Repetition:

- Elektronenbeugung (kaum Roentgenbeugung)
- Diffusion / Surface Phase Formation
  Adsorption / Desorption / Growth
- X-ray Absorption Spectroscopy
- X-ray Microscopy
- Photoelectron Spectroscopy – also for Chemical Analysis

- Dates for Excursion?

Oberflächenphysik

27/04/2010

Local Probes and Experiments I:

Scanning Tunneling Microscopy (STM)
Inelastic Tunneling and
Scanning Tunneling Spectroscopy (STS)

Prof. Dr. Silvia Schintke & Prof. Dr. Thomas A. Jung

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PAUL SCHERRER INSTITUT

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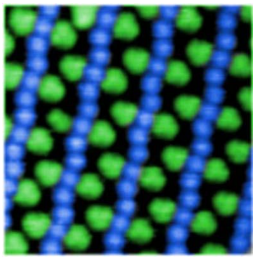
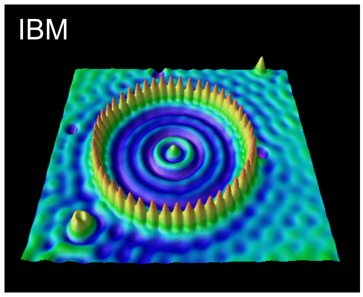
STM – local probe for surface science

surface analysis @ nanoscale
- scanning probe methods (STM/AFM)
  - working principle of STM
  - tunnel current
  - examples and image interpretation
- scanning tunneling spectroscopy (STS)
  - local electronic structure



STM image: self-assembled molecular layer
Nanolab, Uni Basel

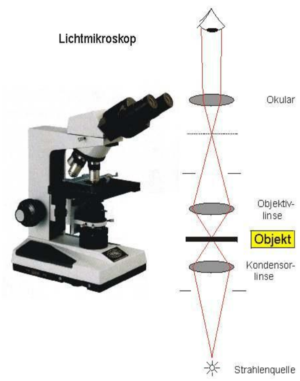
surface modifications @ nanoscale
- manipulation of atoms or adsorbates
- nanoindentation

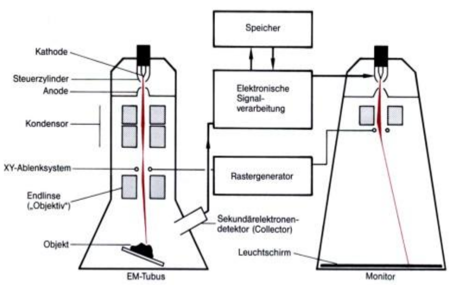


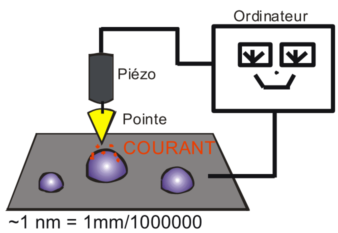
Microscopes

For the visualisation of millimeter to nanometer structures

Light Microscope	Electron Microscope (SEM)	Scanning Probe Microscope (SPM)
since about 1750	since about 1955	since about 1981





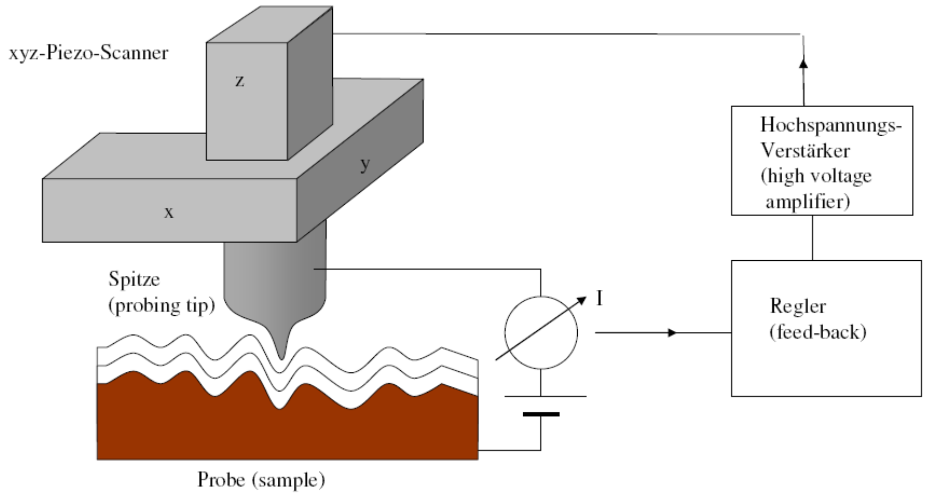


geometric optics
resolution about 500 nm
Light-Intensity contrast

e-beam raster-scan
resolution 5 nm
secondary electron counting
projection image

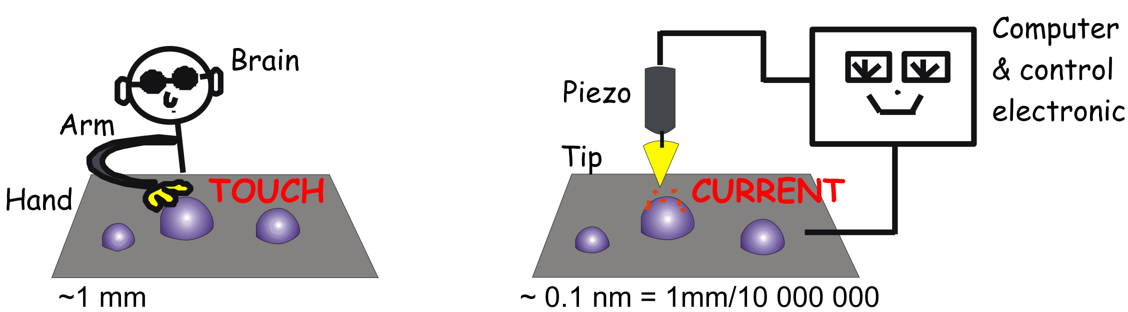
Local probe piezo-scan
resolution 0.1 nm
3D map of surface

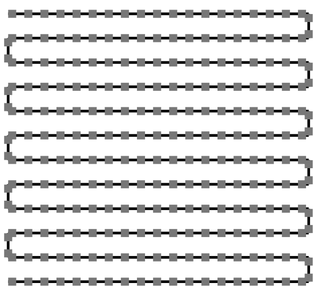
Rastertunnelmikroskop (STM)

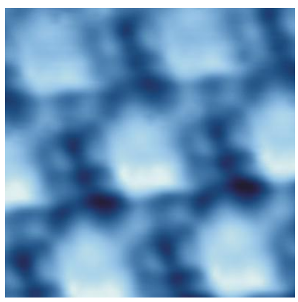


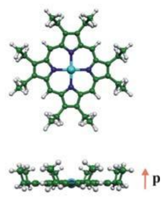
Ein Regler hält den Tunnelstrom (≈pA-nA) zwischen Spitze und Probe konstant. Es werden Kontouren konstanten Tunnelstroms abgerastert.

Scanning Tunneling Microscopy









CuOEP on Cu(111) (averaged image)
3.0 nm × 3.0 nm, U = -0.55 V, I = 24 pA
L.Ramoino, S.Schintke et al., to be published

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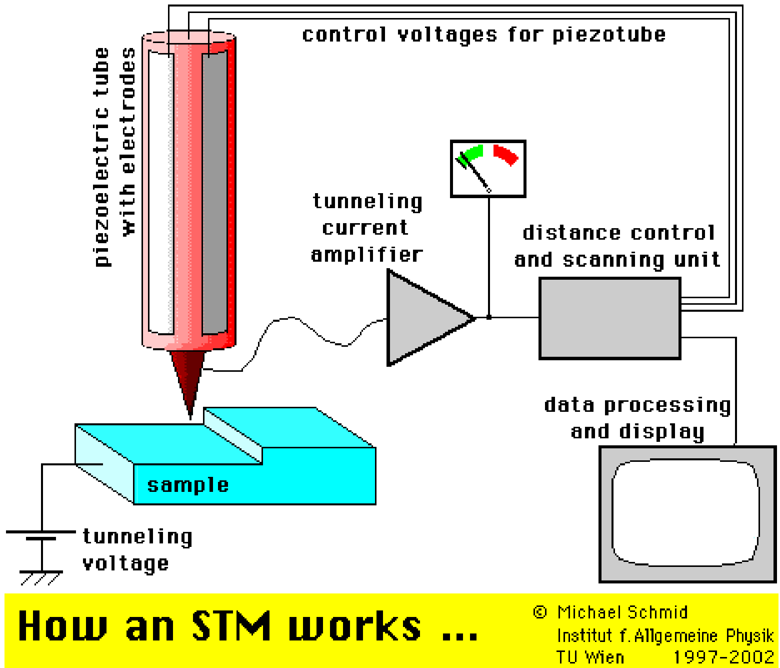
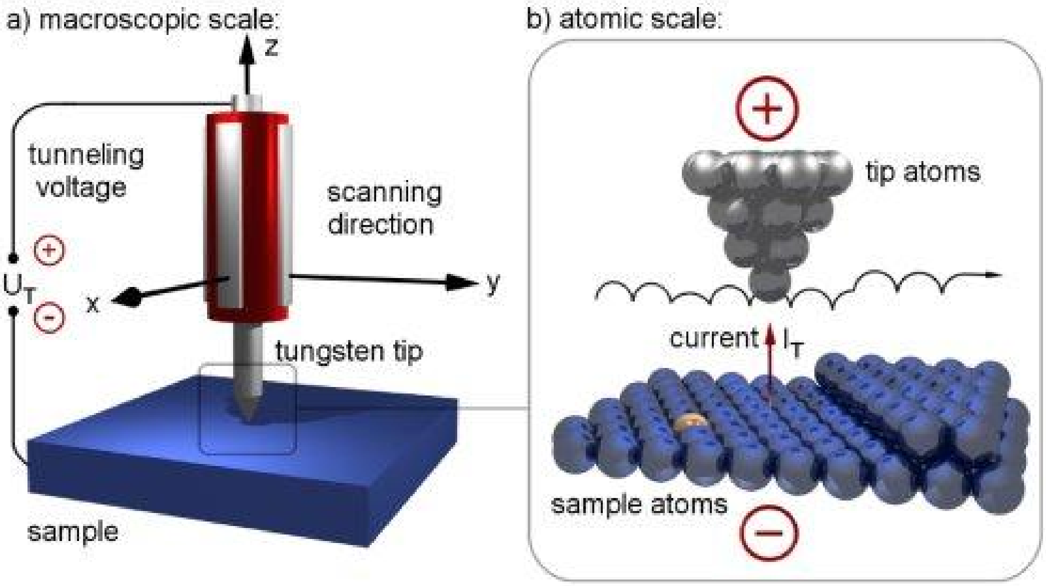
Nanolab, Uni Basel

Image acquisition **(constant current images)**



Piezo unit and tip displacement



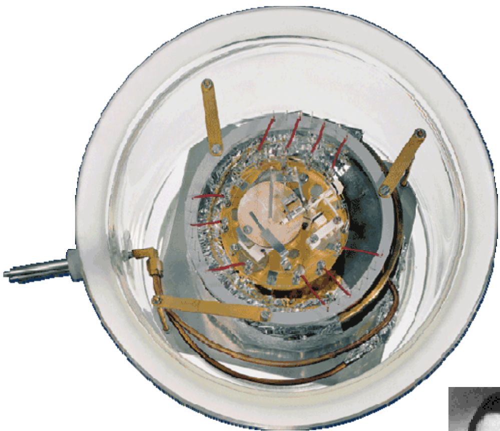
History of Scanning Tunneling Microscopy

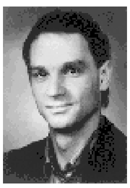
- **1979-1981 Development at IBM Zürich**
  G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel,
  Appl. Phys. Lett 40 (1982), Phys. Rev. Lett. 49, 57 (1982)
- **1986** **Nobel prize of Physics** for Gerd Binnig and Heinrich Rohrer

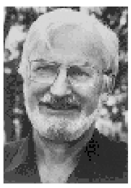
The soccer ball team of the IBM research lab; 15 October 1986
C. Julian Chen: Introduction to Scanning Tunneling Microscopy;
Original photo: Blick

The first Scanning Tunneling Microscope

1981 development at
IBM Rüschlikon, Switzerland

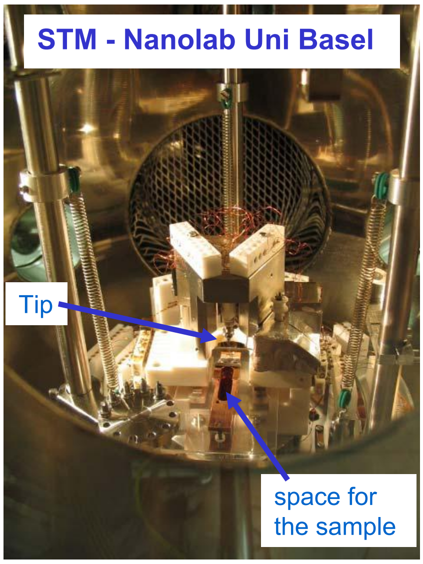




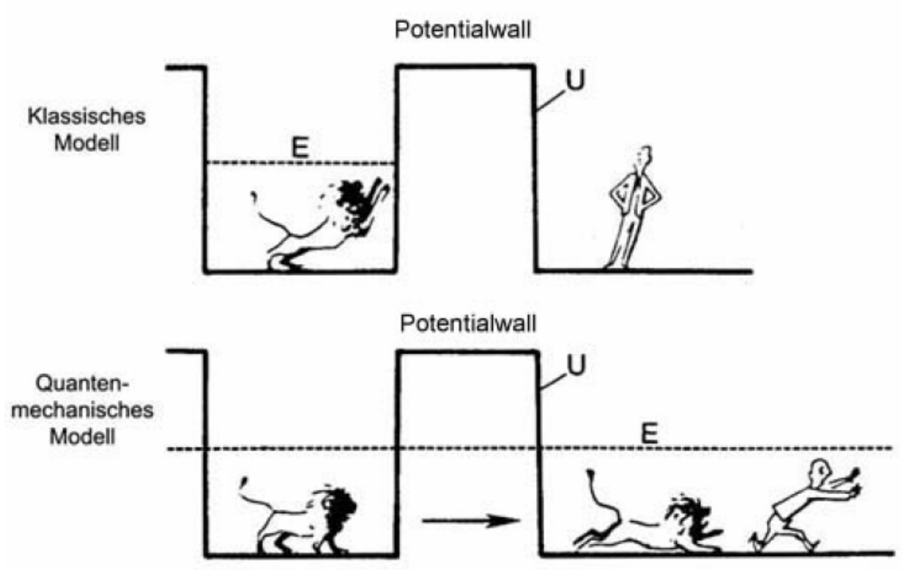


G. Binnig and H. Rohrer
Nobelprize for physics 1986

The « Nanolab » at the University of Basel

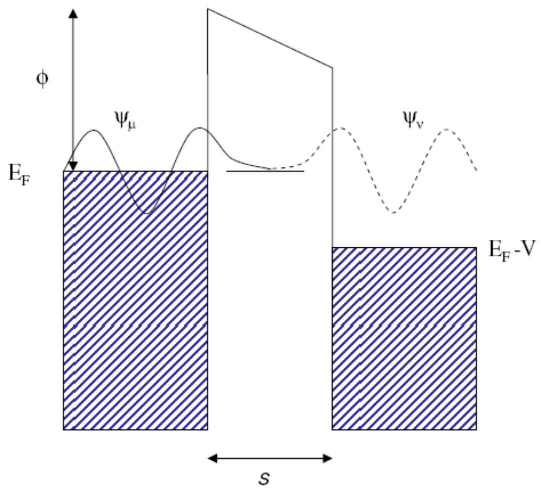


Quantum Mechanic Tunneling



Tunneleffekt

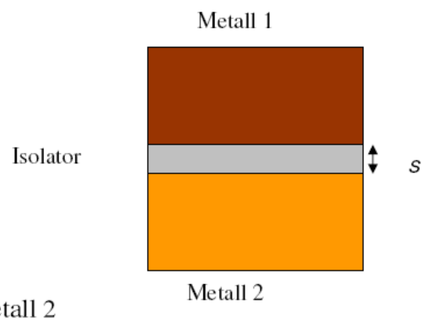
Schon zu Beginn der Quantenmechanik wurde der Tunneleffekt vorausgesagt. Der Überlapp der Wellenfunktionen führt zu einer Transmission von Elektronen durch ein klassisch verbotenenes Gebiet. Zwischen zwei Metallen, die durch Vakuum oder ein Oxid getrennt sind, fliesst ein Tunnelstrom.



Tunneleffekt

$$I = f(U)\exp\left(-A\sqrt{\phi}\, s\right)$$

J. Frenkel, *Phys. Rev.* **B 36**, 1604 (1930)



I: Tunnelstrom
U: Extern angelegte Spannung
s: Distanz zwischen Probe und Spitze
ϕ: Barrierenhöhe

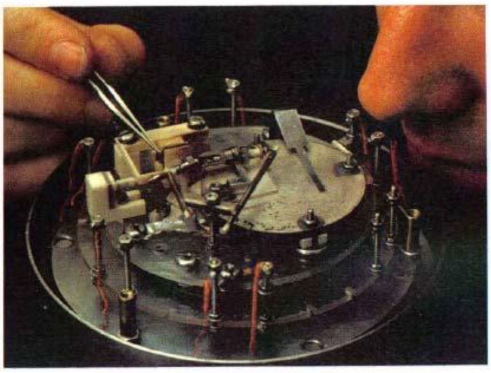
$\phi \approx \frac{\phi_1 + \phi_2}{2}$ ϕ_1, ϕ_2 Austrittsarbeiten von Metall 1 und Metall 2

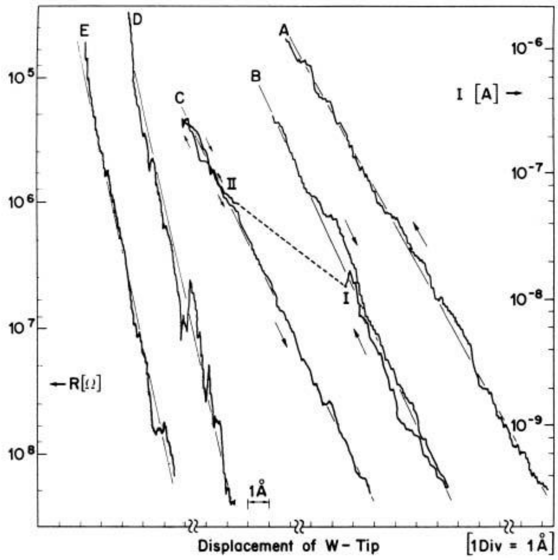
$A = 2\sqrt{\frac{2m}{\hbar^2}} = 1.025$ Å^{-1}eV$^{-1/2}$.

f (U) : Funktion der elektronischen Struktur von Probe und Spitze
Für freie Elektronen f (U) ~ U

Der Tunnelstrom hängt exponentiell vom Abstand s ab. Für typische Austrittsarbeiten von ϕ=4.5eV ändert sich der Strom etwa um eine Grössenordung, wenn die Distanz um 1Å verändert wird. Historisch wurde zuerst das Oxidtunneln realisiert. Erst mit dem STM konnte Vakuumtunneln beobachtet werden.

Tunnelstrom



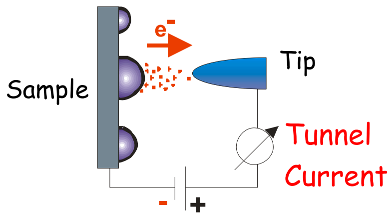


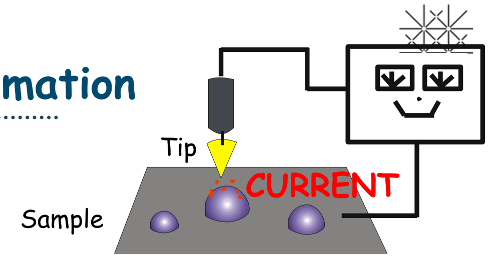
Exponentieller Abfall des Tunnelstromes mit dem Abstand

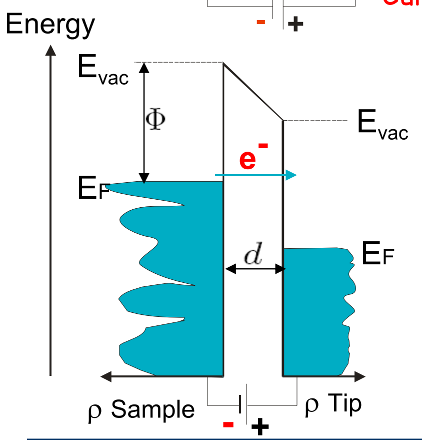
STM

Nanosurf AG, Liestal

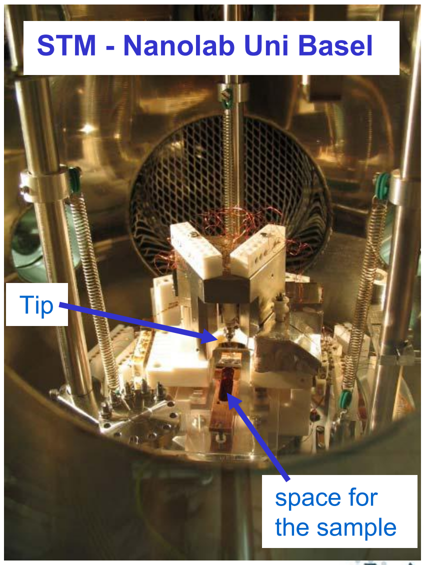
Tunnel Current – simple approximation



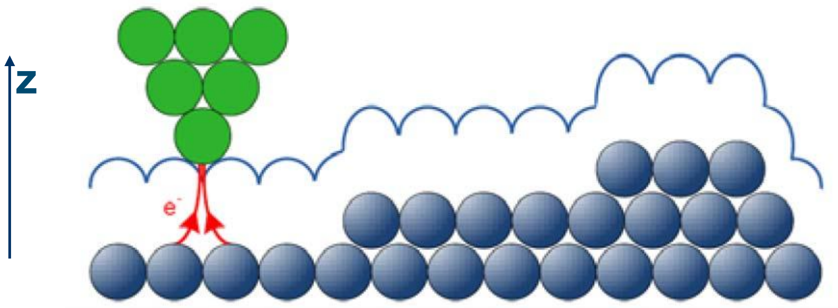




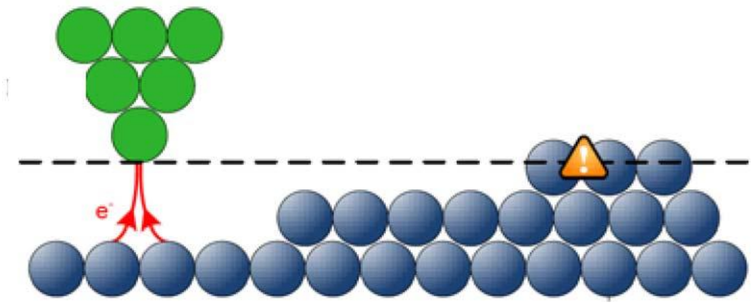
$$I_t \approx c_1 \cdot U_{bias} \cdot e^{-c_2\sqrt{\Phi}\cdot d}$$



Measurement modes: constant current vs constant height



at each position (x,y)
record signal:
tip displacement in z direction

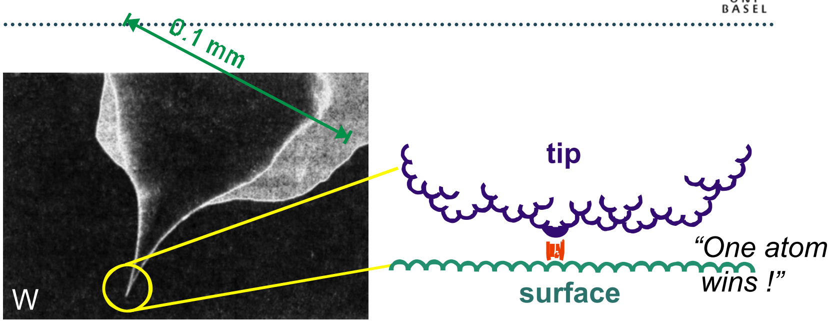


at each position (x,y)
record signal:
tunnel current I_t

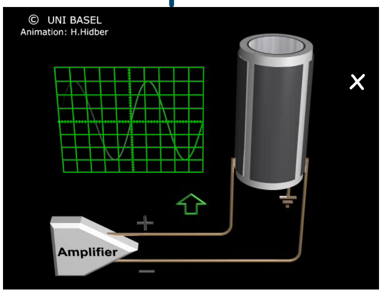
The « finger » and the « arm »

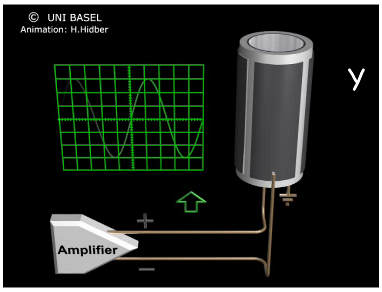
UNI BASEL

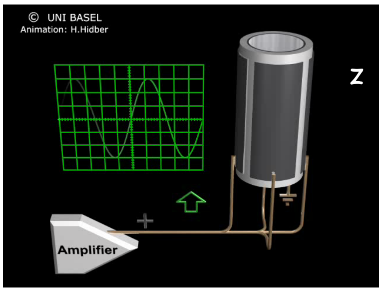
"Finger" = tip



"Arm" = piezoelectric actuator







Animations: H. Hidber, University of Basel

Piezo scan unit

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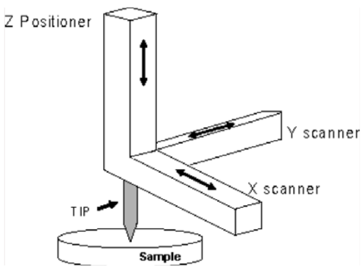
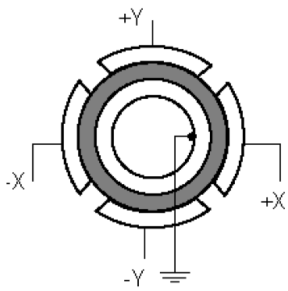
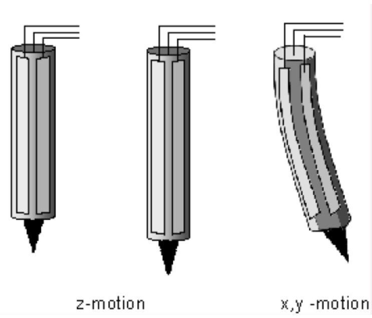
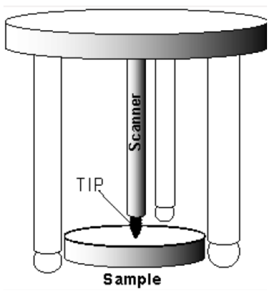


tripod scanner



tube scanner

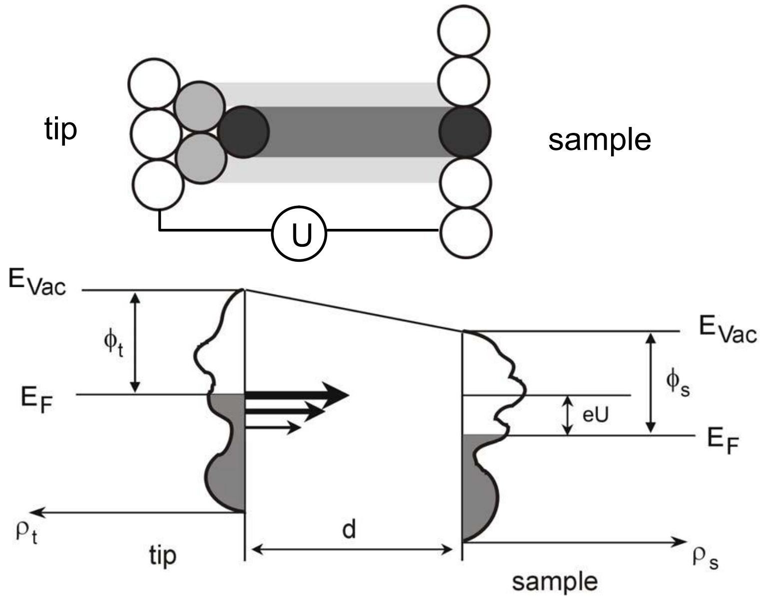




beetle type STM

Principe d'un microscope à effet tunnel

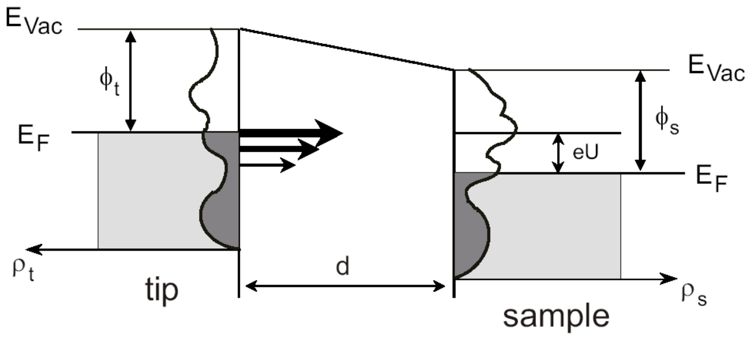
Tunnel Current in STM



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 Current



Bardeen approximation PRL 6, **57** (1961)

$$I \propto \int_0^{eU} \rho_s(E)\rho_t(\pm eU \mp E)T(E,eU)dE$$

$$T(E,eU) = \exp\left(-\frac{2z\sqrt{2m}}{\hbar}\sqrt{\frac{\Phi_s+\Phi_t}{2}+\frac{eU}{2}-E}\right)$$

STM Application
for
Surface Analysis
and
Surface Material Science & Engineering

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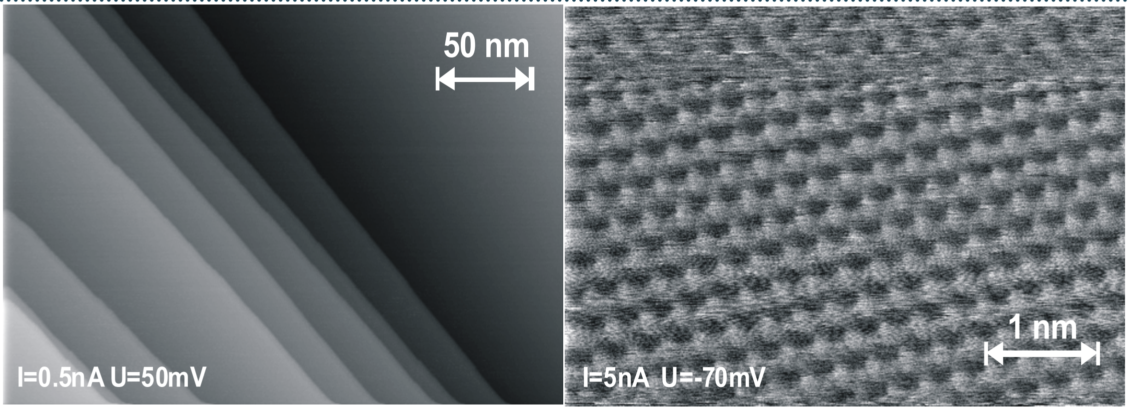
Nanolab, Uni Basel

Atomic resolution
Metals

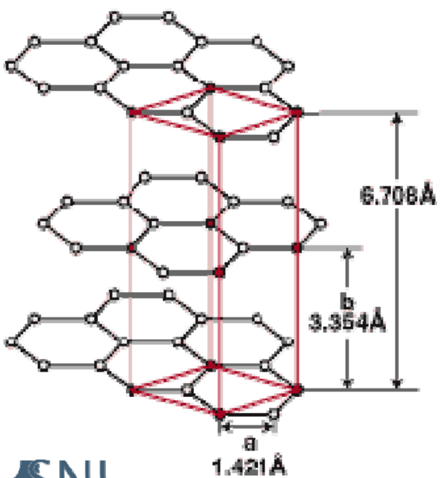


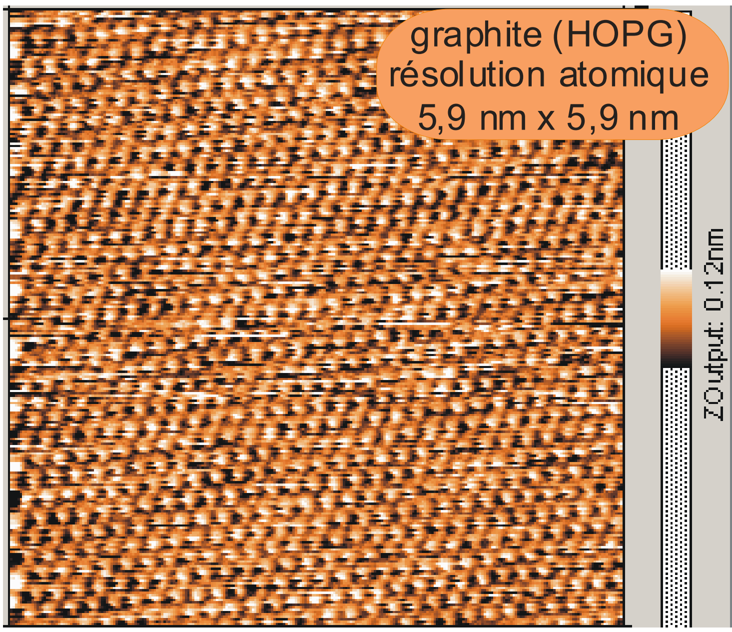
steps of monatomic height atomic resolution
(raw data on Ag(111))

$$I \propto \int_0^{eU} \rho_s(E)\rho_t(\pm eU \mp E)T(E, eU)dE$$

$$T(E, eU) = \exp\left(-\frac{2z\sqrt{2m}}{\hbar}\sqrt{\frac{\Phi_s + \Phi_t}{2} + \frac{eU}{2} - E}\right)$$

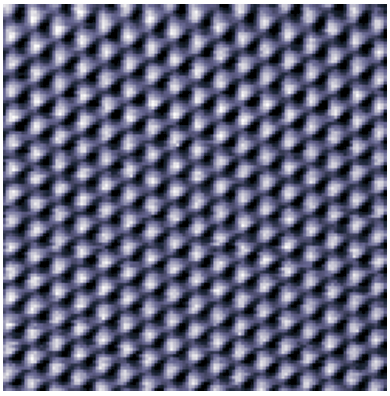
Graphite: HOPG (highly oriented pyrolythic graphite)



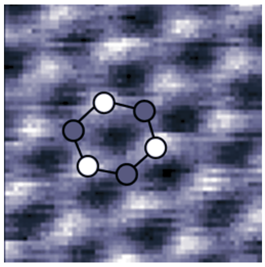


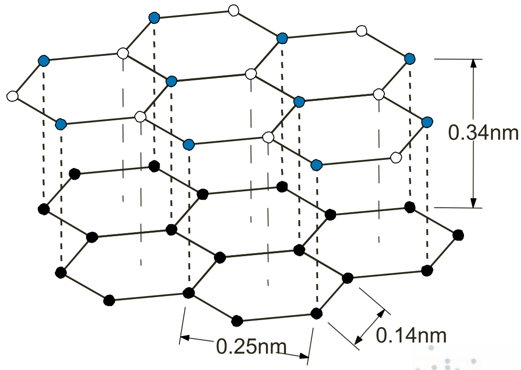
Atomic Resolution Images on HOPG

STM image raw data of HOPG



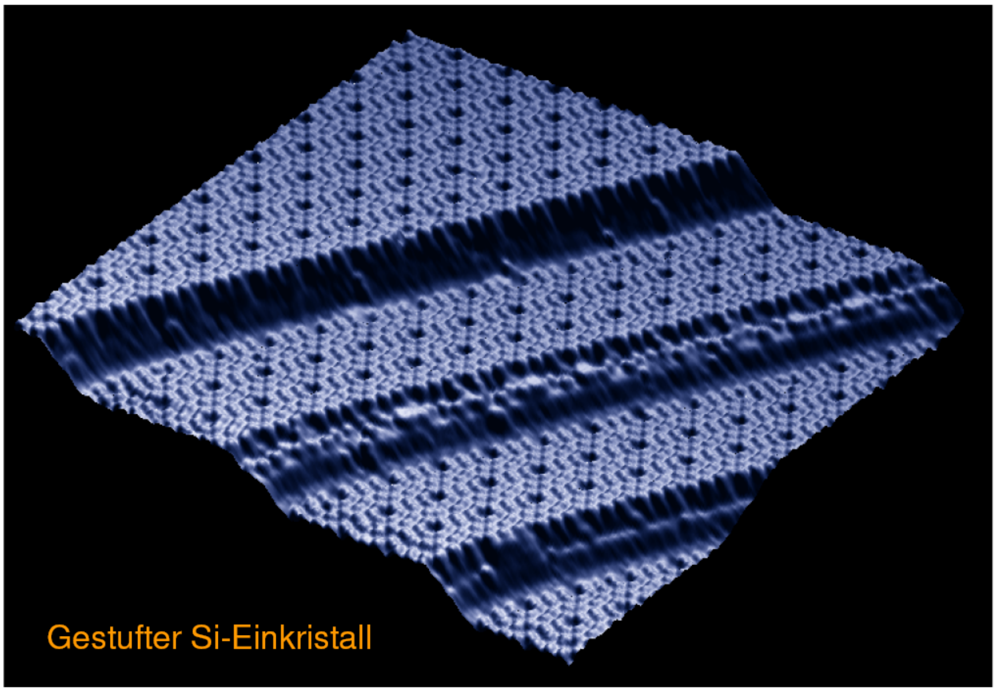
scan size: 4 nm



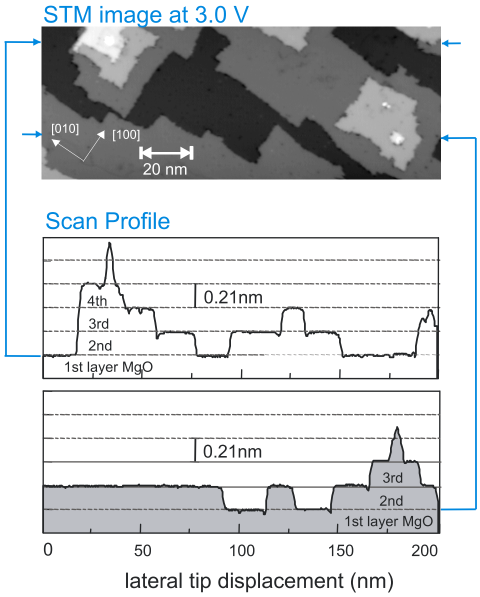


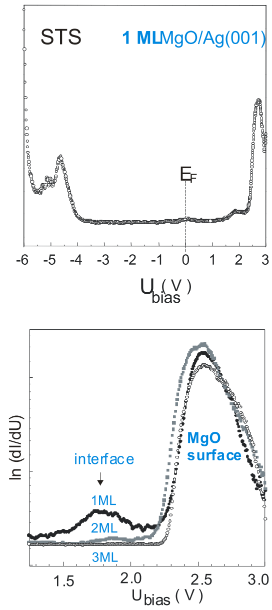
From the lattice model of graphite one can see that there are two different positions of the carbon atoms in the graphite crystal lattice (see e.g. R.C. Tatar)

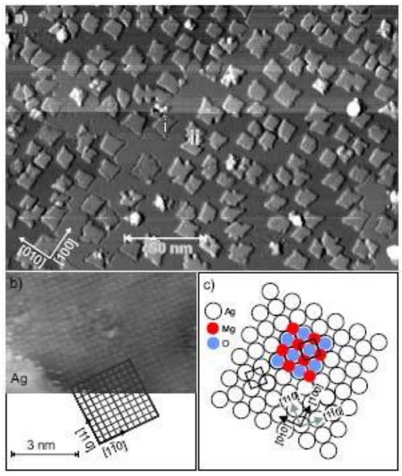
Semiconductors: Silicon



Ultrathin insulators
MgO/Ag(001): Insulator at the limit



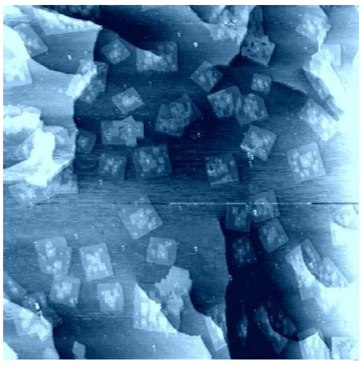




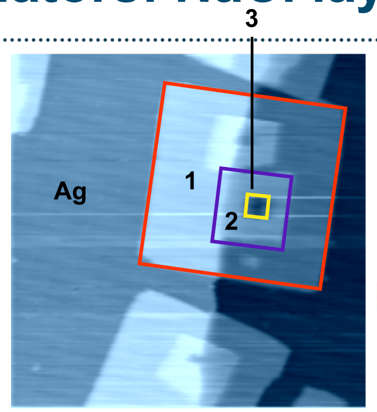
S. Schintke et al., *Insulator at the ultrathin limit: MgO on Ag(001),* Phys. Rev. Lett. **87**, 276801 (2001)

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)

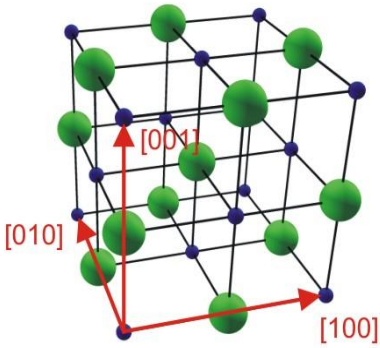
Ultrathin insulators: NaCl layers



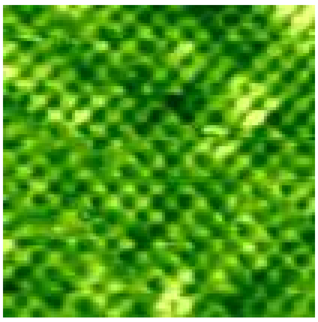
NaCl on Ag(111)
1.25 µm x 1.25 µm



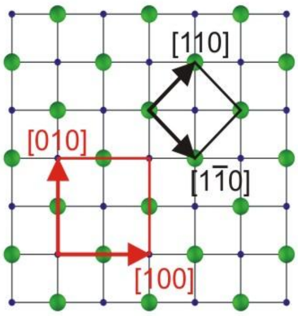
NaCl on Ag(111) 200 nm x 200 nm
U = 4.0 V, I = 15 pA



atomic resolution: <u>one</u> type of the ions is imaged

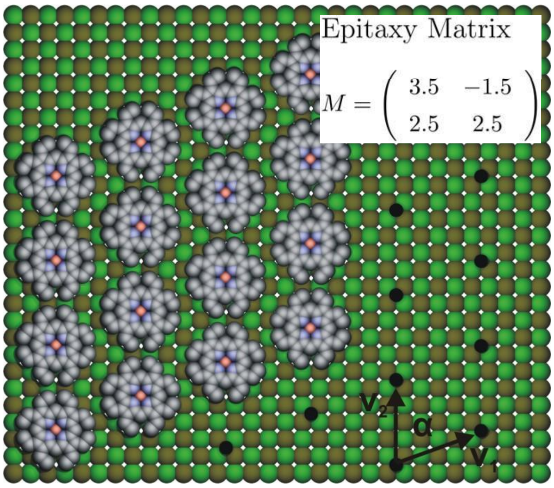


NaCl on Cu(111)
5 nm × 5 nm
U = -1.5 V, 50 pA



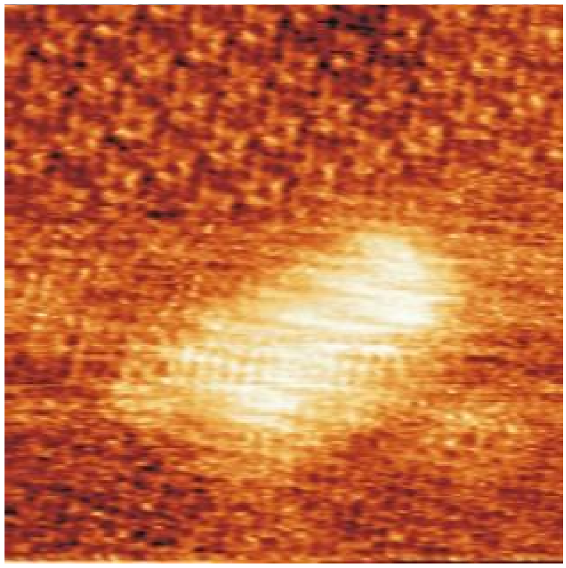
a_0 = 5.65 Å

CuOEP Self-Assembly on Salt



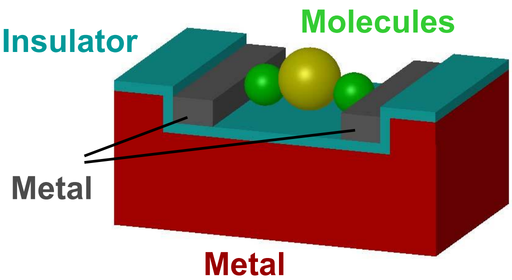
	model	experiment
v_1	14.6 Å	14.3 ± 0.3 Å
v_2	13.5 Å	13.5 ± 0.3 Å
α	68.2°	69.0 ± 1°

CuOEP on NaCl/Ag(111)

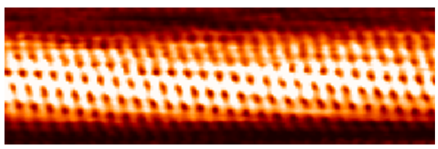


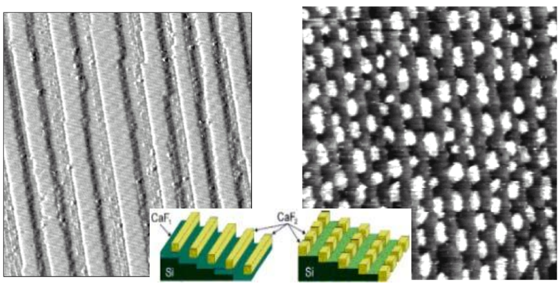
15 × 15 nm, U = -0.25 V, I = 81 pA

Towards Molecular Electronics

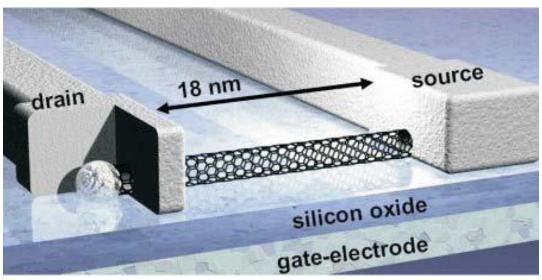


Carbon Nanotube





Himpsel, Jung et al. MRS Bulletin **24** (8) 1999



Infineon: carbon nanotube FET

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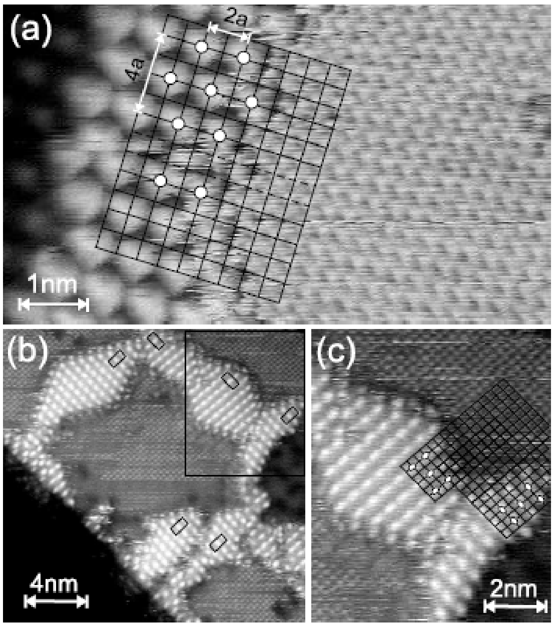
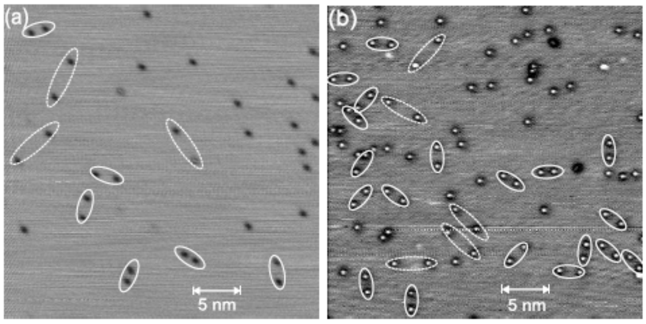
Nanolab, Uni Basel

Oxygen on Ag(001): molecular superstructures; far- ranged dissociation



Atoms



Atoms:
S. Schintke, S. Messerli et al., J. Chem. Phys. 114, 4206 (2001)
Molecules:
S. Messerli, S. Schintke et al., Chem. Phys. Lett. 328, 330 (2000).

Oxygen/Ag(001)

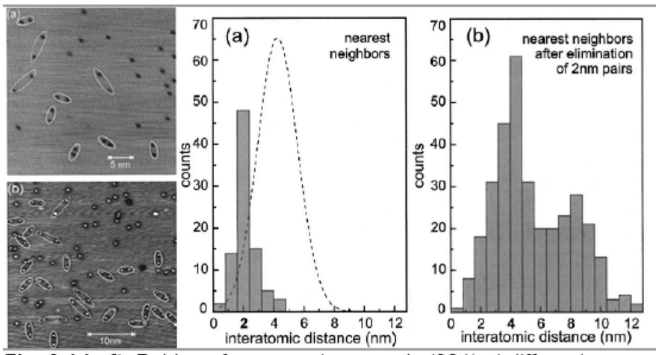


Fig. 3.1 Left: Pairing of oxygen atoms on Ag(001) at different coverages observed in STM images (50 K).
Right: Distribution of interatomic distances analysed from STM data.

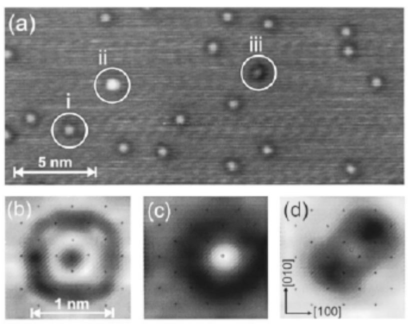
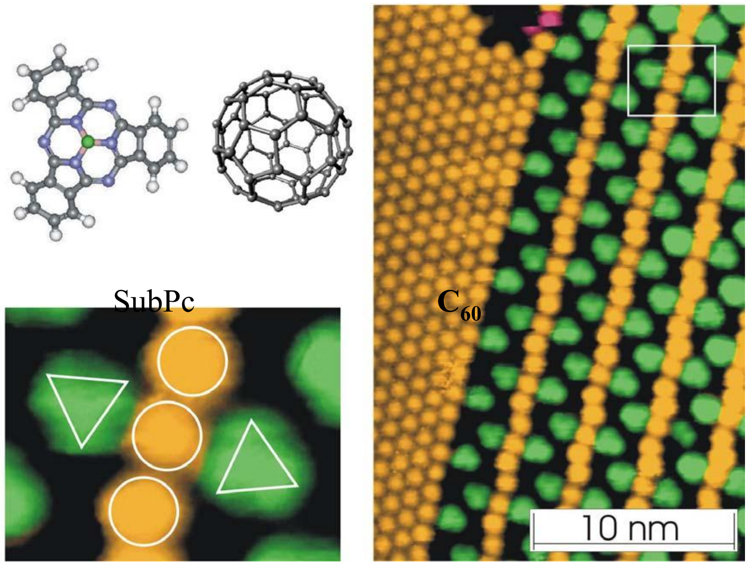


Fig. 3.2: Binding sites of oxygen atoms. Top: experimental STM data (50 K). Bottom: Calculated STM images a) hollow site, b) on-top site, c) bridge site.

S. Schintke, S. Messerli, K. Morgenstern, J. Nieminen, and W.-D. Schneider, Journal of Chemical Physics **114**, 4206-4209 (2001)

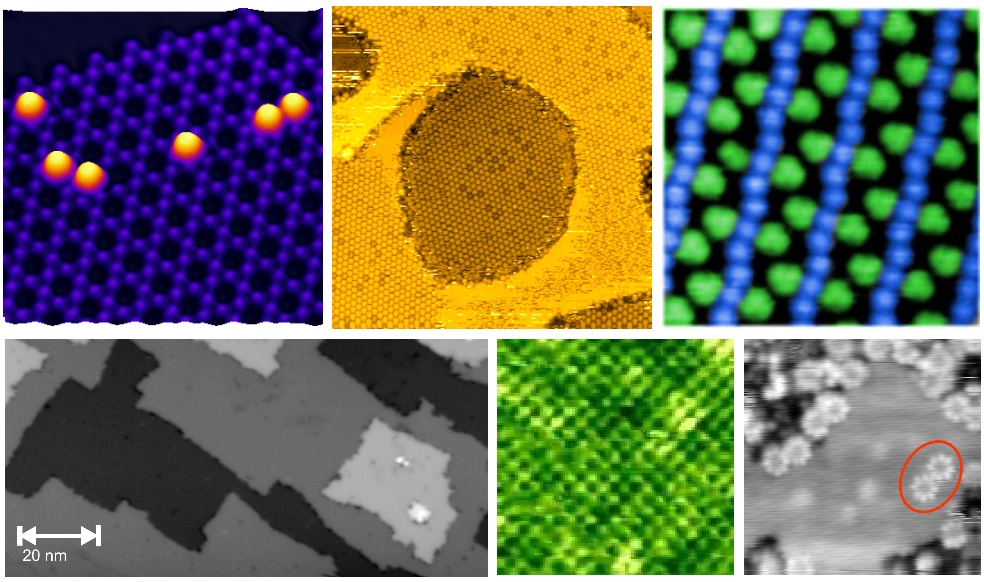
Self-intermixed monolayer



Scan range 4.3nm x 3.2nm. V_{bias}=1.3V, I_t=20pA. Scan range 17nm x 25nm. V_{bias}=1.3V, I_t=20pA.

M. de Wild *et al., ChemPhysChem* **10**, 181 (2002)
M. de Wild *et al., Chimia* **10,** 56 (2002)

Further STM images from research



www.nccr-nano.ch (Uni Basel)

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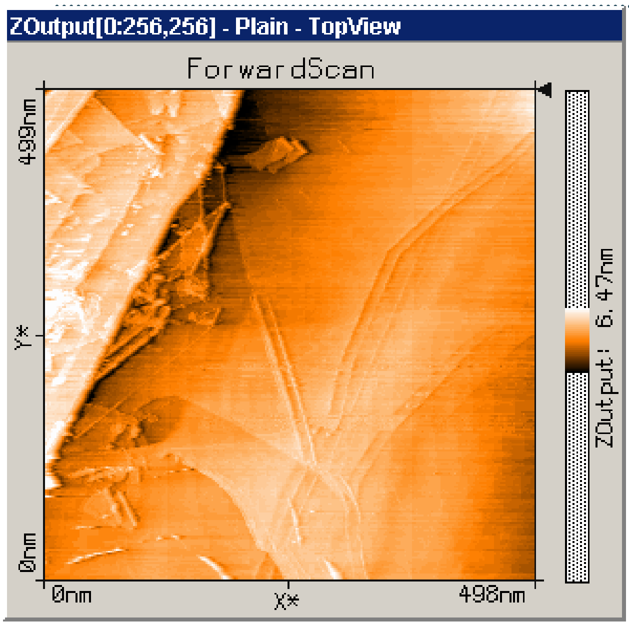
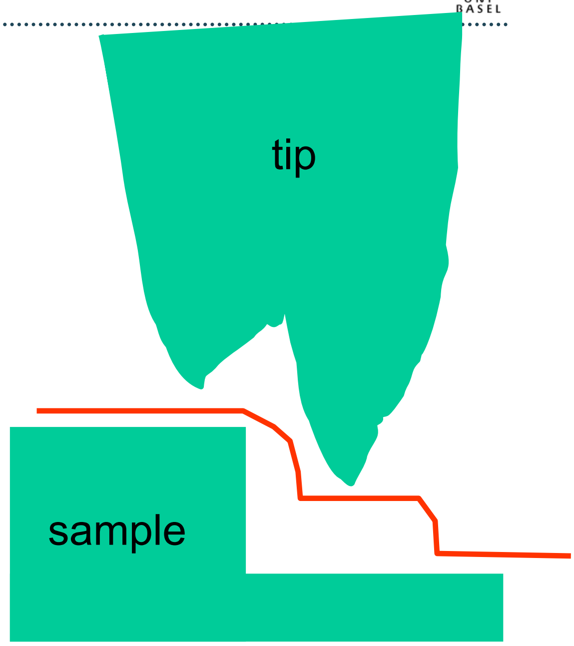
Nanolab, Uni Basel

Artefact: Double Tip Effect





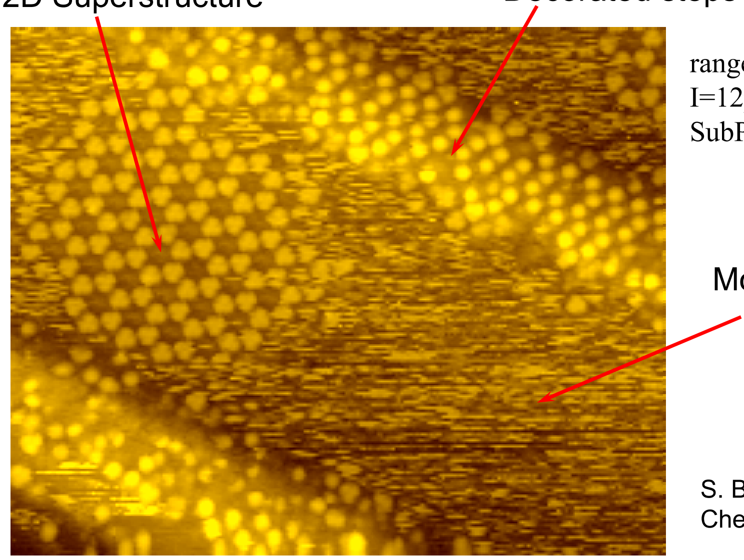
Nanosurf AG - Smart Instruments for Nanoscience & Nanotechnology

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

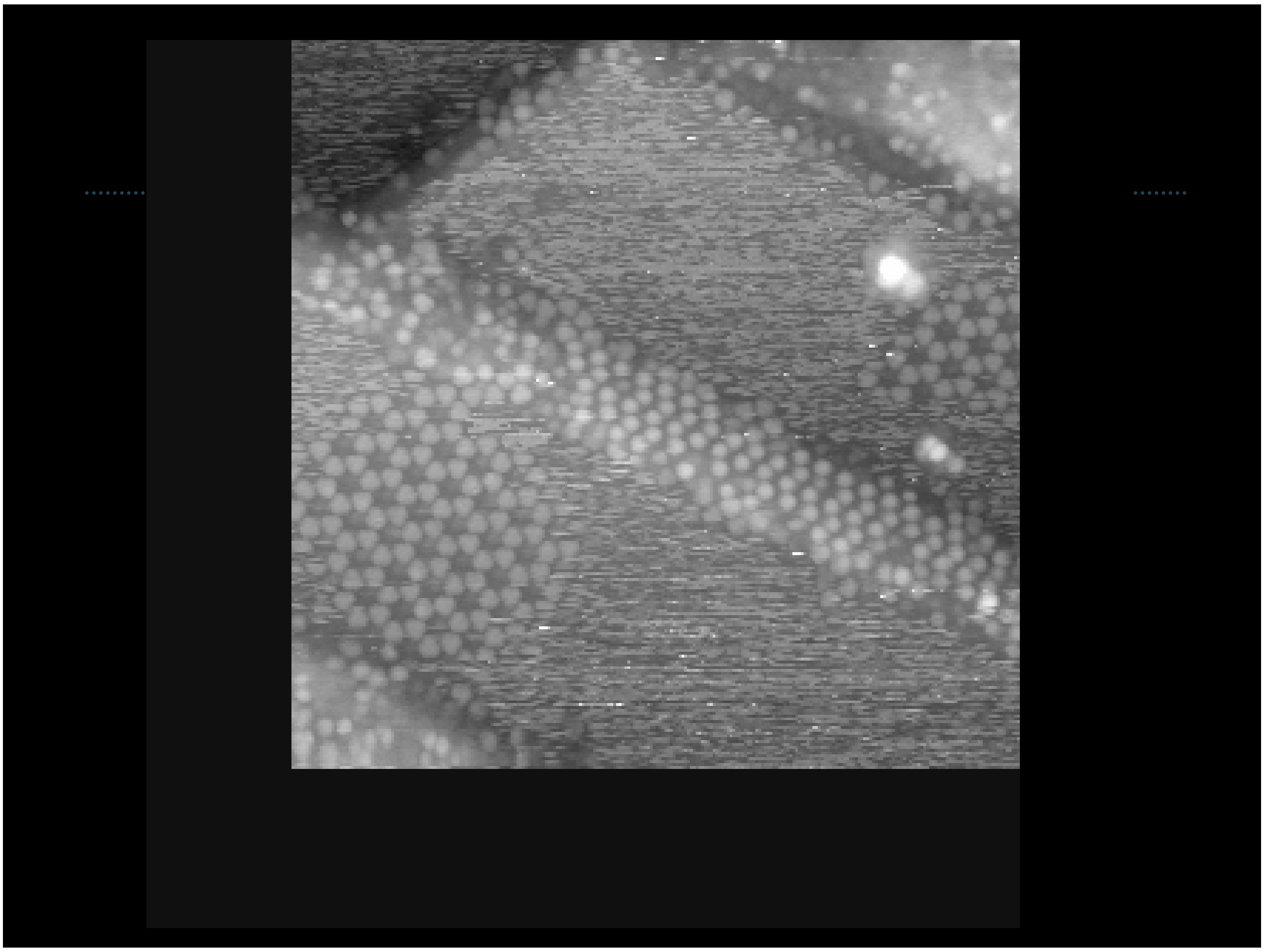
Coexistence of 2D Crystal and 2D Gas Phase



range 54x44nm
I=12pA, U=0.85V
SubPc coverage ~0.3 ML

S. Berner et al.,
Chem. Phys. Lett. **348** (2001) 175

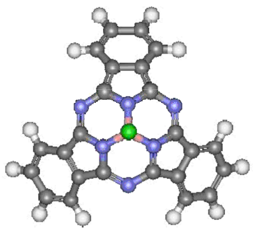
- Streak noise by mobile molecules
- Mobile molecules form 2D gas phase
- Island is in dynamic equilibrium with the surrounding gas phase

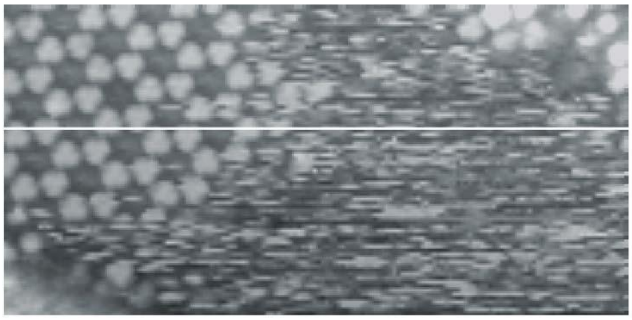


SubPc on Ag(111):

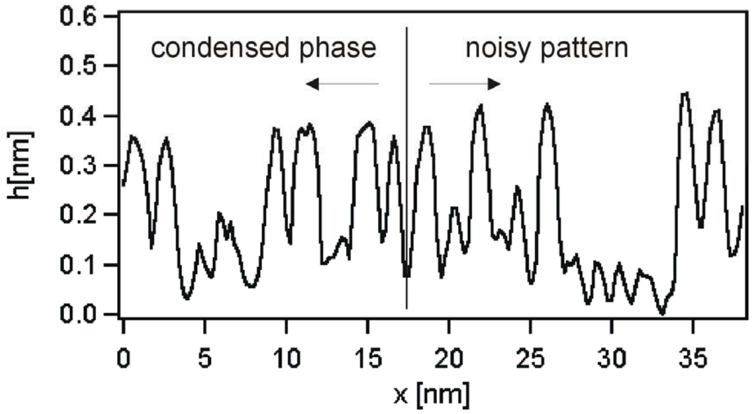
Co-existence of molecular lattice gas and 2D solid

S. Berner et al. Chemical Physics Letters 348 (2001) 175-181



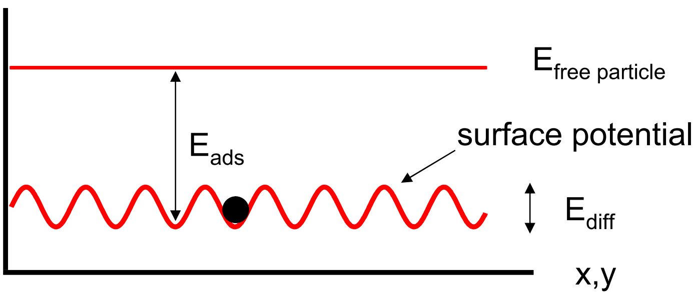


=> 2D lattice gas



Hopping rate:
31 ± 10 s^{-1}

Introduction to Surface Diffusion



- E_{diff} << kT => “free” particles => 2 D gas
- E_{diff} > kT => 2 D lattice gas
- E_{diff} >> kT => immobile particles

Hopping rate $\nu = \nu_0 \cdot \exp - \frac{E_{diff}}{kT}$ $\nu_0 \sim 10^{12}\ s^{-1}$

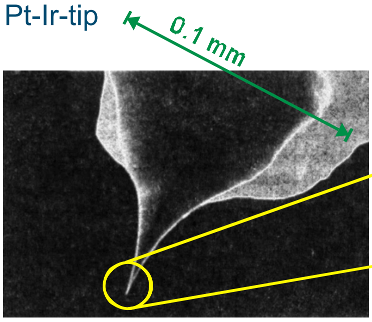
J.V. Barth, Surf. Sci. Rep. **40** (2000) 75

SubPc on Ag(111): $E_{diff} \sim 0.7$ eV

« Nanotool »: STM-Tip

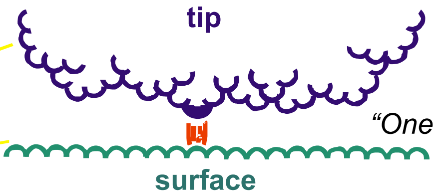
Materials: Tungsten (W), Iridium (Ir), Platinum-Iridium (Pt-Ir), Gold (Au),…
e.g. cut or electrochemically etched

Pt-Ir-tip



Matterhorn (“tip”)

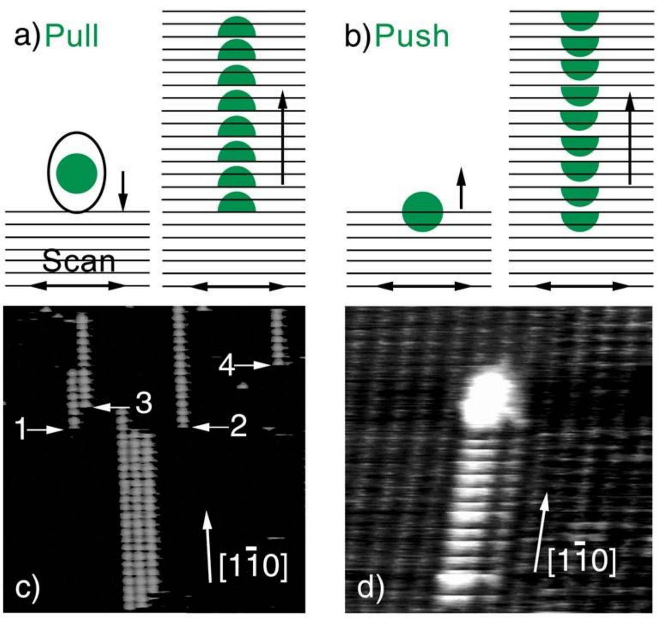
Pingpong-ball (“atom”)



“One atom wins !”

W-tip
Scanning electron micrographe of an STM tip
(Hamann, Hietschold, Rastertunnelmikroskopie)

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).

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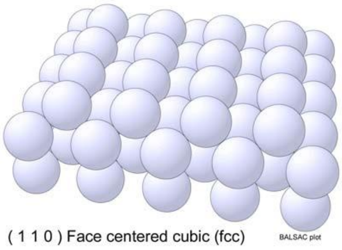
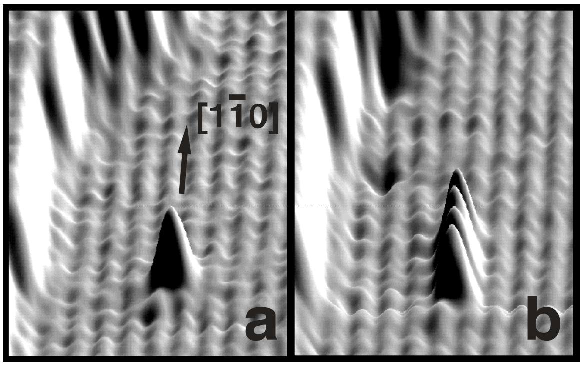
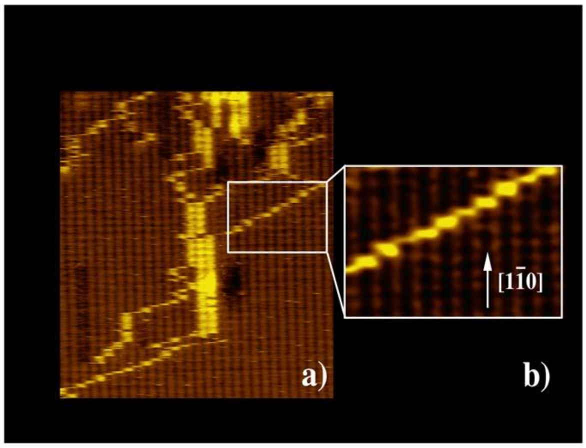
Nanolab, Uni Basel

Tip-sample interaction



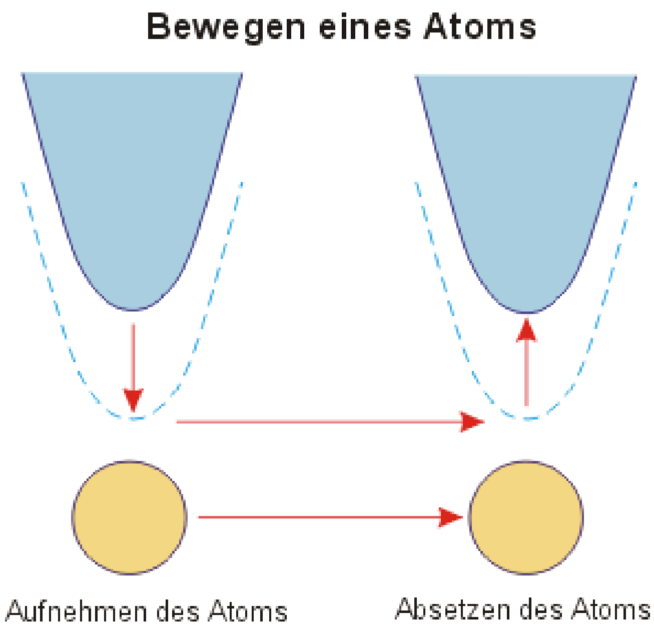
Diagonal Ag adatom motion along
[1-11] direction (atom exchange)





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).

Adsorbate manipulation by STM



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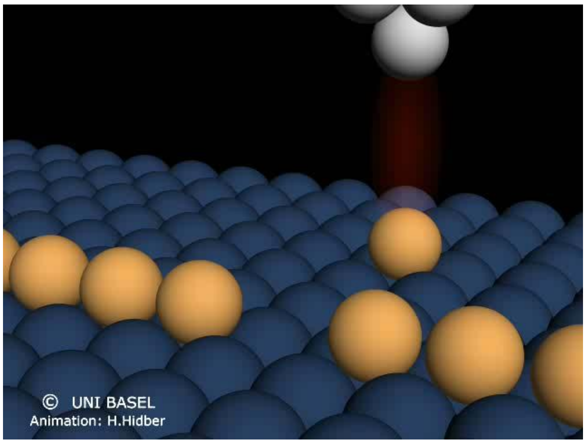
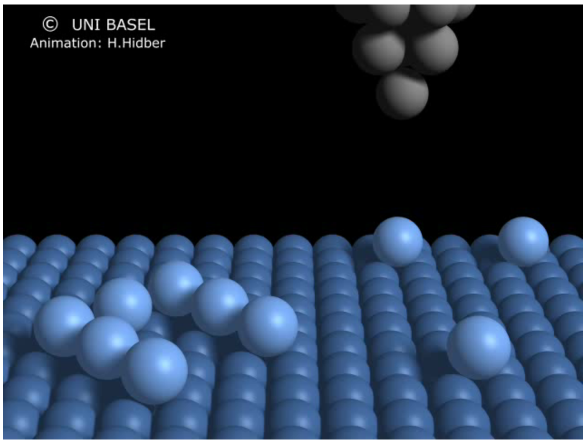
Nanolab, Uni Basel

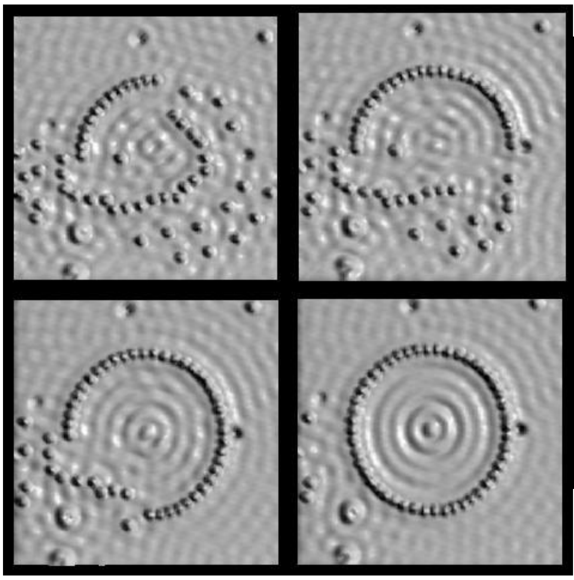
Déplacer des atomes ou molécules

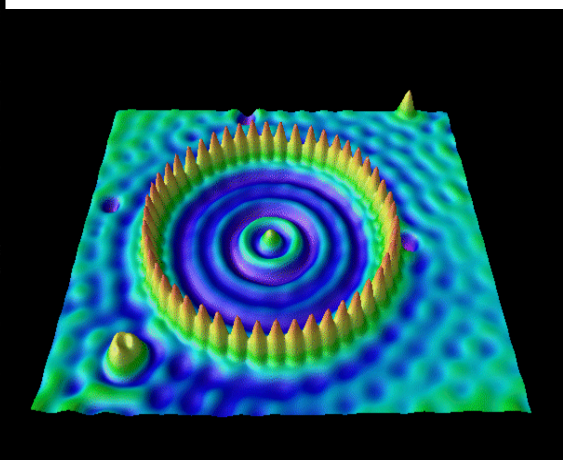




Animations: H. Hidber, Université de Bâle

Quantum Corral





IBM

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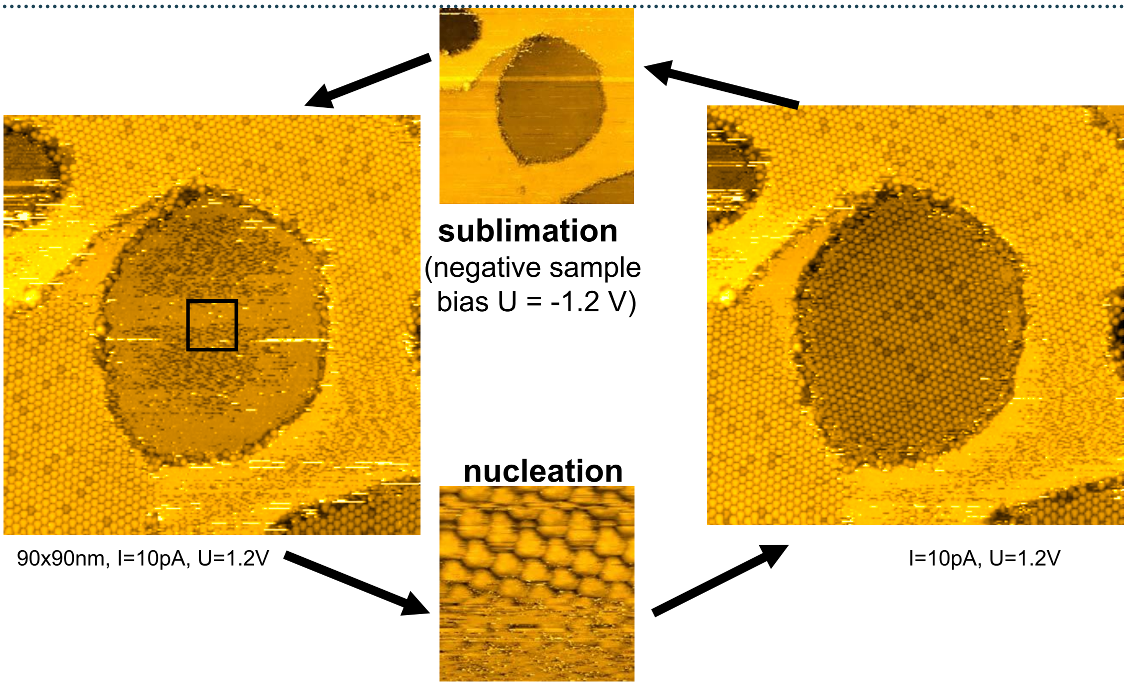
Nanolab, Uni Basel

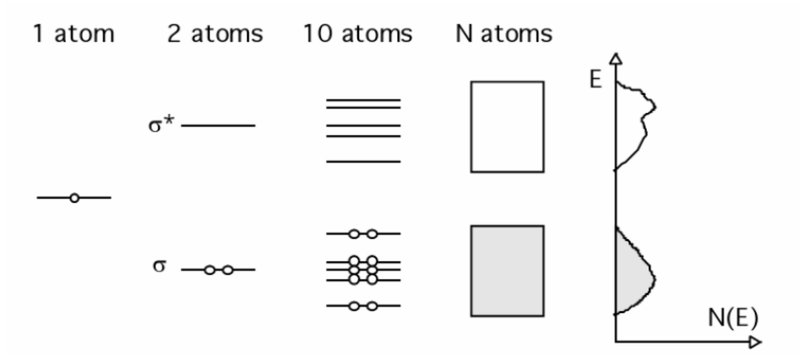
Reversible 2D Phase Transition controlled by the STM tip



Controlled phase transition 2D fluid <=> 2D solid

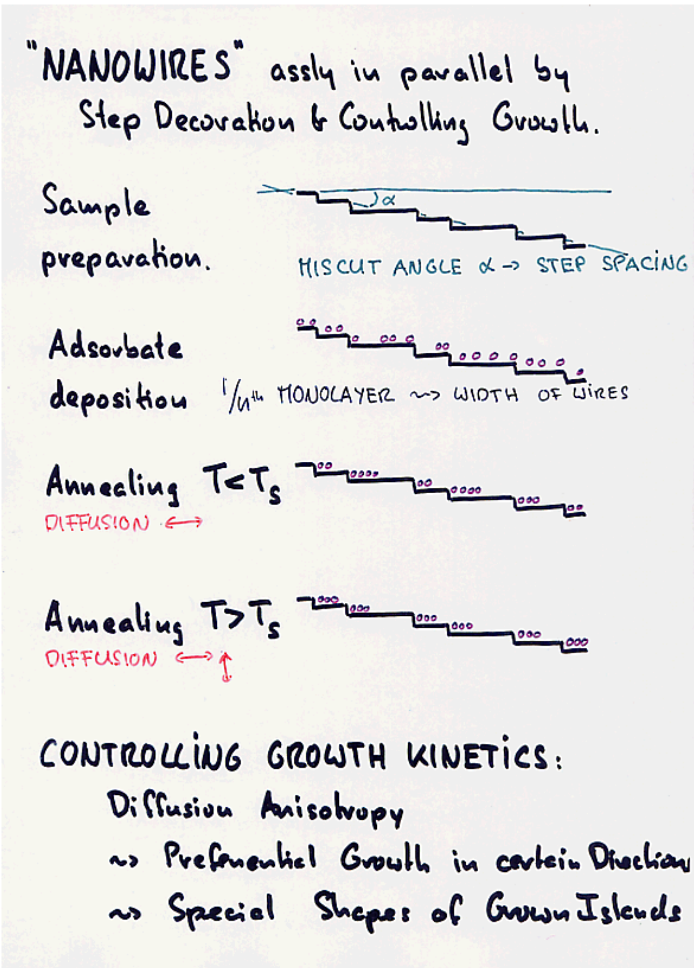
STS (scanning tunneling spectroscopy)

Density of States (DOS)

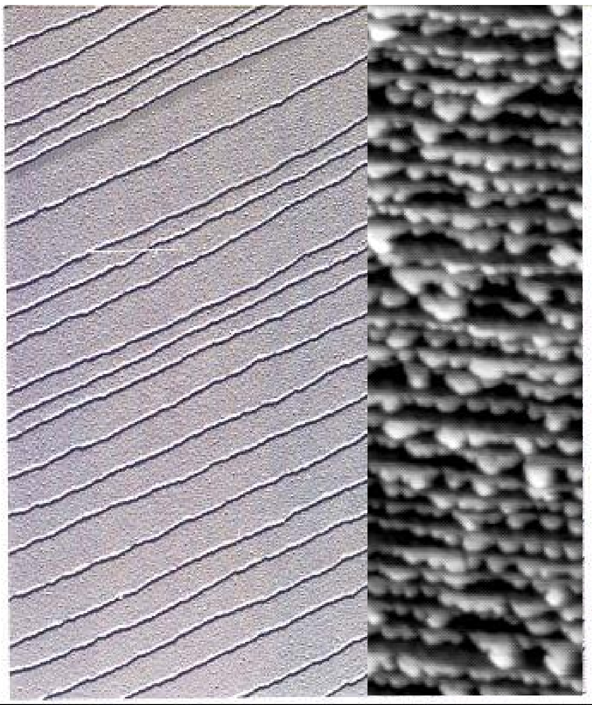


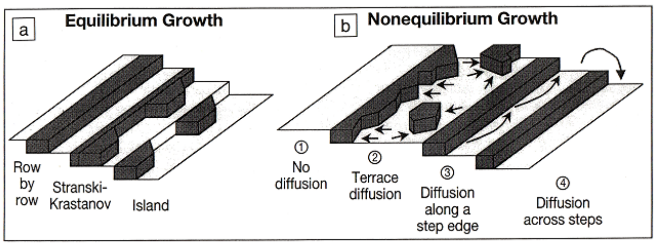
Density of States (DOS), N(E) is the number of energy levels bewteen E and E+dE (states per eV)

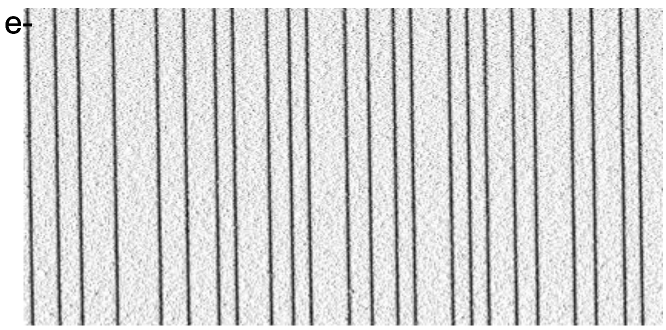
States can have s,p,d,f or mixed (hybrid) character
Bands may be separated by band-gaps E_g



‘Physical’ Self Assembly of e.g. Nanowires

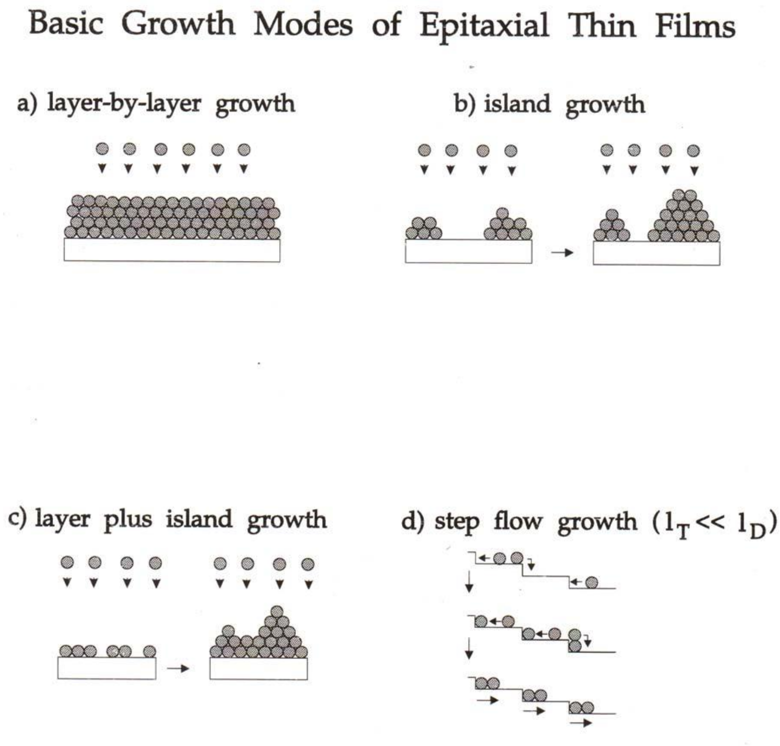


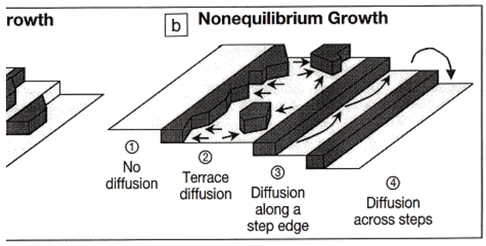


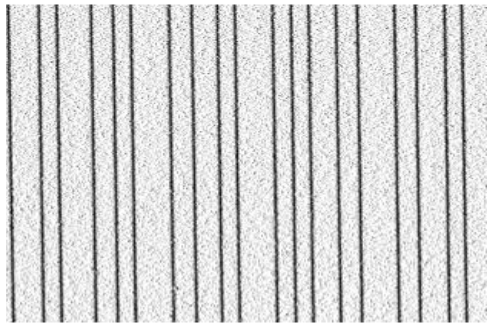


F. Himpsel, Th. Jung et al.
MRS Bulletin **24**, 20--24 (1999).

‘Physical’ Self Assembly of e.g. Nanowires
jumping from 3D to 2D

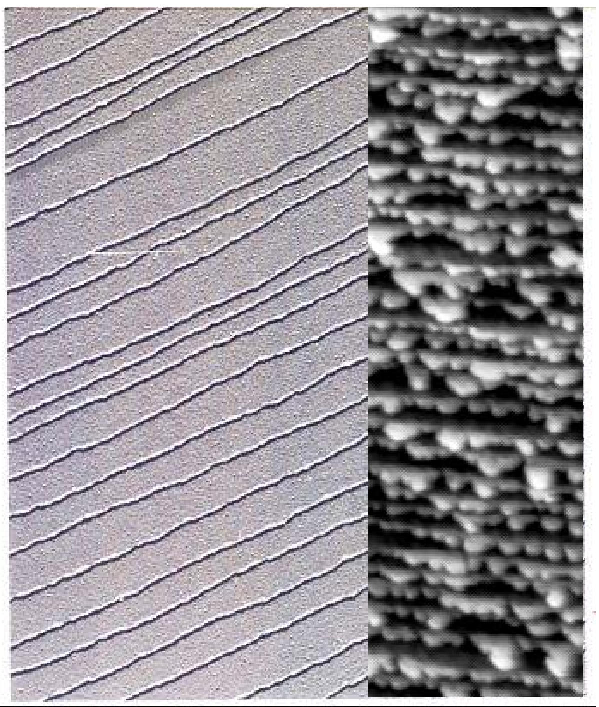


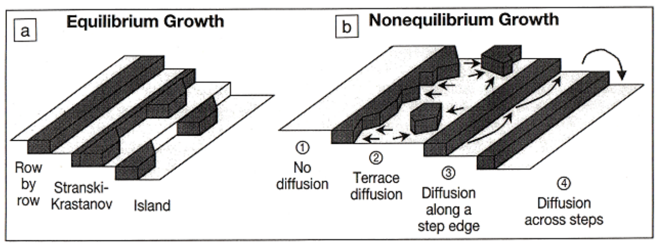




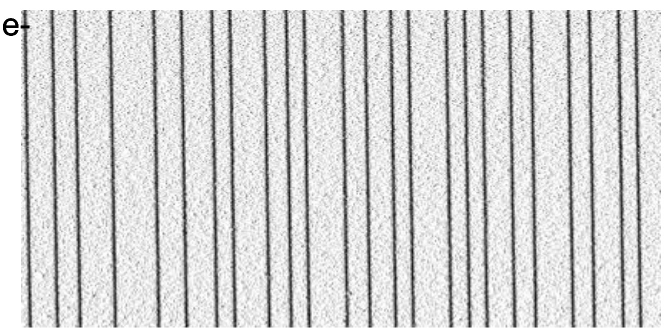
Th. Jung et al.
n **24**, 20--24 (1999).

‘Physical’ Self Assembly of e.g. Nanowires

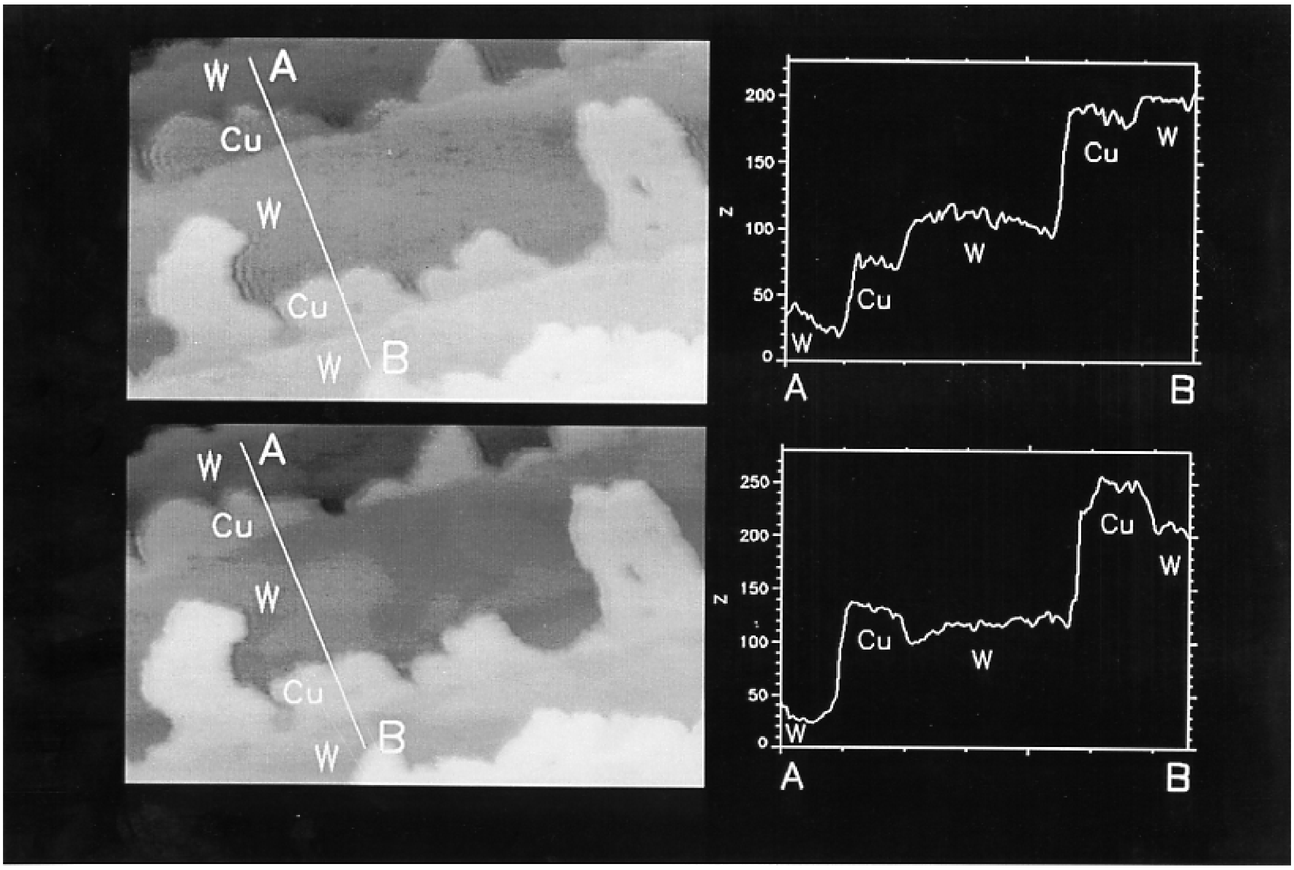




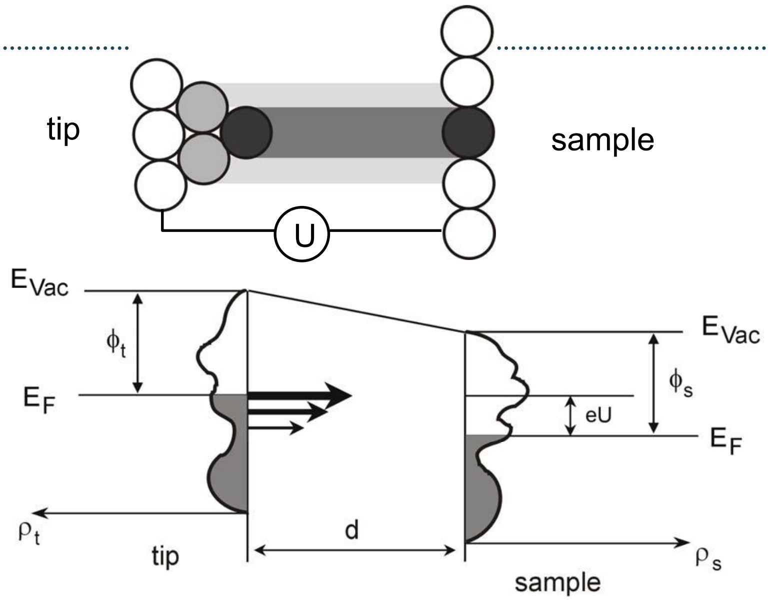
e-



F. Himpsel, Th. Jung et al.
MRS Bulletin **24**, 20--24 (1999).



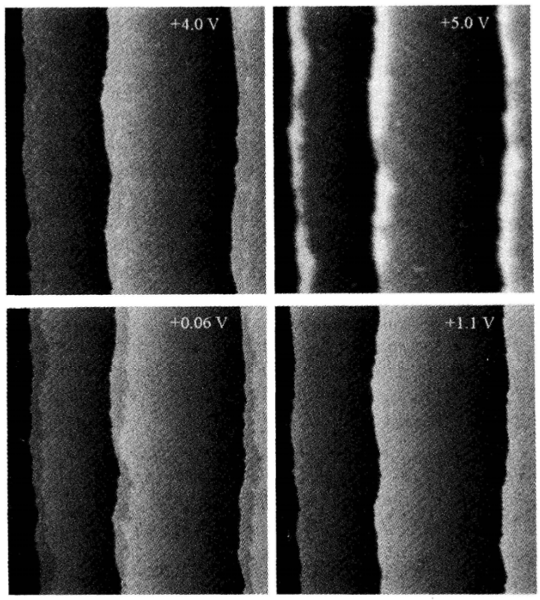
Scanning Tunneling Microscopy



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

Chemical Sensitivity in STM: surface states vs image states



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

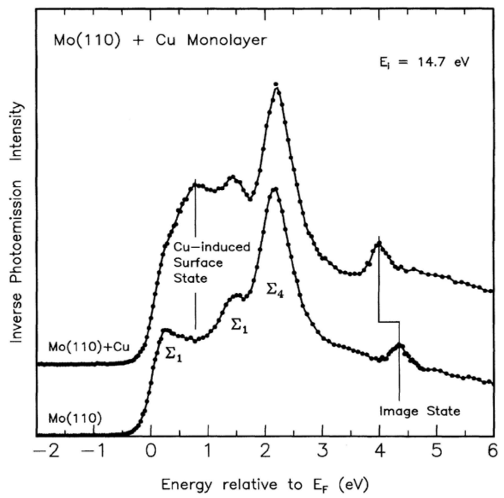
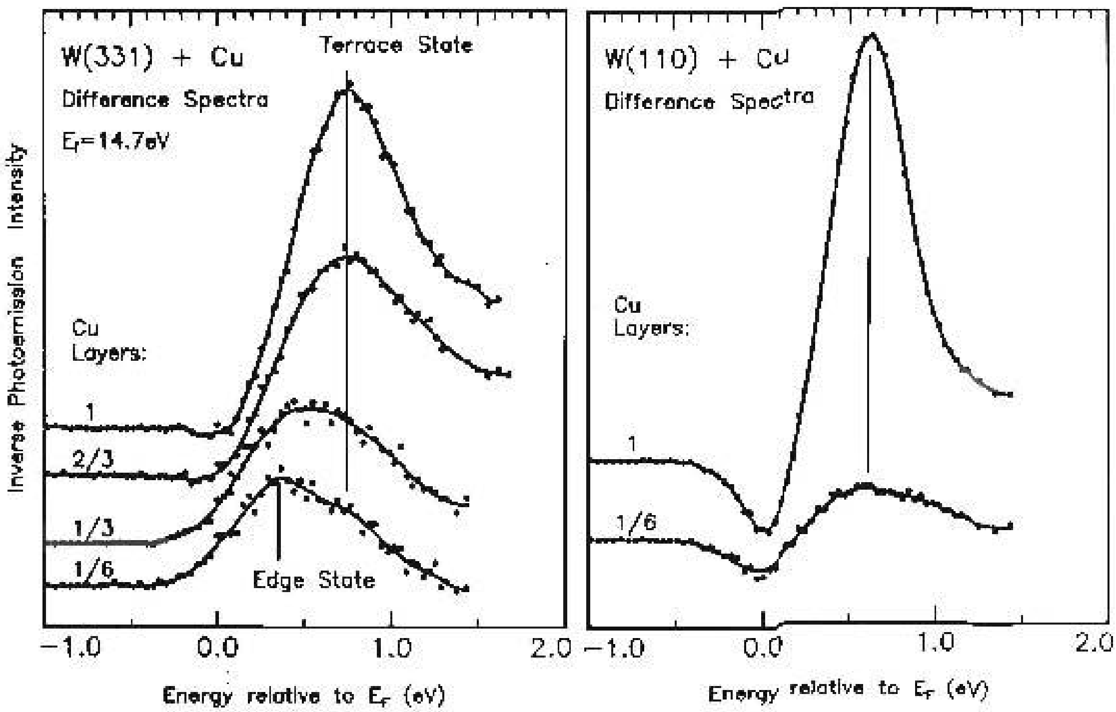


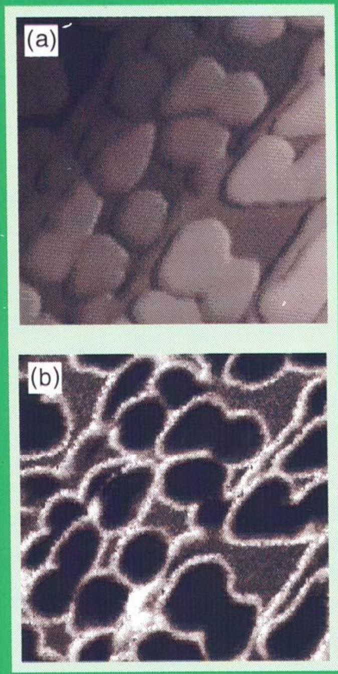
Image State Contrast >>> Surface State Contrast

Stufenzustaende und Oberflaechenzustaende auf W(331)



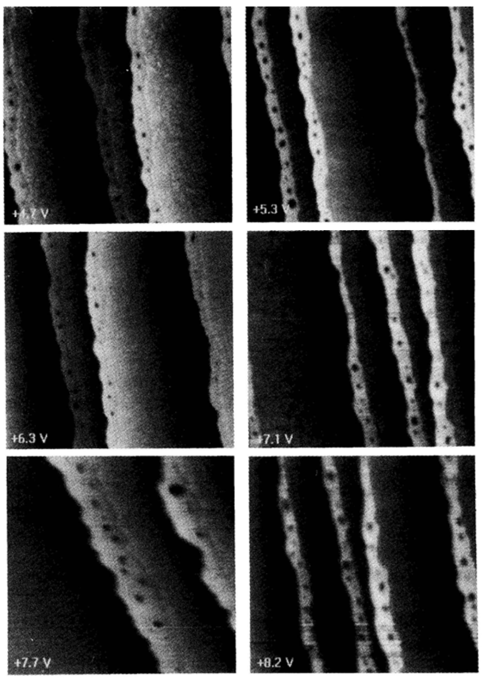
Chemical Information from SPM / Spectroscopy

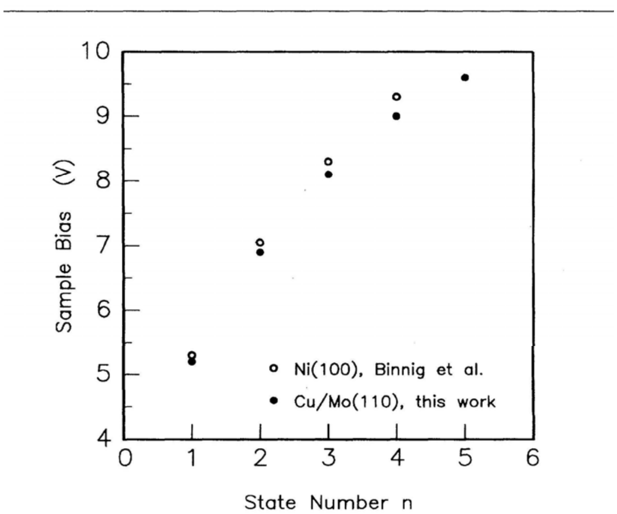
Spectroscopic Changes at the Edge of Fe Islands on W(110)



(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).

Chemical Sensitivity in STM: surface states vs image states

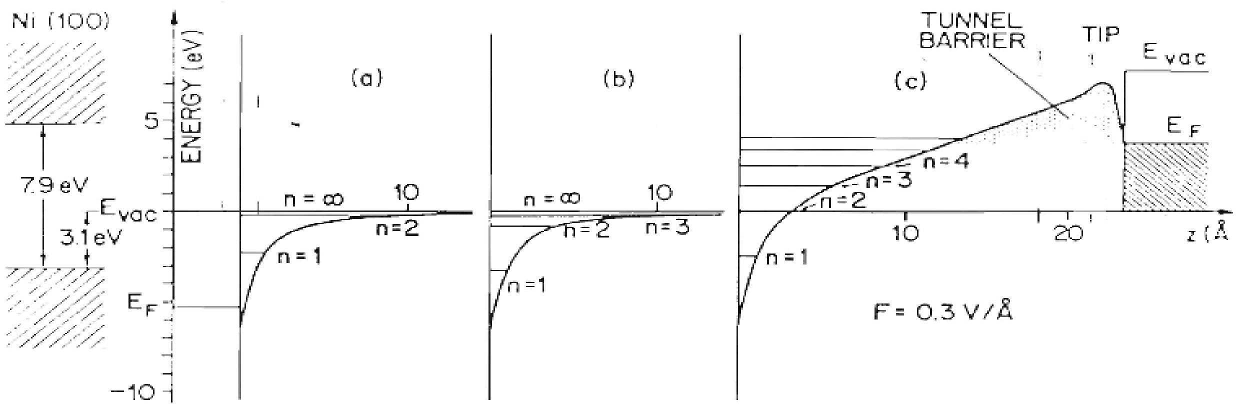




Periodic Contrast Change in U_{gap}: Image Resonant Enhancement !

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

Bildladungspotential ueber leitender Oberflaeche



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