Vorlesung
Analysemethoden II
Andrij Romanyuk

- Di 18.10. statt 8.15 ab 15.00
- Fr 21.10. ganzer Tag

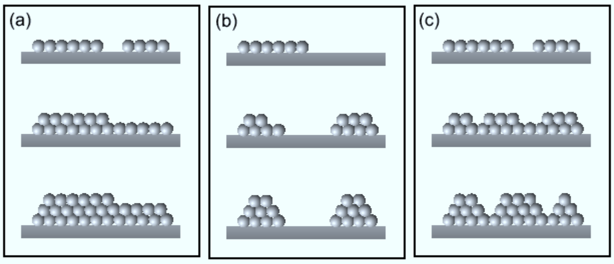
Abtausch der Dozenten besser als Verschiebung → wird versucht.

Repetition:

- Nanostrukturierung: Warum? Wo? Wie? -- Beispiele
- Bottom-Up vs. Top Down
- Bottom-Up Nanostrukturieren:
  → Spielen mit Physikalischen / Chemischen WW
- Oberflaechen und Vakuum Warum? Wieviel?

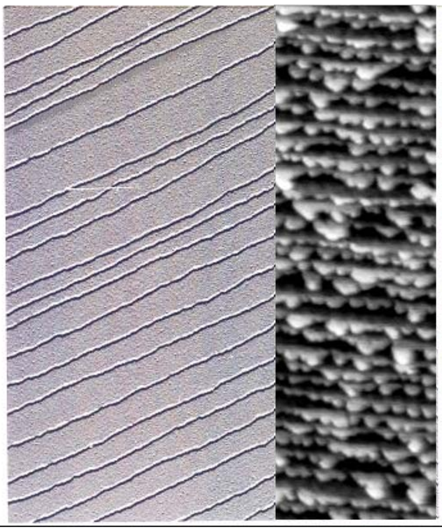
- Diffusion
- Methoden zur Bestimmung
- Bedeutung fuer's Wachstum
- Isotropie / Anisotropie

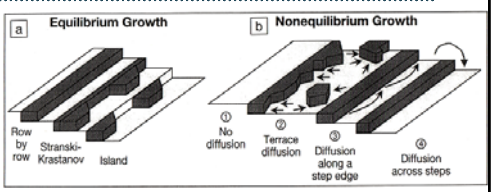
Growth Modes



(a) **Layer-by-layer** or **Frank-van der Merve** mode → 2D islands
(b) **Island** or **Vollmer-Weber** mode → 3D islands
(c) **Layer plus island** or **Stranski-Krastanov** mode → 2D layer + 3D islands

‘Physical’ Self Assembly of e.g. Nanowires





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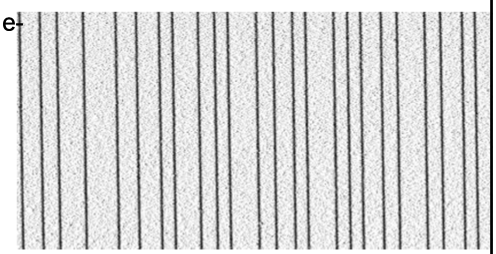
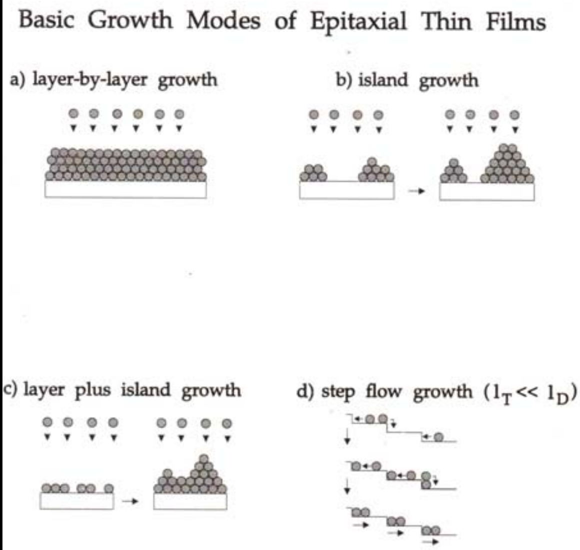
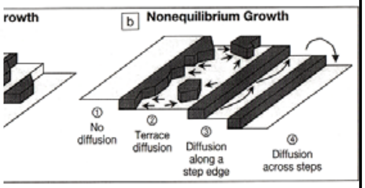
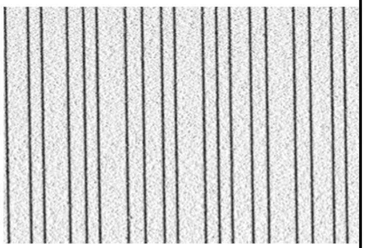


F. Himpsel, Th. Jung et al.
MRS Bulletin **24**, 20--24 (1999).

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



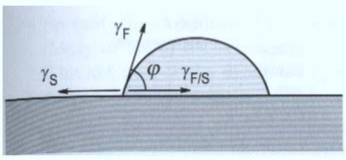




Th. Jung et al.
n **24**, 20--24 (1999).

Growth Modes

- **Surface tension** (γ) = work required to build a surface of unit area (≡ force per unit length)

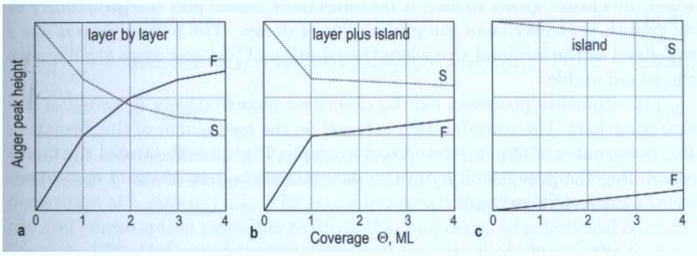


$$\gamma_S = \gamma_{SF} + \gamma_F \cos\varphi$$

- Island growth: $\varphi > 0$ → $\gamma_S < \gamma_{SF} + \gamma_F$
- Layer-by-layer growth: $\varphi = 0$ → $\gamma_S \geq \gamma_{SF} + \gamma_F$

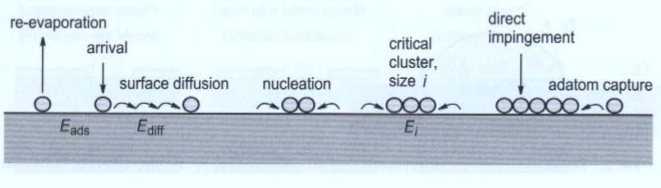
Growth Modes

- Exp: Monitor Auger signals from film and substrate while depositing...



Island Number Density

• Nucleation and growth on surfaces:



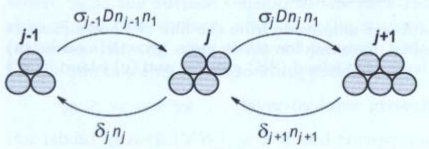
- Diffusion coefficient: $$D = \frac{\nu}{4n_0}\exp\left(-\frac{E_{diff}}{k_B T}\right)$$

- Residence time: $$\tau_{ads} = \frac{1}{\nu}\exp\left(\frac{E_{ads}}{k_B T}\right)$$

• **Critical island size** i: minimal size when the addition of one atom makes the island stable

Island Number Density

• Capture and decay processes → cluster size



• Rate equations:

adatom density

subcritical clusters

$$\frac{dn_1}{dt} = R - \frac{n_1}{\tau_{ads}} + \left(2\delta_2 n_2 + \sum_{j=3}^{i} \delta_j n_j - 2\sigma_1 D n_1^2 - n_1 \sum_{j=2}^{i} \sigma_j D n_j \right) - n_1 \sigma_x D n_x$$

stable clusters

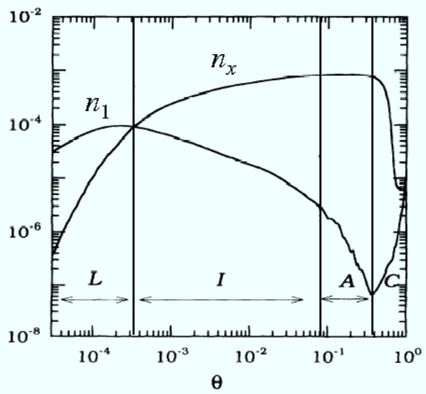
deposition rate

$$\frac{dn_j}{dt} = n_1 \sigma_{j-1} D n_{j-1} - \delta_j n_j + \delta_{j+1} n_{j+1} - n_1 \sigma_j D n_j$$ → metastable clusters

$$\frac{dn_x}{dt} = n_1 \sigma_i D n_i$$ → stable clusters

Island Number Density

• Numerical solution for $i = 1$ without re-evaporation (Amar, Family and Lam, PRB 1994):



• Four coverage regimes are found

Island Number Density

(1) Low-coverage nucleation regime: $n_1 >> n_x$

- In such case:

$$n_1 \propto \Theta \qquad n_x \propto \Theta^3$$

When $n_x \sim n_1$ → **(2) Intermediate-coverage regime**

- In such case:

$$n_1 \propto \Theta^{-1/3} \qquad n_x \propto \Theta^{1/3}$$

When mean island separation ~ mean free path of adatoms

→**(3) Aggregation regime** (Θ ~ 0.1-0.4 ML)

When the island join together

→**(4) Coalescence and percolation regime**

Island Number Density

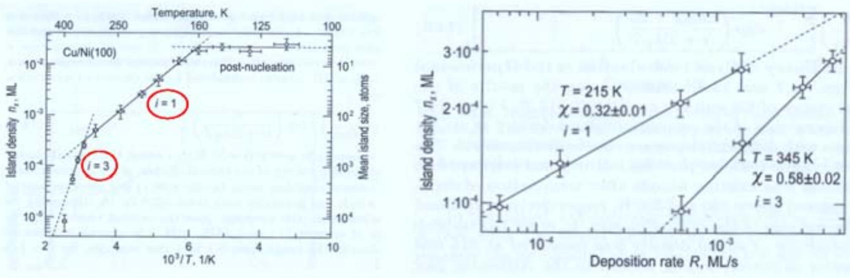
• Saturation density (Venables et al., 1984):

$$n_x = n_0 \eta(\Theta, i)\left(\frac{4R}{\nu_0 n_0}\right)^{\frac{i}{i+2}} \exp\left(\frac{iE_{diff} + E_i}{(i+2)k_B T}\right)$$

χ; binding energy of critical cluster

$$\eta(\Theta, i) \sim 0.1-1$$

• Example: Cu on Ni(100) (Müller et al., PRB 1996)



Island Shape

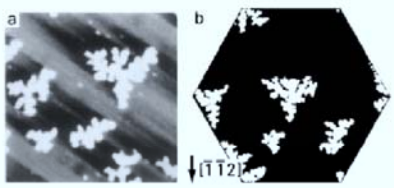
- At low T (slow edge diffusion): **ramified islands**
- **Diffusion-limited-aggregation (DLA) model** (Witten & Sander, PRL 1981):

- Adatoms stick at islands
- Fractal shape
- Branch thickness ~ 1 atom
- No influence of lattice geometry

- In real growth (STM experiments):
  - Fractal shape
  - Branch thickness > 1 atom
  - Influence of lattice geometry

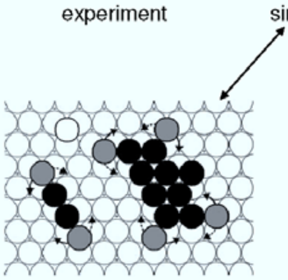
Island Shape

- Example: Pt/Pt(111) (Hohage et al., PRL 1996)



experiment simulation

- Branch thickness ~ 4 atoms
- Trigonal symmetry

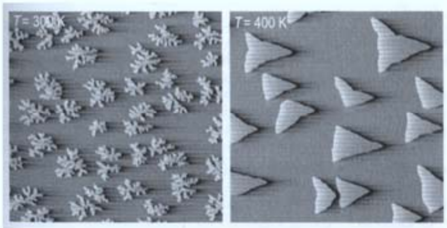


- Higher coordination is preferred

Island Shape

- At higher T: **compact islands**
- Example: Pt/Pt(111) (Bott et al., PRL 1992)

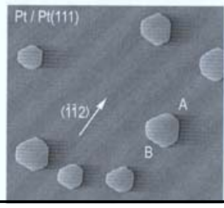
300 K



400 K

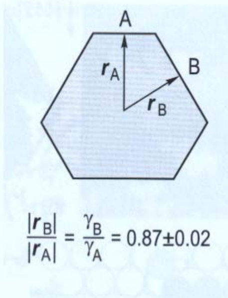
- The equilibrium shape is hexagonal:

(deposition at 425 K + annealing at 700 K)



Island Shape

- **2D Wulff theorem:** In a 2D crystal at equilibrium, the distances of the borders from the crystal center are proportional to their free energy per unit length



- For Pt(111): B/A ~ 0.87

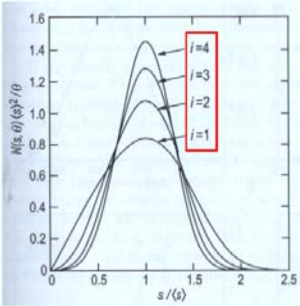
Island Size Distribution

- **Island size distribution** depends on:
  - Critical island size
  - Coverage
  - Substrate structure
  - "Coarsening" (at high Θ)

- From **scaling theory** (Amar et al., PRB 1994):

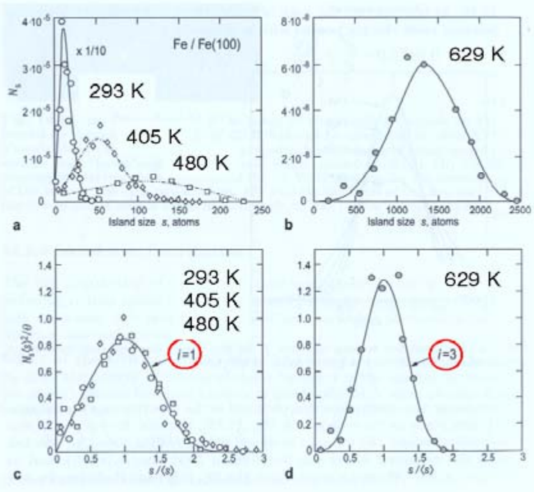
$$N_s = \frac{\Theta}{\langle s \rangle^2} f_i\left(\frac{s}{\langle s \rangle}\right)$$

- Comparing with experimental results
→ critical island size



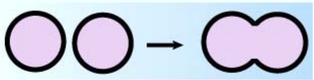
Island Size Distribution

- Example: Fe on Fe(100) (Stroscio et al., PRL1993, Amar et al., PRB 1994)



Coarsening Phenomena

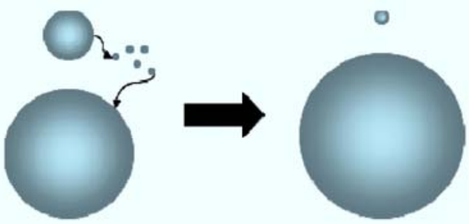
1) Coalescence:



- At 0.1 ML coverage: **dynamic coalescence** (**Smoluchowski ripening**)
- At 0.4-0.5 ML: **static coalescence**
- Higher coverages → **percolation** growth (→ change of physical properties!)

Coarsening Phenomena

2) (Ostwald) Ripening:



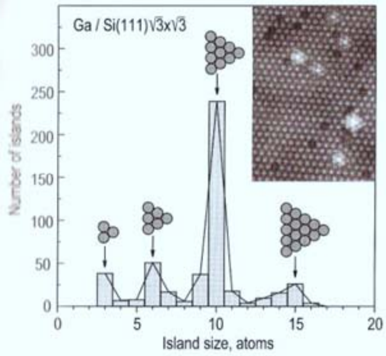
- Chemical potential of a circular island:

$$\mu(r) \propto \frac{\gamma}{r}$$

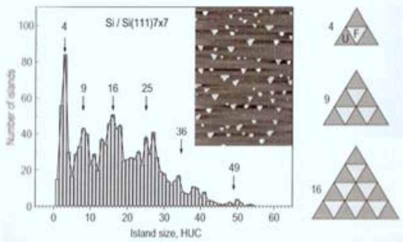
Reducing free energy → net flow from smaller to larger islands!

Magic Islands

• Ga on Si(111)√3x√3 (Lai & Wang, PRL 1998):



• Si on Si(111)7x7 (Voigtländer et al., PRL 199

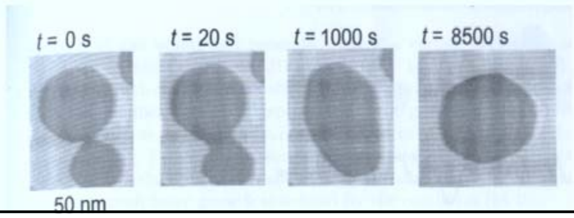


Formation of a new row → high energy cost!

Vacancy Islands

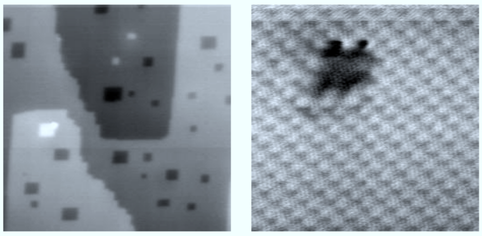
• Ion bombardment → formation of **vacancy islands**

• Analogies with adatom islands



Vacancy Islands

• Electron bombardment on insulating surfaces (Bennewitz et al., SS 2001):

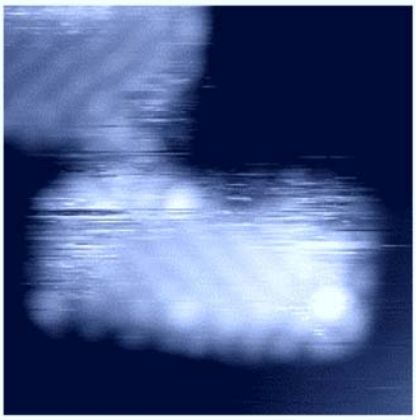


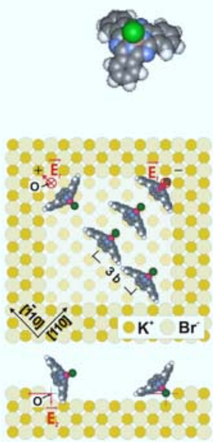
KBr(100)

- Irradiation with 1 keV electrons at 130 ºC
- Rectangular pits with area of 1x1 nm^2 up to 30x30 nm^2
- 1 ML deep (0.33 nm)

Vacancy Islands

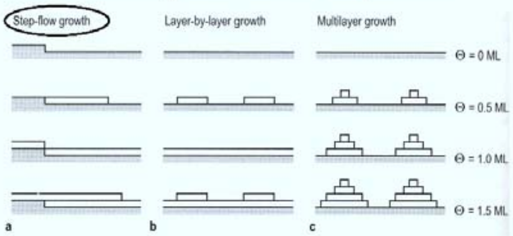
• Vacancy islands can be used as <u>molecular traps</u> (Nony et al., NL 2004)



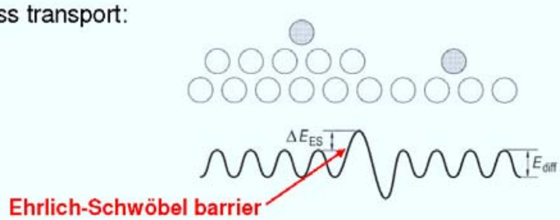


Kinetic Effects in Homoepitaxy

- Thermodynamics → Layer-by-layer growth but…
- Kinetic processes → Other growth modes are possible!

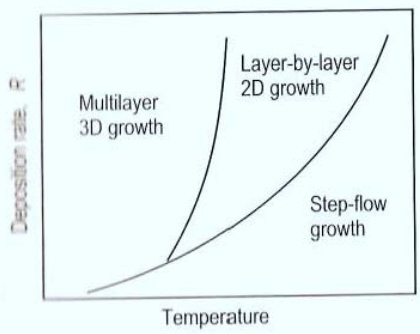


- **Interlayer** mass transport:



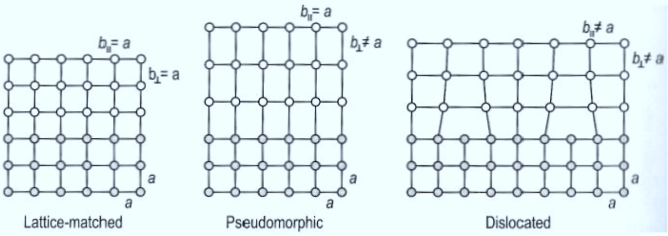
Kinetic Effects in Homoepitaxy

- Deposition rate and Temperature are important!
- Growth mode diagram (Rosenfeld et al., 1997):



Strain Effects in Heteroepitaxy

• Heteroepitaxy growth modes:

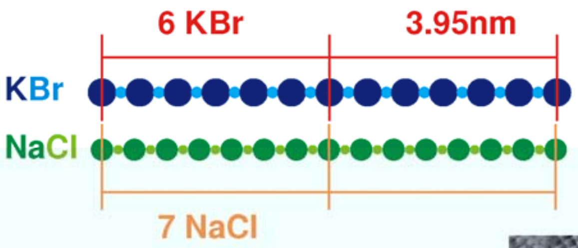


• Lattice **misfit** → elastic strain and dislocations

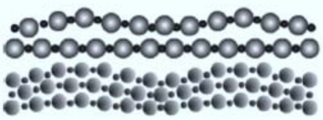
• Pseudomorphic growth below critical misfit and film thickness

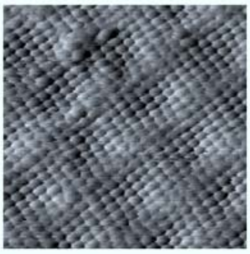
Strain Effects in Heteroepitaxy

• Heteropitaxy on insulating surfaces (Maier et al., PRB 2007):



• A "Moiré pattern" appears (also in the substrate?)

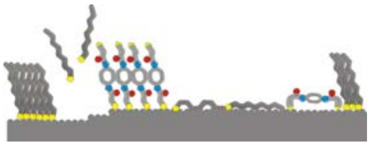


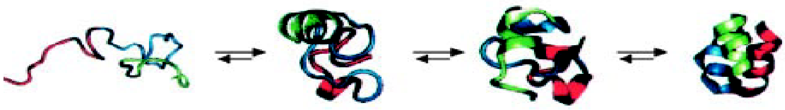


Molecular Self-Assembly

"Molecular self-assembly is the spontaneous association of molecules under equilibrium conditions into stable, structurally well-defined aggregates joined by non-covalent bonds. Molecular self-assembly is ubiquitous in biological systems and underlies the formation of a wide variety of complex biological structures."

G.M. Whitesides, J.P. Mathias and C.T. Seto, *Science* **254**, 1312 (1991)



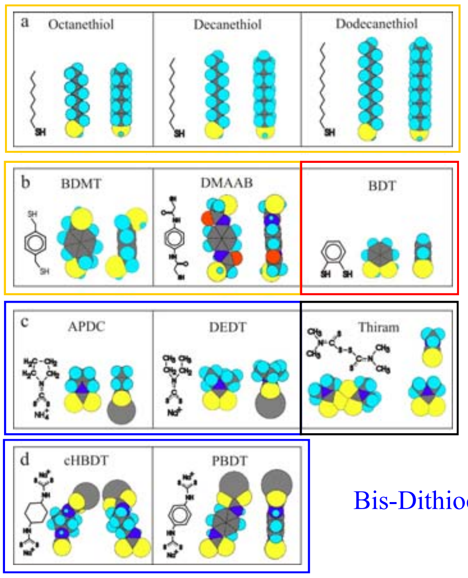


Die untersuchten Moleküle

Monothiole

Dithiole

Dithiocarbamate



1,2-Dithiol

Thiuramdisulfid

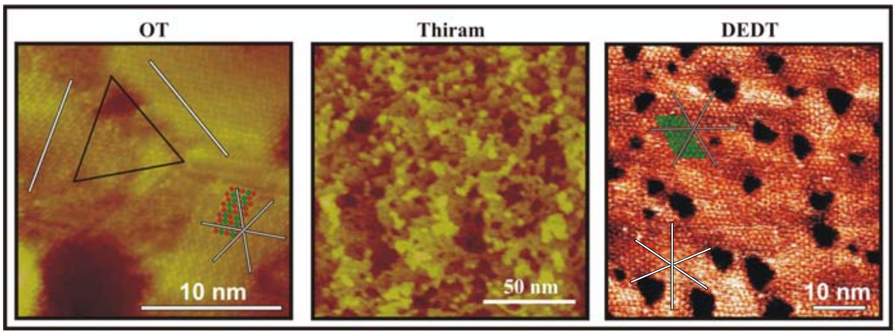
Bis-Dithiocarbamate

STM 2D Self-assembled Monolayer

- etch pits
- domain boundaries
- $(\sqrt{3}\times\sqrt{3})R30°$
- 0.5 nm dot distance

- jagged step edges
- no molecular resolution

- etch pits
- chiral domains
- $(2\sqrt{3}\times 2\sqrt{3})R30°$
- 0.96 nm dot distance



1 Schwefel/Punkt

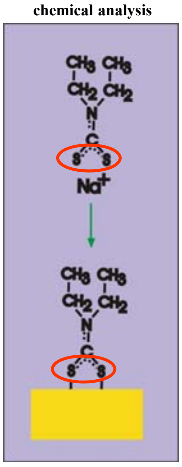
6 Schwefel/Punkt

Untersuchung der Chemisorption

XPS - ESCA

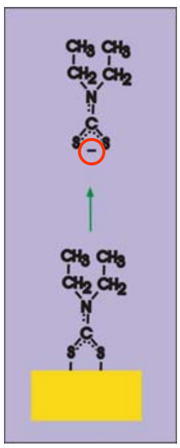
x-Ray photoelectron spectroscopy

Electron spectroscopy for chemical analysis

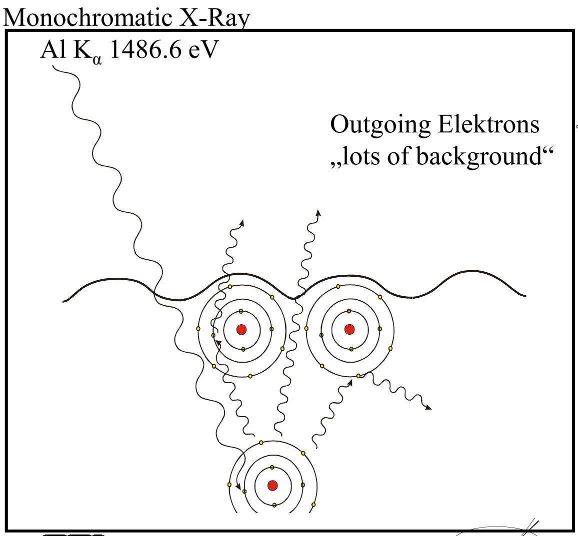


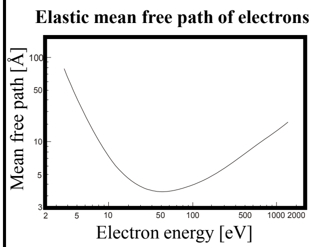
CV

Cyclic voltammetry



X-Ray Photoelectron Spectroscopy - XPS





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XPS signal and chemical Shift

$$E_{kin} = h\nu - E_b - \Phi$$ (Conservation of energy)

Given by the X-ray source: **constant**

Given by the Bulk properties: **small and almost constant**

Represents strength of interaction between ELECTRONS and the NUCLEUS

(Chemistry) (Physics)

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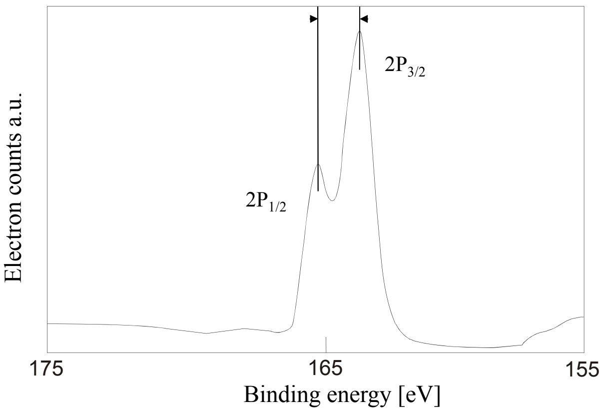
The XPS Sulfursignal

Handbook of X-ray Photoelctron Spectroscopy



- Double Peak (spin-orbit coupling)
- Relation of the Areas 2:1
- $2P_{3/2}$ Maxima @ 164 eV
- Energishift 1.18 eV

Theoretical Peakshape : Convolution of a Lorenzian and a Gaussian

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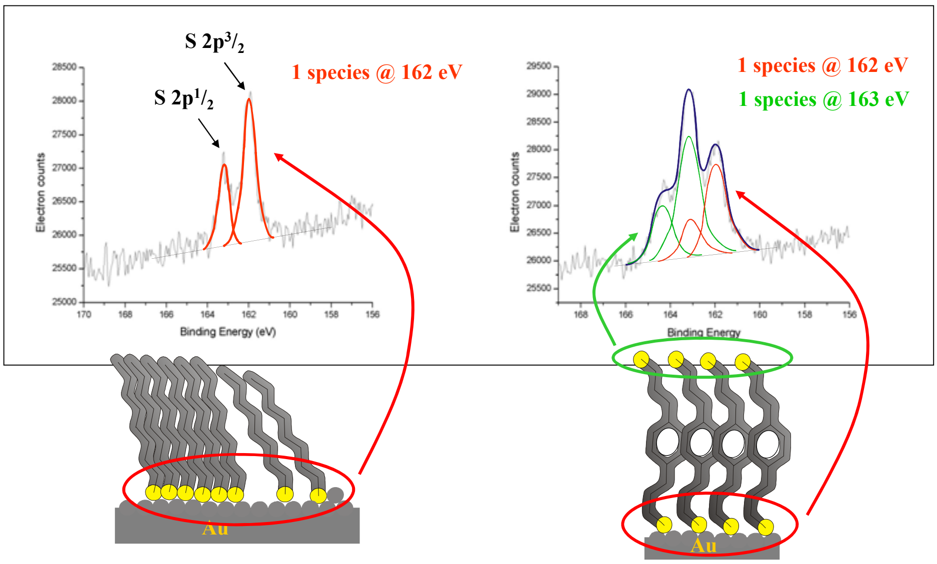
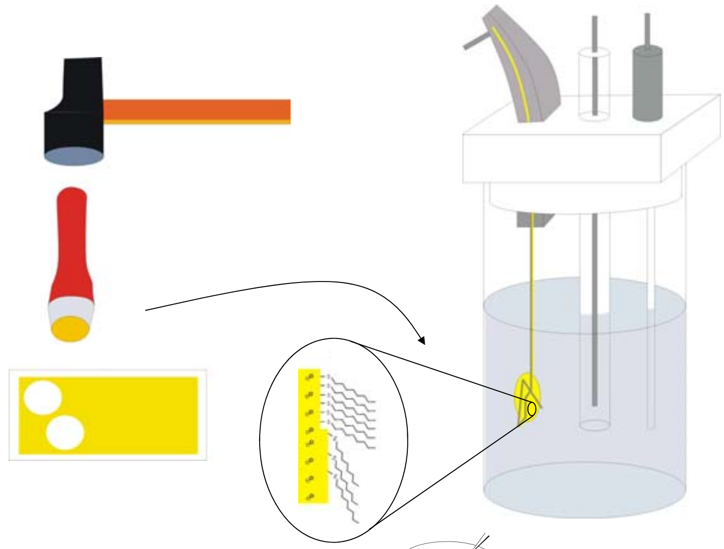
XPS Signale von Thiolen und Dithiolen auf Gold



Cyclic Voltammetry - Reductive Desorption



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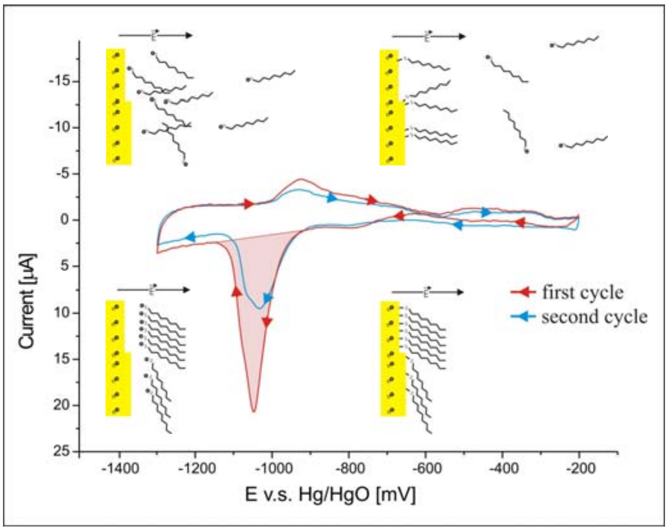
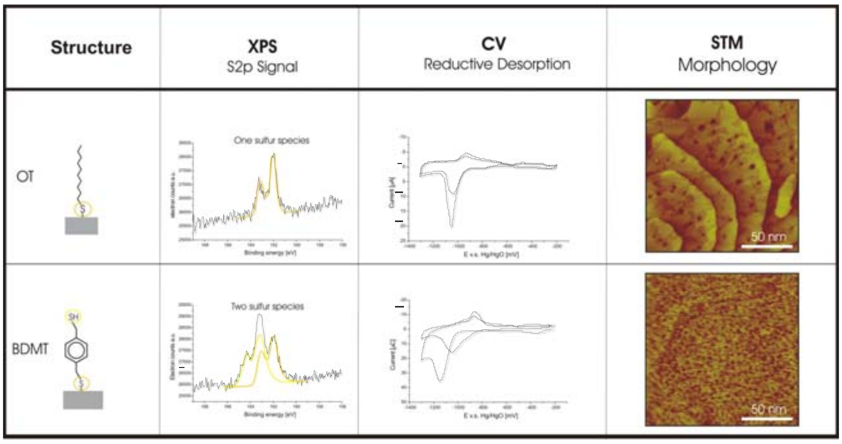
Reductive Desorption
of dodecanethiol from gold



Chemical Interaction at the surface

Thiols and Dithiols



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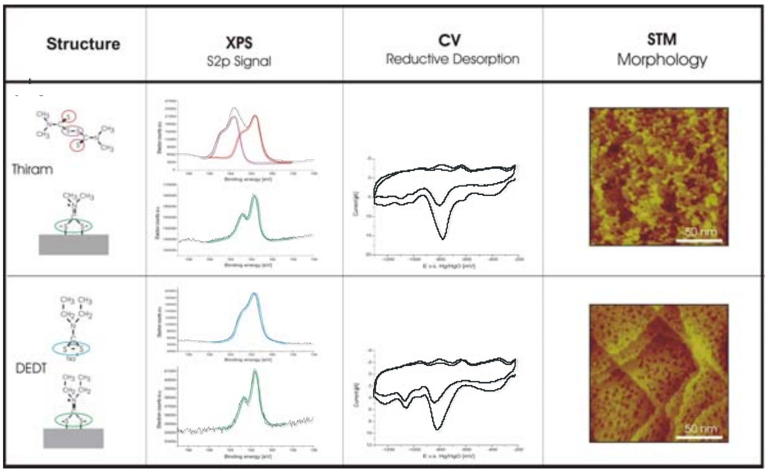
Chemical Interaction at the surface

Thiurames and Dithiocarbamates



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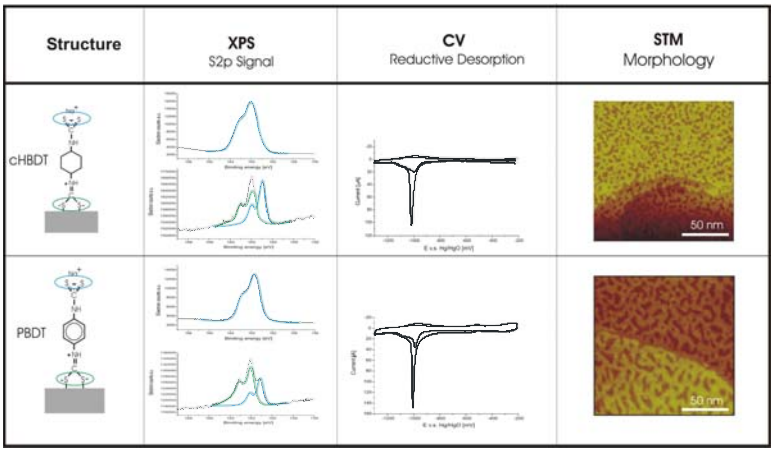
Chemical Interaction at the surface

Bis Dithiocarbamates



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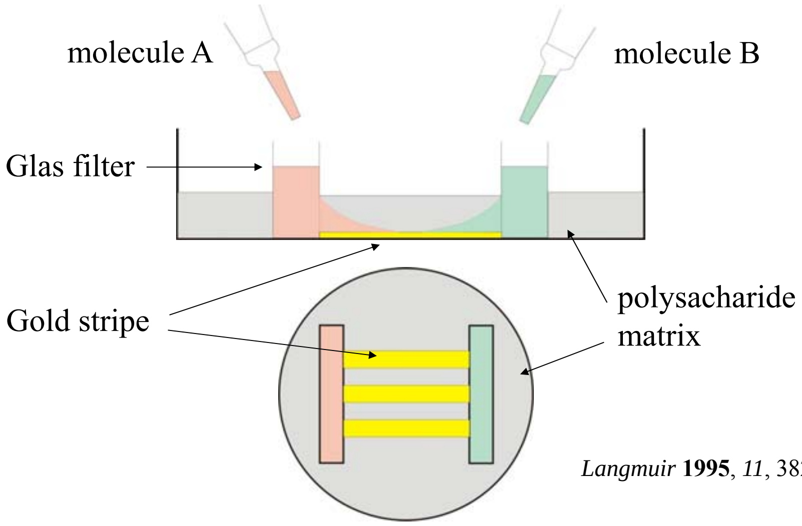
SONY

Gel-Assembly from Liedberg and Tengvall



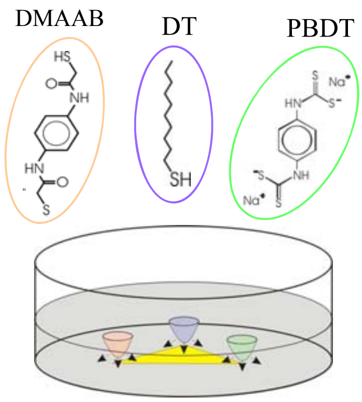
Langmuir **1995**, *11*, 3821-3827

PAUL SCHERRER INSTITUT

SONY

Gel-Assembly I

Spatial resolved assembly



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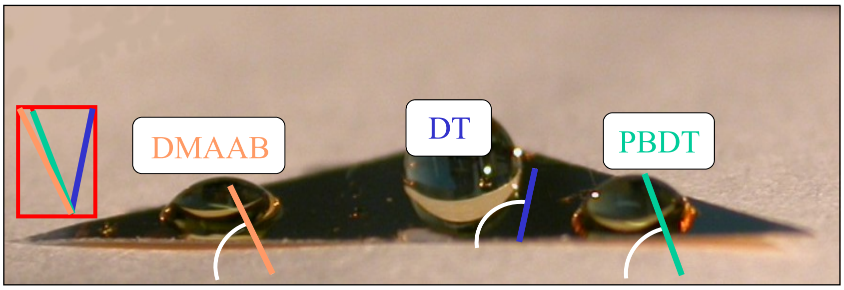
SONY

Gel-Assembly – Contact Angle

Contact Angles of a Molecular Gradient Assembly



WICHTIG: Strukturieren mit Molekuelen

Vgl: Micro-Contact Printing, Dip-Pen Lithography, Nanografting, …
Tuning von Oberflaechenenergien ~> Stabilisatoren / Emulgatoren fuer Nanopartikel
3D → colloidale Prozesse fuer Nanopartikel → kuenstliche Membransysteme,

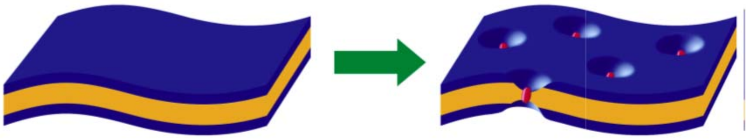
NANO

Block Copolymer Membranes as Mimics of Biological Membranes

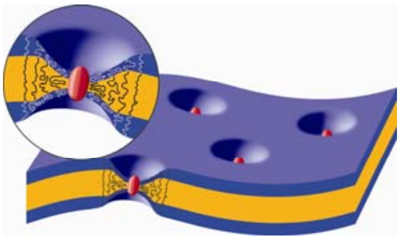
Zur Anzeige wird der QuickTime™ Dekompressor „TIFF (Unkomprimiert)" benötigt.

M.S. Bretscher, *Scientific American*, **1985**, *253(4)*, 86-90

Block Copolymer Membranes with Inserted Membrane Proteins



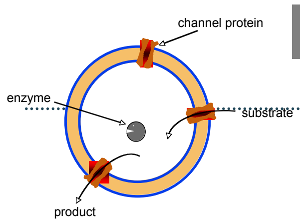
Nardin et al. *Angew. Chem.*, **2000**, *117*, 4247

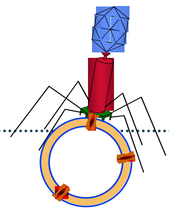


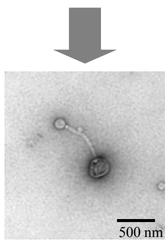
- Polymer chains can be compressed
(increase in the local surface energy but decrease in the stretching energy!)
- Polydispersity allows small chains to segregate around a membrane protein

Pata et al. *Biophysical Journal*, **2003**, *85 (3)*, 2111

The Nanoreactor

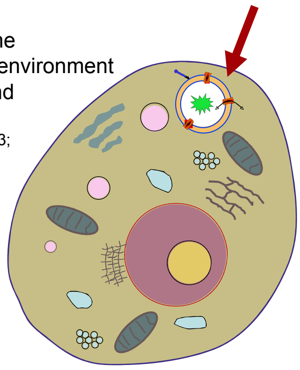






- full activity of encapsulated enzyme
- protection against hostile outside environment
- activation / deactivation on demand

Nardin et al, *Chem. Commun* **2000**, 1433; *Eur. Phys. J. E* **2001**, *4*, 403; ...



Biological recognition!

A. Graff, et al., *Proc. Natl. Acad. Sci.USA* ,**2002**, *99*, 5064

Cell-specific integration of artificial organelles

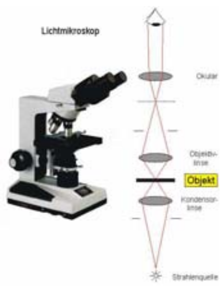
N. Ben-Haim et al, *Nano Lett.* **2008**, *8*, 1368

Microscopes

For the visualisation of millimeter to nanometer structures

Light Microscope

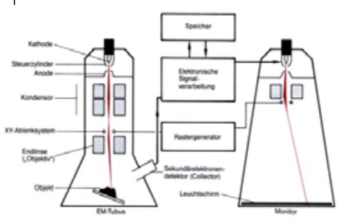
since about 1750



geometric optics
resolution about 500 nm
Light-Intensity contrast

Electron Microscope (SEM)

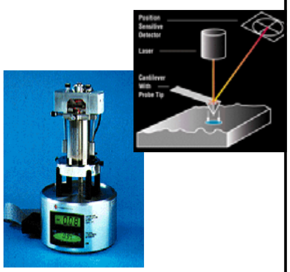
since about 1955



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

Scanning Probe Microscope

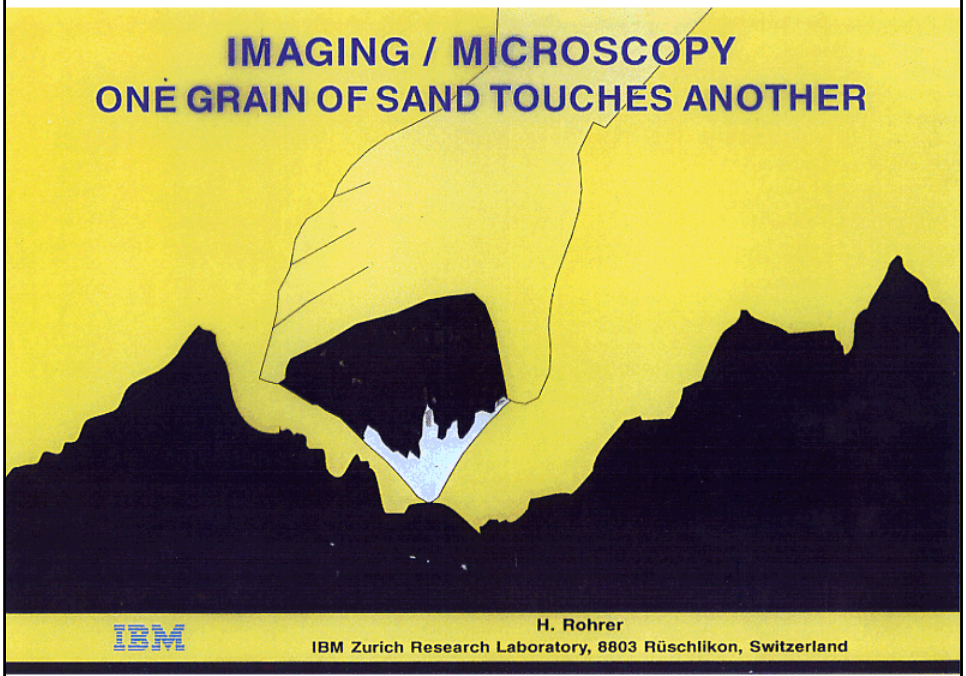
since about 1981

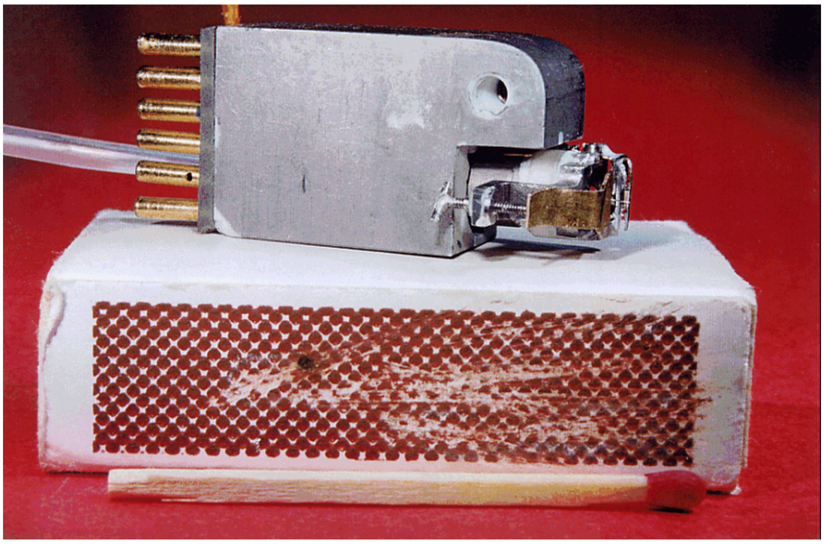


deflection sensor
piezo-scan
resolution 0.2 nm
3d topographic map

N.B.
Ein Bild sagt mehr als tausend Worte (Daten)

Es wird oft behauptet, es handele sich um ein chinesisches Sprichwort. Auch Konfuzius wird oft als Urheber genannt. Der erste gedruckte Nachweis findet sich jedoch im englischen Sprachraum. Am 8. Dezember 1921 veröffentlichete Fred R. Barnard in der Zeitschrift "Printers' Ink" eine Anzeige mit dem Slogan "One Look is Worth A Thousand Words." Es handelte sich um eine Fachzeitschrift der Werbebranche. Die Anzeige warb für den Gebrauch von Bildern in Werbeaufdrucken auf Autos. Am 10. März 1927 erschien eine zweite Anzeige mit der Phrase "One Picture is Worth Ten Thousand Words". Dort wird behauptet, es handele sich um ein chinesisches Sprichwort. Das Buch "The Home Book of Proverbs, Maxims, and Familiar Phrases" zitiert den Autor Barnard, der sagte, er habe den Slogan "als chinesisches Sprichwort betitelt, damit die Leute es ernst nehmen".





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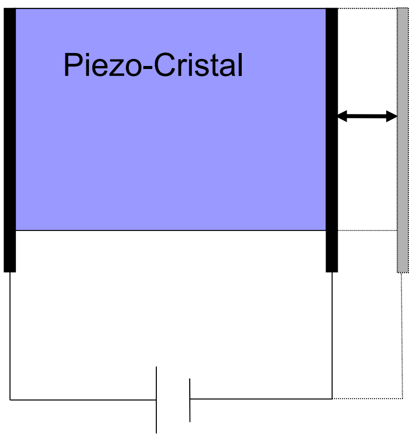
The Piezo Scanner



E-field modifies X-tal structure and elongation

DC voltage
-220 to +220 V

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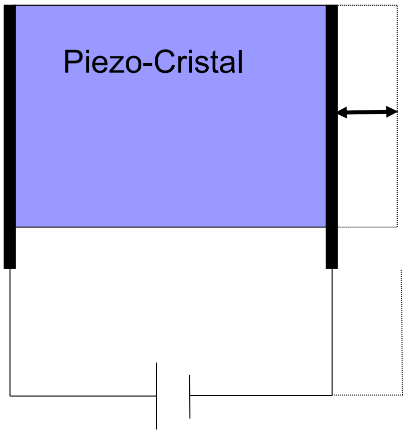
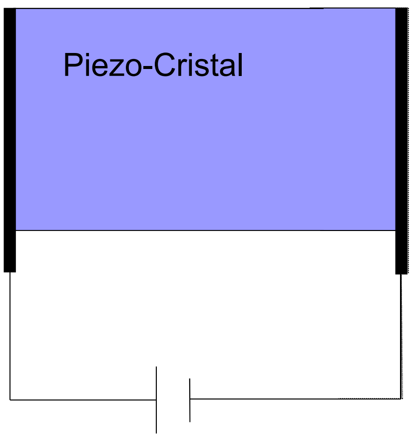
The Piezo Scanner



contracted !

DC voltage
-220 to +220 V

The Piezo Scanner

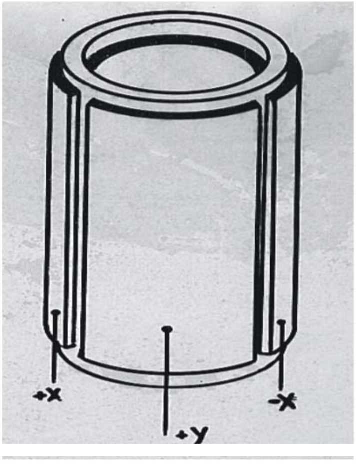


extended !

DC voltage
-220 to +220 Volt

XYZ – Scanning unit

'precision at your fingertips'



Precision: 1/100th Angstrom

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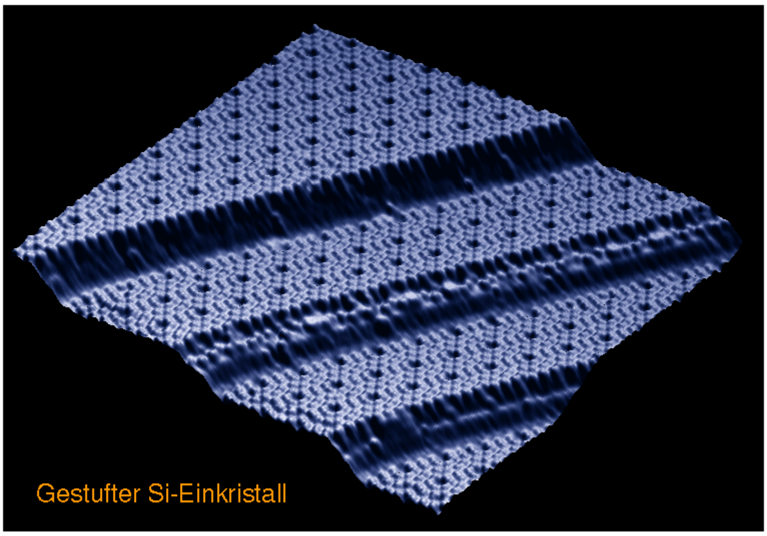

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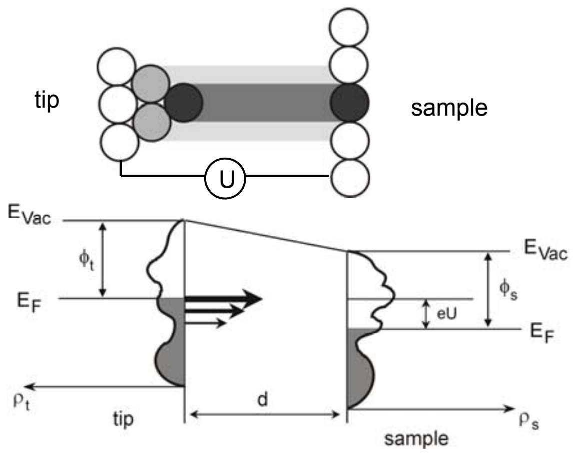
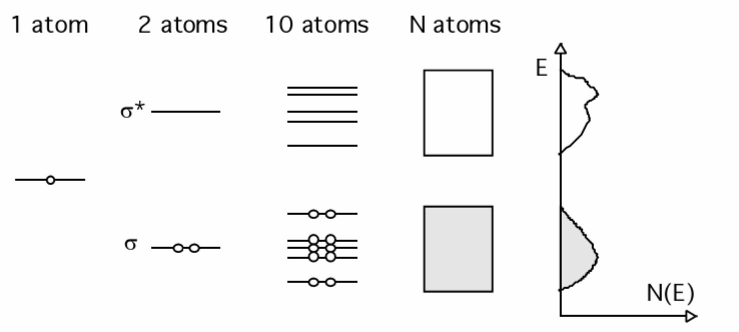
Scanning Tunneling Microscopy



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

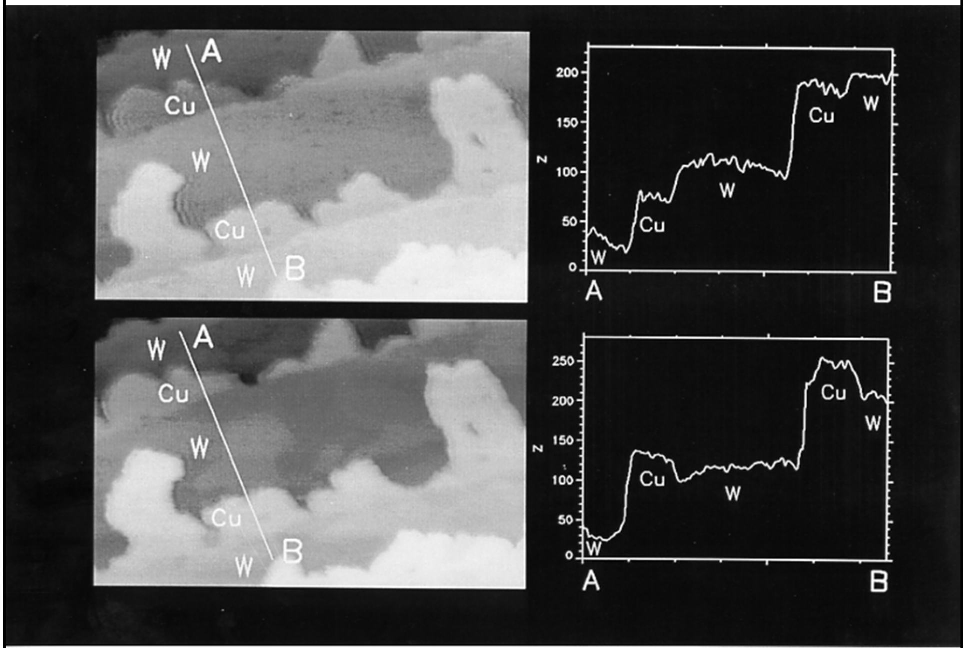
=> sensitivity to local electronic structure of the sample

Density of States (DOS)



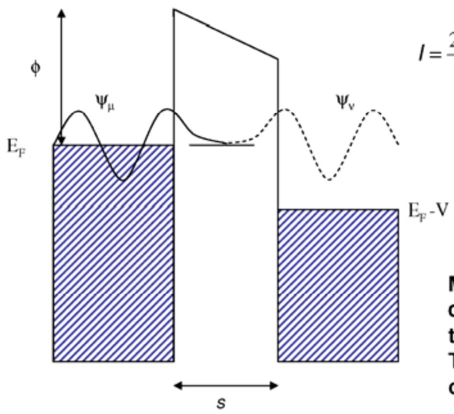
Density of States (DOS), N(E) is the number of energy levels bewteen E and E+dE (states per eV)

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



Calculation of tunneling current

The tunneling current is related to the overlap of electron wave functions. According to the Bardeen formalism the current can be approximated as:



$$I = \frac{2\pi e}{\hbar}\sum_{\mu\nu} f(E_\mu)[1 - f(E_\nu - eV)]\delta(E_\mu - E_\nu)|M_{\mu\nu}|^2$$

$f(E)$ is the Fermi function

$$M_{\mu\nu} = \frac{\hbar^2}{2m}\int d\vec{S}\cdot\left(\psi_\mu^*\vec{\nabla}\psi_\nu - \psi_\nu\vec{\nabla}\psi_\mu^*\right)$$

$M_{\mu\nu}$ is the so-called matrix element describing the probability of a transition from state μ into state ν. The integral is a surface integral over the current density of ψ.

J. Bardeen, *Phys. Rev. Lett.* 6, 57 (1961)

Tunnelspektroskopie auf Supraleitern

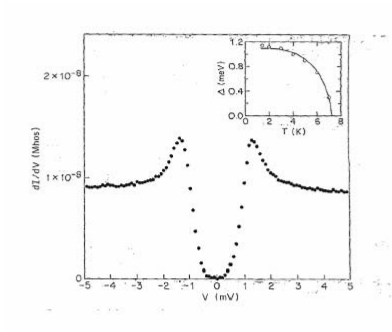


Fig. 2.7. dI/dV vs. bias voltage V for $NbSe_2$ at 0T applied magnetic field used to determine the gap at 1.45K. Inset: The gap vs. temperature and the corresponding BCS-fit. From [35].

H.Hess et al., Phys.Rev. Lett. 62(2), 214(1989)

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Inelastische Tunnelspektroskopie

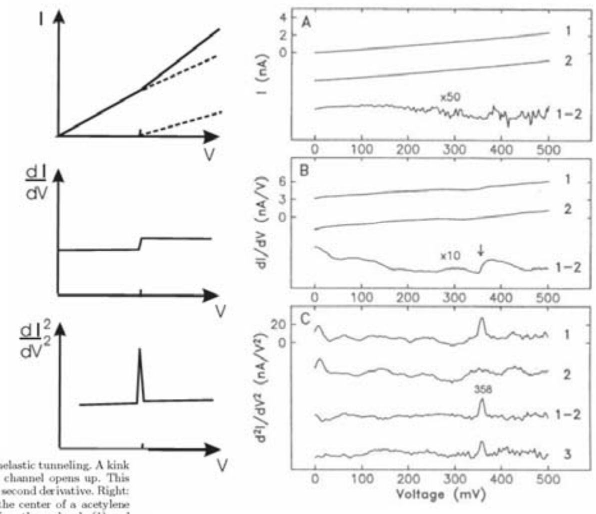
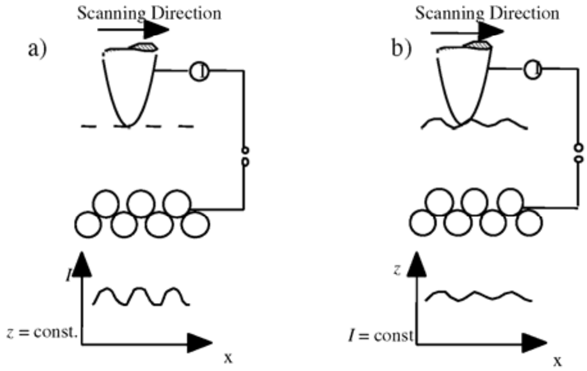


Fig. 2.8. Left:Current vs. voltage curves with elastic and inelastic tunneling. A kink is observed when the inelastic electron tunneling current channel opens up. This kink becomes a step in the first derivative and a peak in the second derivative. Right: (A) I-V-curves recorded with the STM tip directly over the center of a acetylene molecule (1) and over the bare Cu(100) surface. (B) dI/dV on the molecule (1) and on the substrate (2). (C) dI^2/dV^2 on the molecule (1) and on the substrate (2). The difference spectrum (1-2) shows a peak at 358mV. (3) is an average of 279 scans. From [41].

B.Stipe,M.Rezaei,W.Ho:Science 280, 1732 (1998)

Operating modes



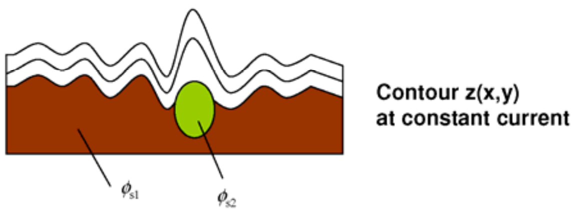
Constant height   Constant current

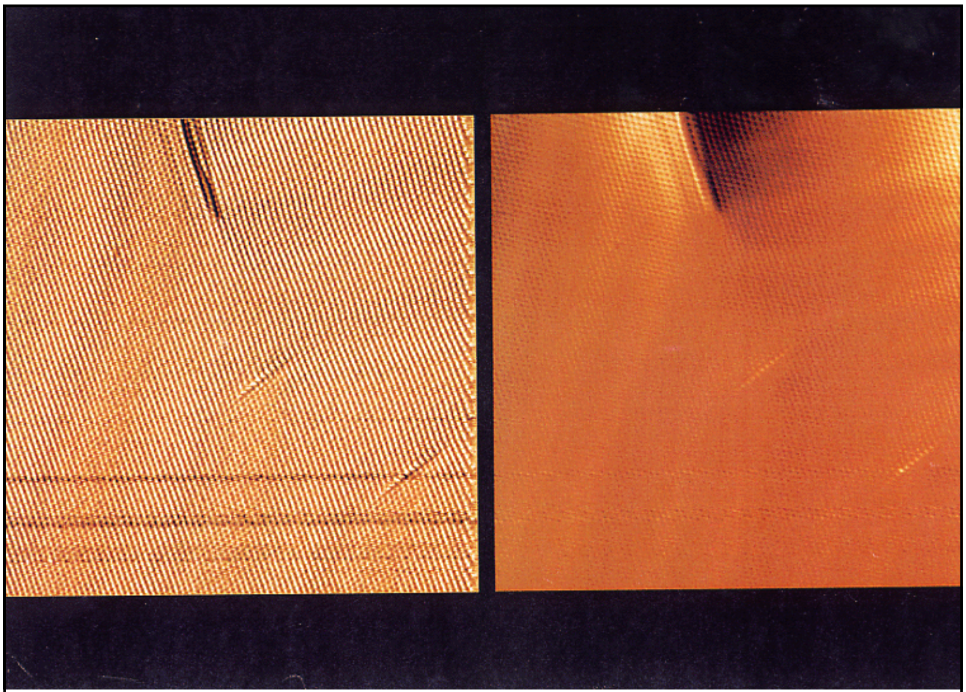
Constant current mode

$$\ln(I) = \text{konst.} \quad \Rightarrow \quad \sqrt{\phi}\, s = \text{konst.}$$

If barrier height constant ⇨ **s=constant**

If barrier height varies ⇨ **$\phi(x,y)$, $s(x,y)$ affect topography z(x,y)**





Crystal grains and their boundary

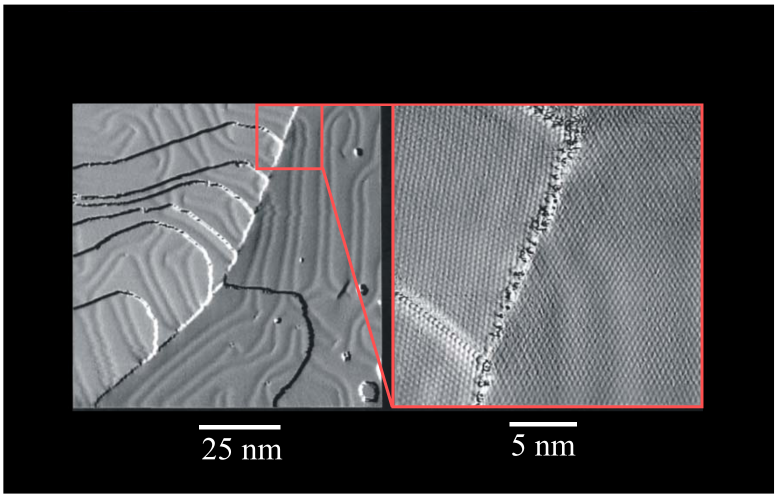


Abbildung von Legierungen

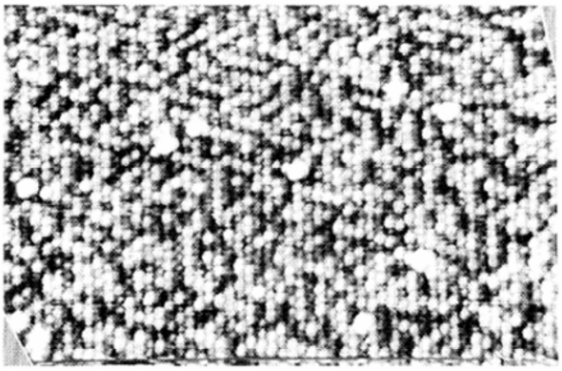
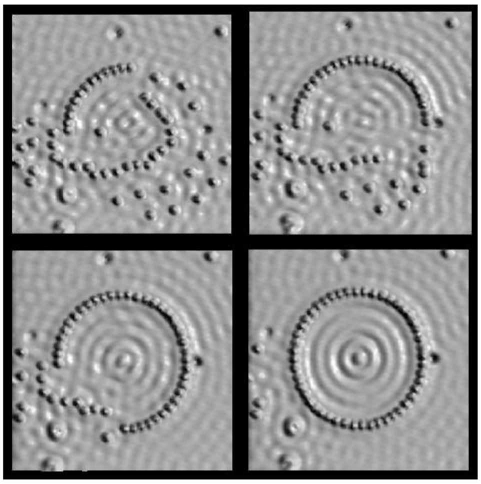


Fig. 2.14. STM image of the (111) surface of a $Pt_{25}Ni_{75}$ single crystal. A voltage of 5mV and current of 16nA were applied. A rather strong "chemical" contrast is observed, where the dark species is attributed to Pt und the bright features to Ni. The contrast is related to the interaction between tip adsorbates and the surface. Image size is 125Åx 100Å. From [50].



M.F. Crommie, C.P. Lutz and D.M. Eigler, *Nature* 363 (1993)

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Oberflächenzustände auf Cu(111)

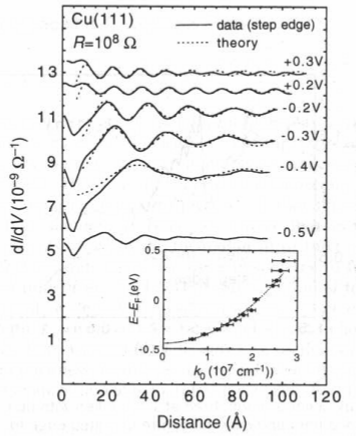


Fig. 2.16. Spatial dependence of dI/dV across a step edge on Cu(111) at 4K. For details see text. From [80].

„Confined electrons“

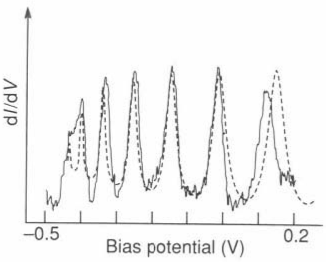
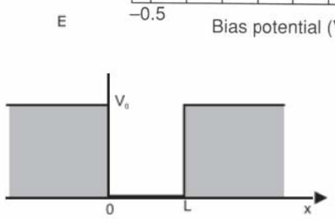


Fig. 2.18. The experimental (solid line) and theoretical (dashed line) voltage dependence of dI/dV, with the top of a STM located at the center of a 88.7Å diameter, 60-atom circle of Fe atoms on a Cu(111) surface. From [84].



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

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

Abbilden von Molekülen

Fig. 2.15. Constant current STM image of Cu-tetra 3,5 di-t-butylphenyl porphyrin (Cu-TBPP) molecules on Ag(100) at low molecular coverage. The monatomic Ag-substrate steps are decorated by the molecules. Image size is 68x68nm^2. I_t=150pA and U=1V. Courtesy of M. de Wild, S. Berner, H. Suzuki and T. Jung.

Manipulation mit dem STM

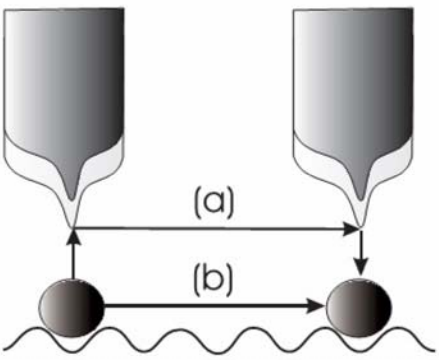
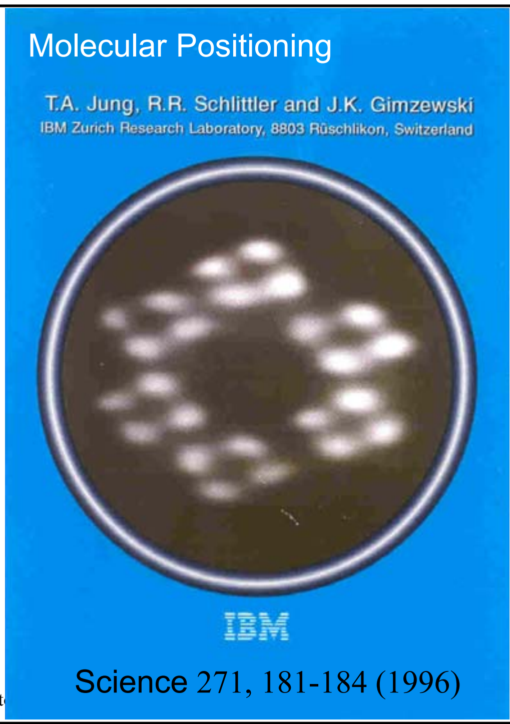


Fig. 2.9. Modes to manipulate single adatoms: (a) Vertical manipulation. (b) Lateral manipulation. In case (a), the adatom forms a strong bond with the tip, is detached from the surface, transported by the tip and redeposited on the surface. In case (b), the interaction has to be strong enough to overcome the corrugation of the interaction potential, which is closely related to the diffusion barrier.



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Manipulation mit dem STM

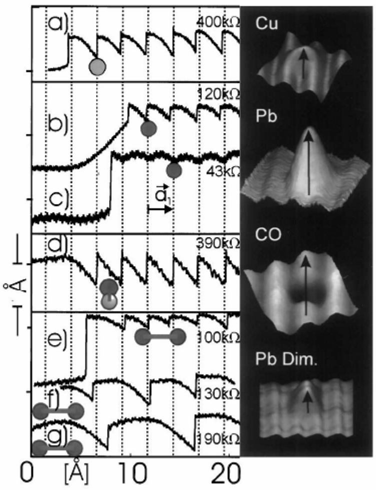

Fig. 2.10. Tip height curves are shown during manipulation of a Cu atom (a), a Pb atom (b,c), a CO molecule (d), and a Pb dimer (e)-(g) along the [1$\bar{1}$0] of the Cu(211) surface. The tip movement is from the left to the right, and the tunneling resistances are indicated. The vertical dotted lines 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].

L.Bartels,G.Meyer,K.H.Rieder:Phys.Rev.Lett. 79(4),697(1997)

Scanning Probe Microscopy

- Real Space (not reciprocal space) experiments with individual objects
- Many different eperimental qualities (electronic, optic, mechanic, reactivity...) but semi-quantitative.
- Versatile tool to solve fundamental and applied problems at surfaces and interfaces

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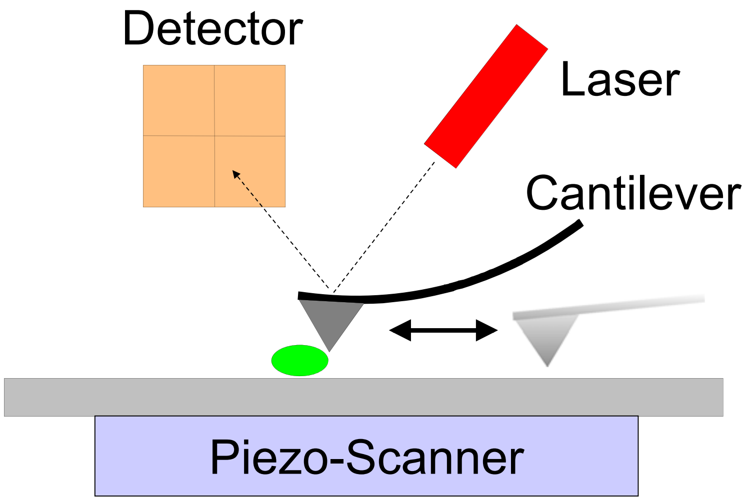
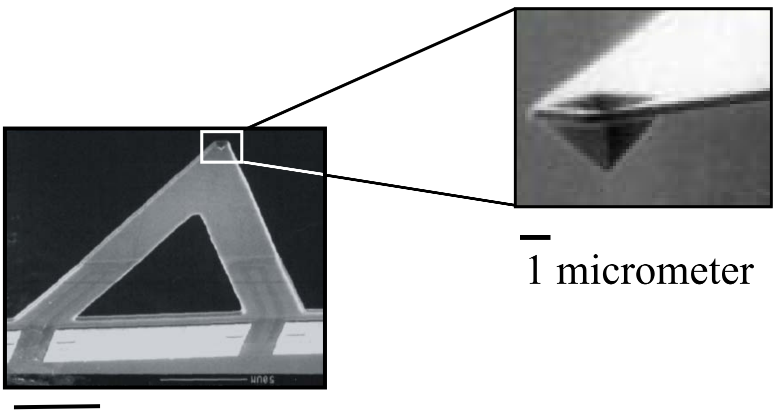
AFM - “Hands & Eyes“



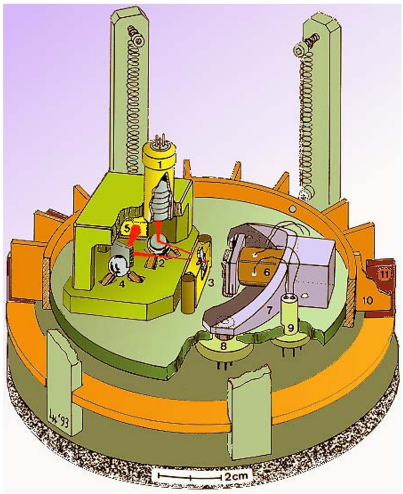
Cantilever with integrated Tip



1 micrometer

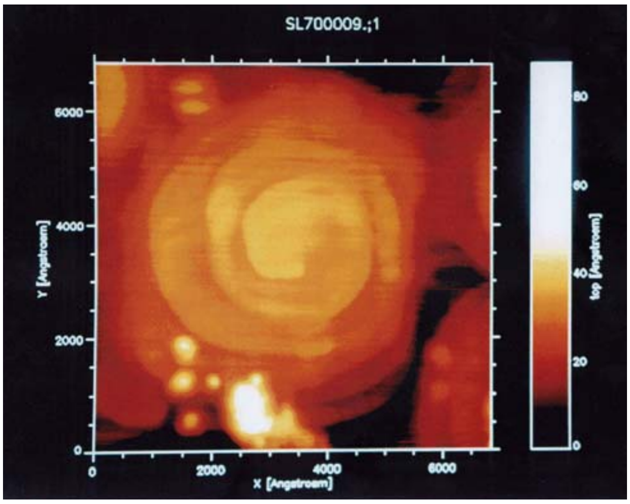
50 micrometers

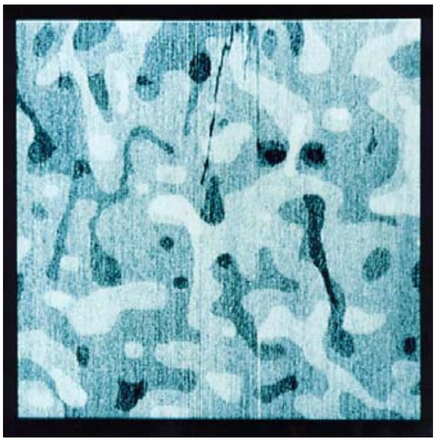
Examples



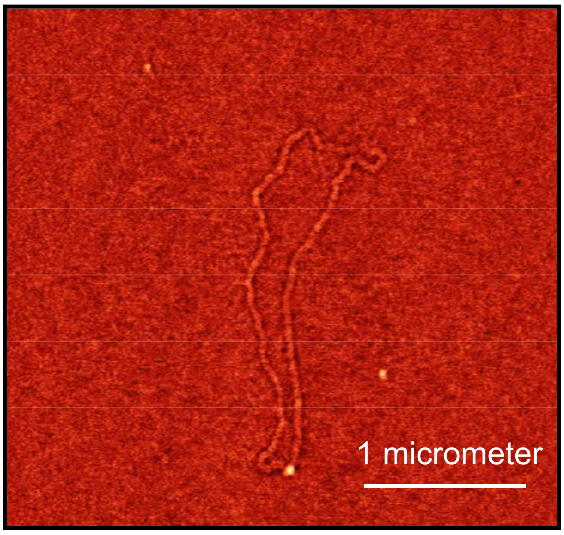
„Screw Dislocation“ on High Tc YBCO

~ 400 nm diameter

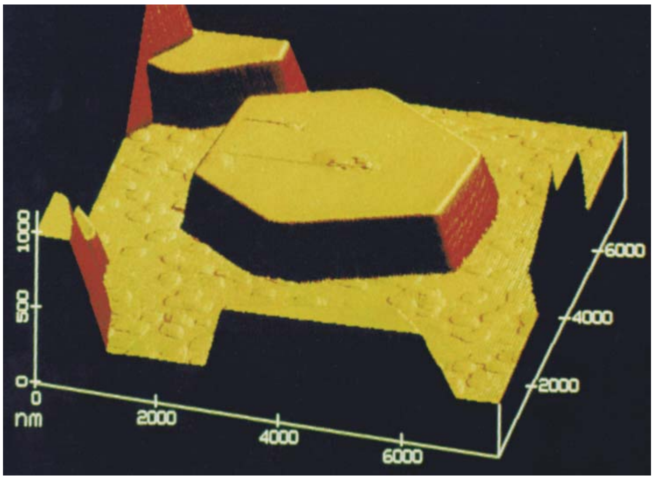




DNA-Molecule

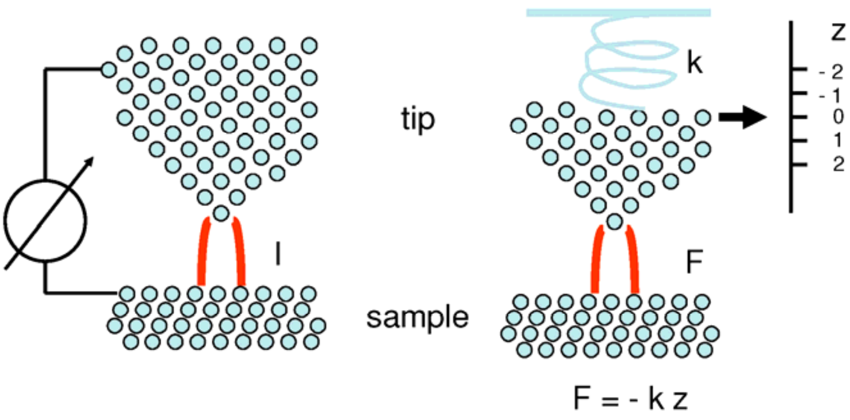


T-(tabular) AgBr grain
of a photographic emulsion (Ilford)

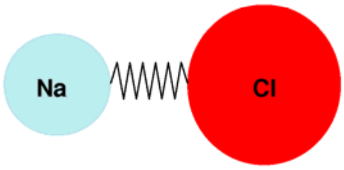


Scanning X Microscopy

S T**unneling** **M** **S** F**orce** **M**

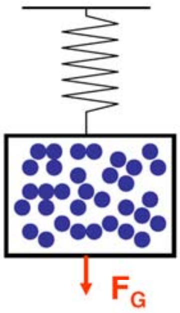


Force between two atoms



Chemical bond
F_{chem} = 1eV/ 0.1 nm
1.6 nN

Sensing Forces



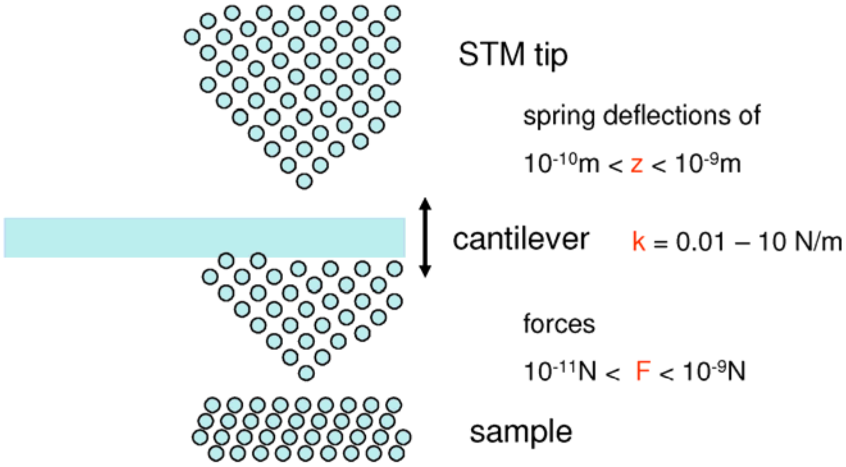
1 nm³ water (33 molecules)

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

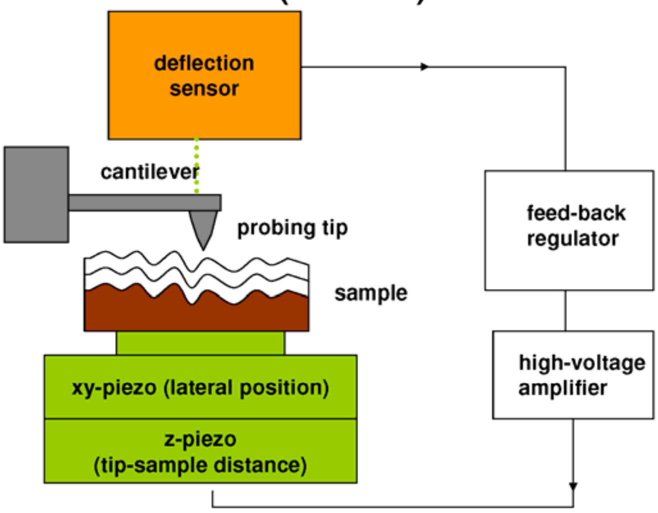
0.01 g

F= 0.1 mN = 10^5 nN

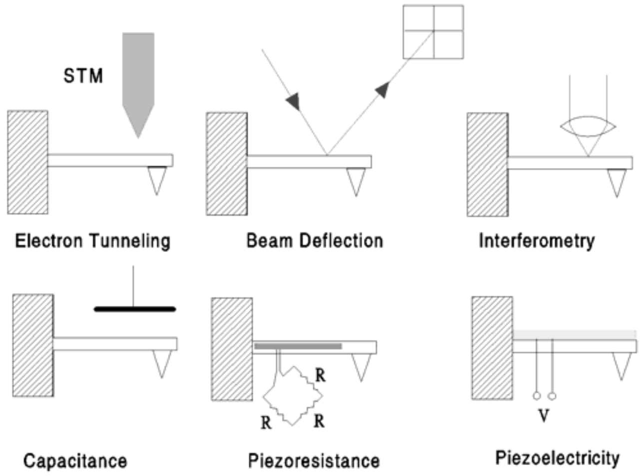
Principle of First Atomic Force Microscope



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)**

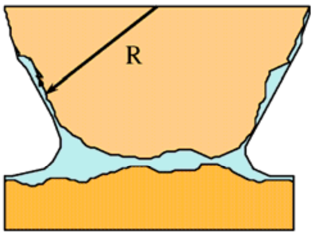
Capillary forces

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

$\gamma(H_2O) = 0.074$N/m R=100nm

Contact angle foir hydrophilic surfaces $\Theta \approx 0°$

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



Van der Waals forces in vacuum

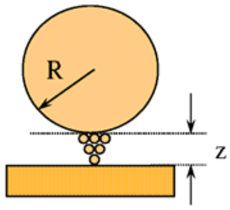
- No capillary forces (no water)
- Van der Waals and electrostatic forces dominate

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

$B=3K/4\,(\varepsilon_s-1)(\varepsilon_t-1)/\,[(\varepsilon_t+1)(\varepsilon_t+2)]$
K=1.41eV

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

$\Rightarrow$ R=100nm, z=1nm



graphite-graphite	8nN
diamond-diamond	17nN
metal-graphite	10nN
SiO_2-graphite	1.2nN

Van der Waals forces in liquids

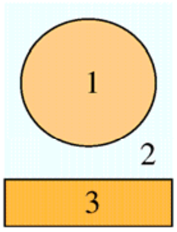
- capillary forces are eliminated
- Van der Waals can be repulsive:

  U » $(n_1^2 - n_3^2)(n_2^2 - n_3^2)$

  For $n_1 < n_2 < n_3$ result negative van der Waals forces.

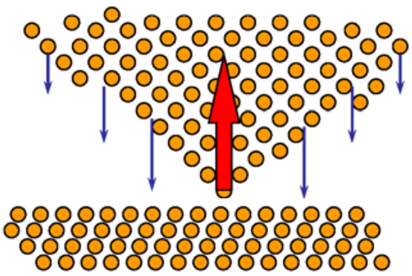
  Mc Lachlan, *Proc. Roy. Soc.* A 271, 38 (1963)
- Observation of very weak forces (10pN) by Ohnesorge und Binnig. Atomic resolution of a calcite surface.

  F. Ohnesorge and G. Binnig, *Science* 260, 1451 (1993)
- For hydrophobic surfaces entrpoy effects can increase the net forces.

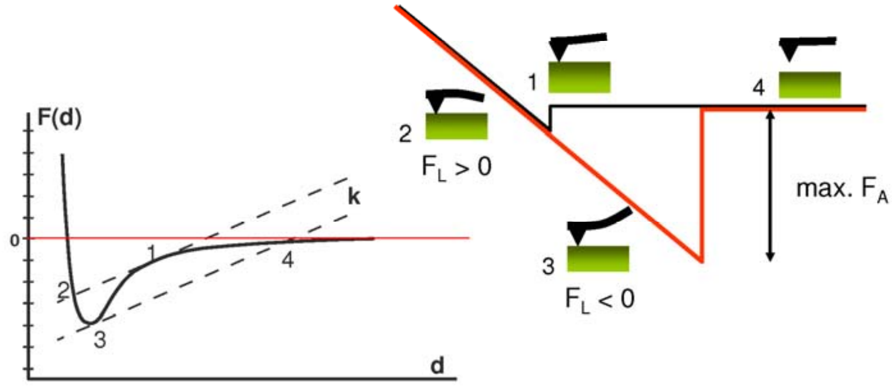


Estimation of forces

- 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

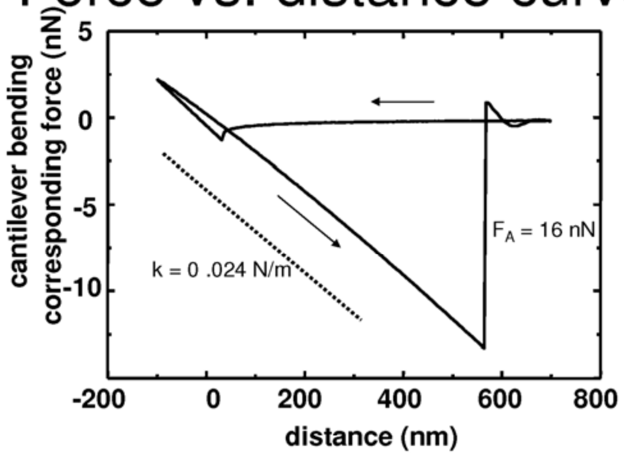


F(d): Interaction force between tip and sample

d: tip sample distance

k: spring constant of cantilever

Force vs. distance curves



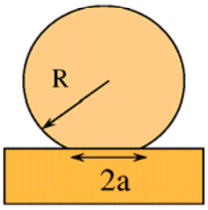
Contact area

The contact area is given by

$2a = 2\,E^{*}(F\,R)^{1/3}$ (Hertz theory)

- in air: 5-100nm
- in liqiuds: atomic resolution
  F. Ohnesorge and G. Binnig, Science 260, 1451 (1993)
- in ultra-high vacuum: 1-10 nm

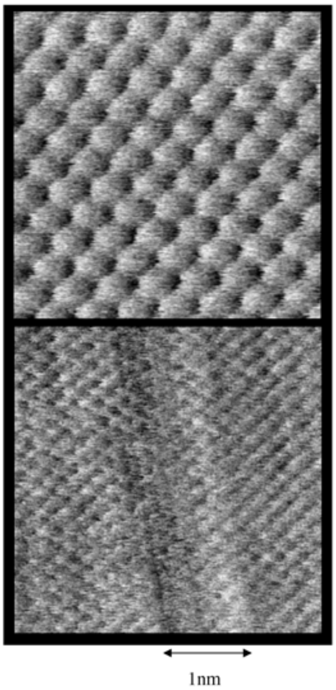
Best resolution in ultra-high vacuum:



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)

C_{60}-molecules: R. Lüthi et al., *Z.f. Phys. B* 95, 1 (1994)

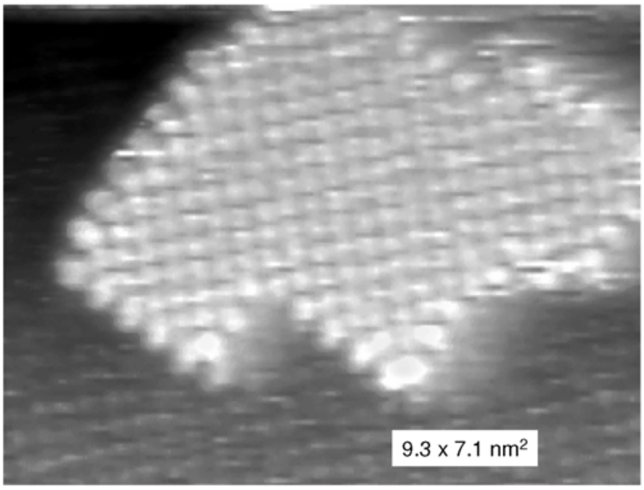


AFM on NaF(001)

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

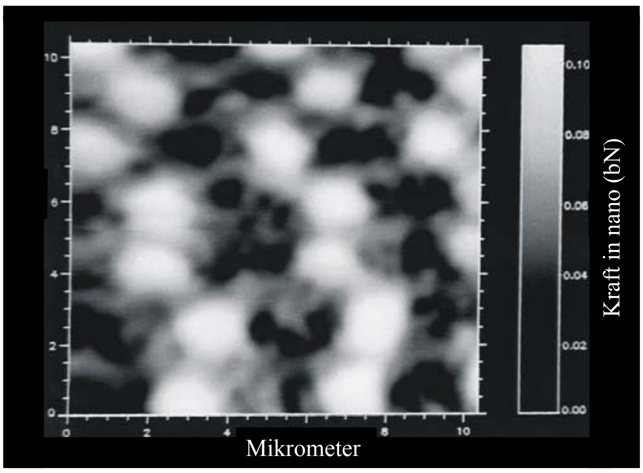
⇒ 1 nm contact radius

True atomic resolution on insulators



NaCl-island imaged by nc-AFM

Magnetic domains on Computer HD



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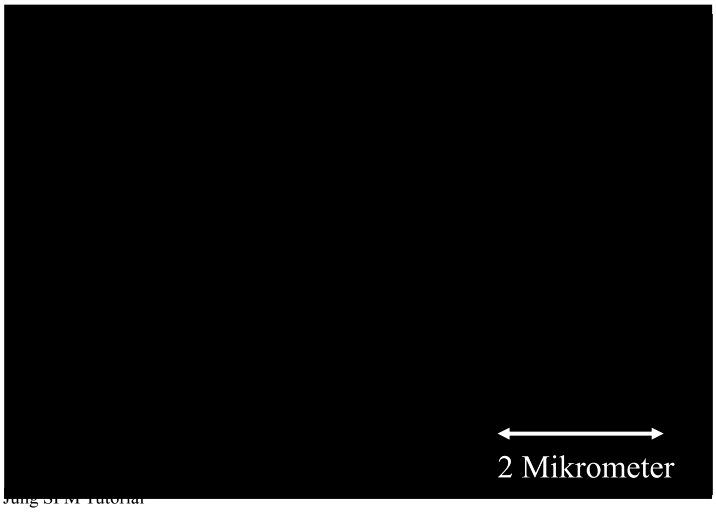
Indentation Hardness

tip-tools – materials testing and data storage



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„HEUREKA“

— writing in between the lines of a CD

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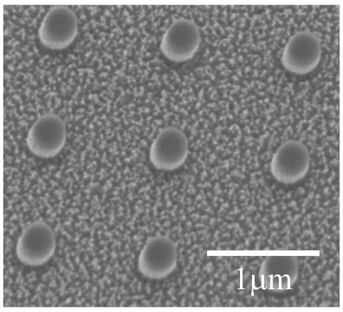
Nano-Fracture / Nano-Wear

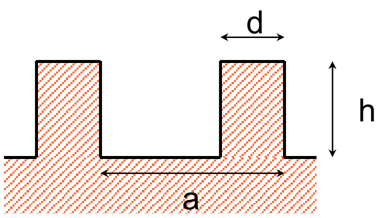
Fracture is a macroscopic phenomenon which crucially depends on microscopic properties

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

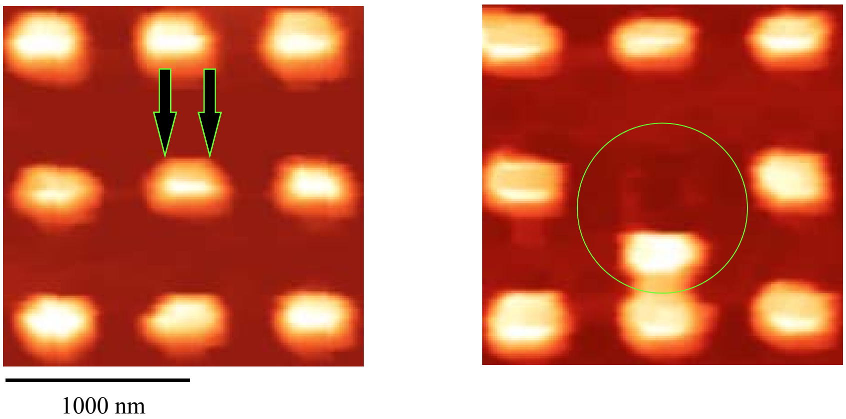
Well defined model system

- Nanotower arrays produced by lithography technique



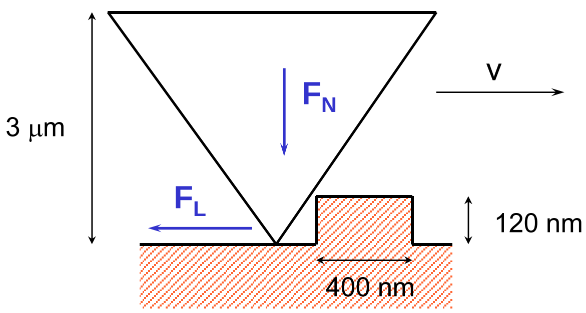


Nanotower Fracture Experiments



breaking off and removing nanotowers

Lateral force measurement



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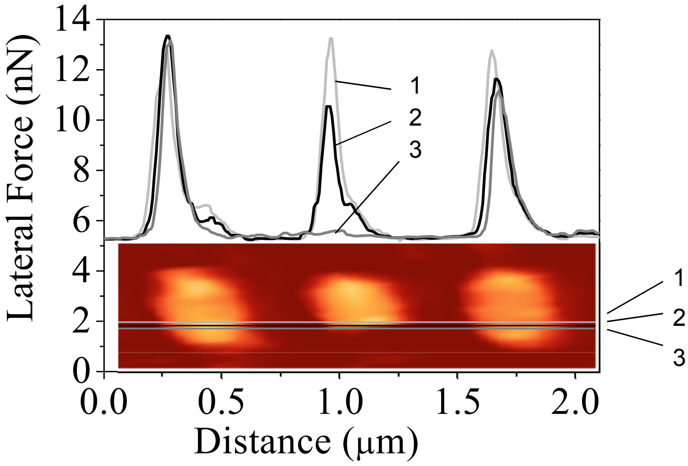
Lateral forces during fracture



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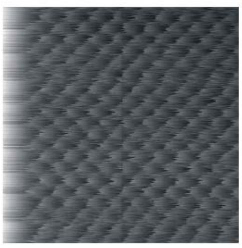
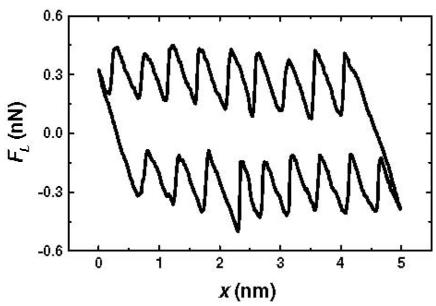
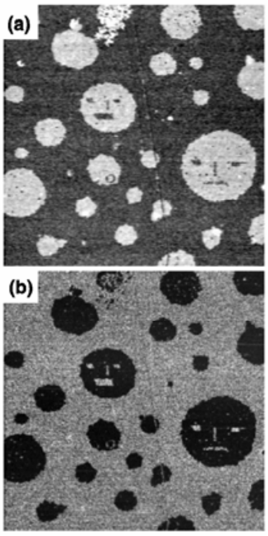
Atomic-scale stick-slip





⇒See part II

Friction contrast



Topography

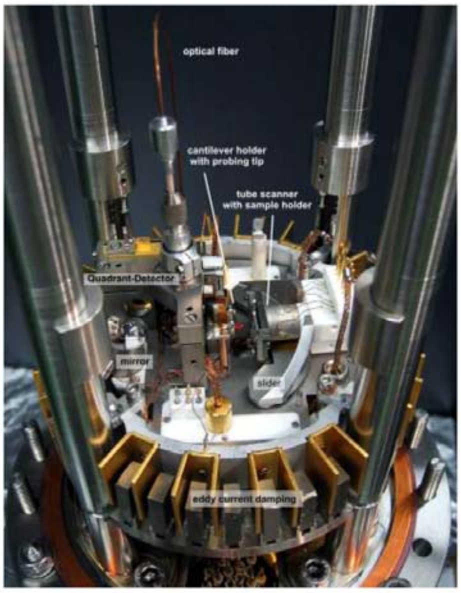
Lateral Force

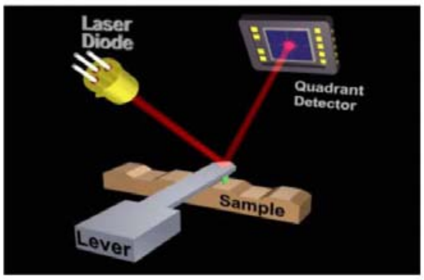
2.8x2.8µm^2

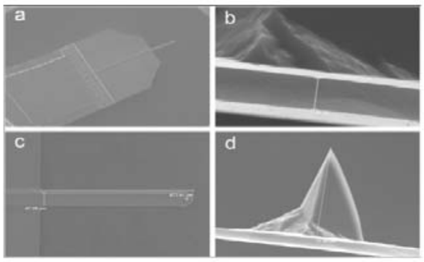
Mixed Langmuir-Blodgett films
($C_{21}H_{43}COO^-$/$C_9F_{19}C_2H_4OCC_2H_4COO^-$)

E. Meyer et al.
Thin Solid Films **220**, 132 (1992)

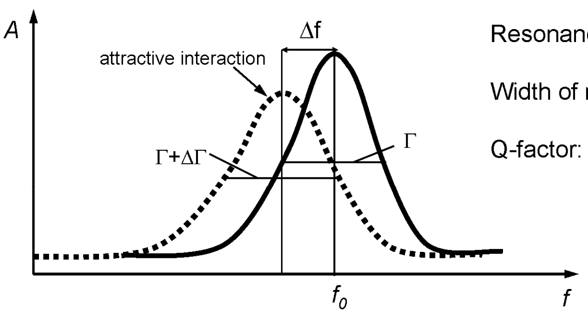
Noncontact-AFM (nc-AFM)







Quantitative understanding of nc-AFM



Resonance frequency: f_0

Width of resonance curve (FWHM): Γ

Q-factor: $Q = \frac{2\pi \cdot f_0}{\Gamma}$

Conservative forces $\Rightarrow$ shift of resonance curve Δf
Dissipative forces $\Rightarrow$ broadening of curve $\Delta\Gamma$

Forces in nc-AFM

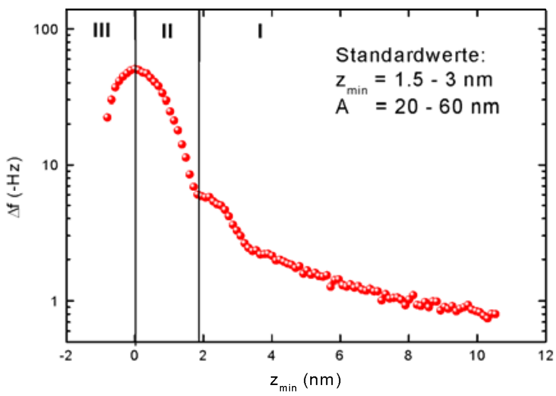
Frequency modulation: $f_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}}$ $\Delta f = -\frac{f_0}{2k}\frac{\partial F_{tot}}{\partial z}$

$\Rightarrow$ measured topography = surface of constant $\frac{\partial F}{\partial z}$

$$F_{tot} = F_{chem} + F_{mag} + F_{el} + F_{vdW}$$

- F_{chem}: bonding between tip and sample atoms (only for d < 5 Å)
- F_{mag}: only for magnetically sensitive tips
- $F_{el} = -\frac{1}{2}\frac{\partial C}{\partial z}V^2$
- $F_{vdW} = -\frac{HR}{6d^2}$

Dynamic Mode, non-contact

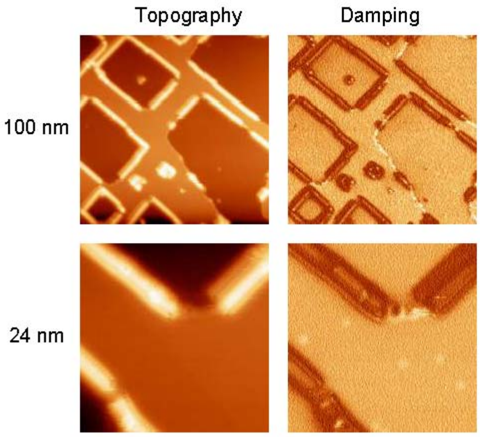


region I:
attractive forces
non-contact mode

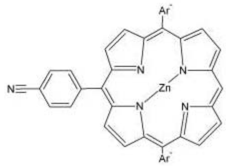
region II:
attractive forces
atomic resolution

region III:
repulsive forces
tapping mode

Molecular nanowires on KBr



- "Asymmetric" porphyrins on KBr with pits
- Straight edges are decorated
- Image height approx 1nm, Single molecules ?



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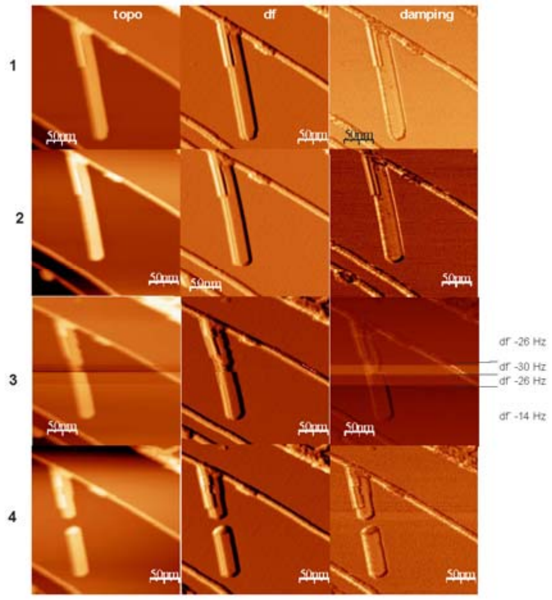
Cutting a molecular wire



Wieviel Kraft braucht man für einen molekularen Schalter?

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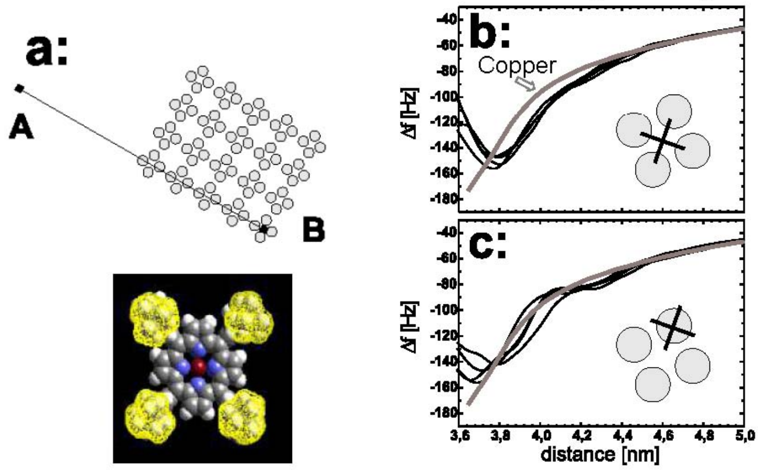
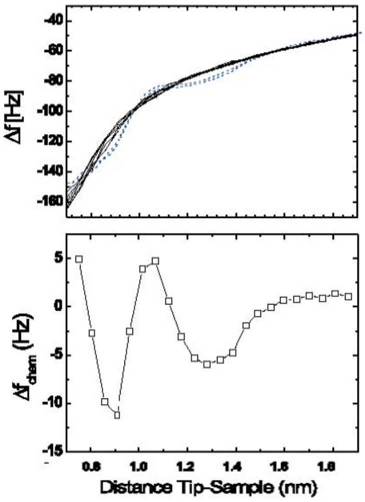
Force spectroscopy of Cu-TBPP molecules on Cu(100)



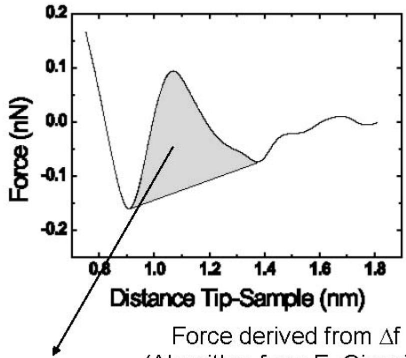
20 Curves on 4x5 Cu-TBPP island; thermal drift 5nm/h

Ch. Loppacher et al., PRL **90**, 066107 (2003)

Force spectroscopy above a leg of Cu-TBPP



Difference (Δf_{leg} - Δf_{Cu})



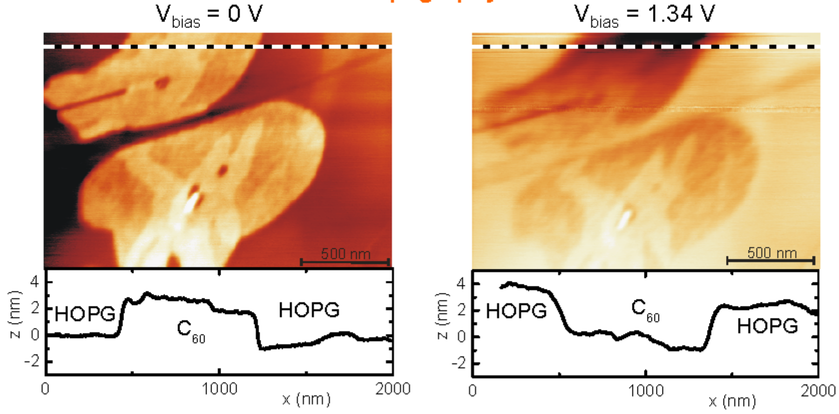
Force derived from Δf
(Algorithm from F. Giessibl)

47×10^{-21} J

P<7fW

10^{-4} switching energy
of a state-of-the-art transistor

inhomogeneous sample: HOPG + ½ monolayer C60

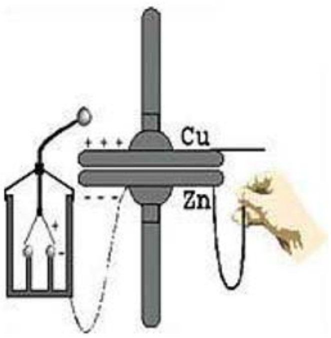


→ contrast inversal: HOPG ↔ C_{60}

S. Sadewasser et al., PRL 91 266101 (2003)

Makroskopische Kelvin-Sonde

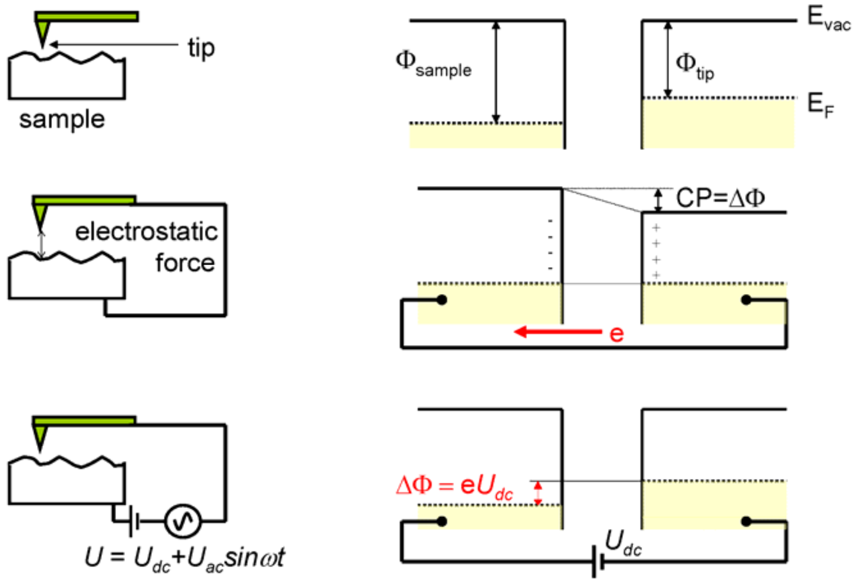
Lord Kelvin 1861



Verschiebestrom

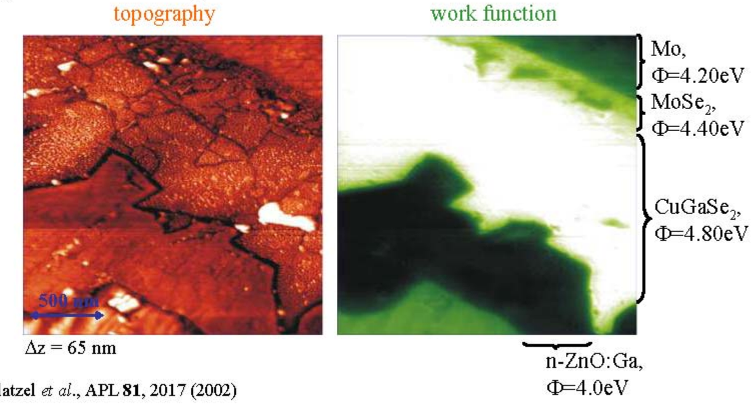
$I(t) = (U_{dc} - U_{CPD})\, f\ \Delta C \cos \omega t.$

Kelvin Principle



Polished Cross Section of a $CuGaSe_2$ Solar Cell

$CuGaSe_2$ solar cell device: V_{oc} = 820 mV, η = 4.6 %
polished and Ar-ion sputtered cross section



Glatzel *et al.*, APL **81**, 2017 (2002)

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