## IMAGING / MICROSCOPY ONE GRAIN OF SAND TOUCHES ANOTHER

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TDM

## **Repetition VII**

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



### **Scanning Tunneling Microscopy**



=> sensitivity to local electronic structure of the sample



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=> sensitivity to local electronic structure of the sample

# Chemical Sensitivity in STM: surface states vs image states



# Chemical Sensitivity in STM: surface states vs image states







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

## **Bildladungspotential ueber leitender Oberflaeche**



a) idealer Leiterb) hohe Stufendichtec) Potentialverschiebung im STM



## **Scanning Tunneling Microscopy**



=> sensitivity to local electronic structure of the sample



### **Molecular Motion Constrained to Two Dimensions**

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



Molecular structure influences: STM - Contrast DE Adsorption Mobility



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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).

## Stufenzustaende und Oberflaechenzustaende auf W(331)



## Dimensionalitaet 3D(bulk) – 2D (flaeche) – 1D (draht) – 0D (punkt)

- Wachstumsverhalten
- Elektronische Zustaende
- ... andere kooperative Phaenomene



## **Scientific Background: Chemical Imaging**





Chemical imaging of insulators by STM J. Viernow et al., *Phys Rev. B 59 (1999) 10356* 

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

CaF<sub>2</sub> nanowires' and 'dots' can be produced by combination of:

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



Self organised Growth of CaF<sub>2</sub> on Si(111) J. Viernow et al., *Appl.Phys.Lett.* **72** (1998) 948 J.-L. Lin et al., *J.Appl.Phys.* **84** (1998) 255

## **One-dimensional confinement of molecules via selective adsorption**



 $CaF_2 / CaF_1$  wires

After deposition of DPP molecules

After subsequent annealing

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

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## **One-dimensional confinement of molecules via selective adsorption**





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

N NANO



#### sublimation of NaCl

- Evaporator rate ~ 1 Å / min
- Substrate temperature ~ 400 K



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

## sublimation of Mg in oxygen background

- Evaporator rate ~ 1 Å / min
- Substrate temperature ~ 500 K
- oxygen 1·10<sup>-6</sup> mbar



S. Schintke, Seminar @ MIT, April 2006



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)

S. Schintke, Seminar @ MIT, April 2006



U N I B A S E L

## **NaCl layers**



NaCl on Ag(111) 1.25 μm x 1.25 μm



3

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<sub>0</sub> = 5.65 Å

## **CuOEP on NaCl/Metal**



#### Substrate

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

#### Molecule deposition: sublimation

- Evaporation rate ~ 1-2 Å / min
- Substrate temperature ~ 300 K



#### copper(II) octaethyl-porphyrin (CuOEP)



S. Schintke, Seminar @ MIT, April 2006



## **CuOEP Self-Assembly on Salt**



	model	experiment
$\mathbf{v}_1$	14.6 Å	$14.3$ $\pm$ 0.3 Å
$v_2$	13.5 Å	$13.5\pm0.3$ Å
$\alpha$	$68.2^{\circ}$	$69.0 \pm 1^{\circ}$

L. Ramoino, M. von Arx, S. Schintke et al. Chem. Phys. Lett. **417**, 22 (2006)

#### CuOEP on NaCl/Ag(111)



15 × 15 nm, U = -0.25 V, I = 81 pA



S. Schintke, Seminar @ MIT, April 2006



## **CuOEP molecules on metal and NaCl/metal**



BASE



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



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

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





## **Bias dependence: CuOEP on NaCl/Pd(111)**

S. Schintke et al. submitted (2007)



15 x 15 nm

Small broadening of the HOMO on NaCl

=> confirming decoupling from metal

• CuOEP on Pd(111): eight lobe structure => HOMO level broadening





## Isolated molecule on ultrathin insulator CuOEP on NaCl/Pd(111)

#### S. Schintke et al. submitted (2007)



Resonant tunneling via HOMO states  $\Rightarrow$  eight lobe structure

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

2Å

2Å

Compare: simulated STM images => adsorption geometry: porphine ring towards substrate



STM-



HOMO



LUMO







## **Scanning Tunneling Microscopy**





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

=> sensitivity to local electronic structure of the sample



## **STS (scanning tunneling spectroscopy)**



## Density of States (DOS)



Density of States (DOS), N(E) is the number of energy levels 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  $\mathsf{E}_{\mathsf{q}}$ 





## Voltage dependence of tunneling current



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

$$I \propto \int_{0}^{eV} N_1(E) N_2(E - eV) T(E, V) dE$$

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

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

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





## Spektroskopie



#### Spektroskopie

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

Information über lokale elektronische Zustandsdichten N(E) enthalten in

I/U



 $\frac{dI/dU}{\frac{dI}{dU}/\frac{I}{U}} = \frac{d\ln I}{d\ln U}$ CCT's mit +U und -U

Stabilisierungsspannung  $U_0$  und U sind Parameter

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





## 2. STM beyond imaging



- STM a tool for nanofabrication: Adsorbate manipulation

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





### **Tip-sample interaction**





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



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#### Tip-sample interaction

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ANOSCIENCE

INSTITUTE





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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#### Déplacer des atomes ou molécules



Animations: H. Hidber, Université de Bâle





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#### **Quantum Corral**

...











## Oberflächenzustände auf Cu(111)









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#### "Confined electrons"





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



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## Construction of exciting molecular cascades at IBM Almaden



•3-input sorter cascade with electrical schematic •AND Gate T. A. Jung SPM Tutorial

#### **Atomic Scale Memory at a Silicon Surface**

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



10nm

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

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





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

#### **Molecular Positioning**

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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  $[1\overline{1}0]$  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)

#### **Reversible 2D Phase Transition controlled by the STM tip**





#### SWISS NANOSCIENCE

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

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#### **SubPc Adsorption Geometry**



Ag(111)

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





#### Microscopic Model



#### Model Tip Induced Diffusion

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



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



Induced diffusion due to electric field: Stroscio & Eigler, Science **254** (1991) 1319 © Prof. Dr. S. Schintke, HEIG-VD & Prof. MingQar& FSQTAS Jurf. Sci. **395** (1998) 342 Nanolab, Uni Basel

## AFM - "Hands & Eyes"



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## **Cantilever with integrated Tip**



#### 50 micrometers

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## Examples



### "Screw Dislocation" on High Tc YBCO

~ 400 nm diameter





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#### **DNA-Molecule**



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



#### Scanning X Microscopy S Tunneling M S Force M



#### Force between two atoms



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

## **Sensing Forces**





1 nm<sup>3</sup> water (33 molecules) 0.01 g  $F_{G}=10^{-23} N = 10^{-14} nN$   $F= 0.1 mN = 10^{5} nN$ 

## Principle of First Atomic Force Microscope





#### **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<sub>2</sub>O) = 0.074N/m *R*=100nm Contact angle foir hydrophilic surfaces  $\Theta \approx 0^{\circ}$ 

 $\Rightarrow$  F<sub>max</sub> = 90nN



# 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 ( $\epsilon_s$ -1)(  $\epsilon_t$ -1)/ [( $\epsilon_t$ +1)(  $\epsilon_t$ +2)] K=1.41eV

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

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

graphite-graphite	8 n N
diamond-diamond	17 n N
m etal-graphite	10 n N
SiO <sub>2</sub> -graphite	1.2 n N



## 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.







F(d): Interaction force between tip and sample

d: tip sample distance

k: spring constant of cantilever



#### Contact area

The contact area is given by

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

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



Steps on NaCI: 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<sub>60</sub>-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
- $\Rightarrow$  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



# "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





1000 nm

### breaking off and removing nanotowers

# Lateral force measurement



# Lateral forces during fracture



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# Atomic-scale stick-slip



⇒See part II

# Friction contrast



Topography

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

Lateral Force

2.8x2.8µm<sup>2</sup>

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

# Noncontact-AFM (nc-AFM)







#### Quantitative understanding of nc-AFM



# Forces in nc-AFM

Frequency modulation:

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

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



# 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**



# 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



#### inhomogeneous sample: HOPG + 1/2 monolayer C60



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**

