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Topics in Nanotechnology – part 6

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Scanning tools for nanotechnology investigations

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Outlook

• The development of nanotechnology requires advanced tools for the nanostructure analysis

• Scanning Probe Microscopy (SPM) provide tools able to measure (quantitatively) physical properties at the very local (atomic) scale: general features of SPM

• Scanning Tunneling Microscope (STM): what is it measuring, and how?

• A few words on Scsnning Force Microscopy (AFM/SFFM,...)

• How the excellent space control achieved in SPM can be used for *nanomanipulation* (i.e., nanofabrication or nanostructuring purposes): a few examples

Need for highly detailed investigation tools

- Due to diffraction, optical methods fail in poviding the required space resolution
- Nanometer or even sub-nanometer resolution can be achieved by using electron microscopy (SEM, TEM)

BUT

- Contrast mechanism in electron microscopy are often indirect (they imply many effects)
- Morphology can be quantitatively derived only for the in-plane features (poor info on the relative height)
- Samples must be frequently prepared (made conductive, cut in thin slices,...)
- Specific physical quantities (e.g., the local density of states, the magnetic or electical polarization,...) cannot be directly measured

Ability to measure local ("point") physical quantities is required to investigate nanotechnolgoy products

Basics of Scanning Probe Microscopy (SPM)

Scanning: piezoelectric translator Probe: tip probing local properties Microscopy: sub-micrometer resolution (+ system to control tip/sample distance + electronics for instrument operation)

Developed starting since '80s thanks to:

Piezo translators with sub-nm resolution;
sub-nm probes



Various physical quantities can be measured point-by-point during the scan and an image (i.e., a map of the quantity) can be built

A few examples of SPMs



Depending on the probe and on its interaction with the surface, a variety of quantities can be investigated

A few details: piezoelectric scanner



Basics of Scanning Tunneling Microscopy



- \checkmark Probe is a conductive tip
- ✓ Sample (surface) is mostly conductive or semiconductive
- \checkmark A bias voltage is applied between sample and tip
- \checkmark Tip is kept at small distance from the surface (typ < 1 nm)
- ✓ Tunneling current (typ in the pA range) is measured

STM tip (probe) preparation



Fig. 4.12. (a) Schematic diagram of the electrochemical cell showing the tungsten wire (anode) being etched in NaOH. The cathode consists of a stainless-steel cylinder which surrounds the anode. (b) Sketch of the etching mechanism showing the "flow" of the tungstate anion down the sides of wire in solution [4.13]

| cathode: | 6H2O + 6e- | \rightarrow 3H ₂ (g) + 60H ⁻ | SRP = -2.45 V |
|----------|-------------|--|---------------|
| anode: | W(s) + 80H- | $\rightarrow \mathrm{WO_4^2} + 4\mathrm{H_2O} + 6\mathrm{e^-}$ | SOP = +1.05 V |

 $W(s) + 2OH^- + 2H_2O \rightarrow WO_4^2 + 3H_2(g)$ $E^0 = -1.43 V$.

Electrochemical etching of W or Pt/Ir typ used



Tunneling current

2.1. Electron Tunneling



The probability of finding an electron behind the barrier of the width d is $W(d) = |\Psi(d)|^2 = |\Psi(0)|^2 e^{-2\kappa \delta}$

Exponential decrease

In scanning tunnneling microscopy a small bias voltage V is applied so that due to the electric field the tunneling of electrons results in a tunneling current I. The height of the barrier can roughly be approximated by the average workfunction of sample and tip. $\Phi = 1/2(\Phi_{supple} + \Phi_{tip})$

If the voltage is much smaller than the workfunction eV << 0, the inverse decay length for all tunneling electrons can be simplified to

$$\kappa \approx \frac{\sqrt{2m\Phi}}{\hbar}$$

The current is proportional to the probability of electrons to tunnel through the barrier:

$$I \propto \sum_{E_n = E_{F} = V}^{E_{F}} \left| \Psi_n(0) \right|^2 e^{-2\kappa d}$$

By using the definition of the local density of states for $\epsilon \rightarrow 0$

$$\rho(z, E) \equiv \frac{1}{\epsilon} \sum_{E_{n} = E - \epsilon}^{E} \left| \Psi_{n}(z) \right|^{2}$$

the current can be expressed by

 $I \propto V \rho_{sa}(0, E_F) e^{-2\kappa d}$ $= V\rho_{ss}(0, E_F)e^{-i.025\sqrt{\Phi}d}$ where $[d] = \mathring{A}; [\Phi] = eV;$

With 5eV as typical example for a workfunction value a change of 1Å in distance causes a change of nearly one order of magnitude in current. This facilitates the high vertical resolution.

Also

$$I \propto V \rho_{rs}(d, E_F)$$

which means that the current is proportional to the local density of states of the sample at the Fermi energy at a distance d, i.e. the position of the tip.

A more exact calculation of the current density of the square barrier problem requires the Schrödinger's equation to be solved in the three regions: before, in and behind the barrier The coefficients have to be adapted so that the overall solution is continually differentiable Defining the transition probability as

$$T = \frac{J_T}{j_i}$$

vields

$$T = \frac{16E(V-E)}{V^2} e^{-2z\delta};$$

 $\kappa = \sqrt{\frac{2m(V-E)}{\hbar^2}}$

with the approximation $\kappa d >> 1$.

The current density itself is defined as

$$\mathbf{j}_{z} = -\frac{\mathrm{i}\hbar}{2\mathrm{m}} \left(\Psi^{*}(z) \frac{\mathrm{d}\Psi}{\mathrm{d}z} - \Psi(z) \frac{\mathrm{d}\Psi^{*}}{\mathrm{d}z} \right)$$

For a nonsquare potential the WKB method must be used. This is more adequate as the potential is changed by the applied voltage and influenced by the image force on the electron. The WKB method yields a transition probability of

$$T(E) \propto \exp\left(-\frac{2}{\hbar}\int_{0}^{1}\sqrt{2mV(z)-E}dz\right)$$

Modes of operation in STM



2.2 Operating Modes of the Scanning Tunneling Microscope

Up to now, the theoretical background of a scanning tunnelling microscope has been presented, but nothing has been said about the experimental operation of a scanning tunnelling microscope. The simplest way to obtain a scanning tunnelling microscope image is to directly measure the variation of the tunnel current as a function of the scanning position while keeping the distance between tip and sample surface constant. A so-called current image is then obtained. Instead of directly recording the atomic variation of the current, however, the usual procedure is to keep the tunnel current constant while scanning over the surface. This is done by changing the distance between tip and surface using a feedback loop (Figure 8). In order to got an image, the voltage required at the piezoelectric crystal to adjust the distance is recorded. One obtains a so-called constant-current STM image.

Feedback loop used to keep constant the tunneling current => "absolute" topography map



Fig. 1.2a,b. Schematic view of two modes of operation in STM [1, 10]. S is the gap between the tip and the sample. I and V_T are the tunneling current and bias voltage, respectively, and V_z is the feedback voltage controlling the tip height along the z direction. (a) constant-current mode and (b) constant-height mode



Fig. 4.27. Block diagram of the STM control, data acquisition and display system indicating all of the equipment connections

2.2. Bardeen Approach Bardeen (quantum) approach to tunneling

Another way of describing electron tunneling comes from Bardeen's approach which makes use of the time dependent perturbation theory. The probability of an electron in the state $\Psi_{at} \stackrel{E_{\Psi}}{\to} to tunnel$

into a state
$$\times \operatorname{at}^{\mathbf{E}_{\mathbf{x}}}$$
 is given by Fermi's Golden Rule

$$\mathbf{w} = \frac{2\pi}{\hbar} |\mathbf{M}|^2 \delta(\mathbf{E}_{\psi} - \mathbf{E}_{\chi})$$

Quantum mech. Treatment

The tunneling matrix element is given by an integral over a surface in the barrier region lying between the tip and the sample:

$$M = \frac{\hbar}{2m} \int_{z=z_0} \left(\chi^* \frac{\partial \Psi}{\partial z} - \Psi \frac{\partial \chi^*}{\partial z} \right) dS$$

Applying a bias voltage V and approximating the Fermi distribution as a step function (kT $\ll \Delta$ $E_{modulion}$), the current is

$$I = \frac{4\pi}{\hbar} \int_{0}^{e^{v}} \rho_{sa} (E_{F} - eV + \varepsilon) \rho_{sp} (E_{F} + \varepsilon) |M|^{2} d\varepsilon \quad (**)$$

Hence the current is given by a combination of the local densities of states of the sample and the tip, weighted by the tunneling matrix element M.



naging the occupied states of C(0001)3x3

Imaging the unoccupied states of SiC(0001)3x3



 $\delta(E_{\psi} - E_{x})$ means that an electron can only tunnel if there is an unoccupied state with the same energy in the other electrode (thus inelastic tunneling is not treated). In case of a negative potential on the sample the occupied states generate the current, whereas in case of a positive bias the unoccupied states of the sample are of importance. Therefore, as shown below, by altering the voltage, a complete different image can be detected as other states contribute to the tunneling current. This is used in tunneling spectroscopy. It should finally be mentioned that the probability of tunneling (expressed by M²) is larger for electrons which are close to the fermi edge due to the lower barrier. Local density of states is actually imaged in STM

Tunneling current and STM

2.1 Theoretical Fundamentals of the Scanning Tunneling Microscope

How does a measuring instrument function that allows us to see ringle atoms. In the case of a scanning tunnelling microscope a fine metallic tip is used as the probe (called tunnelling tip) (see Figure 3). This tip is approached toward the surface until a current flows when a voltage is applied between the tip and the sample surface. This hapens at distances in the order of 1 ran. The current is called tunnel current since it is based on the quantum-mechanical tunnel effect. After a tunnelling cortact is established, the tip is moved over the surface by a plezoelectric scanning unit, whose mechanical extension can be controlled by applying appropriate voltages. The scanning unit is typically capable of scanning an area of a few turn up to several µm. This allows us to obtain a microsscopic image of the spatial variation of the tunnel current. Hence the name sconning tunnelling microscope.

- A metallic tip is moved as probe towards a conducting surface up to a distance of about 1 nm
- With an applied voltage a current flows due to the tunnel effect (tunnel current)
- The spatial variation of the tunnel current is measured by scanning over the sample surface
- A microscopic image of the surface is produced

At this stage we have to ask what kind of atomic-scale structures can be made visible by the scanning tunnelling microscope utilising the tunnel effect? These structures must by nature correspond to electrical states from or into which the electrons can tunnel. In the turnelling process, the electrons must tunnel through the vacuum barrier between tunnelling in and sample, which represents a potential barrier tunnel effect allows a particle (here an electron) to tunnel through this potential barrier even though the electron's energy is lower than the barrier height. The probability of such a process decreases exponentially with the geometrical distance between the tip and the sample and with increasing barrier beight. An experimental apparatus making use of the runnel effect must therefore minimize the potential barrier to be tunneled through. This is realised in the scanning tunnelling microscope configuration by moving the tip very close (about 1 im) to the surface. The electrons can then pass between the surface and the tunnel current is fixed by <u>applying a voltage between sample and</u>

In order to explain and interpret the images of the surface states obtained in this way, efforts to develop a theory were made very soon after the invention of the scianing tunnelling microscope. One of the possible theoretical approaches is based on Bardeen's icea of applying a transfer Hamiltonian operator to the tunnelling process [2]. This had the advantage of adequately describing the many-particle nature of the tunnel junction. In the model, a weak overlap of the wave functions of the surface states of the two electrodes (tunnelling tip and sample surface) is assumed to allow a perturbation calculation. On this basis, Tersoff and Hamaan developed a <u>simple theory</u> of scanning tunnelling microscopy [3], [4] Hence follows the tunnel current:

 $T \sim V \cdot \rho_{tip}(W_E) \cdot \rho_{kample}(n_1, W_F)$

The tunnelling tip is assumed to be a metallic s-orbital as shown schematically in Figure 4. In addition, it is assumed that (ow voltages $f(), c_n$, much smaller than the work function) are applied. $\mu_{app}(W_F)$ is the density of states of the tip and $\mu_{approx}(r_0, W_F)$ is that of the sample surface at the centre r_0 of the tip orbital and at the Fermi energy W_F Eq. (1) shows that at low voltage the scanning tunnelling microscope thus images the electronic density of states at the sample surface near the Fermi energy. However, this result also means that the scanning tunnelling microscope images do not directly show the atoms, but rather the electronic states bound to the atoms, as can be seen in Eq. (1), the tips density of states in the measurement in the same way as the density of states of the simple. It is therefore desirable to know the exact electronic state of the tip, but unfortunately, in practice, every tip is different and the details remain unknown.

- Weak overlap of the wave functions of the surface states of the two electrodes (tunnelling tip and sample surface)
- Tunnelling tip approximated as an s-orbital
- Low voltages (V ≪ work function)



Figure 4: Schematic representation of the tunnelling geometry in the Tersoff-Hamann model.



(1)

Figure 5t At high voltages not only the states near the Fermi energy W_1 contribute to the current but all states whose energy ranges between W_2 and $W_1 + eV$.



- · The tunnel current is proportional to the local density of states of the sample
- The scanning tunnelling microscope images the electronic local density of states of the sample near the Fermi energy.

In a first approximation the density of surface states decreases exponentially into the vacuum with the effective inverse decay length k_{eff}

$$k_{\rm eff} = \sqrt{\frac{2m_{\rm e}B}{\hbar^2} + |k_{\rm u}|^2} \tag{2}$$

 m_e is the electron mass and k_1 is the parallel wave vector of the tunnelling electrons. *B* is the barrier height, which is approximately a function of the applied voltage *V* and the work functions Φ_{unref} and ϕ_{in} of the sample and tip [5], respectively:

$$B = \frac{\Phi_{tip} + \Phi_{sample}}{2} - \frac{|eV|}{2}$$
(3)

The tunnel current thus decreases exponentially with the tip-sample distance z:

$$(1 - exp \left| -2k_{\text{eff}} z \right|$$
(4)

The exponential current-voltage dependence is quite essential for the high measurement accuracy of a scanning tunnelling microscope, since even small changes in distance may cause a large change in the tunnel current. Thus the tip just meeds one microtip, which is only about 0.1 nm closer to the surface than the next one, and still all current flows over only the closest microtip. Thus even apparently wide tips can yield atomic resolution via one microtip.

The description of the tunnel current by Eq. (1) however, has an important restriction; it strictly speaking only applies & low voltages [2] in particular for the investigation of semiconductor surfaces voltages of the order of 2 in 3 V are required due to the existence of a band gap. Thus the theory must be extended. The simplest extension yields:

 $\underline{T(W,V)}$ is a transmission coefficient which depends on the energy of the electrons and the applied voltage. The tunnel current is composed of the product of the density of states of the tip and sample at all the different electron energies that are allowed to participate in the tunnelling process (Figure 5). For example, an image measured at -2 V applied to the sample, consequently shows all occupied sample states with an energy between the Fermi energy and 2 eV below the Fermi energy. Tunnelling at a positive voltages analogously provides a measurement of the empty surface states in an energy interval determined again by the voltage.

In order to illustrate this effect more clearly, in the following the InP(110) surface will be presented. On InP(110) surfaces two electrical states exist near the surface in occupied state below the valence band edge and an empty state above the conduction band edge (Figure 6). All the other states are located geometrically deeper in the crystal or emergetically deeper in the bands. They thus contribute little to the tunnel current.

Da R. Waser Ed., Nanoelectronics and information technology (Wiley-VCH, 2003)

Lateral resolution in STM

d=6Å

Tip

2.3. Lateral resolution

The lateral resolution of STM can not be understood in terms of a Fraunhofer diffraction resolution. The corresponding wave length of the tunneling electron would be $\lambda > 10$ Å. Therefore the STM works in the near-field regime. The overall geometric curvature of the tip with a radius of curvature of e.g. 1000 Å and $\kappa = 1$ Å⁻¹ would give rise to a resolution of about 50 Å.

The actual atomic resolution can only be understood in a quantum mechanical view: The most prominent model in this respect is the **s-wave-tip model**. The tip is regarded as a protuding piece of Sommerfeld metal with a Radius of curvature R (see Figure). It is assumed that only the s-wave solutions of this quantum mechanical problem (spherical potential well) are important. Thus, at low bias the tunneling current is proportional to the local density of states at the center of cuvature of the tip I₀:

$$I \varpropto \sum_{E_{\mu} = E_{\mu} \rightarrow V}^{E_{\mu}} \left| \Psi_{\mu}(\mathbf{r}_{0}) \right|^{2} = eV\rho_{sa}(\mathbf{r}_{0}, E_{F})$$

In this model only the properties of the sample contribute to the STM image which is quite easy to handle. But it cannot explain the atomic resolution.



Calculations and experiments showed that there is often a d22 like state near the fermi edge present at the apex atom which also predominantely contributes to the tunneling current. It is understood that this state (and also the p, like state) is advantageous for a "sharp,, tip. Since the tunneling current is a convolution of the tip state and the sample state, there is a symmetry between both: By interchanging the electronic state of the tip and the sample state, the image should be the same (reciprocity principle). This can also explain the fact that the corrugation amplitude of an STM image is often larger than that of the LDOS of the sample (measured by helium scattering). In this case the tip traces a fictitious surface with a d2² like state. The state of the tip atom is dependent on the material and the orientation. As the tip is quite difficult to handle, it is one of the most difficult problems in a STM experiment.



Fig. 1. 1. Comparison of the resolution range of STM with that of other microscopes [1, 1]. [HM: High-resolution optical Microscope. PCM: Phase Contrast Microscope. (S)TEM: (Scanning) Transmission Electron Microscope. FIM: Field Ion Microscope. REM: Reflection Electron Microscope]

"Atomic" resolution achieved in STM

Atomic resolution in STM

(Highly Oriented Pyrolithic) Graphite substrates well suited as test samples



Bias polarity-related contrast mechanisms





located above the P atoms, whereas the empty state is bound to the In atoms (Figure 7a,b). The P and In atoms are alternately arranged in zigzag rows. At negative sample voltages, the scanning turnelling microscope probes the occupied states located at the P sublattice, whose electrons tunnel into the empty states of the tunnelling tip (Figure 6a). Conversely, only the empty surface states at the In sublattice are probed at positive voltages applied to the sample (Figure 6b) [6] – [8]. If the voltage polarity is changed every scan line, i.e. the occupied and the empty states are probed each alternating scan line, the two resulting images can be superimposed and the zigzag rows of alternating "In" and "P" atoms become visible (Figure 7c).

In the special case of the InP(110) surface, the occupied surface state is spatially

Apart from the spatial distribution of the density of states, its energy dependence is also of interest, and it should be possible to determine this dependence from current-voltage characteristics using Eq. (5) In order to do so, however, information is required about the transmission coefficient, which turns out to be a great obstacle even if approximations [9] are used. Therefore, in most cases, an experimentally viable approach is used, in which the density of states is approximated as follows [10], [11];

$$\rho_{\rm sample}(eV) \approx (dUdV)/(UV)$$

(6)

It is thus possible to experimentally measure the density of states as a function of the energy relative to the Fermi level.

Figure 7:

(a) Schematic top view and
(b) side view of the (110) surfaces of
III-V compound semiconductors.
(c) Superposition of two scanning
tunnelling microscope images measured at positive (red) and negative
(green) voltage. The density of state
maxima correspond to the surface
states at the In and P atoms, respectively.

Contrast mechanisms related to bias polarity

STM spectroscopy



A few words on other SPMs



Cantilevers for the SFM (AFM)



Fig. 5.2a-d. Fabrication of thin-film microcantilevers. (a) A thin film of SiO_2 or Si_3N_4 is formed on the surface of a (100) Si wafer and patterned to define the shape of the cantilever and to create openings on the top and bottom of the wafer. (b) The windows are aligned along (111) planes. (c) Anisotropic etching of the exposed Si with KOH undercuts the cantilever and self-terminates at the (111) planes as shown. (d) A small Si chip is cut from the wafer to serve as a pedestal for mounting the cantilever in the AFM [5,4]



Fig. 5.4a-e. Fabrication of Si_3N_4 microcantilevers with integrated pyramidal tips (a) to (e) illustrate the steps in the fabrication process, see text [5,4]

Advanced microfabrication tools needed to obtain suitable probes



Fig. 5.5a-d. SEM micrographs of Si₃ N_d cantilevers with integrated pyramidal tips. (a) The Si₃ N_d film is attached to the surface of a glass block with dimensions of $2 \times 3 \times 0.7 \text{ mm}^3$. Four cantilevers protrude from the edge of the block. (b) Four pyramidal tips can be seen at the end of this V-shaped cantilever. (c) The pyramidal tips are hollow when viewed from the back side. (d) Each tip has very smooth sidewalls, and the tip appears to terminate virtually at apoint, with less than 30 nm radius [5.4]

Scanning Force Microscope (SFM) I

3.2 The Operation Principle of Scanning Force Microscope

The main electronic components of the SFM are the same as for the STM, only the topography of the scanned surface is reconstructed by analysing the deflection of the tip at the end of a spring. Today, the interferometrical and optical lever method dominate commercial SFM apparatus. The most common method for detecting the deflection of cantilever is by measuring the position of a reflected laser-beam on a photosensitive detector. The principle of this optical lever method is presented in Figure 18 a. Without

cantilever displacement both quadrants of the photodiode (A and B) have the same irradiation $P_A = P_B = P/2$ (*P* represents the total light intensity). The change of the irradiated area in the quadrants A and B is a linear function of the displacement.

$$\propto \Delta d = 2\sin\{\Theta\} \cdot S_2 = 2\Theta \cdot S_2 = 3S_2 \cdot \delta/L \tag{10}$$

For small angles $\sin(\Theta) \approx \Theta$ and Θ may be evaluated from the relation $\Theta = 3b/2L$ (Figure 18b). For $P_{\rm A}$ and $P_{\rm B}$ one would get approximately $P_{\rm A} = P/2 \cdot (d + \Delta d)/2$ and $P_{\rm B} = P/2 \cdot (d - \Delta d)/2$. Using the simple difference between $P_{\rm A}$ and $P_{\rm B}$ would lead to

 $\Delta P = P \cdot 3S \delta / (Ld)$ but in this case one cannot distinguish between the displacement δ of the cantilever and the variation in the laser power P. Hence the normalised difference is used, which is only dependent of δ :

$$\frac{P_{\rm A} - P_{\rm B}}{P_{\rm A} + P_{\rm B}} = \delta \cdot \frac{3S_2}{Ld}$$

(11)

The "lever amplification" $\Delta d/\delta = 3S_2/L$ is about a factor of one thousand. On the basis of this kind of technique one is able to detect changes in the postion of a castilever of the order of 0.01 nm.

For large distances between the tip and the sample the bending of the cantilever by attractive forces is negligible. After the cantilever is brought closer to the surface of the sample (point "a" Figure 18c) the van der Waals forces induce a strong deflection of the cantilever and, simultaneously, the cantilever is moving towards the surface. This increases the forces on the cantilever, which is a kind of positive feedback and brings the cantilever to a direct contact with the sample surface (point "b"). However, when the cantilever is brought even closer in contact to the sample, it actually begins to bend in the opposite direction as a result of a repulsive interaction ("b-c"). In the range ("b-c") the position of the laser beam on both quadrants, which is proportional to the force, is a linear function of distance. On reversal this characteristic shows a hysteresis, bhis means that the cantilever loses contact with the surface a distance (point "d") which is much larger than the distance on approaching the surface (point "a").

Up to now, the actual probe, i.e. the tip of the leaf spring, has not been discussed in detail. Its preparation is particularly demanding since the tip and the sensitive spring should be one piece. Moreover, the cantilever should be as small as possible. Nowadays, such scanning tips are commercially available (in contrast to the tunnelling tips, which you should prepare yourself). Figure 19 shows such a spring with tip (cantilever) made of Si. The characteristic parameters of a cantilever has been presented in Figure 18b. The spring constant $k = Ead_{L}^{2}/4L^{2} \sim 0.1 - 10$ N/m of the cantilever enables topographical analysis with atomic resolution.

For the realisation of a scanning force microscope, the force measurement must be supplemented by a feedback control, in analogy to the scanning tunnelling microscope. The controller keeps the amplitude of the vibration of the cantilever (the tip), and thus also the distance, constant. During scanning the feedback controller retracts the sample with the scanneer of a piezoelectric ceramic or shifts towards the cantilever until the vibration amplitude has reached the setpoint value again. The principle of height regultion is exactly the same as for the scanning tunnelling microscope. The scanning force micrographs thus show areas of constant effective force constant. If the surface is chemically homogeneous and if only van der Waals forces act on the tip, the SFM image shows the topography of the surface.



nic

-0.10

0.4

0.5

Distance (nm)

Figure 18: The amplification of the cantilever motion through the optical lever ann method. (a) Optical Isser path in the standard AFM set-up. (b) Cantilever beam in beading. (c) Cantilever force as a function of the distance tip – sample distance

Contact mode of operation



Figure 19: Scanning electron micrograph of a cantilever made of Si. [24].

Scanning Force Microscope (SFM) II

3.1 Theoretical Principles of the Scanning Force Microscope.

As already mentioned above, van der Waals forces lead to an attractive interaction between the tip on the spring and the sample surface. Figure 15 shows schematically the van der Waals potential between two atoms. The potential can be described in a simpler classical picture as the interaction potential between the time dependent dipole moments of the two atoms. Although the centres of gravity of the electronic charge density and the charge of nucleus are exactly overlapping on a time average, the separation of the centres of gravity is soatially fluctuating in every moment. This produces statistical fluctuations of the atoms' dipole moments. The dipole moment of an atom can again induce a dipole moment in the neighbouring atom and the induced dipole moment acts back on the first atom. This creates a dipole-dipole interaction on basis of the fluctuating dipole moments. This interaction decreases with d^e in the case of small distances d (Lenard-Jones potential). At larger distances, the interaction potential decreases more rapidly (d^{2}) . This arises from the fact that the interaction between dipole moments occurs through the exchange of virtual photons. If the transit time of the virtual photon between atoms 1 and 2 is longer than the typical fluctuation time of the instantaneous dipole moment, the virtual photon weakens the interaction. This range of the van der Waals interaction is therefore called retarded, whereas that at short distances is unretarded.



Figure 15: The van der Waals potential Ubetween two atoms, d_i is the critical distance above which the transit time effects weaken the interaction [23].



Figure 17: Resonance curves of the tip without and with interaction with a van der Waals potential. The interaction leads to a shift $\Delta \omega$ of the resonance frequency with the consequence that the tip excited with the frequency ω_m has a vibration amplitude $a(\omega)$ attenuated by Δa [23].



Figure 16: Schematic representation of the effect of the van der Waals interaction potential on the vibration frequency of the spring with tip. As the tip approaches the surface, the resonance frequency of the leaf spring is shifted. (from [23]). In escanning three microscope is not based on the interaction of individual atoms only. Both the sample and the tip are large in comparison to the distance. In order to obtain their interaction, all forces between the atoms of both bodies need to be integrated. The result of this is known for simple bodies and geometries. In all cases, the summation leads to a weaker decrease of the interaction. A single atom at distance d relative to a half-space leads to an interaction potential of

$$U = -\frac{C\pi\rho}{6} \cdot \frac{1}{d^3}$$
(7)

where C is the interaction constant of the van der Waals potential and Δ the density of the solid. C is basically determined by the electronic polarizabilities of the atoms in the half-space and of the single atom. If one has two spheres with radii R_1 and R_2 at distance d (distance between sphere surfaces) one obtains an interaction potential of

$$U = -\frac{AR_1R_2}{\delta(R_1 + R_2)} \frac{I}{d}$$
(8)

where A is the so-called Hamaker constant. It is materials specific and essentially contains the densities of the two bodies and the interaction constant C of the van der Waals potential. If a sphere with radius R has a distance d from a half-space, an interaction potential of

$$U = -\frac{AR}{6} \cdot \frac{1}{d}$$
(9)

is obtained from Eq. (8). This case describes the geometry in a scanning force microscope best and is most widely used. The distance dependence of the van der Waals potential thus obtained is used analogously to the distance dependence of the tunnel current in a scanning tunnelling microscope to achieve a high resolution of the scanning force microscope. However, since the distance dependence is much weaker, the sensitiv-Dynamic operation of the scanning force microscope is lower.

The dynamic operation method of a scanning force microscope has proved to be particularly useful. In this method the nominal force constant of the van der Waals potential, i.e. the second derivative of the potential, is exploited. This can be measured by using a vibrating tip Figure 16). If a tip vibrates at distance d, which is outside the interaction range of the van der Waals potential, then the vibration frequency and the amplitude are only determined by the spring constant k of the spring. This corresponds to a harmonic potential. When the tip comes into the interaction range of the van der Waals potential, the harmonic potential and the interaction potential are superimposed thus changing the vibration frequency and the amplitude of the spring.

This is described by modifying the spring constant k of the spring by an additional contribution f of the van der Waals potential. As a consequence, the vibration frequency is shifted to lower frequencies as shown in Figure 17. ω_0 is the resonance frequency without interaction and $\Delta\omega$ the frequency shift to lower values. If an excitation frequency of the tip of $\omega_m > \omega_0$ is selected and kept constant, the amplitude of the vibration decreases as the tip approaches the sample, since the interaction becomes increasingly stronger. Thus, the vibration amplitude also becomes a measure for the distance of the tip from the sample surface. If a spring with low damping Q^{-1} is selected, the resonance curve is steep and the ratio of the amplitude change for a given frequency shift becomes large.

In practice, small amplitudes (approx. 1 nm) in comparison to distance d are used to ensure the linearity of the amplitude signal. With a given measurement accuracy of 1 %, however, this means that the assembly must measure deflection changes (of 0.01 nm, which is achieved most simply by a laser interferometer or optical lever method.

A very few examples of AFM images



TappingMode AFM image of poly(styrene) and poly(methyl methacrylate) blend polymer film. The film was spin-cast on mica substrate from chloroform solution. The surface structure is resulted from the spinodal decomposition. The islands consist of a PMMS-rich phase while the surface matrix composes of a PS-rich phase. 3µm scan courtesy C. Ton-That, Robert Gordon University, U.K.



Atomic resolution image of the titanium oxide layer on top of a titanum substrate. Contact mode AFM in air, commercial silicon nitride cantalever. 5 nm scan courtesy P. Cacciafesta, University of Bristol, UK.



The sample is a strip of adhesive (3M Scotch tape) that has been peeled of a metal surface. The image shows small pits in the sticky surfaces of the adhesive. The image was acquired in TappingMode at frequency of 3 Hz and setpoint of 1.8 V. 2µm scan courtesy L. Scudiero, Washington State University, USA.

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Nanomanipulation by scanning probe techniques I

Main objective:

The excellent space resolution offered by SPM can be exploited also to:

- Manipulate (spatially) nanoparticles on a surface;
- Produce very local modifications of the surface (physical and/or chemical)

5 Manipulation of Atoms and Molecules

The scanning probe microscopes do not only have the ability to image individual atoms. The interaction needed for imaging the surfaces can also be used to manipulate individual adatoms, molecules, or the surface structure itself on the atomic scale. Indeed a large number of works concentrated on the manipulation of individual atoms and in the following novel nanostructures were built. Here we briefly show the work by Eigler and coworkers [44], [45] as examples, followed by a more subtle tip-induced manipulation of atoms, and the tip-induced migration of defects by tip-induced excitement of defects [46], [47]. More recently the group of Rieder could even perform full chemical reactions with single molecules [48]. Three different manipulation modes can by distinguished: the lateral and the vertical manipulation as well as the tunnel current induced changes. The combination of all three modes enables to achieve tip controlled chemical reactions.

Nanomanipulaton shares similar tools as SPM



Figure 32: In the STM imaging mode the tunnel current is kept constant and the cantilever is raised. For manipulation the tip is lowered above an atom dragging it to the desired position, lifting the cantilever losing interaction with the atom [44].

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Nanomanipulation by scanning probe techniques II

In the STM device, the tip is so close to the target as to make the electron current highly spatially confined - it is the key to the extremely high spatial resolution of STM images. The key element in surface modifications is also the STM tip. To affect these modifications one utilizes a variety of tip-sample interactions, including attractive and repulsive forces, electric fields, and the effect of highly spatially confined electron currents. The small distance between tip and sample, which is about one nanometer, causes electrons to tunnel to (or from) a region on the sample that is approximately one nanometer in diameter, with an even smaller major distribution area. Thus, the surface fabrication produced by STM must be performed on the nanometer scale, i.e., STM can nanofabricate Later, we will see that it is also possible to manipulate a single atom or molecule adsorbed on the surface with STM.

Since the invention of STM in 1981, as a nanofabrication tool it has been used in direct surface identation, electron-beam-induced deposition, etching, single-atom manipulation, and so on. All of these techniques have a wide-spread application potential. First, it is possible to reduce the linewidth of large-scale integrated circuits from the micrometer scale to the nanometer scale by lithography, beam-induced deposition and etching, which is one of the goals of high technology. In most cases the resulting feature with dimensions on the order of hundred nm [9.1], but features with dimensions of a few nm have also been achieved [9.2-4]. An exciting possibility will be to use the tip to "operate" on biomolecules such as DNA and proteins. The electronic properties of devices may be dominated by quan-

Nanomanipulation by STM

tum-size effects when their size is reduced to the nanometer or atomic scale. By STM and other techniques, it is possible to discover new phenomena, design new devices and fabricate them. Next, STM can be utilized to repair masks and integrated circuits. The surface topographies can be imaged in situ during the surface fabrication process by STM, which makes it possible to discover defects in masks and circuits, to repair them by surface deposition and etching, and then to examine the final results by STM. Lastly, using the STM as a tool, the essential research on the growth, migration and diffusion of clusters on surfaces, and the interactions between small particles or between substrates and particles can be performed in order to manipulate clusters or atoms on purpose.

Lens-focused electron beams, ion beams and X-rays can also be employed in nanofabrication. Although the STM seems unlikely to become competitive in some areas of nanofabrication such as wafer-scale resist patterning, it has its own characteristics. First, an STM can work in either the tunneling mode or the field-emission mode. When working in the latter, a low applied voltage (higher than a few volts) can produce a strong enough electric field to make electrons emit from the tip over the barrier, because the distance between tip and sample is very small. These emitting electrons with a certain current and energy, will not diverge greatly because of the small separation which results in a nanometer beam diamter on the substrate surface. Unlike conventional high-energy electron lithography, the lowenergy STM beam reduces the problems associated with electron backscattering and the generation of secondary electrons. A resolution of about 10 nm, and exposure rates comparable to those of conventional electron lithography have been achieved. Secondly, by moving the tip to contact the sample, the STM tip can also produce local contact forces and electrostatic forces in a small region on the sample surface to create indentations directly. Lastly, at present, STM is the only instrument that can provide a nmsized beam of very low energy electrons (0 + 20 eV). The importance of electrons with low energy is obvious when it is considered that many of the processes such as migration, bond breaking, chemical reactions that would be interesting to control, have activation energies less than 10 eV per atom which require a low-energy beam.

"Lateral" manipulation of single atoms

5.1 Lateral Manipulation

In the lateral manipulation mode a particle on the sample surface is moved along the surface to the desired location without losing contact to the surface. The motion can be obtained either by dragging or pushing. Figure 31a to d show the build up of a quantum corral by manipulating individual Fe atoms on a Cu(111) surface at 4 K [44]. The final structure of 15 nm diameter consists of 48 Fe atoms. At this stage one may ask how such a fine manipulation can be achieved. The procedure is as follows: Fe atoms are evaporated onto a Cu(111) surface cooled to 4 K. The surface containing statistically distributed Fe atoms is then examined by STM. Normally, no atoms are displaced, but if the distance between tunnelling tip and a Fe atom is reduced, then the tunnelling tip exercises an attractive force on the Fe atom and the Fe atom can be dragged by the tunnelling tip to the desired location on the surface [44], [45]. Once the desired location is reached, the tip is retracted. Increasing the distance between the tip and the sample reduces the tip-Fe atom interactions and, hence, the Fe atom remains at its new position (Figure 32). Figure 31e shows that in this way a whole circle of iron atoms can be built up. The artificially build nanostructure shown in Figure 31 confines the electrons of the two-dimensional surface electron gas on Cu(111). Therefore, as soon as the circle is complete, the electrons are scattered in the circle and form standing electron waves due to quantum mechanics. Figure 31e thus illustrates the wave nature of the electrons.

In a quantum well, due to the quantization of the electron states, not only standing electron waves but also discrete energy values of the electrons are expected. Consequently, increased electron densities should occur at specific energies. As already described, the density of states can be approximately calculated from experimentally measured current-voltage characteristics by calculating (dL'dV)'(LV). For metals, however, LV is generally constant and the sample density of states is therefore proportional to dL'dV. The variation of dL'dV as a function of voltage reflects the density of states variation as a function of energy. Figure 33 shows the density of states thus obtained for three different surface positions. At the centre of the circle, as expected, peaked energy levels occur (curve a), whereas outside the circle no structure in the density of states is measurable (curve c). If the density of states is measured at a distance of 0.9 nm from the circle centre, even more energy levels occur as shown by the arrows in curve b.

This example of spectroscopic measurements and of the spatial distribution of the electron waves in a potential well provides a particularly illustrative picture of quantum mechanics. The construction of different quantum structures by an atom-by-atom manipulation approach using scanning probe microscopes nowadays allows a new look into the quantum world and a direct spatial measurement of the electron waves.



Figure 31:

(a) to (d) show the process of building a quar corral consisting of 48 Fe atoms positioned c Cu(111) surface. The resulting structure and standing waves induced by the quantum confiment of surface electrons in the structure is v in the three-dimensional view
(e) of the quantum corral [44].

Fe quantum corral



Artifical quantum structures can be produced

"Lateral" manipulation and surface reconstruction

Instead of evaporating foreign atoms onto a copper surface it is also possible to reconstruct the substrate surface itself, which is more difficult due to the higher coordination number and binding energy of the atoms located in the surface or in steps [49]. The experiments shown here are carried out on Cu(211) substrates at 30 - 40K. In Figure 34 a sphere model of the copper surface is shown, whereby the atoms are shaded darker the deeper they lie. Lateral manipulation of single Cu atoms parallel and perpendicular to step edges is presented in Figure 35 [49]. A measure for the minimum force necessary to move a copper atom is the tunnel resistance which displays the distance between tip and sample. The tunnel resistance used for motion along a step edge was approx. 700 k Ω and ~500 k Ω for moving them over a step edge. Figure 36a - c demonstrate that it is even possible to "dig out" single copper atoms from even higher coordinated sites. The single Cu atoms leading to a corresponding vacancies in the initial site of the atoms.

Furthermore instead of moving single atoms, the lateral manipulation technique is also capable to move entire molecules. Gimzweski et al. deposited hexa-tert-butyl decacyclene (HB-DC) molecules onto a Cu(100) surface [50]. The decacyclene core of the HB-DC is equipped with six bulky t-butyl-legs (Figure 37). At monolayer coverage, the molecules are immobile, forming a two dimensional van der Waals crystal (Figure 38). Separated HB-DC molecules on a Cu(100) surface are extremely mobile, making it impossible to get STM images with atomic resolution.

For this reason a coverage of just less than one monolayer was chosen and STM images resemble those of the immobilized 2-D lattice at full monolayer coverage. However, there are some random voids. In this layer the molecules can be at sites with different symmetry with respect to the surrounding molecules (Figure 39). Molecules at sites of lower symmetry rotate at speeds higher than the scan rate used for imaging and therefore appear as torus Figure 40a. The molecules at the higher symmetry sites are observed as six-lobed images, proving that they are immobile Figure 40b. Gimzweski used the lateral manipulation to drag a rotating HB-DC molecule from a low symmetry site into a higher symmetry site and the six lobes of the immobilized molecule was again clearly observed.



Figure 38: STM image of an Cu(100) surface after exposure to a full monolayer coverage of HB-DC molecules at room temperature. Image area is 11.4 nm by 11.4 nm [50].



0.26 nm and imaged as a six-loceb structure in registry with the surrounding molecules. Image area is 5.75 nm by 5.75 nm.

"Vertical" manipulation

5.2 Vertical Manipulation

In the vertical manipulation process, the adparticles are transferred from the sample surface to the tip apex and vice versa [51], [52]. The first experiments on vertical STM manipulation were carried out by Eigler "picking up" Xe atoms [51]. The group of Rieder showed that transferring a Xe atom to the tip apex leads to markedly improved resolution [53]. The single Xe atom obviously "sharpens" the tip.

In Figure 41(a) [54], [55] a schematic presentation of the *pick up* process of a Comolecule from Cu(111) is shown. It is well known that CO molecules stand upright on a Cu(111) surface [56] with the carbon atom bonding to the copper atoms. Due to occasional contact between the tip and the surface some copper atoms are transferred to the tip apex. During the transfer of the CO molecule to the tip, the molecule must consequently rotate. A reliable procedure for transferring the CO to the tip and back to the surface requires ramping of the tunneling voltage and the simultaneous decrease of the tip-surface distance. Figure 41b and e show that scanning with a CO molecule on the tip apex leads to a clear chemical contrast. Figure 41b is scanned with a clean metal tip and all adsorbents appear as depressions. After the transfer of the CO molecule to the tip apex (indicated with an white arrow) and rescanning the area, Figure 41c shows that all CO molecules changed their appearance to protrusions. Only the oxygen atom in the upper left part of Figure 41b and c retains its appearance.

In [57] it has been described, how to combine the potential of single atom manipulation of STM and single atom sensitivity of an atom probe mass spectrum to realize an ultimate technique for surface science. The System used by Shimizu et al. consists of an STM, an atom probe, load lock chambers and a mechanism to transfer tip and sample. The tip can be transferred reversibly between the STM and the atom probe stages. To investigate the pick-up of Si atoms during manipulation, a clean Si surface was approached with a clean tungsten tip applying a bias of + 2 V and 0.3 nA at the sample. After manipulation the tip was transferred from the STM to the atom probe. The atom probe analysis showed the formation of to different layers on top of the tip apex. The top most layer was WSi₂ and the next layer was W₅Si₃, finally the clean tungsten surface appeared. Using this combination of an STM and an atom probe could prove that the tips during manipulation do not only adsorb atoms but furthermore depending on the conditions alloys can be formed.



Figure 41:

(a) A sketch of the picking up procedure of CO molecules on Cu(111) surfaces. Notice that the CO molecule stands upright with the carbon atom attached to the surface and has to switch its orientation when being transferred to the tip.
(b), (c) STM images showing the pick up of a CO molecule. Notice the chemical contrast after the pick up [54].

Molecules or atoms can be "trapped" or "released" by the STM tip by varying the bias voltage

STM nanomodifications I

5.3 Effects induced by the Tunnel Current

It is also possible to excite atoms by the tip-sample interactions. Figure 42 shows a set of consecutive STM images acquired with 8 s time interval. The images show that the defects change their lattice positions [58], [59]. The tip can excite defects by several physical mechanism. The case shown here is based on a field-induced migration, due to the strong electrostatic field penetrating into the semiconductor. Defects can, however, also be excited by funnelling of minority carriers into defect states followed by a charge carrier recombination with electron-phonon coupling [47]. There are surely even further mechanisms which may possibly excite atoms on the surface. Which of those will take place depends sensitively on the measurement conditions.

Finally, in Figure 43 the cutting of a carbon nano tube with an AFM is presented [60]. Earlier experiments controlling the length of carbon nano tubes were carried out using a STM [61]. At first the 600 nm² area is scanned then the AFM cantilever is lowered at the positions marked in the left image and for cutting a voltage pulse of -6 V is applied. The image on the right hand side shows the carbon nano tube after cutting.

Defects are "excited" through local tunneling currents



Figure 42: Migration of the phosphorus vacancies on the GaP(110) surface. The chanes of the lattice positions of the vacants cies is induced by the tip of the scanning tunnelling microscopi In this particular case the jungs are field-induced.

STM nanomodifications II

Figure 44: Schematic presentation of

(a), (b) Electron-induced abstraction of

(c) Pulling the iodine atom to a terrace

(d) Bringing together to two phenyl

molecules by lateral manipulation and

(e) electron-induced chemical associa-

(f) Pulling the synthesized molecule by its front end to prove the association.

the tip-induced Ullmann reaction.

the iodine from the iodobenzene.

site.

tion to biphenyl.

5.4 Complex Chemical reactions with the STM

In 1904, Ullmann et al. heated iodobenzene with copper powder as catalyst and discovered the formation of biphenyl with high purity [62]. This aromatic ring coupling mechanism is now nearly 100 years old and known as the Ullmann reaction. Combining the presented STM manipulation methods, namely the moving of adsorbents and the influence via increased tunnel current, it is possible to control this complex chemical reactions at low temperatures step by step. S. H. Hla et al. presented the synthesis of to one biphenyl molecule out of two iodobenzene on a copper surface at 20 K [48].

The synthesis consist of three different steps. First two iodobenzene (C_6H_3 I) have to be dissociated into phenyl (C_6H_3) and iodine (Figure 44a and b). Secondly the two phenyl rings have to be located one to another (Figure 44d and e) and finally in the third step, through tunnelling electrons the two phenyl rings are associated to biphenyl (Figure 44e).

To abstract the iodine from the iodobenzene the STM tip is positioned right above the molecule at a fixed height and a the sample voltage is switched to 1.5 V for several seconds. The energy transfer from a single electron causes the breaking of the C-I bond

Figure 45a – c, [62]. As the bond energies of the C-H and C-C bonds are two and three times higher than the C-I bond, it is not possible to break them with a single electron process at this voltage. After preparing to phenyl reactants and moving away the iodine, the left phenyl Figure 45c is brought close to the other one by lateral manipulation using the tip adsorbate forces Figure 45d. Though the two phenyls are close together they do not join at 20 K. The two phenyls can easily be separated again by lateral manipulation. Both phenyls are still bond to the Cu step edge via their σ_{C-Co} bonds. Figure 46 shows a model where the phenyl is lying with its ð ring on the terrace while one of its C atoms is pointing towards the step edge and σ -bonding to a Cu atom. The final reaction step to associate the two phenyls to biphenyl is done by positioning the tip right above the centre of the phenyl couple and increasing the current drastically. The successful chemical association can be proved by pulling the synthesized molecule by its front end with the STM tip [62].



STM-controlled electrochemical reactions



Figure 45: STM image of the Ullmann synthesis induced by the tip. (a) Two iodobenzene molecules are absorbed at a Cu(111) step edge. Introducing a voltage pulse through the tip abstracts the iodine from the phenyl molecules (b) (the left molecule).

(c) By lateral manipulation the molecules are further separated and

(d) the phenyl molecules are moved together to prepare for their association. (scan area $7\times3~nm^2)$ [48]

Conclusions

✓ Scanning Probe techniques have been developed thanks to advances in material fabrication (atomic probes), electronics (and piezoelectric translators), and *methods of operation* (e.g., the role of feedback)

 \checkmark STM is a powerful technique which, by collecting the local tunneling current, can be used to map the local density of states in conductors or semiconductors, and/or the morphology of the sample in *absolute* terms

✓ AFM/SFFM shares a similar space resolution, but the probed quantities have a "mechanical" nature

✓ Many other SPMs have been developed, and the list is still growing

 \checkmark The excellent space control offered by SPM can be exploited also for fabrication (nanomanipulation) purposes