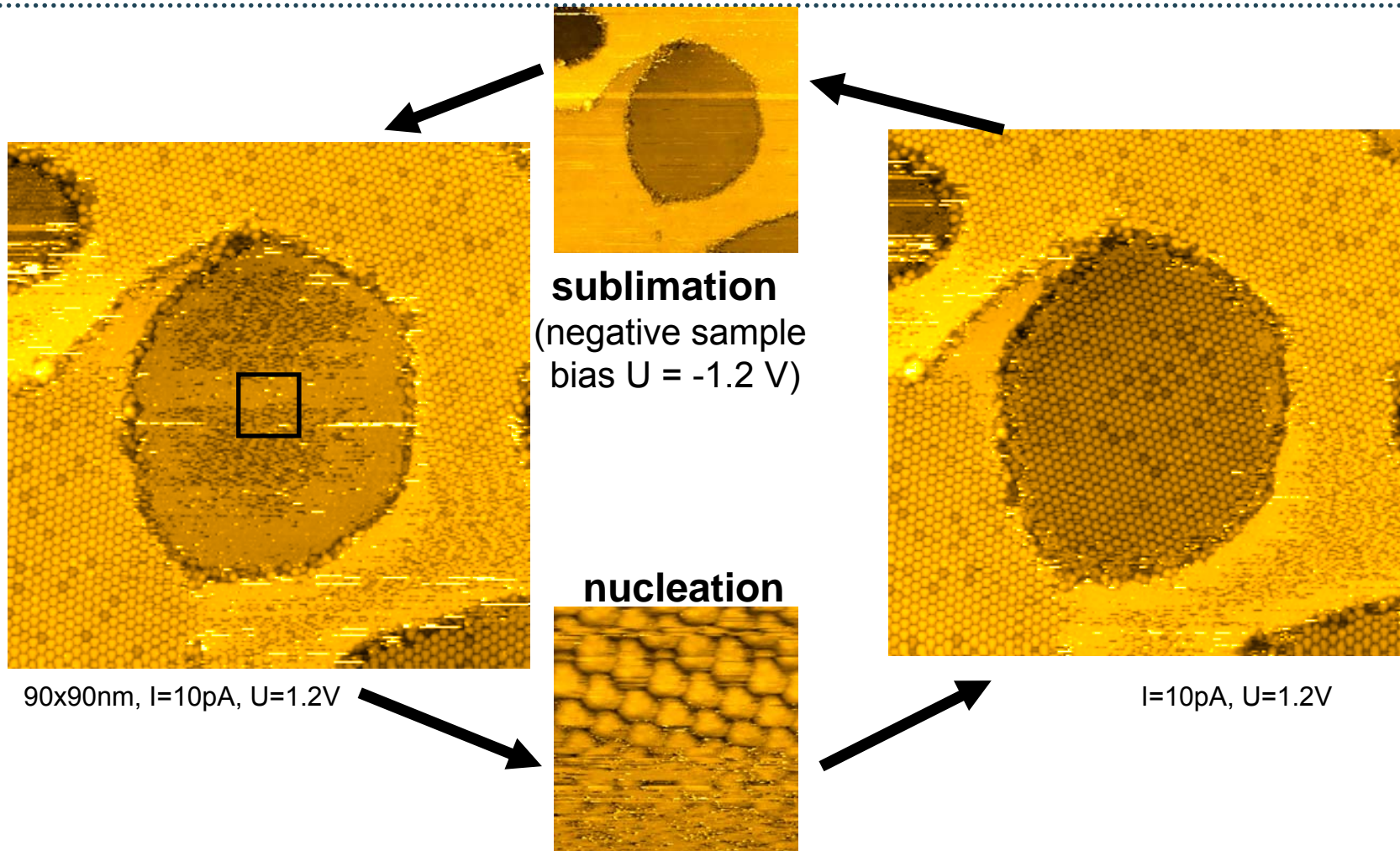


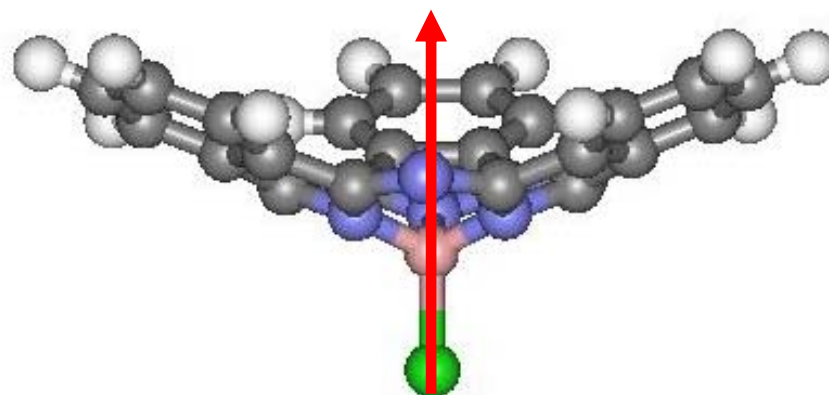
Fig. 2.10. Tip height curves are shown during manipulation of a Cu atom (a), a Pb atom (b,c), a CO molecule (d), and a Pb dimer (e)-(g) along the $[1\bar{1}0]$ of the Cu(211) surface. The tip movement is from the left to the right, and the tunneling resistances are indicated. The vertical dotted lines correspond to fcc sites next to the step edge. The initial sites of the manipulated species are indicated by small sphere models. On the right part STM images of the different adparticles are shown. The arrows indicate the direction of tip movement. From [43].

Reversible 2D Phase Transition controlled by the STM tip



Controlled phase transition 2D fluid \Leftrightarrow 2D solid

SubPc Adsorption Geometry



Ag(111)

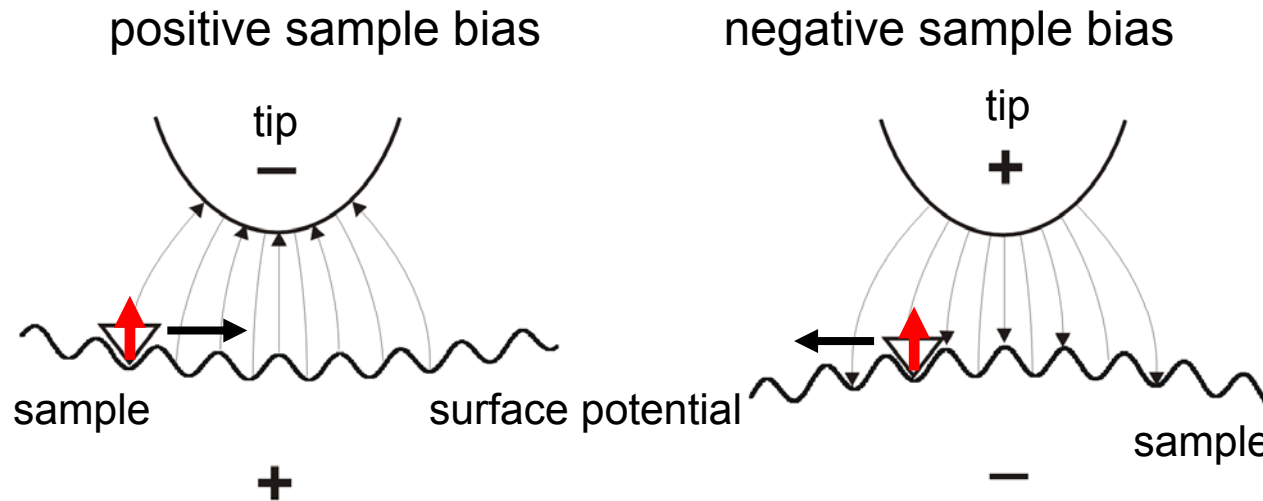
**Adsorption with the Cl toward the Ag
=> dipole moment is pointing away from the surface**

Microscopic Model



Model Tip Induced Diffusion

SubPc dipole moment and inhomogeneity of the electric field of the tip lead to induced diffusion

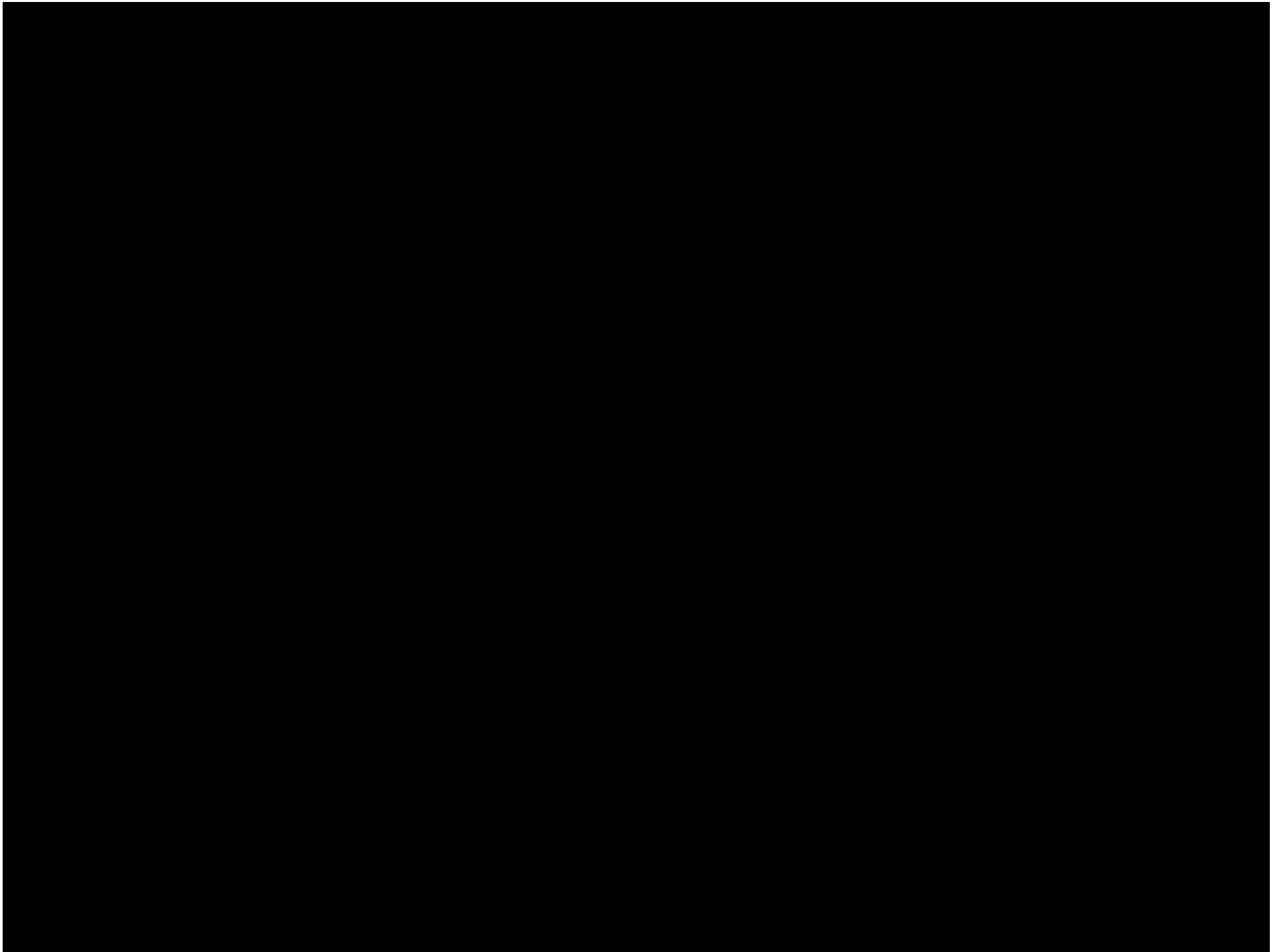


pos. sample bias: diffusion towards the tip
neg. sample bias: diffusion away from the tip

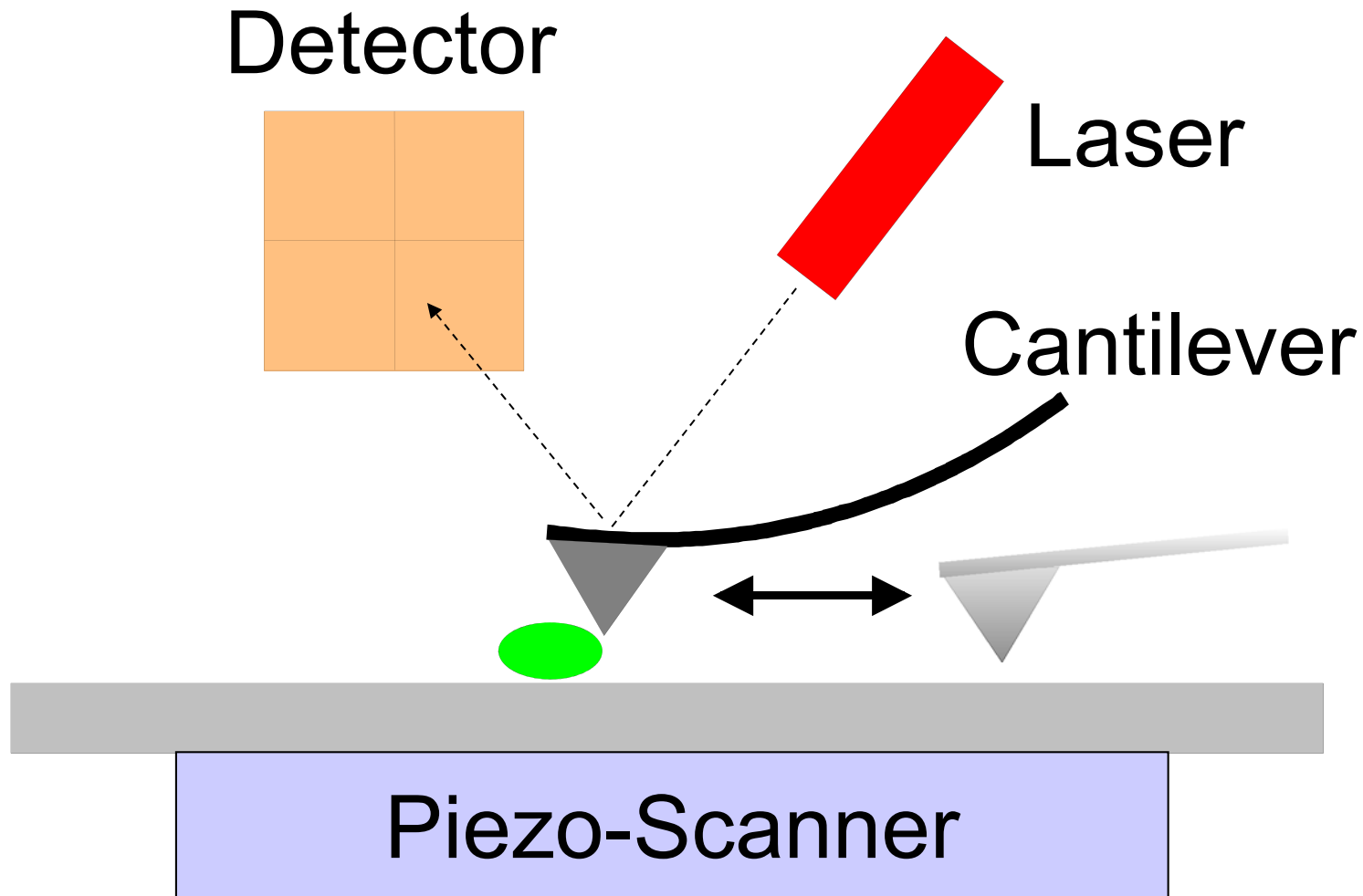
Induced diffusion due to electric field:

Stroscio & Eigler, Science **254** (1991) 1319

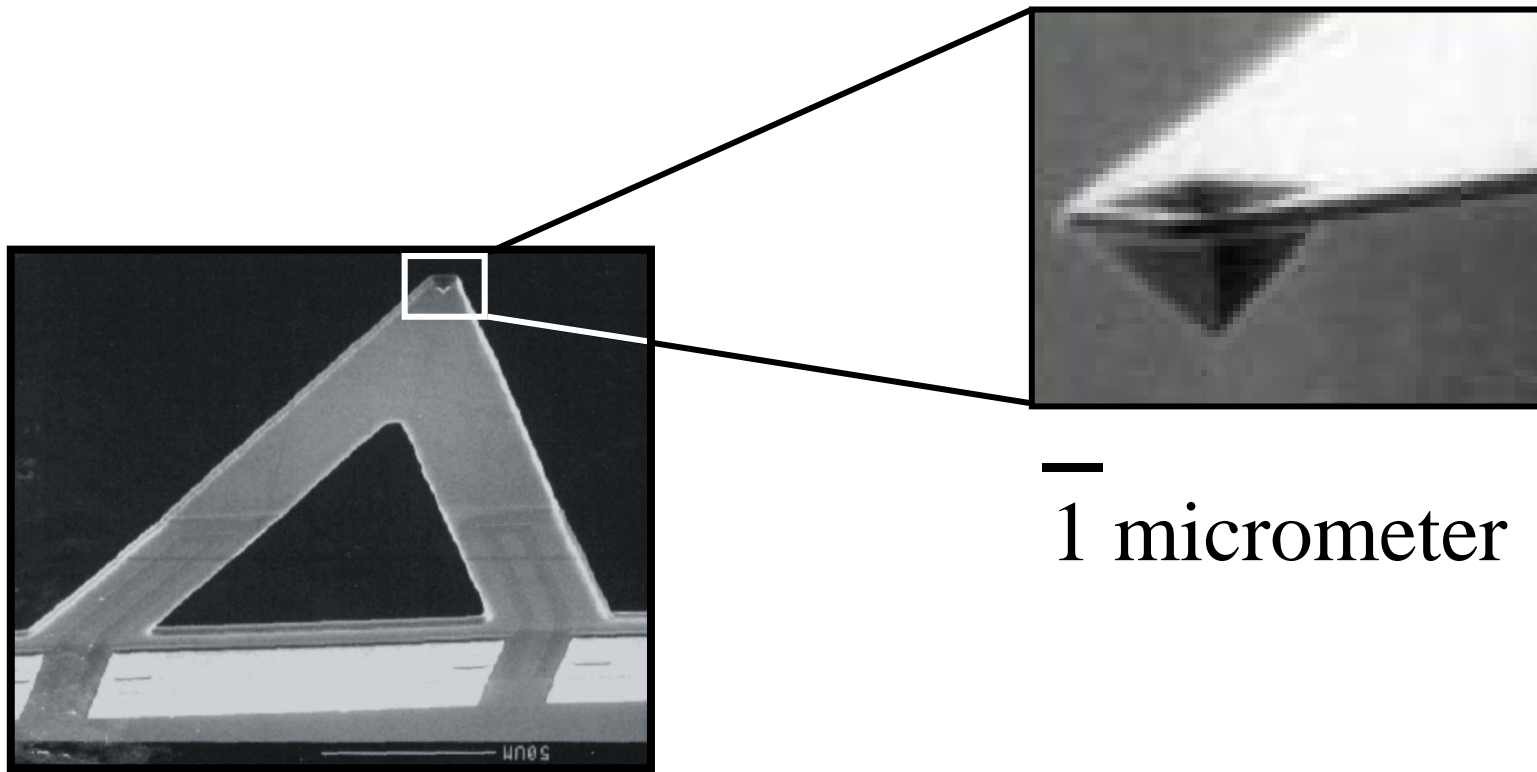
Mingo & Flores, Surf. Sci. **395** (1998) 342



AFM - “Hands & Eyes”



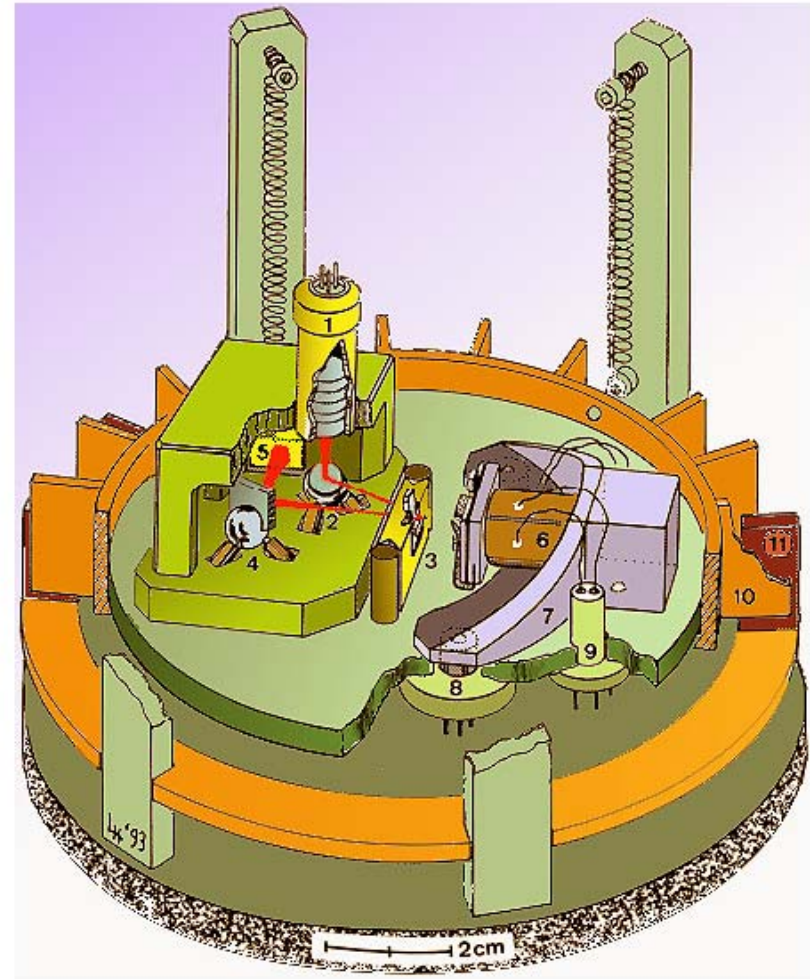
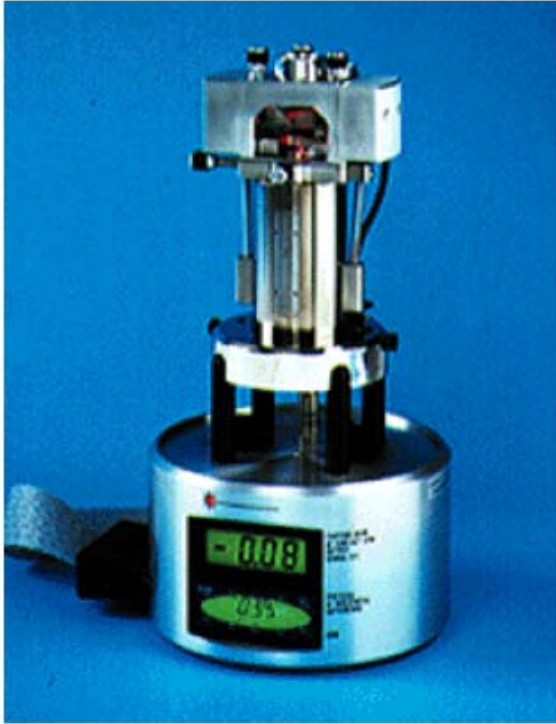
Cantilever with integrated Tip



50 micrometers

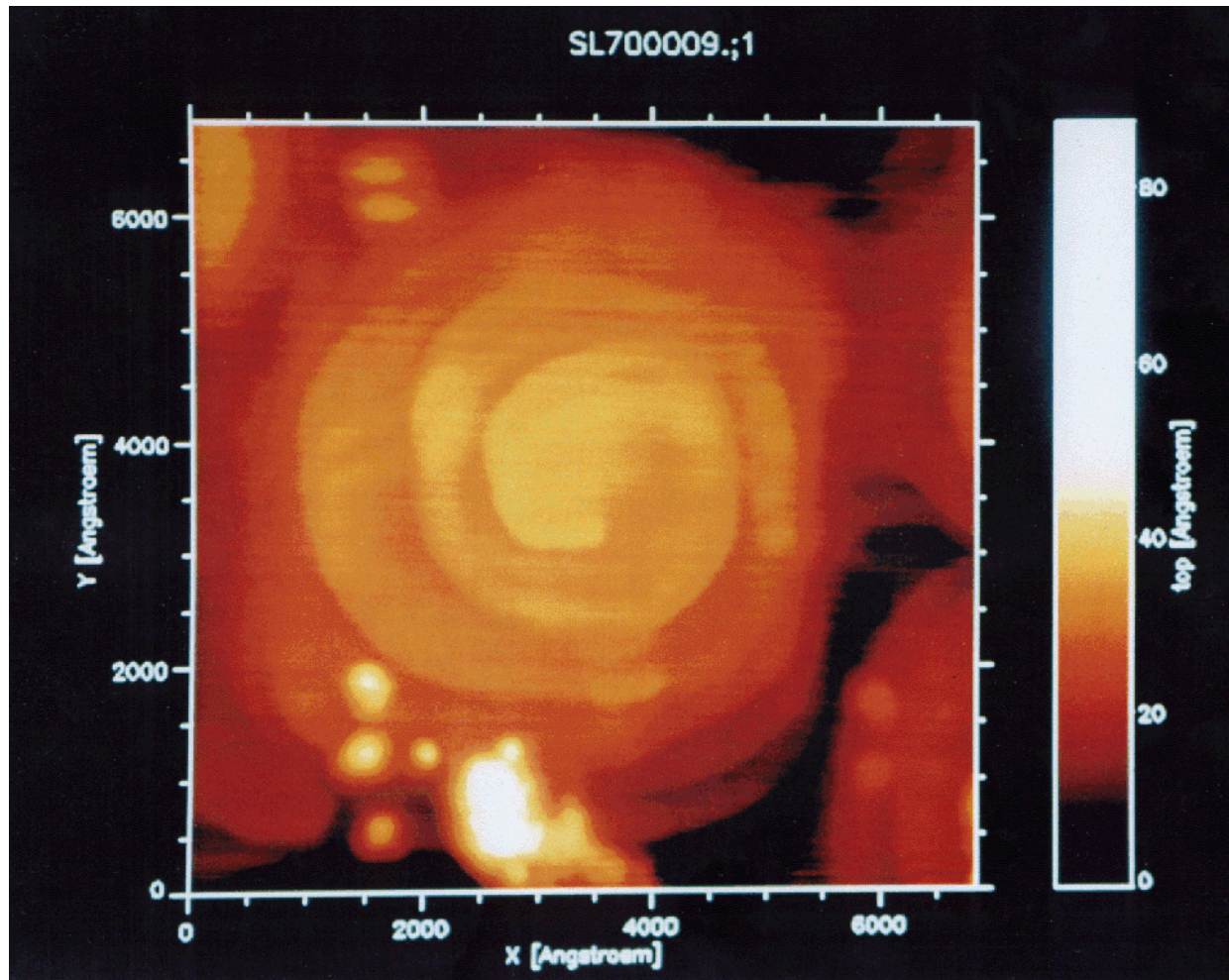
1 micrometer

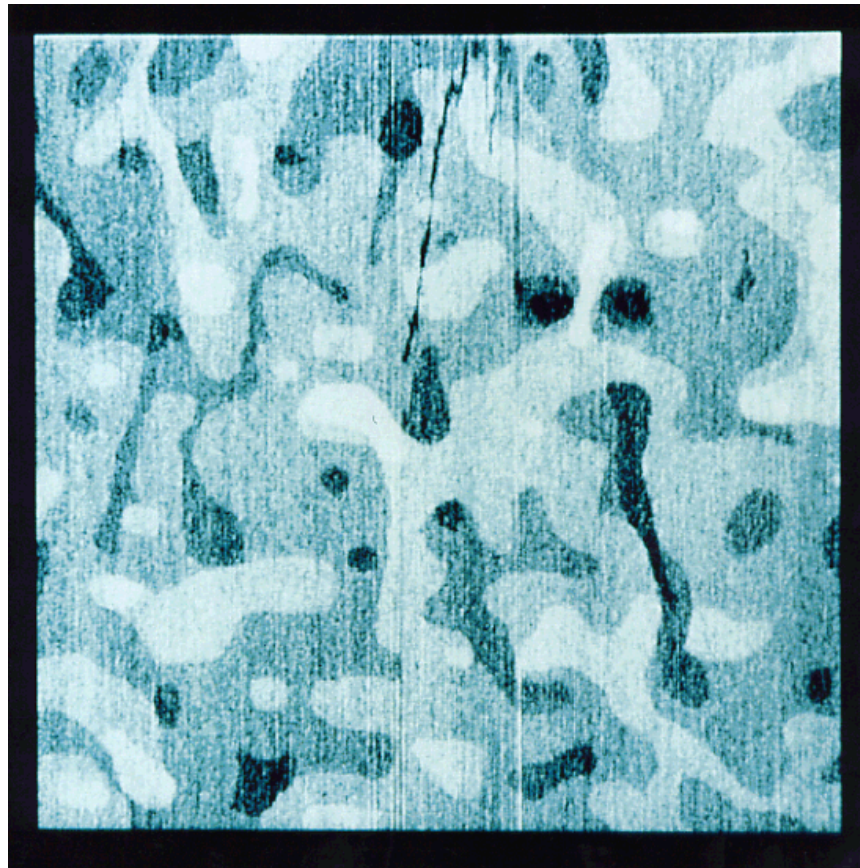
Examples



„Screw Dislocation“ on High Tc YBCO

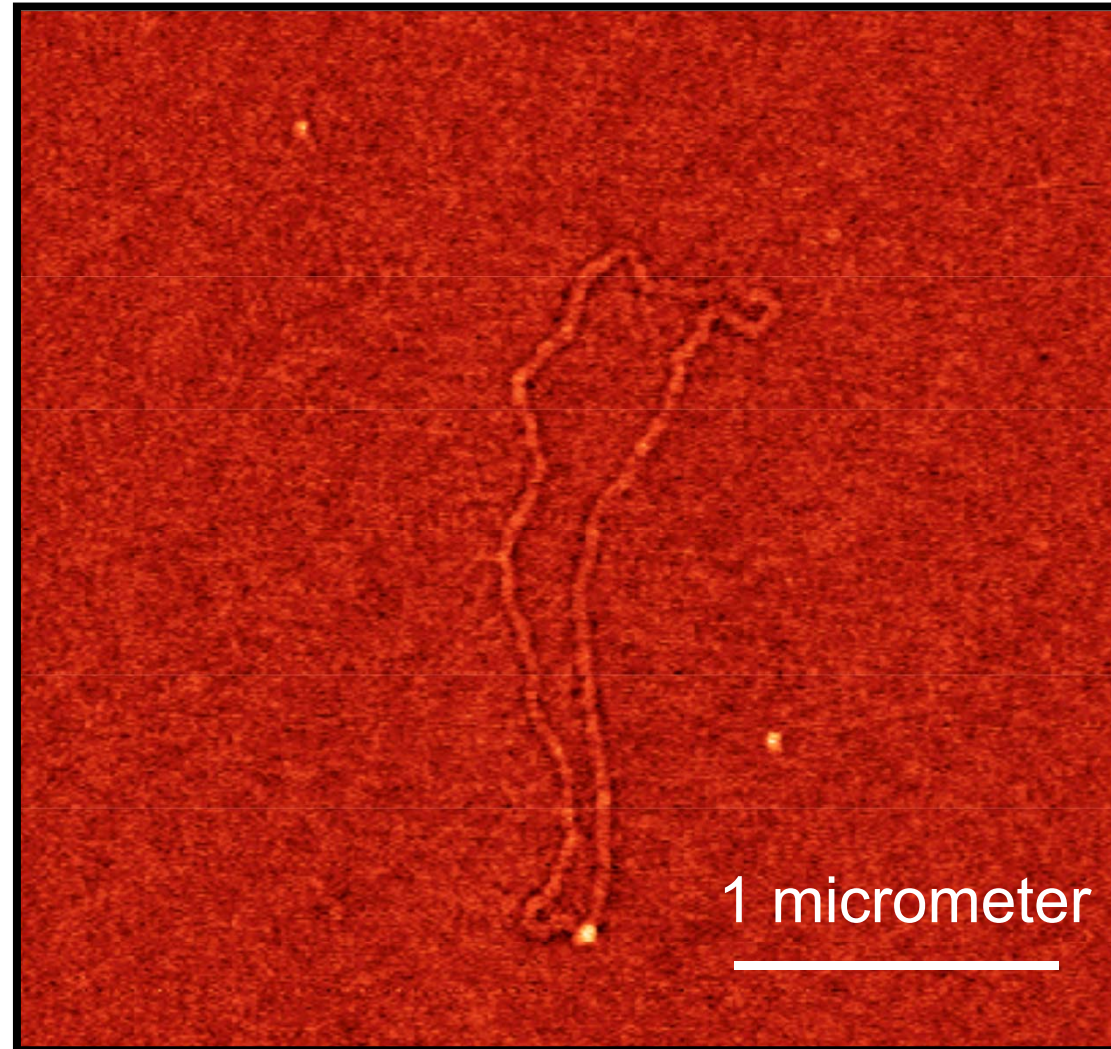
~ 400 nm diameter



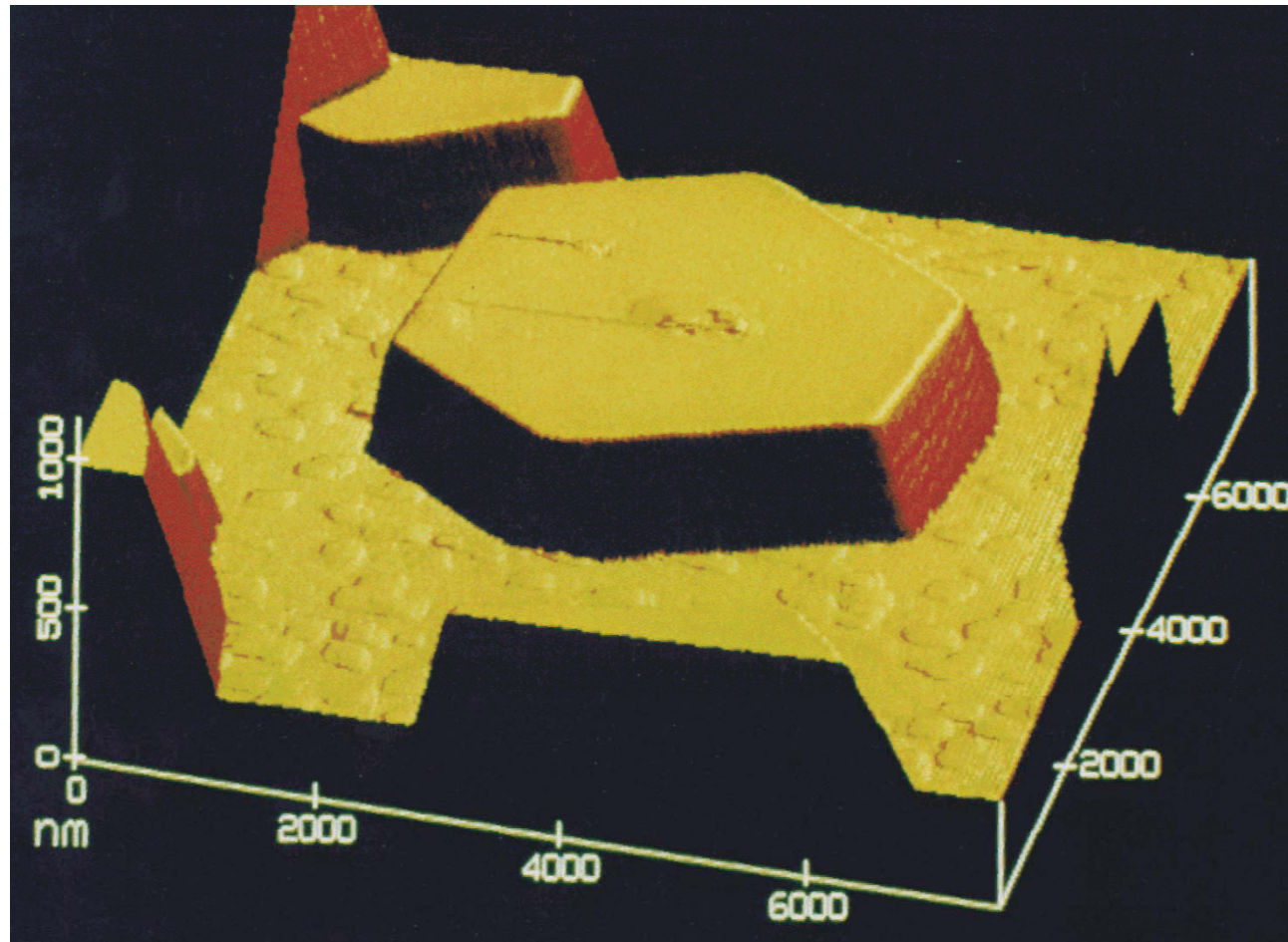


T. A. Jung SPM Tutorial

DNA-Molecule



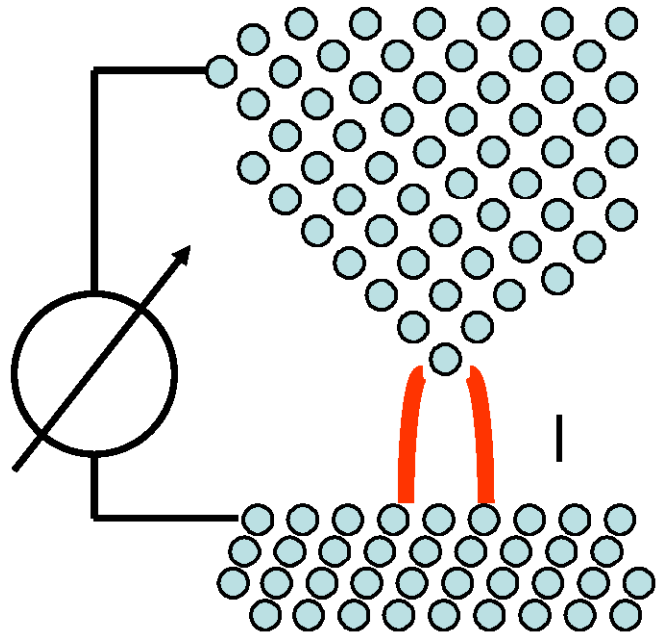
T-(tabular) AgBr grain of a photographic emulsion (Ilford)



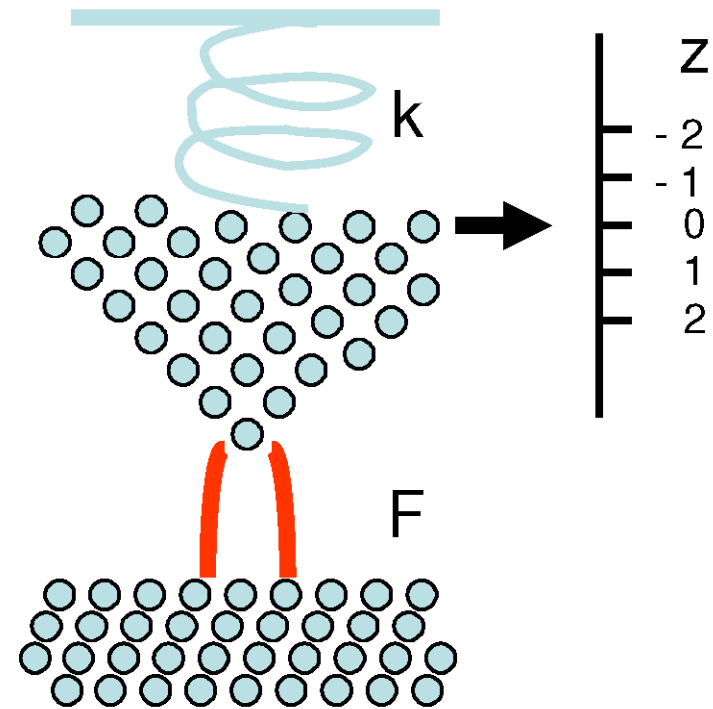
Scanning X Microscopy

S Tunneling M

S Force M

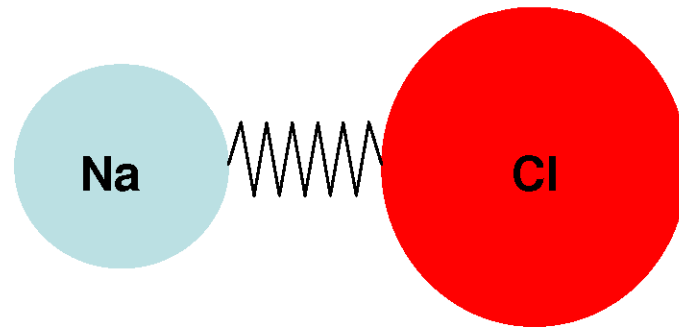


tip
sample



$$F = -kz$$

Force between two atoms

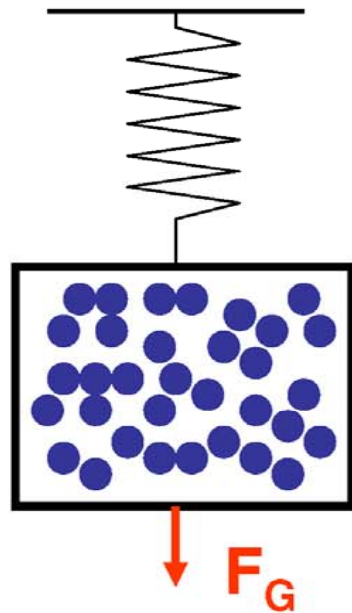


Chemical bond

$$F_{\text{chem}} = 1\text{eV} / 0.1\text{ nm}$$

1.6 nN

Sensing Forces



1 nm³ water (33 molecules)

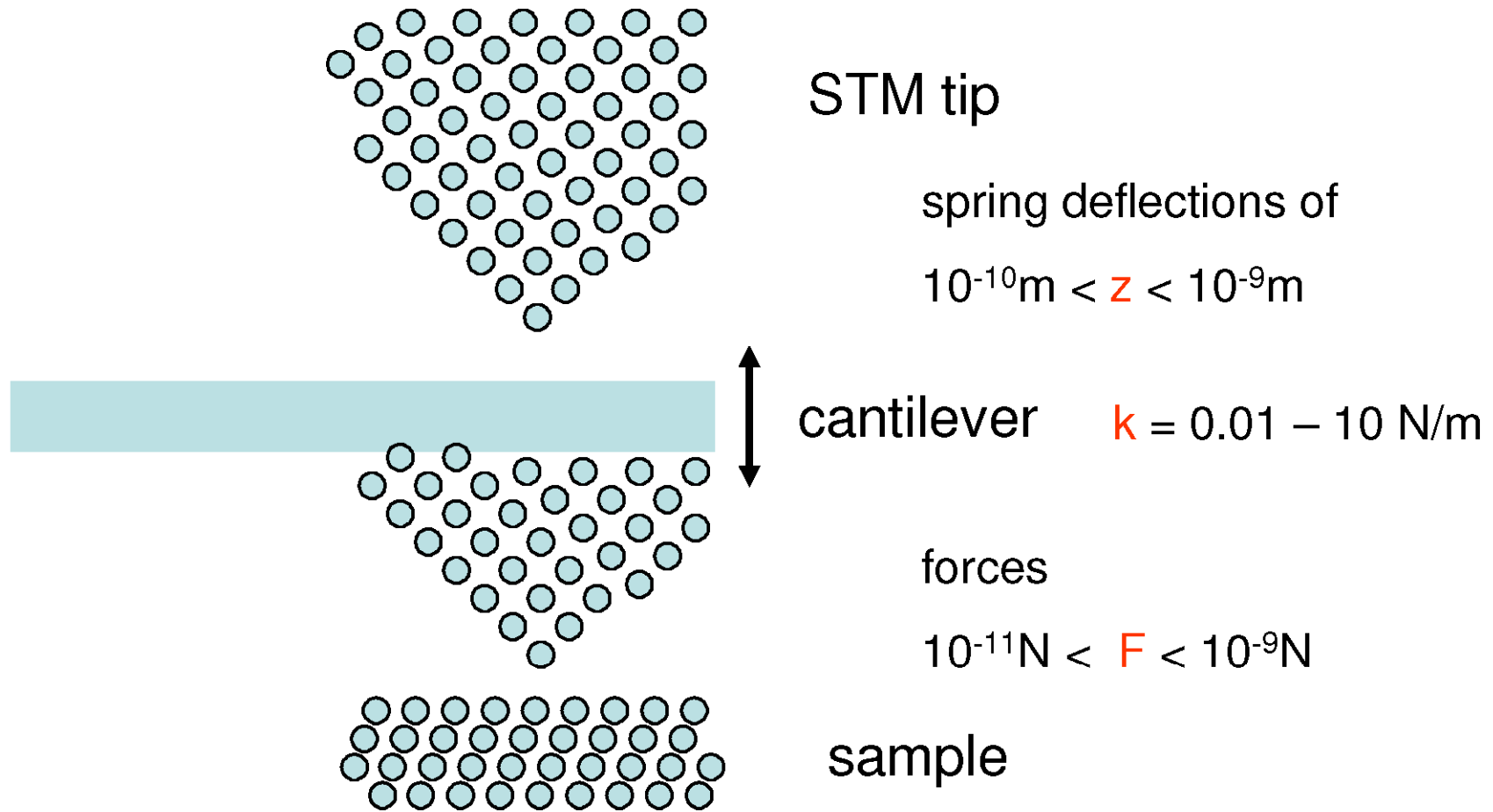
$$F_G = 10^{-23} \text{ N} = 10^{-14} \text{ nN}$$



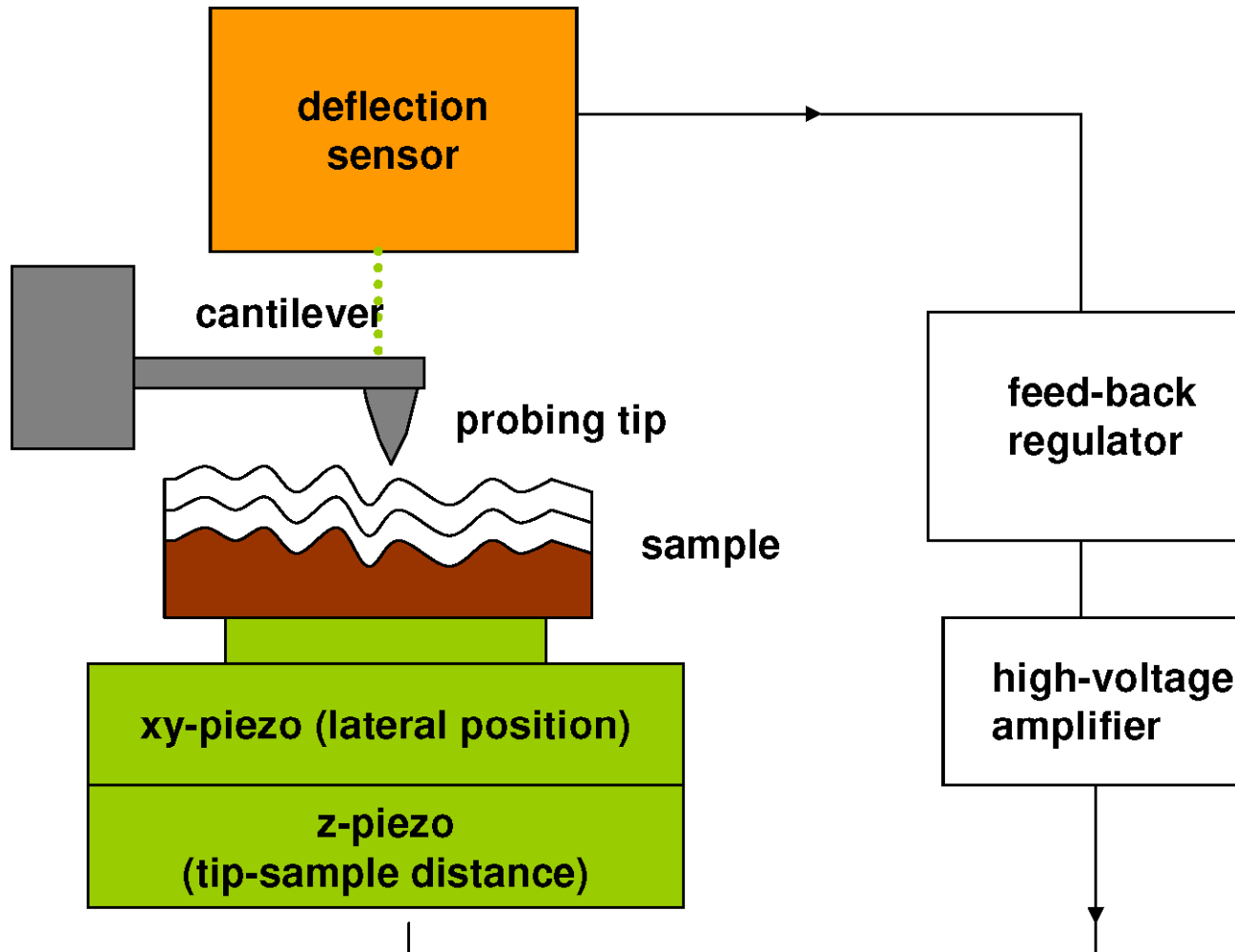
0.01 g

$$F = 0.1 \text{ mN} = 10^5 \text{ nN}$$

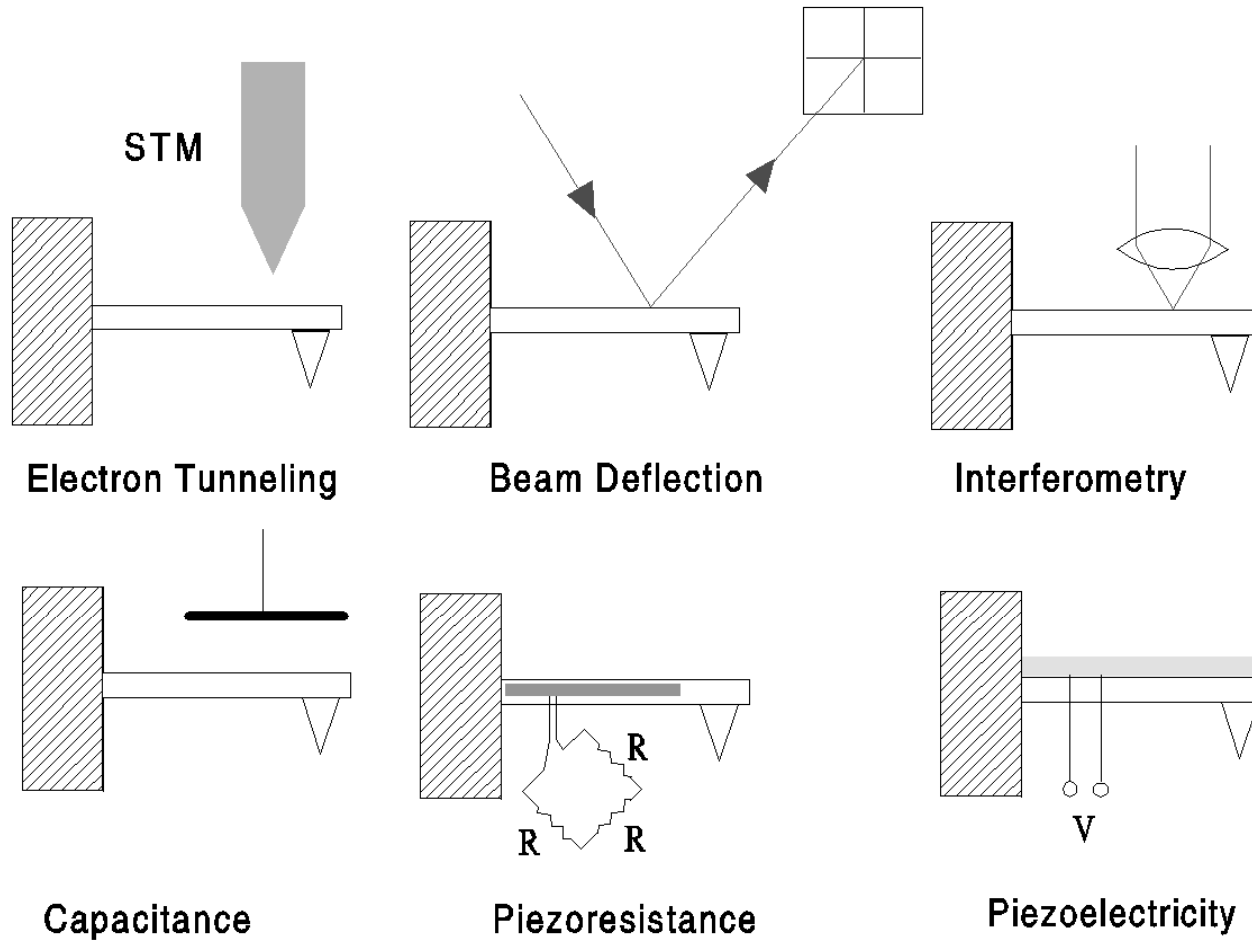
Principle of First Atomic Force Microscope



Scanning Force Microscope (AFM)



Deflection sensors



Relevant forces

- short-range repulsive forces (Pauli exclusion) or ionic repulsion forces
- short-range chemical binding forces
- van der Waals forces (always present, retarded beyond 100 nm)
- electrostatic forces (long-ranged)
- magnetic forces

- interaction in liquids
 - hydrophobic / hydrophilic forces
 - steric forces
 - solvation forces

Literature:

J. Israelachvili

Intermolecular and Surface Forces with Applications to Colloidal and Biological Systems, Academic Press (1985)

D. Tabor

Gases, liquids and solids, Cambridge University Press (1979)

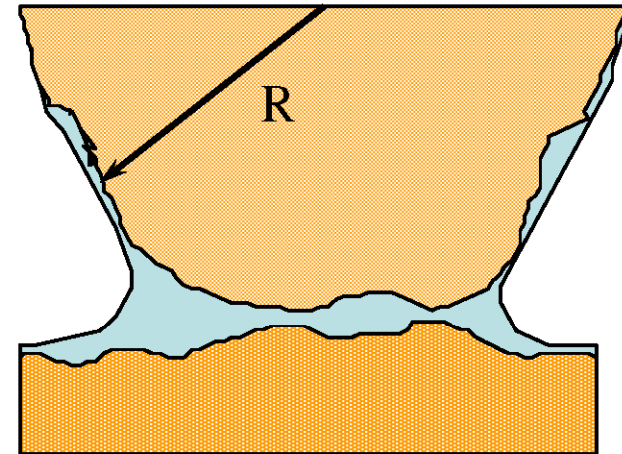
Capillary forces

$$F_{\max} = 4 \pi R \gamma \cos(\Theta)$$

$$\gamma(\text{H}_2\text{O}) = 0.074\text{N/m} \quad R=100\text{nm}$$

Contact angle for hydrophilic surfaces $\Theta \approx 0^\circ$

$$\Rightarrow F_{\max} = 90\text{nN}$$



Van der Waals forces in vacuum

- No capillary forces (no water)
- Van der Waals and electrostatic forces dominate

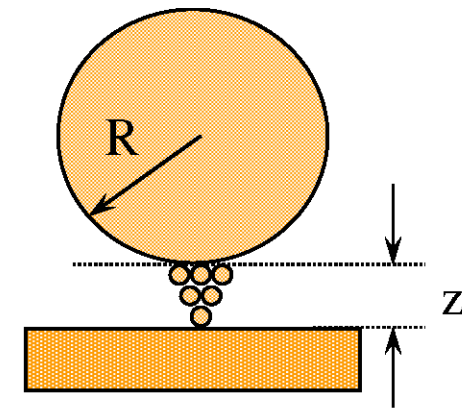
$$F_{\text{vdW}} = - B R/z^2 * 1/(1+z/2 R)^2$$

$$B=3K/4 (\epsilon_s-1)(\epsilon_t-1)/[(\epsilon_t+1)(\epsilon_t+2)]$$

$$K=1.41\text{eV}$$

F.O. Goodman and N. Garcia,
Phys. Rev. B 43, 4728 (91)

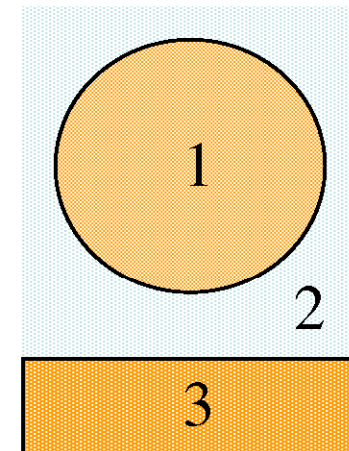
⇒ R=100nm, z=1nm



graphite-graphite	8 nN
diamond-diamond	17 nN
metal-graphite	10 nN
SiO ₂ -graphite	1.2 nN

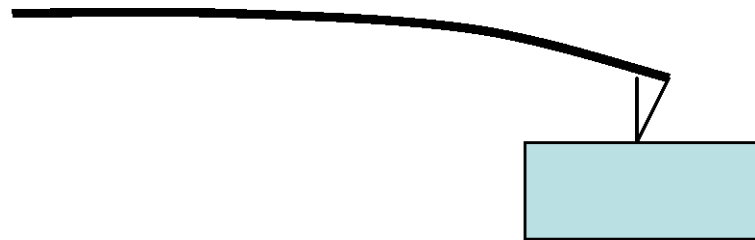
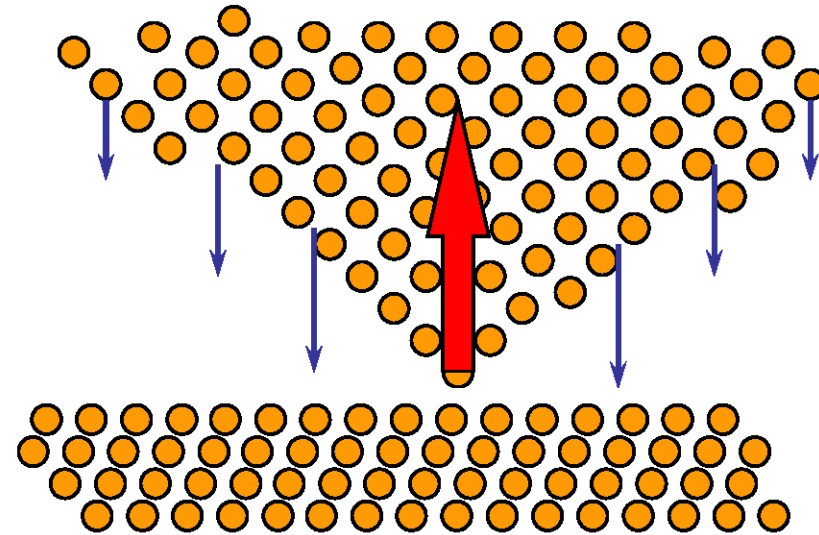
Van der Waals forces in liquids

- capillary forces are eliminated
- Van der Waals can be repulsive:
$$U \gg (n_1^2 - n_3^2)(n_2^2 - n_3^2)$$
For $n_1 < n_2 < n_3$ result negative van der Waals forces.
Mc Lachlan, *Proc. Roy. Soc. A* 271, 38 (1963)
- Observation of very weak forces (10pN) by Ohnesorge und Binnig. Atomic resolution of a calcite surface.
F. Ohnesorge and G. Binnig, *Science* 260, 1451 (1993)
- For hydrophobic surfaces entropy effects can increase the net forces.

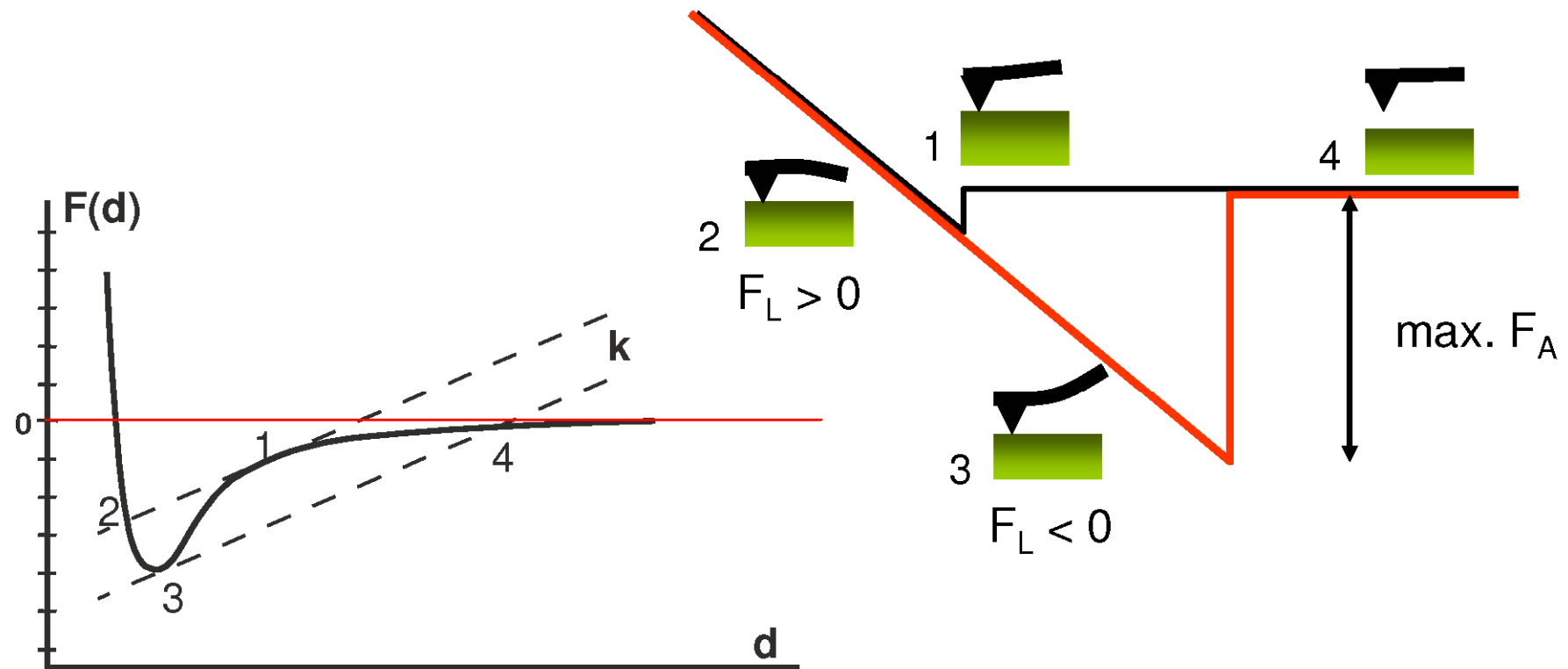


Estimation of forces

- Typical long-range forces:
 - in air: 10-100nN
 - in liquids: 1-100pN
 - in ultra-high vacuum: 0.1-10nN
- Long-range forces are compensated by short-range repulsion. Bending of the cantilever can reduce the repulsive forces.



Force vs. distance curves

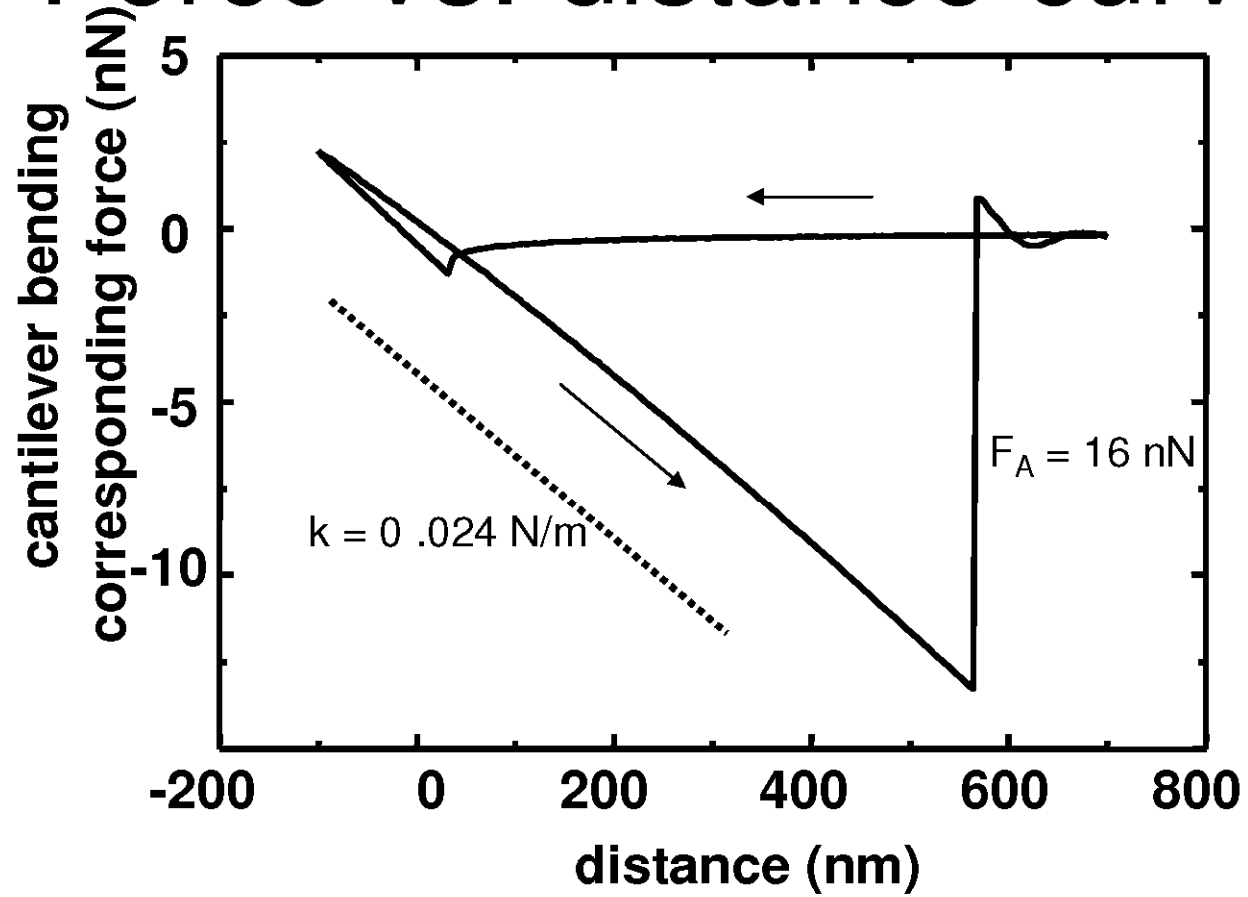


$F(d)$: Interaction force between tip and sample

d : tip sample distance

k : spring constant of cantilever

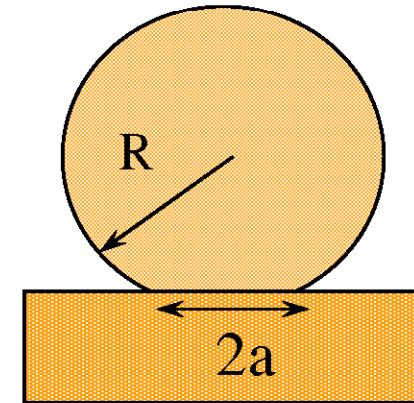
Force vs. distance curves



Contact area

The contact area is given by

- $2a = 2 E^*(F R)^{1/3}$ (Hertz theory)
- in air: 5-100nm
- in liquids: atomic resolution
F. Ohnesorge and G. Binnig, *Science* 260, 1451 (1993)
- in ultra-high vacuum: 1-10 nm
Best resolution in ultra-high vacuum:

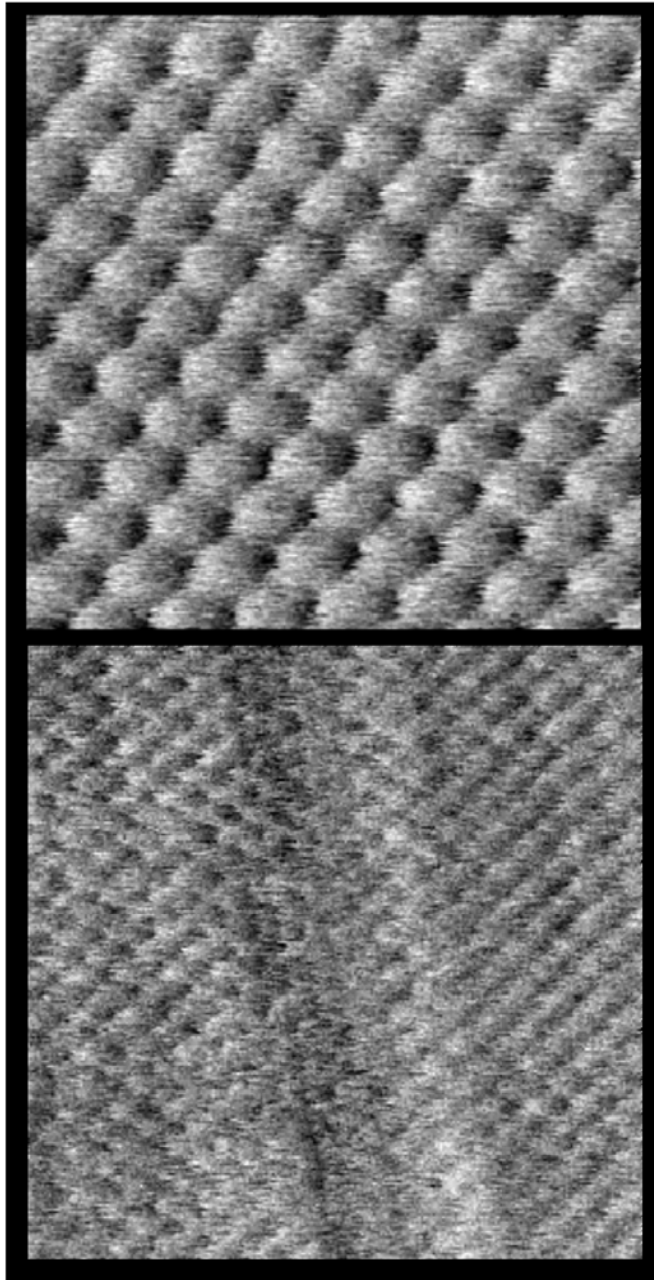


Steps on NaCl: L. Howald et al., *Phys. Rev. B* 49, 5651 (1995)

Si(111)7x7 unit cell: L. Howald et al. *Phys. Rev. B* 51, 5484 (1995)
(chemically modified tip)

C₆₀-molecules: R. Lüthi et al., *Z.f. Phys. B* 95, 1 (1994)

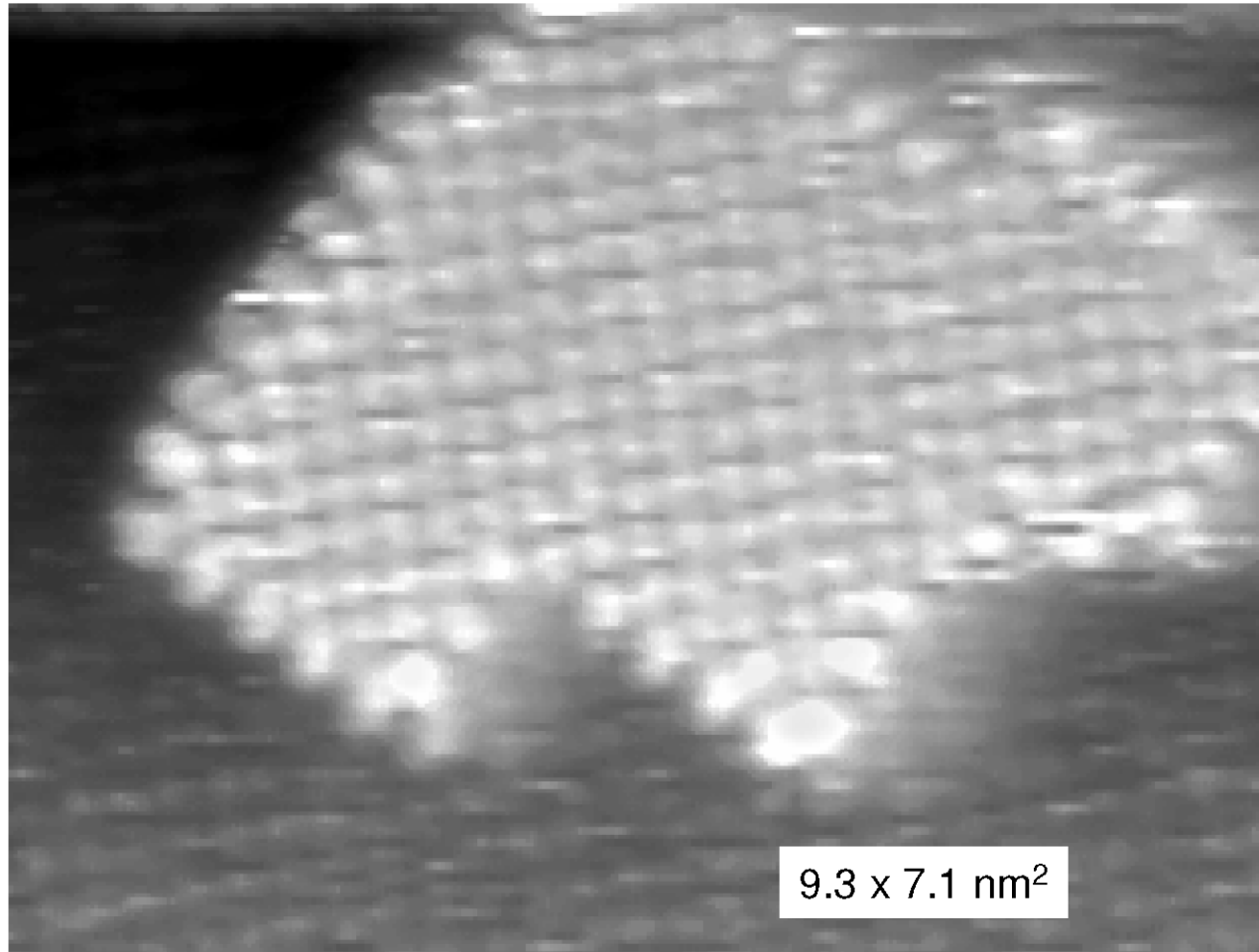
AFM on NaF(001)



- contact mode imaging on NaF(001)
 - observation of the atomic periodicity
 - steps area distorted in a range of 1 nm
- ⇒ 1 nm contact radius

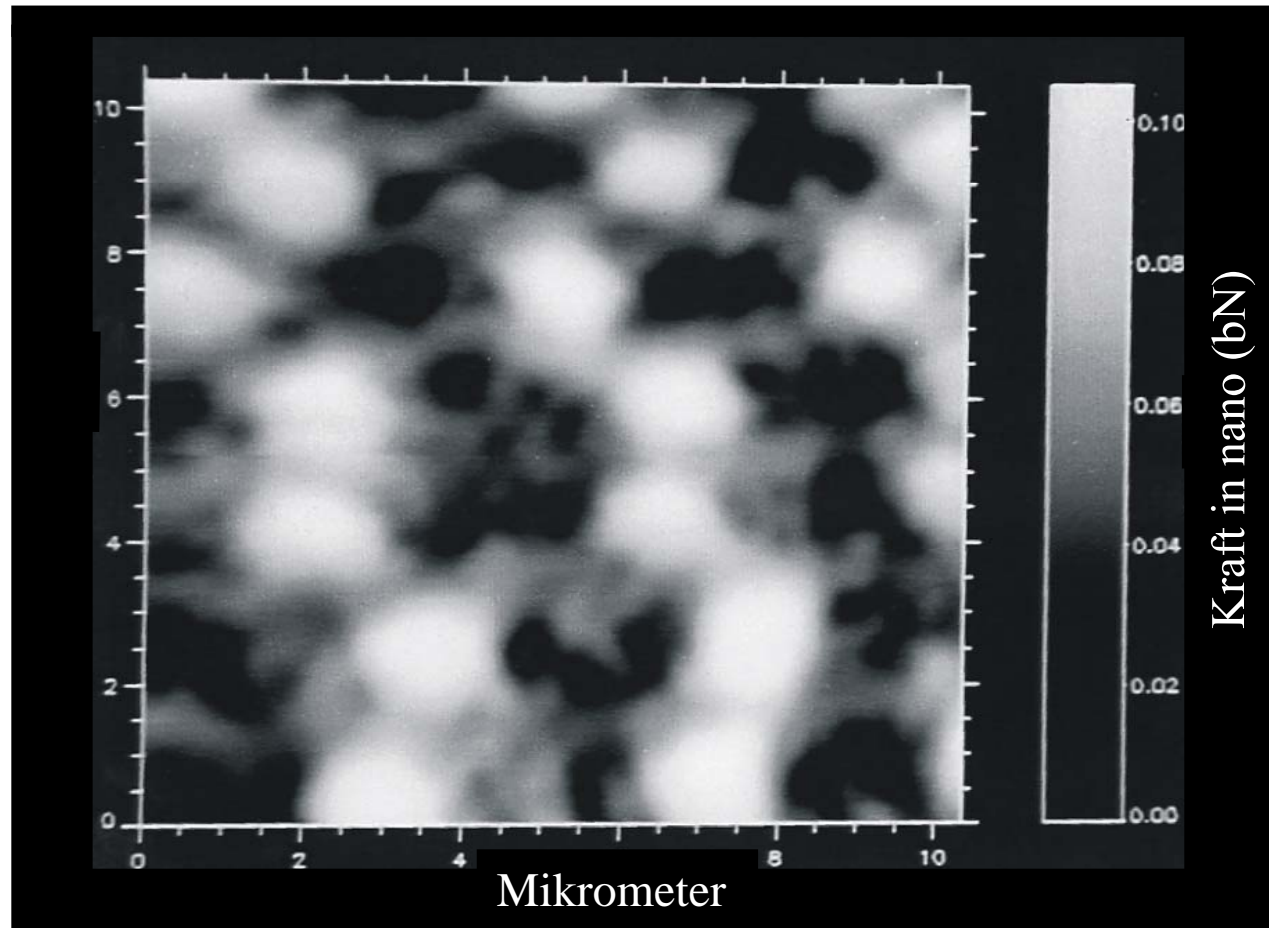
1 nm

True atomic resolution on insulators



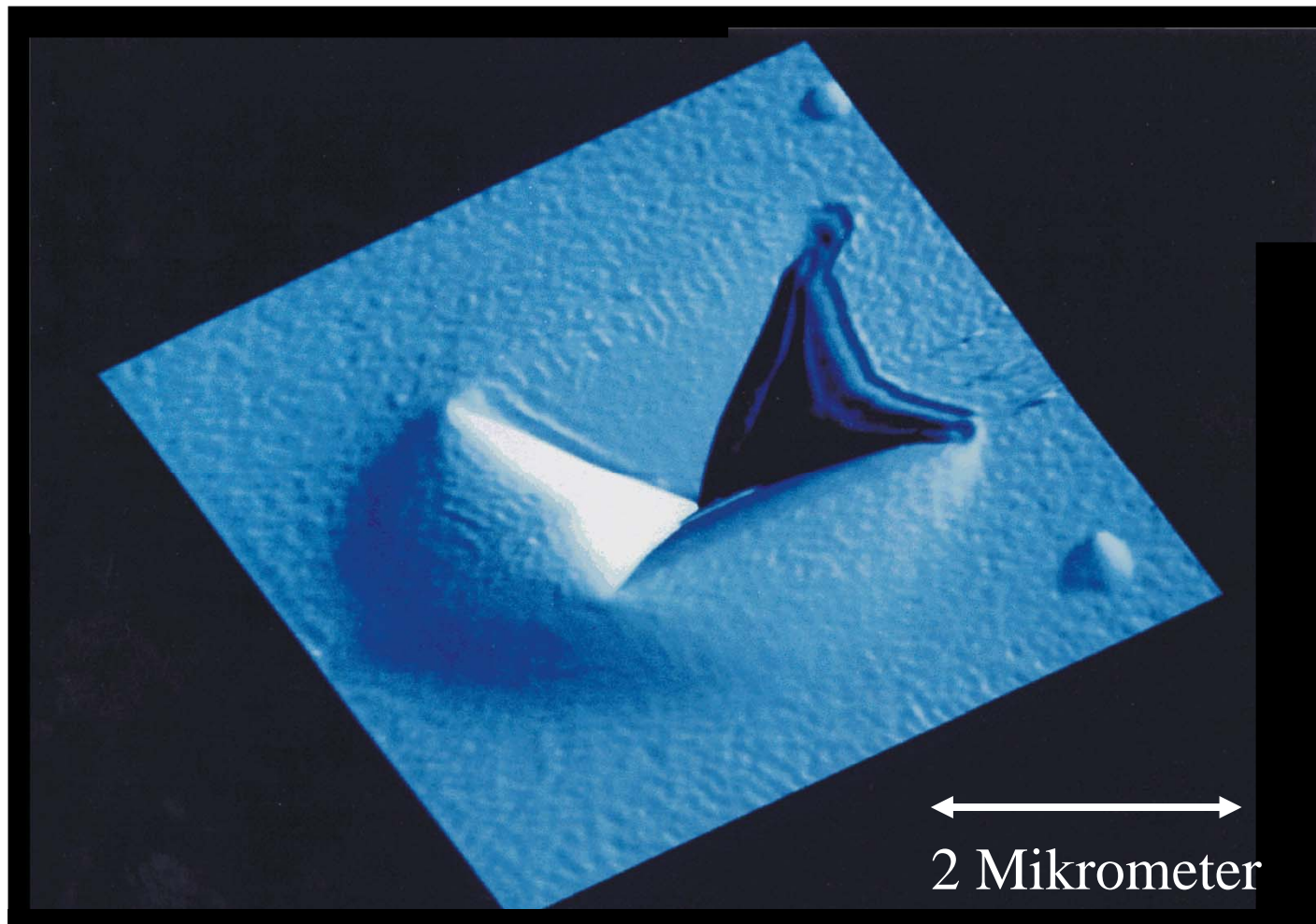
NaCl-island imaged by nc-AFM

Magnetic domains on Computer HD



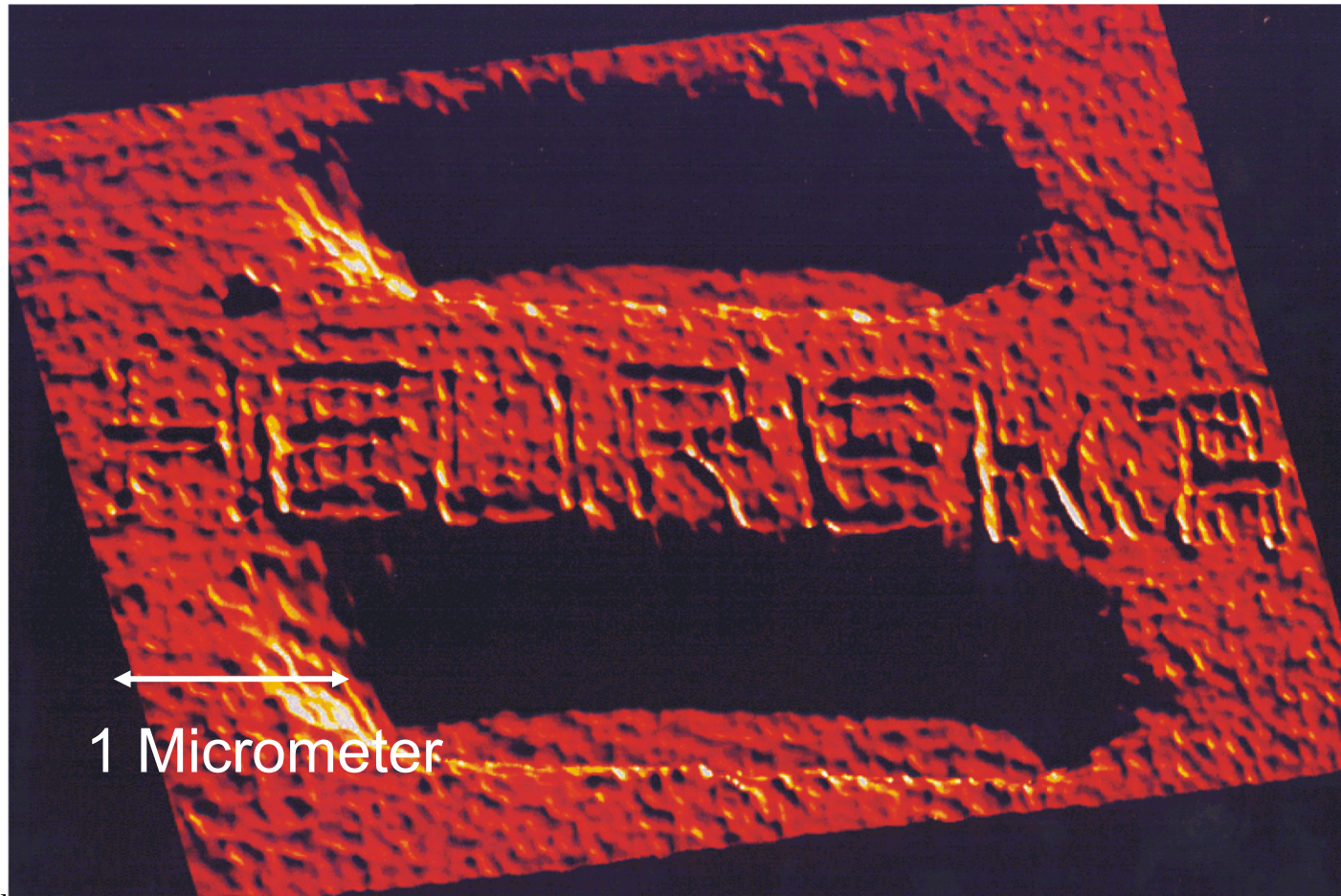
Indentation Hardness

tip-tools – materials testing and data storage



„HEUREKA“

— writing in between the lines of a CD



Nano-Fracture / Nano-Wear

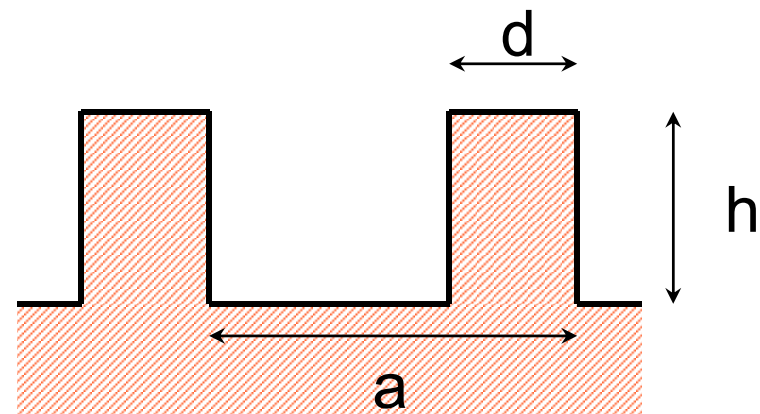
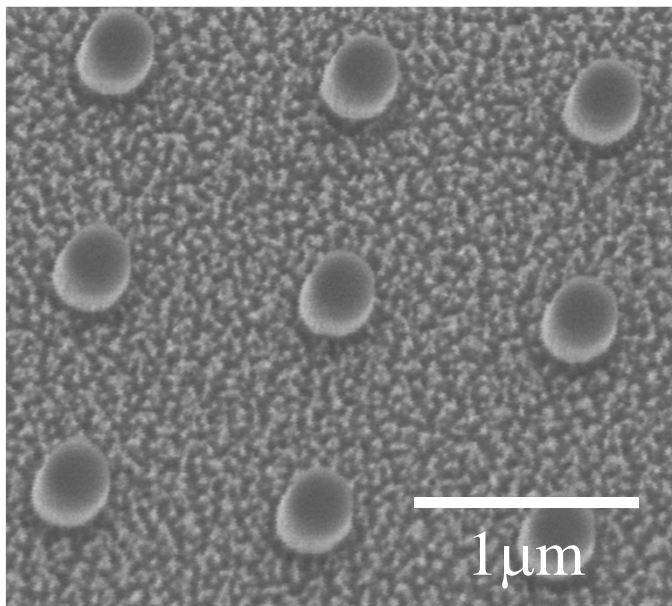


Fracture is a **macroscopic** phenomenon which crucially depends on **microscopic** properties

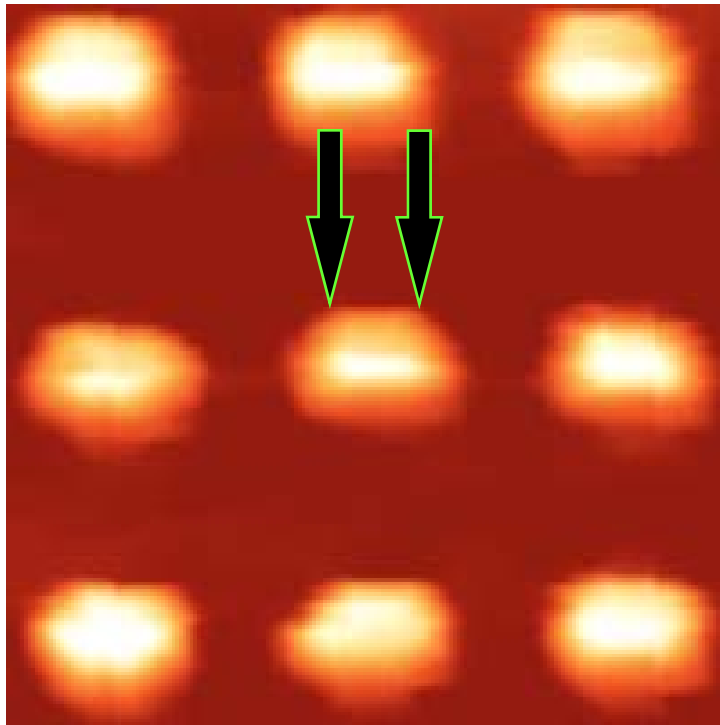
- Crystal structure
- Dislocation lines
- Interfaces
- Crack initiation
- Crack propagation

Well defined model system

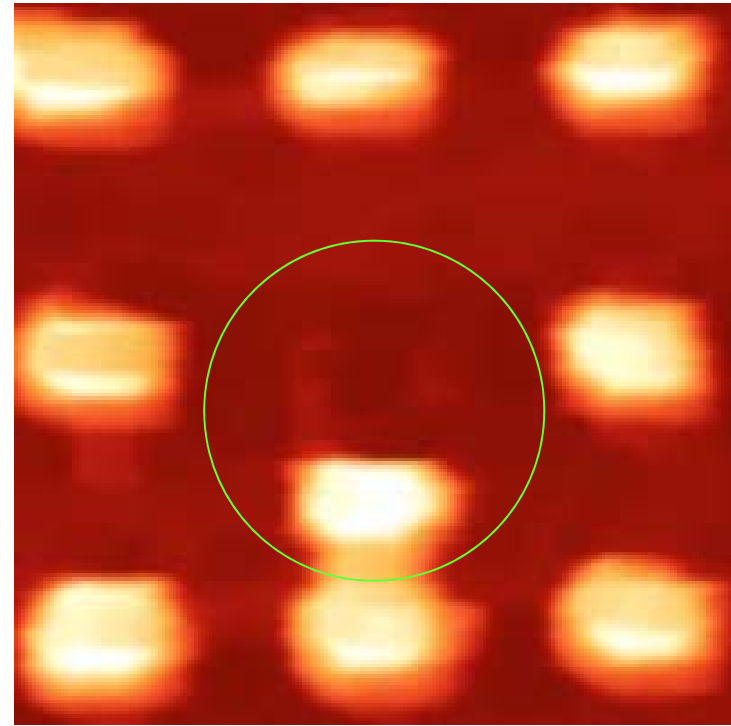
- Nanotower arrays produced by lithography technique



Nanotower Fracture Experiments

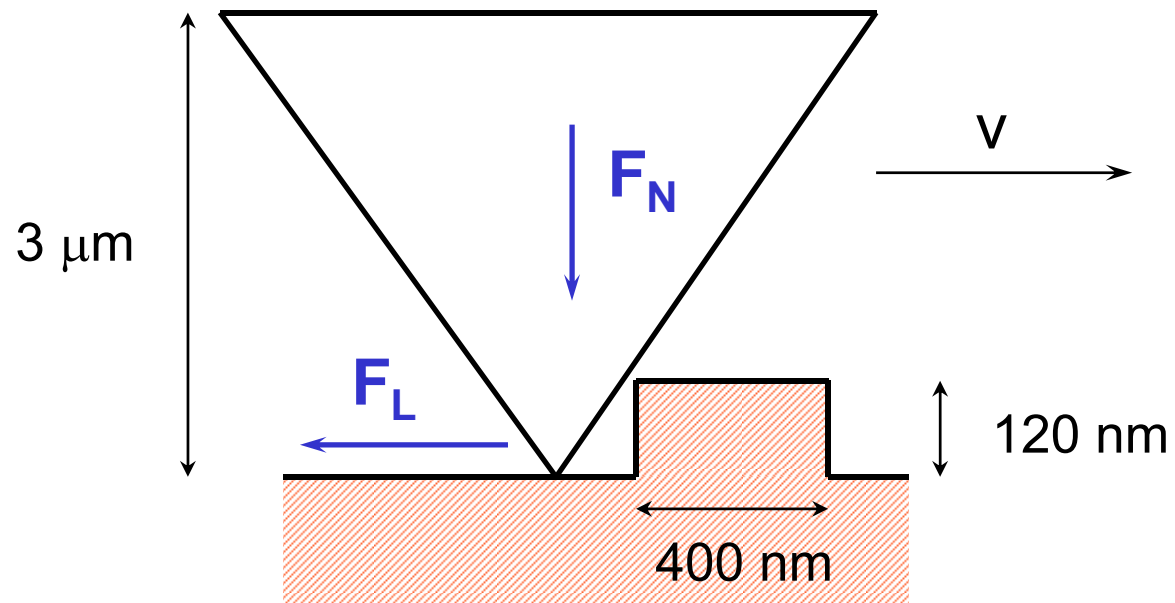


1000 nm

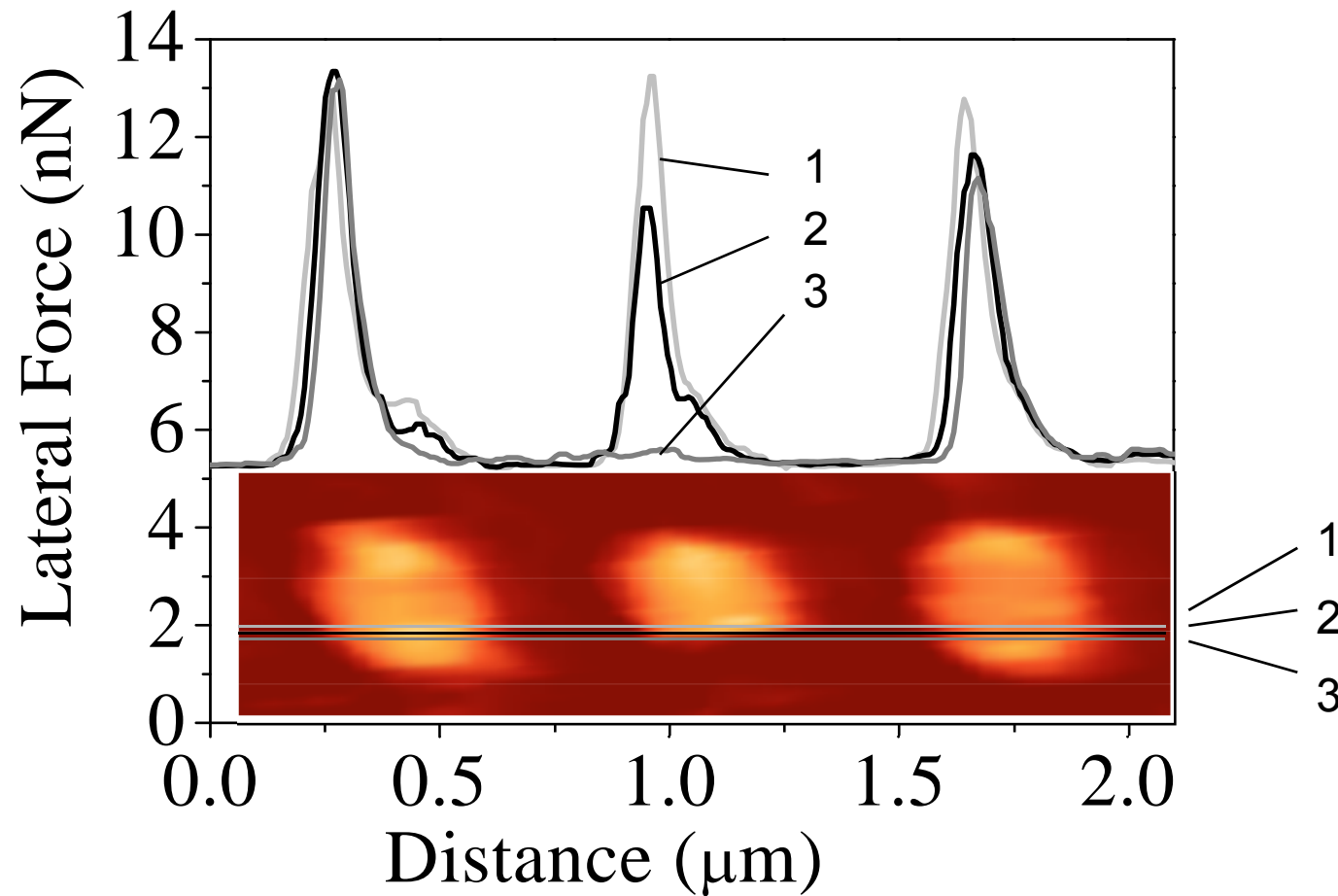


breaking off and removing nanotowers

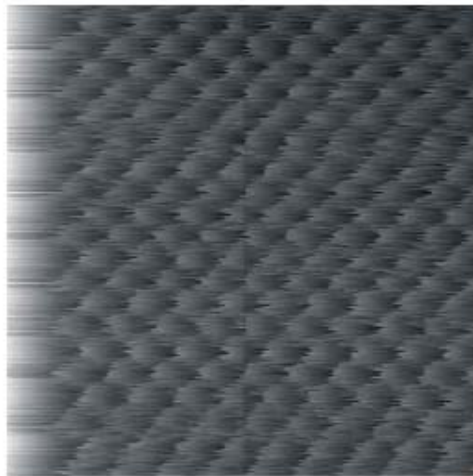
Lateral force measurement



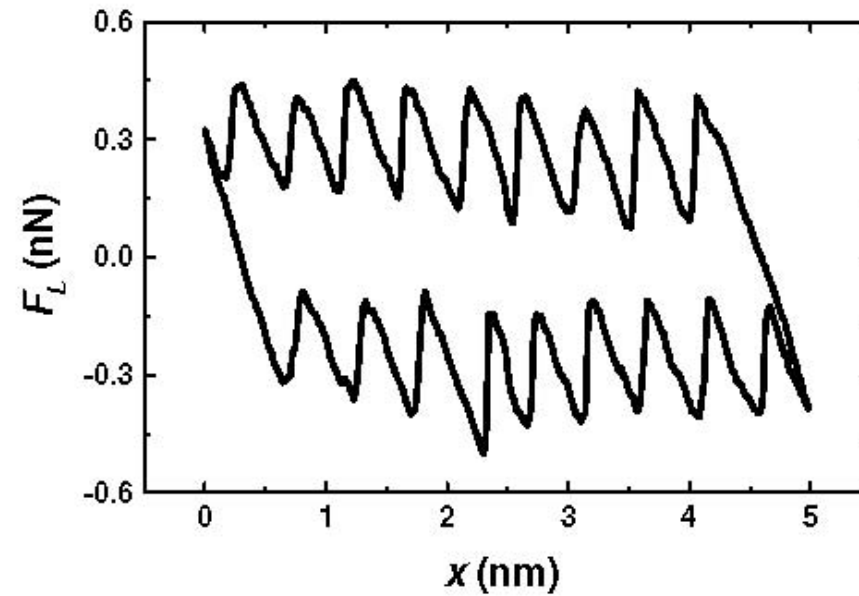
Lateral forces during fracture



Atomic-scale stick-slip

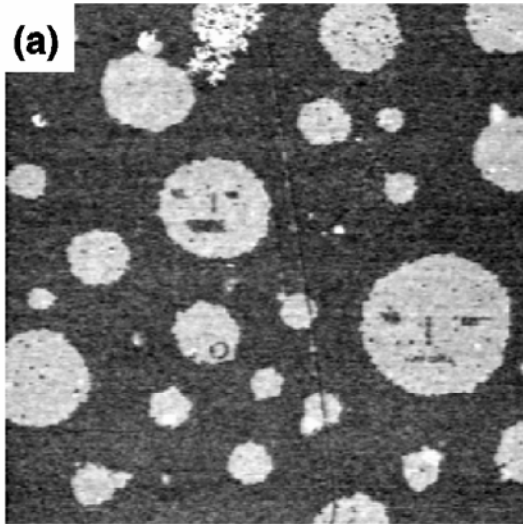


NaCl(100)



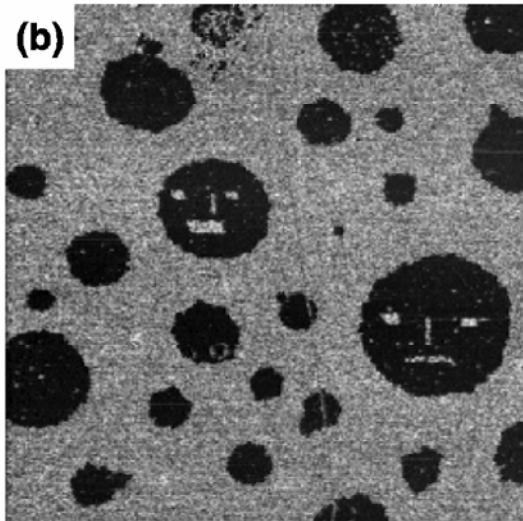
⇒ See part II

Friction contrast



Topography

Mixed Langmuir-Blodgett films
($\text{C}_{21}\text{H}_{43}\text{COO}^- / \text{C}_9\text{F}_{19}\text{C}_2\text{H}_4\text{OCC}_2\text{H}_4\text{COO}^-$)



Lateral Force

2.8x2.8 μm^2

E. Meyer et al.

Thin Solid Films **220**, 132 (1992)

