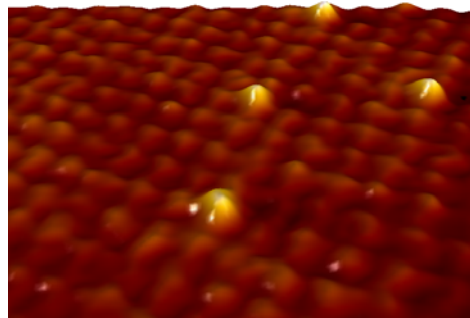


Rastersondenmikroskopie

Themen:

- Rastersondenmikroskopie (**S**canning **P**robe **M**icroscopy)
- Rastertunnelmikroskopie (**S**canning **T**unneling **M**icroscopy)
 - Prinzip und experimentelle Realisierung
 - in situ Anwendung
- Rasterkraftmikroskopie (**A**tomic **F**orce **M**icroscopy)
 - Prinzip
 - Anwendungen
 - lokale Kraftmessungen

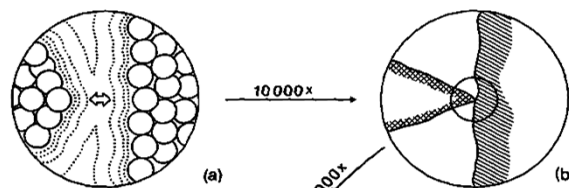


Rastersondenmikroskopie (SPM)

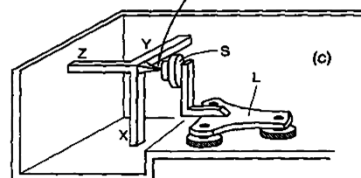
Prinzip Rastersondenmikroskopie:

Bilderzeugung über Abrastern der Oberfläche mit lokaler, abstandsempfindlicher Sonde

Abstandsmessung über lokalen Effekt mit starker Abstandsabhängigkeit

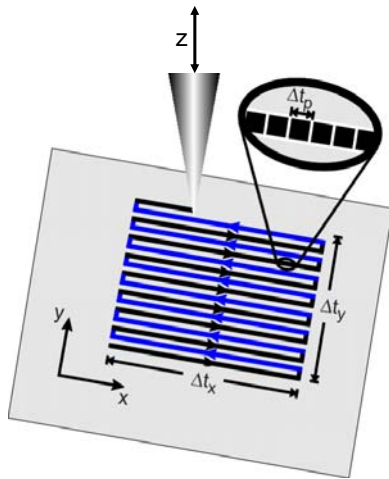


Bilderzeugung über Abrastern der Probe

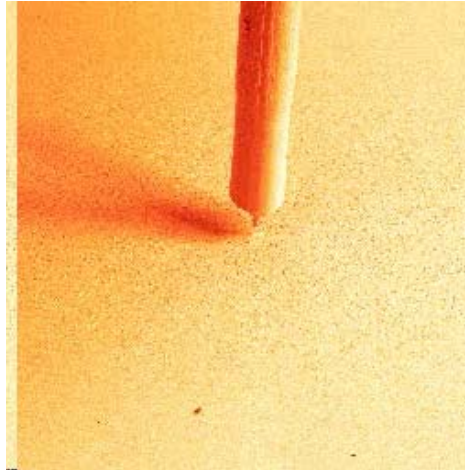


G. Binnig, H. Rohrer, *Surf. Sci.* 152/153, 17 (1985)

Rastersondenmikroskopie (SPM)

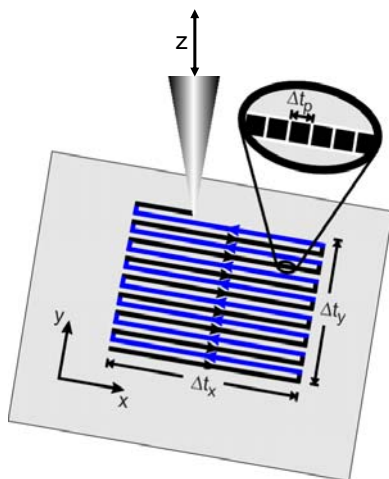


Spitzenbewegung eines Rastertunnelmikroskops während Bilderzeugung (sichtbar gemacht im Elektronenmikroskop)

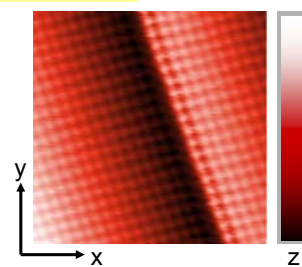


<http://www.fz-juelich.de/>

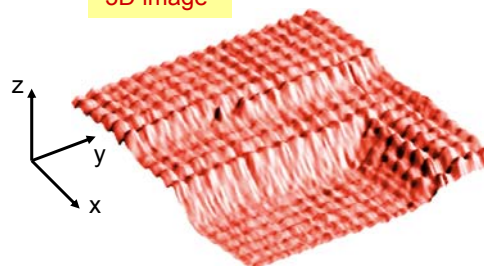
Rastersondenmikroskopie (SPM)



Topview image



3D image



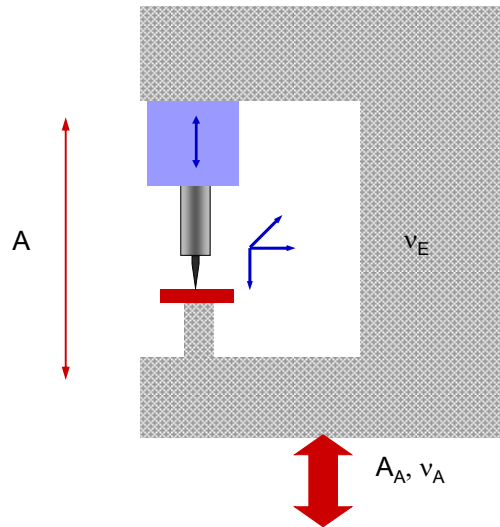
Rastersondenmikroskopie (SPM)

Mechanische Stabilität

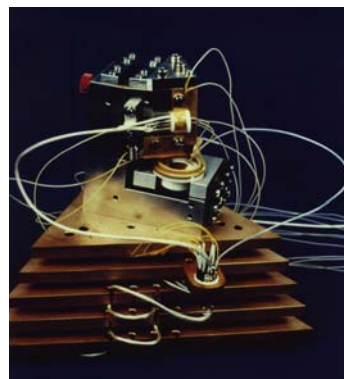
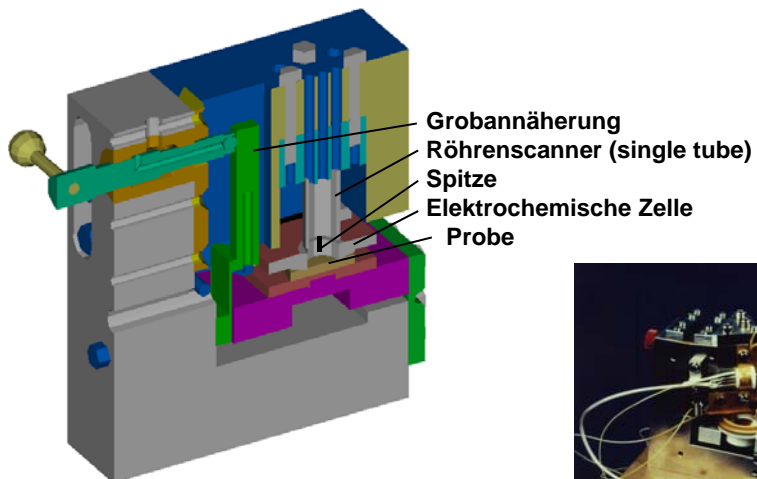
Probleme und Artefakte

- Piezo Nichtlinearitäten
- Creep
- Drift

Schematischer Aufbau

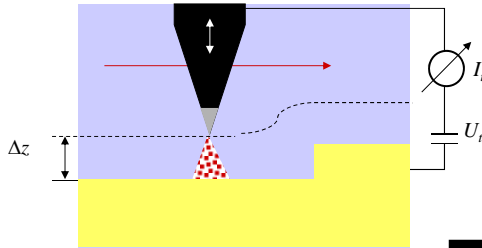


Rastersondenmikroskopie (SPM)

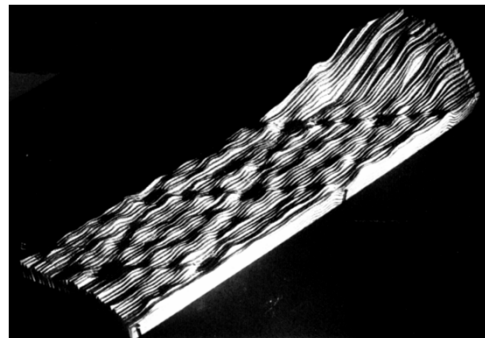
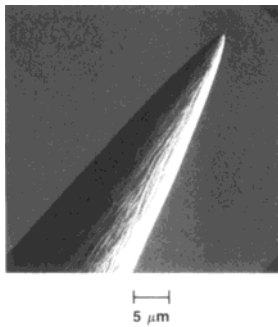


Rastertunnelmikroskopie (STM)

Prinzip: Abstandsmessung über quantenmechanischen Tunneleffekt



G. Binnig, et al.,
Phys.Rev.Lett.
50, 120 (1982)

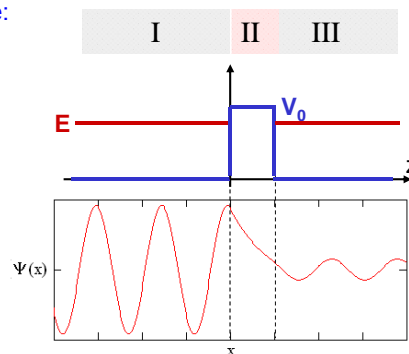


Rastertunnelmikroskopie (STM)

Prinzip: Abstandsmessung über quantenmechanischen Tunneleffekt

Elektronentransmission durch Potentialbarriere:

- Bereich I, III:
ebene Wellen
 $k = \sqrt{2mE} / \hbar$
 - Bereich II:
exponentieller Abfall
 $\alpha = \sqrt{2m(V_0 - E)} / \hbar$
- Transmission durch klassisch verbotenes Gebiet der Breite a .



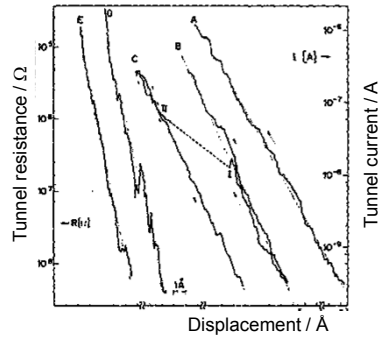
- Transmissionskoeffizient:

$$T = \frac{k \cdot |A'|^2}{k \cdot |A|^2} = \frac{1 - E/V_0}{1 - E/V_0 + (V_0/4E) \cdot \sinh^2(\alpha \cdot a)}$$

$$\approx \frac{16E}{V_0^2} (V_0 - E) \cdot e^{-2\alpha a} \quad \text{für } \alpha \cdot a \gg 1$$

Rastertunnelmikroskopie (STM)

Exponentielle Abstandsabhängigkeit



G. Binnig, *Appl. Phys. Lett.* **40**, 178 (1982)

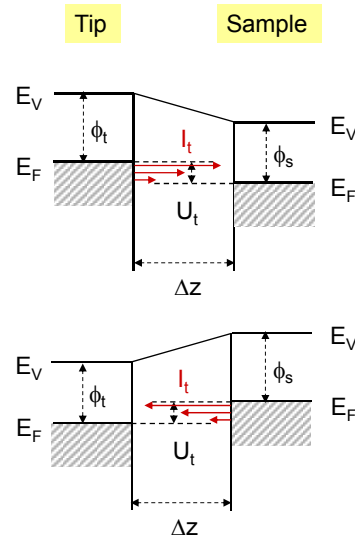
Tunnelstrom:

$$I_t \propto U_t \cdot \exp(-\text{const.} \cdot \sqrt{\phi} \cdot \Delta z)$$

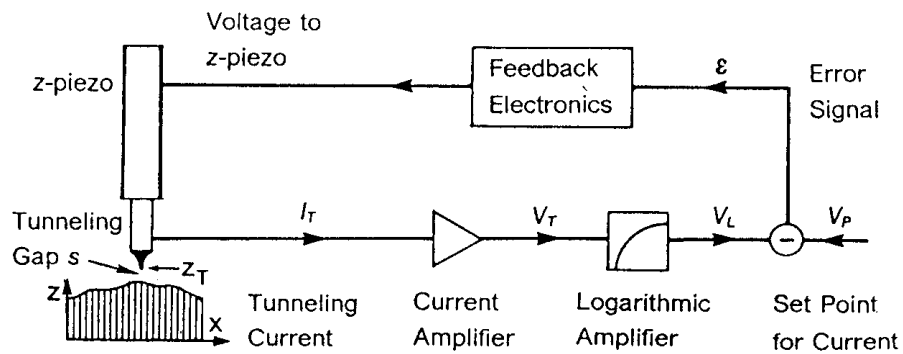
$$\text{const.} \approx 1 \text{ \AA}^{-1} \text{eV}^{-1/2}$$

ϕ = eff. Tunnelbarriere

Abhängigkeit von Tunnelspannung U_t



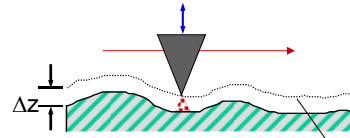
Rastertunnelmikroskopie (STM)



Rastertunnelmikroskopie (STM)

Constant Current Mode

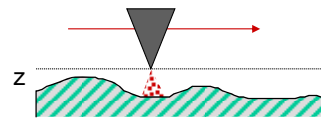
- konstanter Strom (typ. 10 pA - 10 nA)
- Feedback-kontrollierte Spitzenbewegung
- Messsignal: z-Bewegung
- Absolute Höheninformation
- langsame Spitzenbewegung



Tersoff-Hamann Modell:
Linien gleicher lokaler Zustands-
Dichte am Fermi-niveau

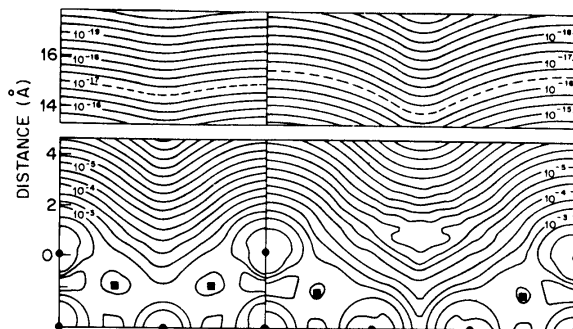
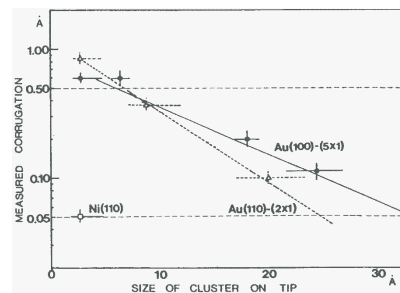
Constant Height Mode

- Feedback-Kontrolle der mittleren
Spitzenhöhe ($z = 3 - 10 \text{ \AA}$)
- Messsignal: I_t
- keine absolute Höheninformation
- schnelle Spitzenbewegung möglich
→ nur für sehr glatte Oberflächen



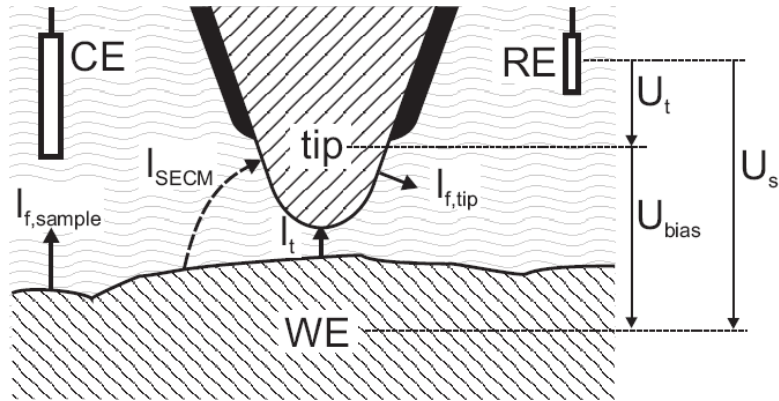
Rastertunnelmikroskopie (STM)

STM Bildkontrast nach Tersoff/Hamann
Theorie (U_t klein, Spitze = s-Orbital):
STM Bilder zeigen Linien konstanter
lokaler Zustandsdichte am Fermi-
Niveau



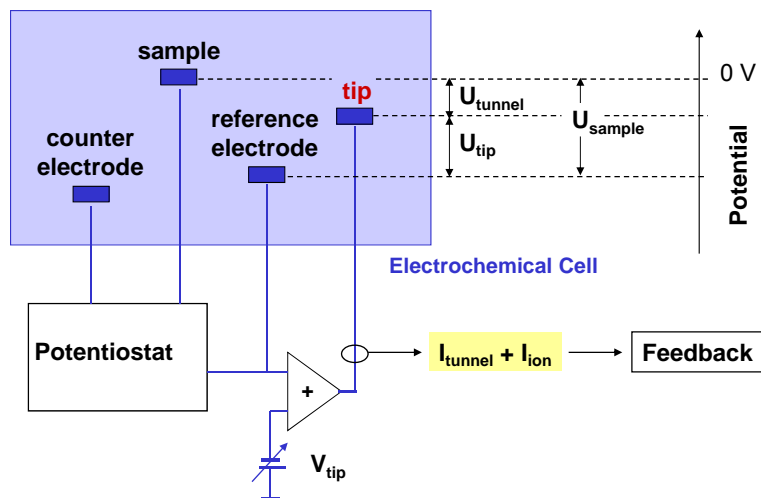
J. Tersoff and D. R. Hamann,
Phys.Rev.Lett. 50, 1998 (1983)

In-situ electrochemical STM



In-situ electrochemical STM

tip potential controlled versus electrolyte
(.Bipotentiostatic setup')



In-situ electrochemical STM: STM tips

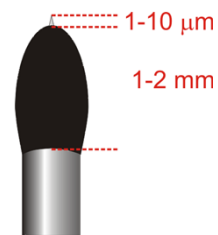
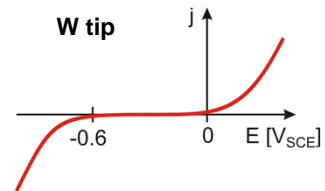
Problems:

- Faradaic processes (currents, tip changes)
- Double layer capacity (noise)

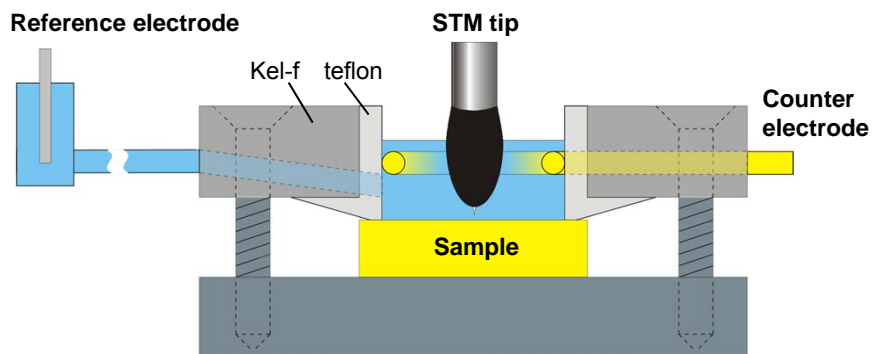
Solved by:

- controlled tip potential
- tip coating
 - apiezon wax
 - polyethylene
 - electrophoretic paints
 - glas
 - nail polish

→ faradaic currents <10 pA
tip capacitance < 10 pF



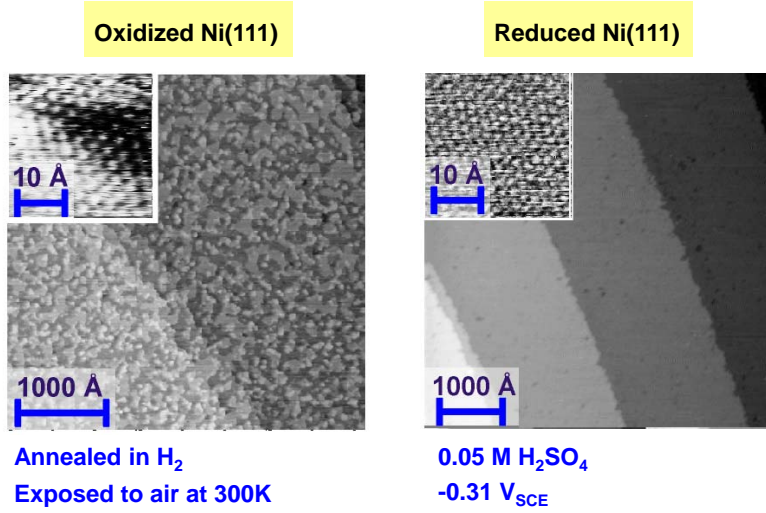
Electrochemical cells for in-situ STM



Reference electrodes:

- wire (Pt, Pd/H, Cu)
- conventional RE + liquid bridge

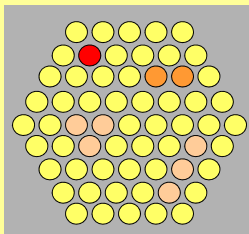
Electrode surface structure: Ni



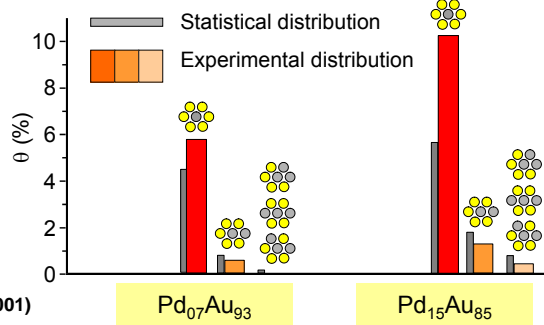
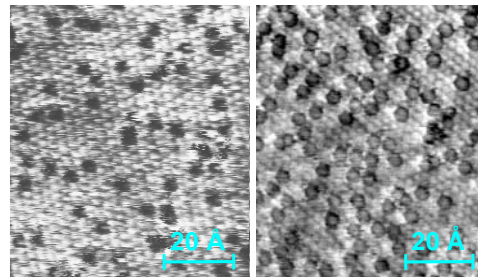
Electrode surface structure: AuPd alloy films on Au(111)

Statistical analysis of STM images:

→ surface density of Pd atom ensembles (monomers, dimers, trimers)



→ tendency towards 2D mixing

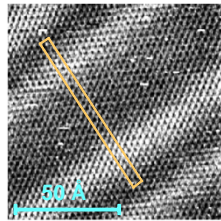
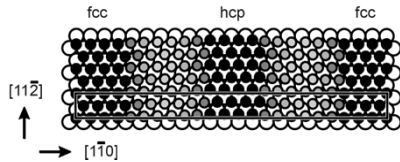


F. Maroun et al., *Science* 293, 1811 (2001)

Au(111) reconstruction

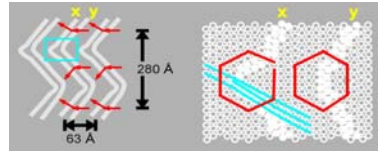
Atomic structure:

- $(\sqrt{3} \times 22)$ unit cell
- 4% uniaxial compressed surface layer
- 2 dislocations per unit cell
- fcc and hcp stacking regions



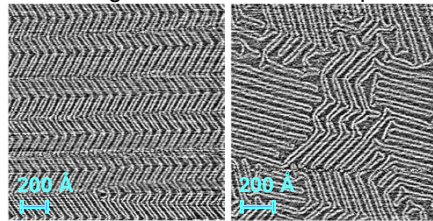
Mesoscopic structure:

rotational domains → stress relief



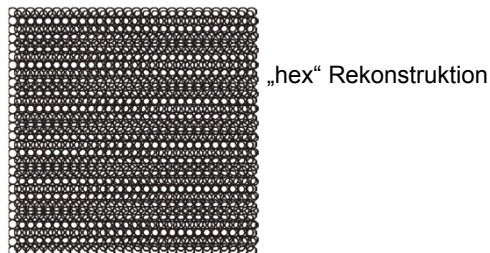
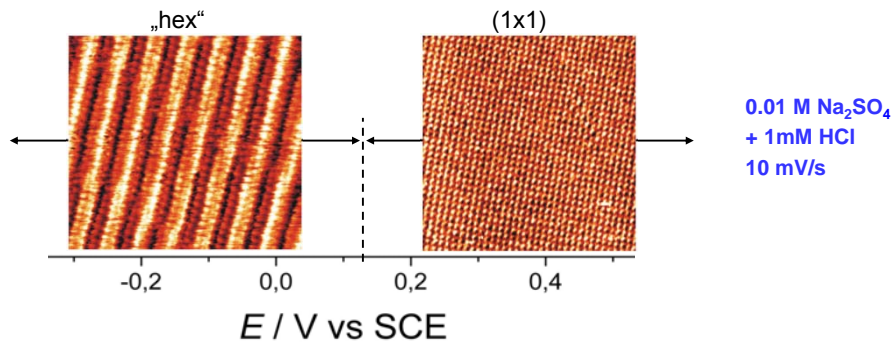
Thermal annealing
→ herringbone

Electrochemical
→ random pattern

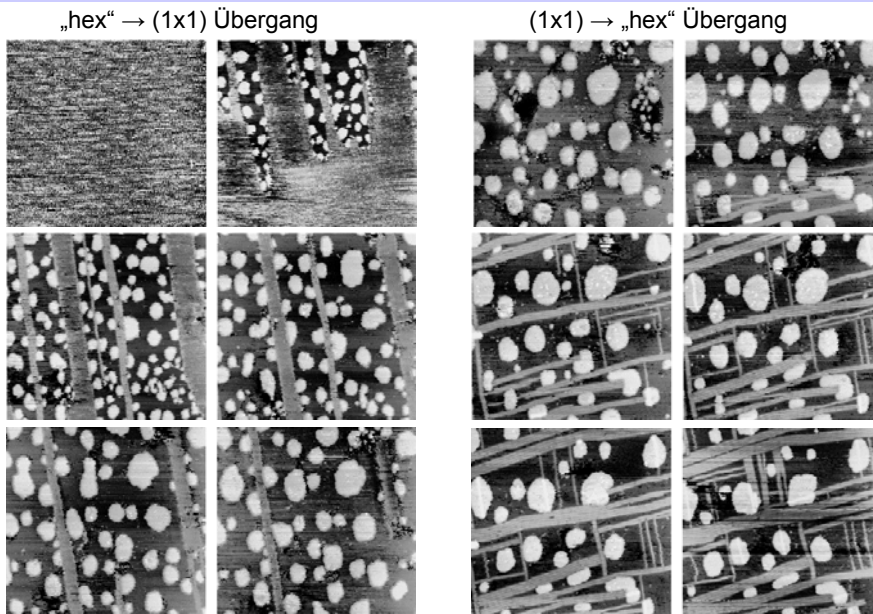


Potential-induzierte Strukturänderungen

2D Phasenübergang zwischen rekonstruierter und unrekonstruierter Au(100) Oberfläche



Potential-induzierte Strukturänderungen

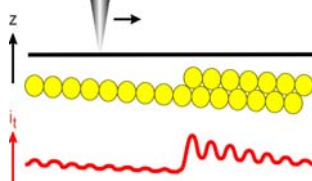


134 x 96 nm²

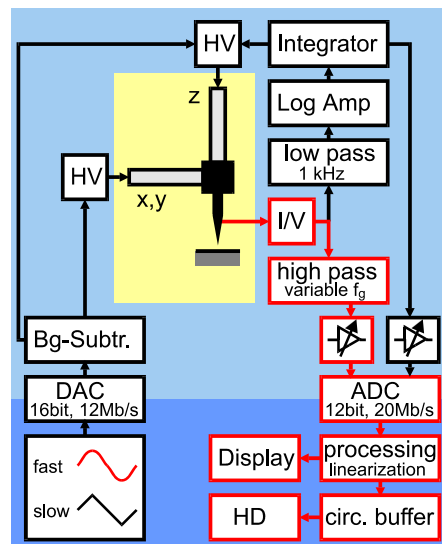
O.M. Magnussen, et al., *Surf. Sci.*, 296, 310 (1993)

Video-STM

- constant height mode (dl/dt)

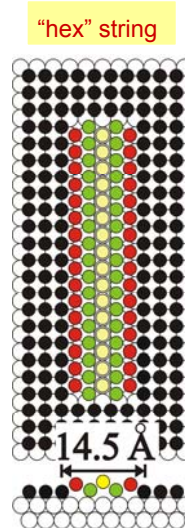
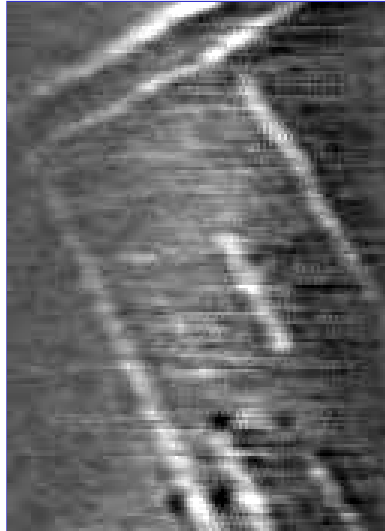


- PC-based, data-stream oriented image acquisition
- fast online-display
- sophisticated offline post-processing



Mobility of metal nanostructures

0.01 M Na₂SO₄ + 1mM HCl
-0.21 V_{SCE}
160 Å × 210 Å
20 images/s

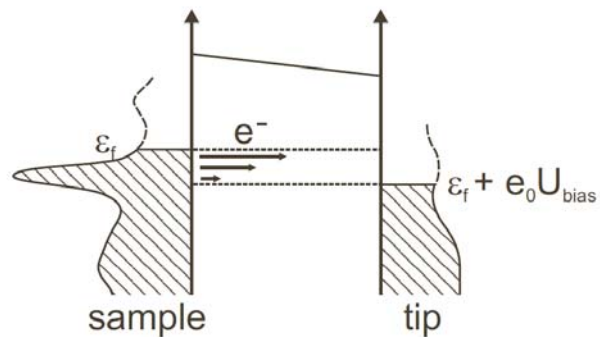


M. Labayen et al., *Nature Materials* 2, 783 (2003)

Rastertunnelspektroskopie

Tunnelstrom abhängig von:

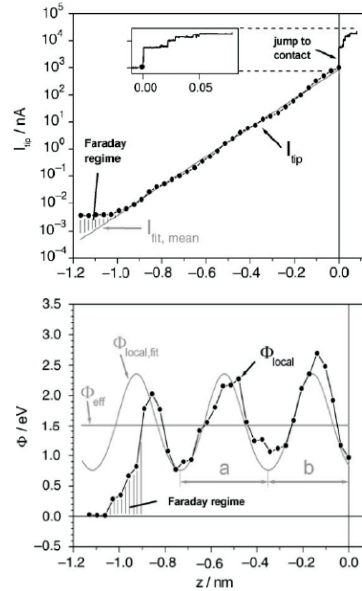
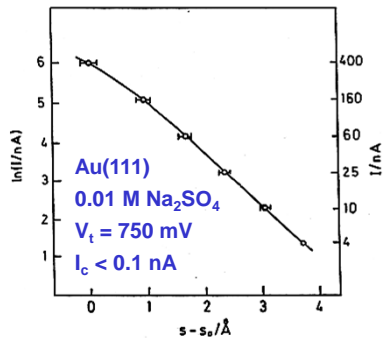
- Lokale Zustandsdichte besetzter Zustände in Probe in Energieintervall $e_0 U_{\text{bias}}$
- Lokale Zustandsdichte unbesetzter Zustände in Spitze in Energieintervall $e_0 U_{\text{bias}}$
- Lokale Tunnelwahrscheinlichkeit (\rightarrow Tunnelbarriere)



Current-distance characteristics

Tunneling barrier in electrolytes:

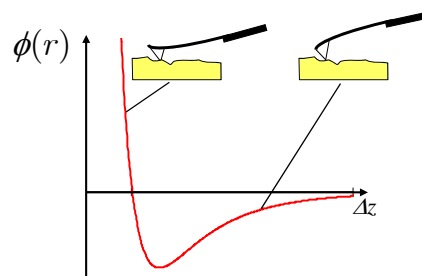
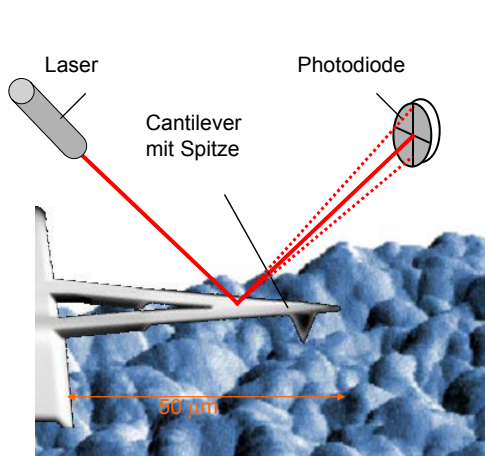
- On clean electrode surfaces $\phi^i \approx 1$ eV
- oscillations in ϕ due to liquid structure



M.Hugelmann, W.Schindler, *Surf. Sci. Lett.* 541, L643 (2003).

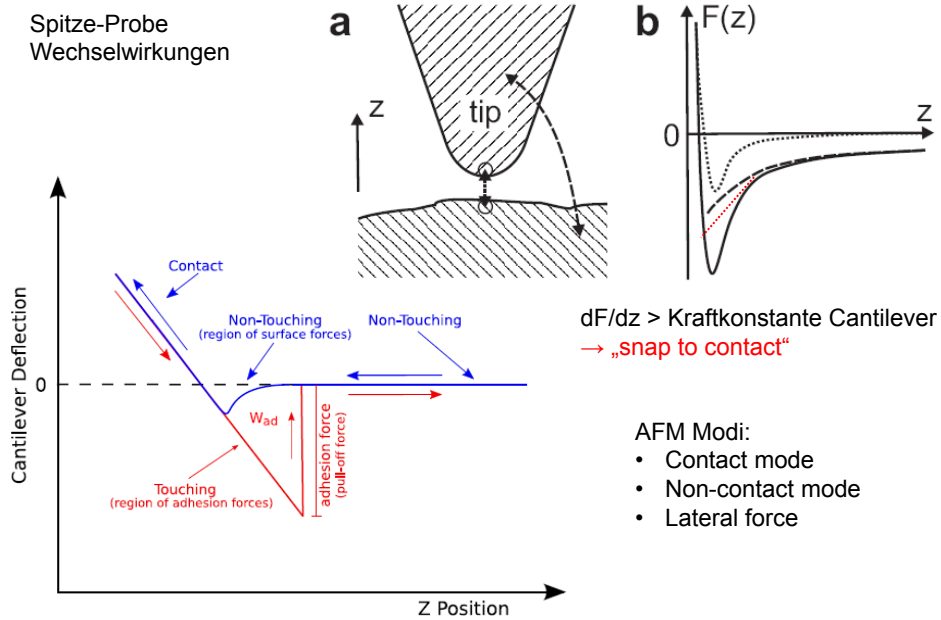
Rasterkraftmikroskopie (AFM)

AFM: Abstandsmessung über mechanische Kraft Spitze-Probe
 → Verbiegung von Federbalken („Cantilever“)



- geringere Auflösung als STM
- auch nichtleitende Substrate
- Wechselwirkungen variierbar über Modifikation der Spitze

Rasterkraftmikroskopie (AFM)



Rasterkraftmikroskopie (AFM)

Dynamische AFM Messungen:

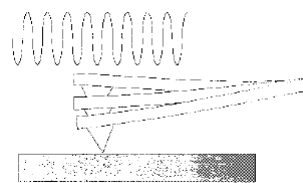
- oszillierender Cantilever
- Messung der Änderungen in Amplitude, und Phase (od. Frequenz) nahe der Probe

→ Typen:

- non-contact
- tapping-mode
- frequenzmoduliertes AFM

Vorteile:

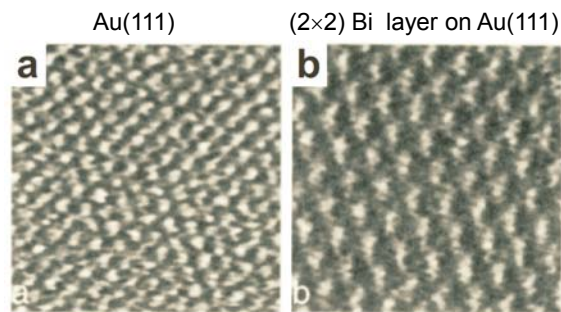
- höhere Auflösung
- Untersuchung weicherer Proben
- Sensitivität auf Materialeigenschaften (Adhäsion, Steifigkeit)



In-situ AFM at solid-liquid interfaces

In-situ AFM:

- Simple combination with electrochemical experiment
- Atomic resolution possible



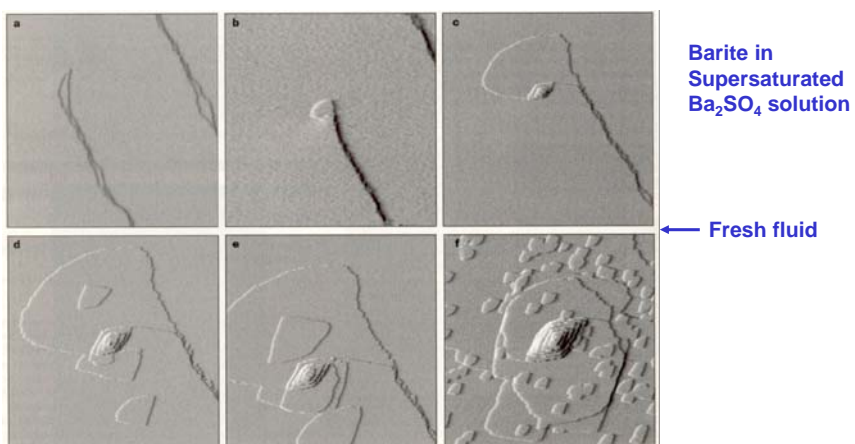
In situ contact mode AFM in 0.1 M HClO₄ solution

C.-H.Chen, A.A.Gewirth, *J. Am. Chem. Soc.* 114, 5439 (1992)

In-situ AFM at solid-liquid interfaces

In-situ AFM:

- Studies of insulators possible → studies of mineralization

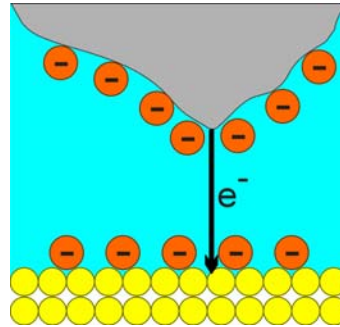


C.M. Pina, et al., *Nature* 395, 483 (1998)

Tip effects

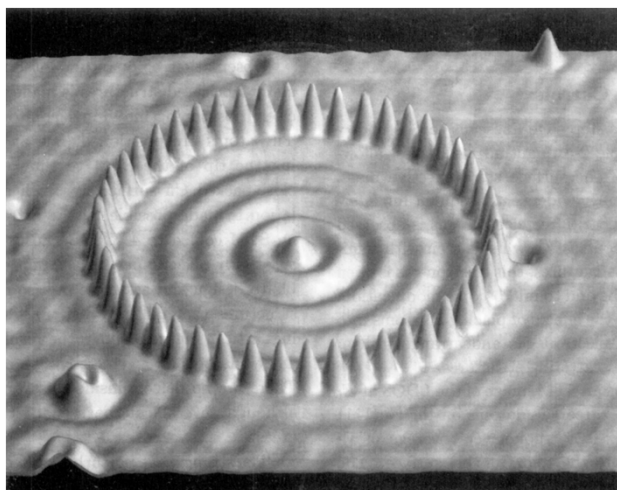
Problem: modification of structure / dynamic behavior due to presence of STM tip

- direct effects:
 - mechanical interactions (for $d_{\text{tunnel}} \ll \lambda$)
 - e_{tunnel} induced effects
 - exchange processes between tip and sample
- electrostatic effects (for $d_{\text{tunnel}} < d_{\text{DL, tip}} + d_{\text{DL, sample}}$)
- geometric effects (shielding, accumulation) for processes involving exchange with solution



Spectroscopy of STM-made nanostructures

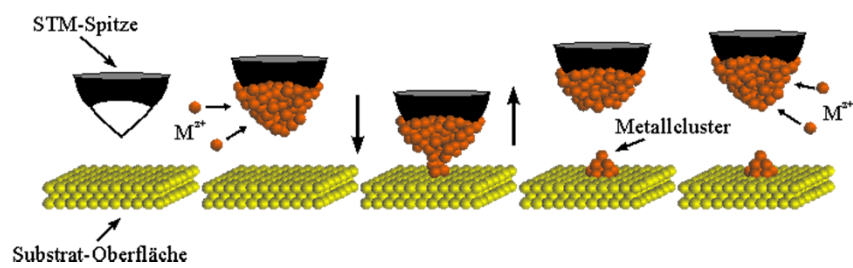
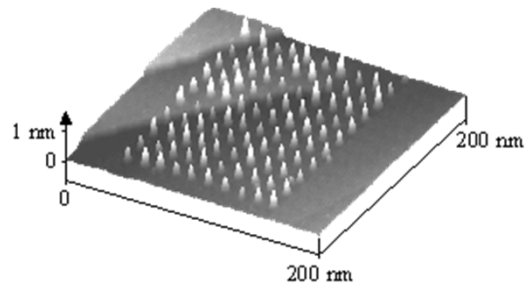
Electron standing waves in artificial quantum corrals



F.C. Crommie, et al., *Science* 263, 218 (1999)

Nanostructure formation: Cu / Au(111)

- Electrochemical deposition on tip
- Mechanical contact → neck formation and breaking



D.M. Kolb, et al., *Science* 275, 1097 (1997)